

### PROBLEM 8. (Solution)

In part f) the equation for the self-dissociation of propanol is unbalanced and should of course be:



### PROBLEM 9. (Solution)

Part c) should read:

- c). If all  $\text{Li}_{(s)}$  were converted to  $\text{Li}_{2(g)}$ , then there would be 19.117 moles  $\text{Li}_{2(g)}$  in a volume of  $5.9474 \times 10^8$  litres, corresponding to  $[\text{Li}_{2(g)}] = 3.2143 \times 10^{-8} \text{ mol L}^{-1}$ , or a total pressure of  $1.2233 \times 10^{-3}$  Torr.

### PROBLEM 10. (Solution)

The 9th line of part d) should read:

$$\text{Mass of } \mathbf{Y}^{i-} = \text{mass } (\mathbf{X}) - \underline{\text{molar}} \text{ mass } (\text{H}^+) \times \text{moles } (\text{OH}^-)$$

### PROBLEM 13.

The amount of sample should be 0.50 g (not 5.00 g) so the second paragraph should begin:

She weighs out  $0.50 \pm 0.01$  g of each sample ...

*The solution should then read:*

- b). Analysis of results:

$$\begin{aligned} \text{moles } \text{M}^+ \text{ in } 0.5 \text{ g} &= \text{moles } \text{OH}^- \times (250 \text{ mL} / 50 \text{ mL}) \times (100 \text{ mL} / 40 \text{ mL}) \\ &= \text{titre volume} \times 0.0326 \text{ mol L}^{-1} \times 5 \times 2.5 \end{aligned}$$

$$M_r(\text{MX}) = \text{sample mass (0.5 g)} / \text{moles } \text{M}^+ \text{ in } 0.5 \text{ g}$$

*The values in the table for possible molecular masses of the unknowns are unchanged.*

**PROBLEM 18. (Solution)**

- a). If we denote the initial activity as  $I_0$  (i.e.  $7.0 \times 10^7$  Bq mL<sup>-1</sup> in each case), and  $I_t$  as the activity after a time  $t$  has elapsed, then  $I_t$  is defined as  $I_t = I_0 e^{-(t / t_{1/2})}$ .

*This equation is incorrect and the sentence should read:*

- a). If we denote the initial activity as  $I_0$  (i.e.  $7.0 \times 10^7$  Bq mL<sup>-1</sup> in each case), and  $I_t$  as the activity after a time  $t$  has elapsed, then  $I_t$  is defined as  $I_t = I_0 e^{-(\ln 2 \ t / t_{1/2})}$   
or  $I_t = I_0 2^{-(t / t_{1/2})}$

*Using the correct equation, the table of nuclide activities is as follows:*

nuclide	$I_t$ (Bq mL <sup>-1</sup> )	$I_t$ after dilution (Bq mL <sup>-1</sup> )
<sup>71</sup> Zn	12100	4.83
<sup>67</sup> Ga	$6.97 \times 10^7$	$2.79 \times 10^4$
<sup>68</sup> Ge	$6.9996 \times 10^7$	$2.80 \times 10^4$

*Using the correct equation, the answers to part d) are also changed slightly to:*

In the 1 mL dose at  $t = 8$  hr,

$$I_t = I_0 2^{-(t / t_{1/2})} \times V_{\text{dose}} / V_{\text{total}} = 1.09 \times 10^8 \text{ Bq} \times 2^{-(8/78.25)} \times 1/100$$

$$I_t = 1.015 \times 10^6 \text{ Bq.}$$

- ii). The residual activity of the 1 mL dose after a further hour would be

$$I_t = 1.015 \times 10^6 \text{ Bq} \times 2^{-(1/78.25)} = 1.006 \times 10^6 \text{ Bq.}$$

Comparison of this activity, with that observed for the 1 mL blood sample, yields the dilution factor:

$$\text{Dilution factor} = 1.006 \times 10^6 / 105.6 = 9531.$$

The patient's blood volume is thus 9.53 litres.

**PROBLEM 20 (Solution).**

The current solution to part a) assumes STP, but NO<sub>2</sub> is a liquid at a 0°C! However, because we are only *estimating* an upper limit for the concentration of NO<sub>2</sub>, let's assume 25°C. The calculation then becomes:

$$\begin{aligned}[\text{NO}_2] &= 0.21 \text{ (mole \% of O}_2\text{)} / 24.484 \text{ L mol}^{-1} \text{ (molar volume at 25}^\circ\text{C)} \\ &= 8.6 \times 10^{-3} \text{ mol L}^{-1}\end{aligned}$$

### PROBLEM 21.

- c). [You should assume that the total metal ion concentration is much less than 0.05 mol L<sup>-1</sup>. ]

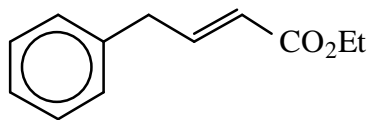
*should be*

[You should assume that the total metal ion concentration is much less than 0.005 mol L<sup>-1</sup>. ]

*The answers are unchanged.*

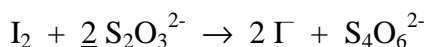
### PROBLEM 26 (Solution).

The correct structure for the Wittig product (xxi) is an ethyl ester (not a methyl ester):



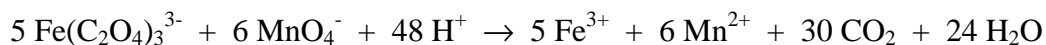
### PROBLEM 29.

The equation for the reaction of iodine and thiosulphate is unbalanced and should of course be:

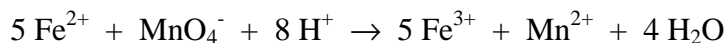


### PROBLEM 30.

In the section: **Analysis for oxalate and iron** the equation for the reaction of tris(oxalato)ferrate(III) and acidified permanganate is unbalanced and should of course be:



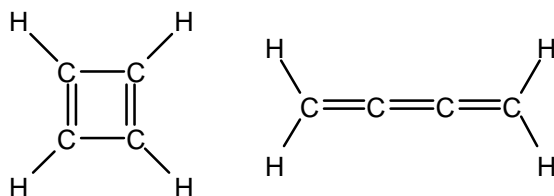
Also, the equation for the oxidation of iron(III) by permanganate incorrectly has Fe<sup>3+</sup> as a reactant and of course should be:



## Worked solutions to the problems

### PROBLEM 1.

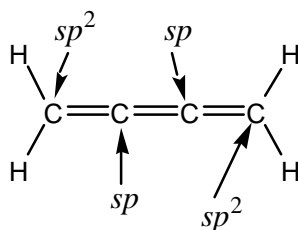
a).



Cyclobutadiene

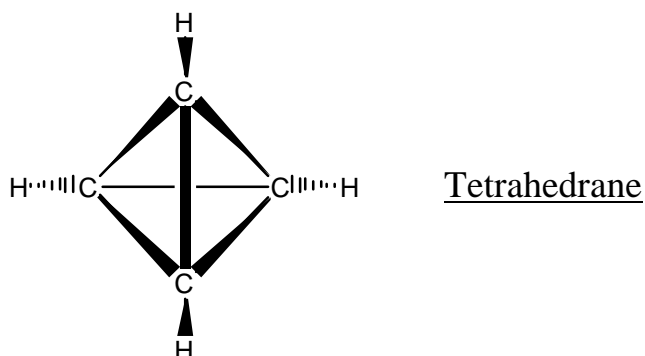
Butatriene

b). The hybridization at each carbon atom is as below:



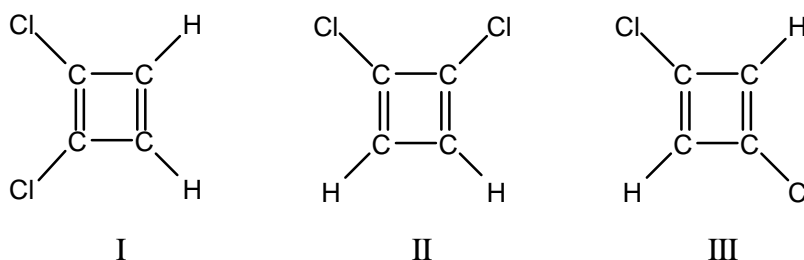
The central C=C bond is between two carbons of  $sp$  hybridization; other C=C bonds are between an  $sp$ -hybridized and an  $sp^2$ -hybridized C atom. The greater the proportion of  $s$ -character in the hybridized orbital, the more 'squat' is the orbital and hence the shorter the  $\sigma$ -bond which results. Therefore the central C=C bond is shorter than the other two.

c).



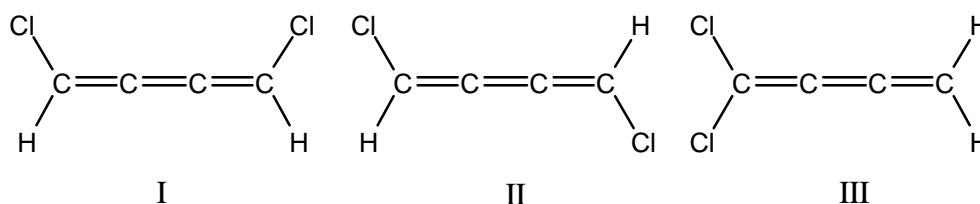
- d). (i) one  
(ii) one  
(iii) one

e). (i) Arguably three:

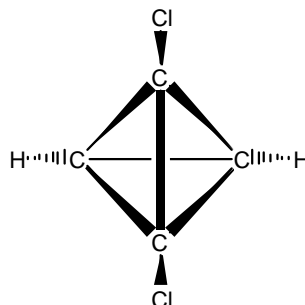


Since cyclobutadiene is not aromatic, I and II aren't properly different canonical forms but are distinct isomers (nevertheless, they may not exist separately).

(ii) Three:

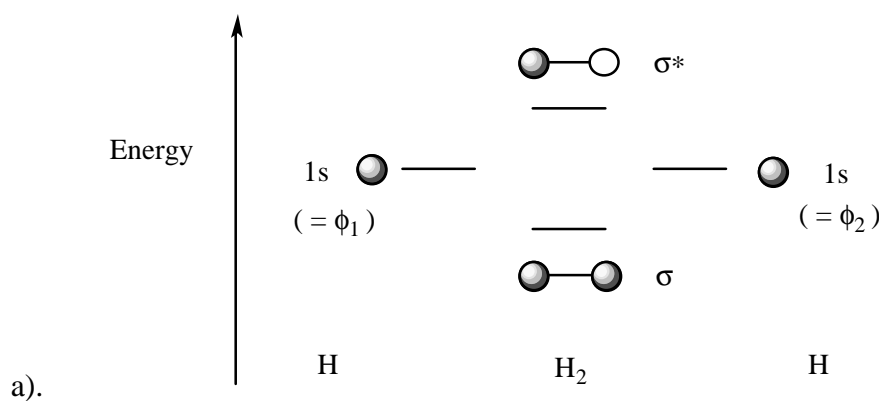


(iii) One:



f). The melting points of the isomers should correlate with their dipole moments. By symmetry, II has zero dipole moment and so has the lowest melting point. Of the other two, III will have a larger dipole moment than I (because the dipole in III lies along the long horizontal axis, whereas that in I lies along the short vertical axis). So III will have the highest melting point.

## PROBLEM 2.

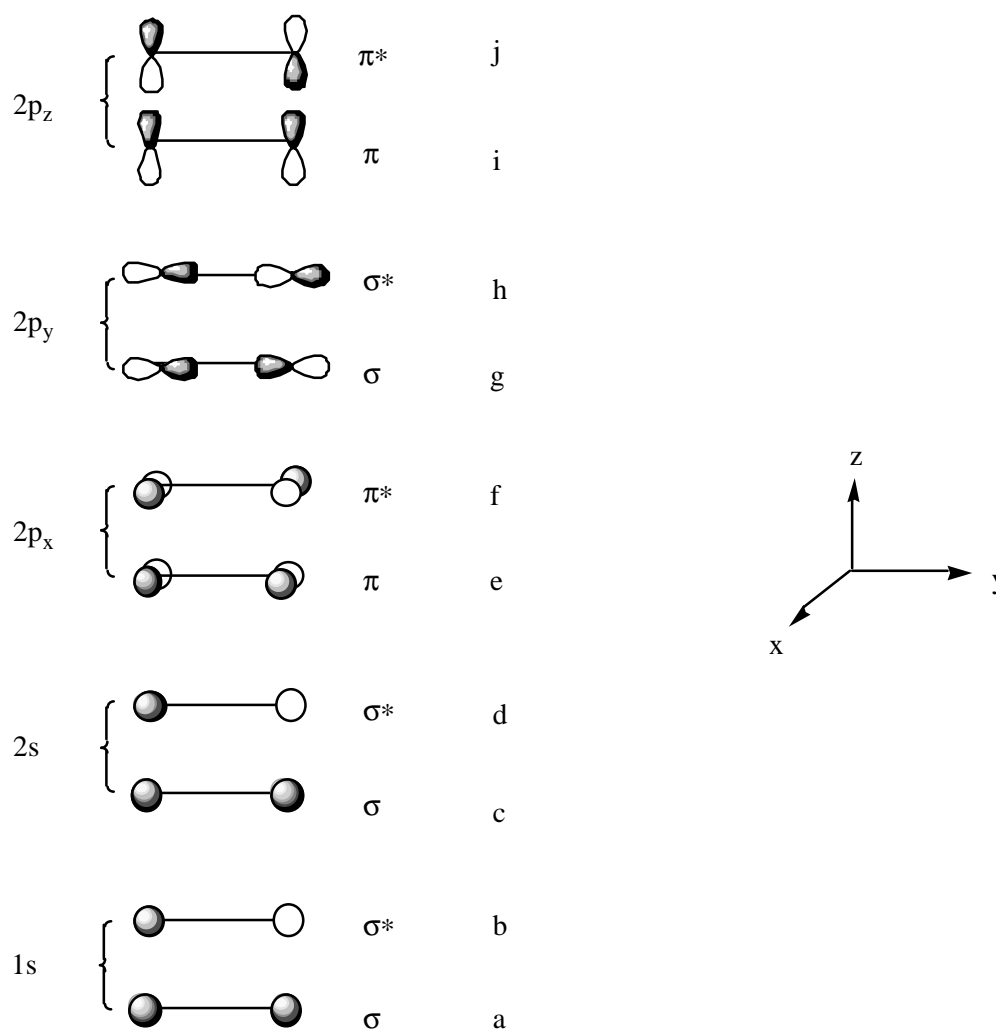


- b). The molecular orbitals of  $H_2$  are formed by combining, in equal amounts, the 1s atomic orbitals on each of the hydrogen atoms. Two molecular orbitals are formed: one lying higher in energy than the 1s atomic orbitals, and the other lying lower in energy. The lower MO is formed from the in-phase combination of the 1s atomic orbitals on each hydrogen atom. The higher MO is formed from the out-of-phase combination. With reference to the above diagram we may write:

$$\sigma = \phi_1 + \phi_2 \quad \text{and} \quad \sigma^* = \phi_1 - \phi_2$$

- c). It is called an antibonding molecular orbital because it results in a net decrease in electron density between the atoms.

d).



$O_2$

- e). The end-on overlap of two p atomic orbitals in g is much better than the side-on overlap in e or i. Thus the amount of bonding character in g is larger and hence the energy of the orbital is lower.

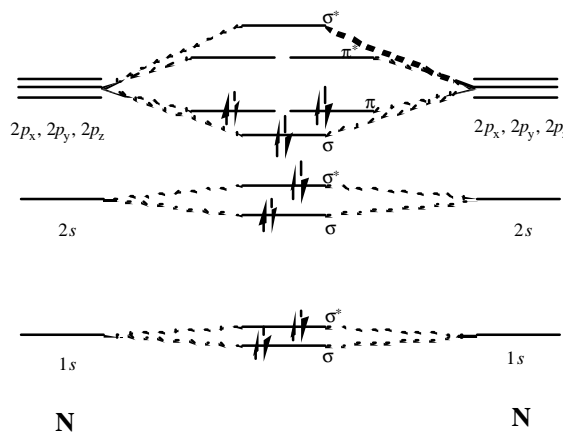
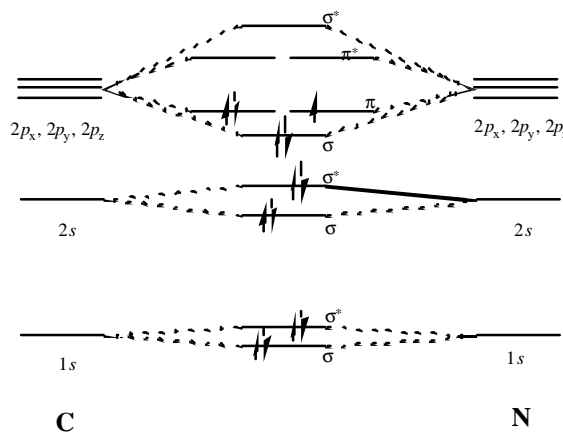
A similar reason explains the energy of h vs f and j. The overlap in h is again better than in f or j. Thus the amount of anti-bonding character in h is larger and hence the energy of the orbital is higher.

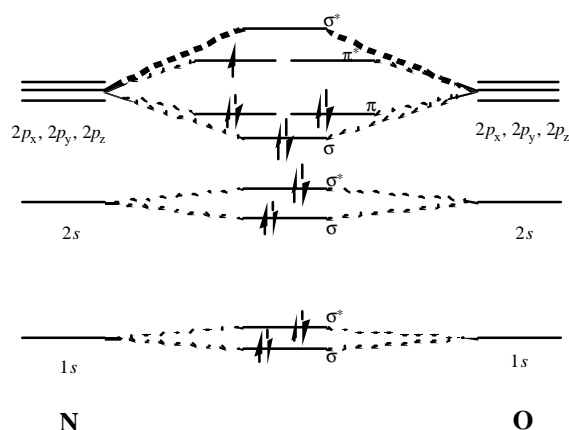
- f). Orbitals e and i both arise from the side-on overlap of p atomic orbitals. The p orbitals in the x direction are, of course, identical to those in the z direction (x and z are completely arbitrary designations on our part) and so the resulting molecular orbitals are identical.
- g). As we stretch the O<sub>2</sub> molecule the overlap between the atomic orbitals on one oxygen and those on the other atom decreases. Thus the anti-bonding character in molecular orbital j decreases and hence its energy is lowered.

Because the end-on overlap in orbital h is greater to begin with than the side-on overlap in j, the overlap will decrease faster in h as the O<sub>2</sub> molecule is stretched. Thus the anti-bonding character decreases more rapidly, and hence the energy of h is lowered much faster.

### PROBLEM 3.

- a). We can construct MO diagrams as follows:

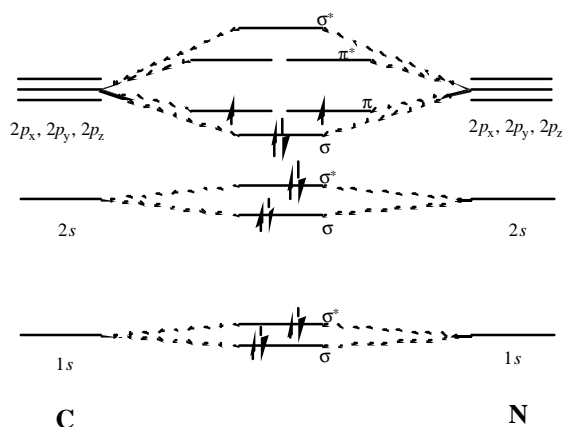




These diagrams ignore differences in energy levels between different nuclei, but give the correct qualitative trends for determination of bond orders.

Molecular orbitals arising from the 1s and 2s atomic orbitals are filled in all cases, and give rise to no net bonding character. Bond order is found from the difference in occupancy of bonding and antibonding orbitals arising from the 2p atomic orbitals. CN has 5 electrons in the  $\sigma$  and  $\pi$  bonding orbitals derived from the 2p orbitals, and none in the corresponding antibonding orbitals, and therefore has a bond order of 2.5.  $\text{N}_2$  has an excess of six electrons in bonding orbitals, so bond order = 3. NO has five more electrons in bonding orbitals than in antibonding orbitals, so its bond order is 2.5.

- b). Here we need to consider the electronic configuration arising from electron loss. For  $\text{CN}^+$ , the new electron configuration will be

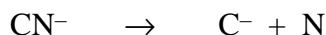


For  $\text{N}_2^+$ , an electron is removed from one of the  $\pi$  bonding orbitals of  $\text{N}_2$ , while for  $\text{NO}^+$  the electron in the  $\pi^*$  antibonding orbital of NO is removed. Removal of an antibonding electron will convey some stabilization on  $\text{NO}^+$ : electrons removed for the other species are from bonding orbitals, so NO will have the lowest ionization energy. Ionization of each of CN and  $\text{N}_2$  requires removal of one

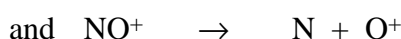
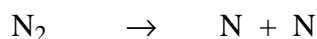


electron from an electron pair in a bonding orbital, so  $\text{IE}(\text{CN})$  and  $\text{IE}(\text{N}_2)$  should be similar. We would expect that  $\text{IE}(\text{N}_2)$  should be somewhat higher than  $\text{IE}(\text{CN})$ , however, because the overlap between atomic orbitals on two N atoms will be better than that between atomic orbitals on C and on N, so  $\text{N}_2$  should have the highest ionization energy. Literature values for these quantities ( $\text{IE}(\text{CN}) = 1359 \text{ kJ mol}^{-1}$ ,  $\text{IE}(\text{N}_2) = 1503 \text{ kJ mol}^{-1}$ ,  $\text{IE}(\text{NO}) = 894 \text{ kJ mol}^{-1}$ ) support these expectations. Note that  $\text{IE}(\text{NO})$  is much lower than the other two ionization energies, indicating the greater ease of removing an electron from an antibonding orbital rather than a bonding one.

- c). Formation of  $\text{N}_2^-$  or  $\text{NO}^-$  involves addition of an electron to an antibonding orbital in each case. In contrast, formation of  $\text{CN}^-$  involves placing the additional electron in the  $\pi$  bonding orbital (which also achieves an electronic structure isoelectronic with that of  $\text{N}_2$ ). Thus we would expect CN to have the highest electron affinity, and this is borne out by the literature values ( $\text{EA}(\text{CN}) = 369 \text{ kJ mol}^{-1}$ ,  $\text{EA}(\text{N}_2) \sim 0 \text{ kJ mol}^{-1}$ ,  $\text{EA}(\text{NO}) \sim 9 \text{ kJ mol}^{-1}$ ).
- d). There are two competing effects here. Firstly, overlap will generally be strongest between atomic orbitals of identical nuclei; thus we would expect  $\text{N}_2$  to have the highest bond strength. However, the comparison is more complex because  $\text{NO}^+$  and  $\text{CN}^-$  are charged species: the dissociation processes are, respectively,



(since C turns out to have a higher electron affinity than N),



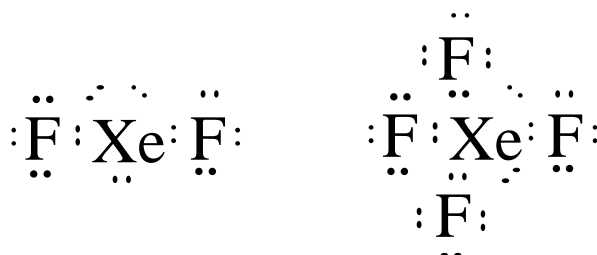
(since O happens to have a lower ionization energy than N).

Bond formation tends to stabilize a charge, whether positive or negative, and so despite the inherently better overlap in  $\text{N}_2$ , it will not necessarily be  $\text{N}_2$  which has the highest bond strength of the three isoelectronic species. In the absence of further information, the question can't be answered with confidence.

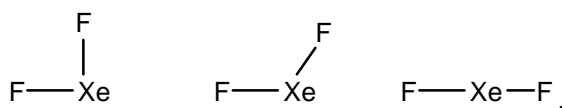
(For the record, current literature values yield  $D[(\text{C}-\text{N})^-] = 994 \text{ kJ mol}^{-1}$ ;  $D(\text{N}-\text{N}) = 946 \text{ kJ mol}^{-1}$ ; and  $D[(\text{N}-\text{O})^+] = 1051 \text{ kJ mol}^{-1}$ . So charge delocalization wins out over better N-N overlap in both cases.)

**PROBLEM 4.**

a).

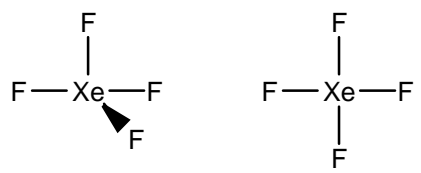


$\text{XeF}_2$  has 5 electron pairs on Xe, so the structure will be based on a trigonal bipyramidal electron configuration. Of the three possibilities,



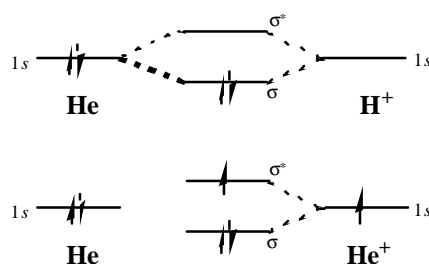
the linear structure minimizes the repulsion between the lone pairs (which will be held closer to Xe than the electrons involved in Xe-F bonds) and so the linear geometry is favoured.

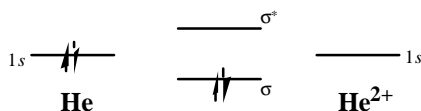
$\text{XeF}_4$  has 6 electron pairs on Xe, so the structure will be based on an octahedral configuration. Of the two possibilities,



The planar structure minimizes the lone-pair repulsion and is consequently favoured.

- b). F always has an oxidation number of -1. Therefore the oxidation numbers of Xe are +2 ( $\text{XeF}_2$ ) and +4 ( $\text{XeF}_4$ ). These species are powerful oxidizing agents!
- c). Ignoring energy level differences for H and He, we can draw the following MO diagrams:





From these diagrams, we can see that HeH<sup>+</sup> and He<sub>2</sub><sup>2+</sup> both have a bond order of 1, while He<sub>2</sub><sup>+</sup> has a bond order of 0.5.

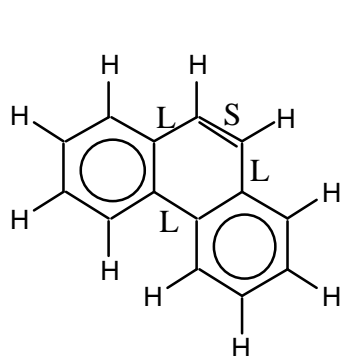
- d). Group II elements will have low second ionization energies (because Be<sup>+</sup> → Be<sup>2+</sup> or Mg<sup>+</sup> → Mg<sup>2+</sup> yields a closed-shell, 1s<sup>2</sup> or 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 'noble gas' configuration). Mg<sup>2+</sup> has better shielding than Be<sup>2+</sup>, so IE(Mg<sup>+</sup>) < IE(Be<sup>+</sup>). Therefore Mg is the best candidate for 'Z'.
- e). Of Mg's neighbours: Ca will have the lowest second ionization energy of {Be, Na, Al, Ca} for reasons analogous to those above. So Ca is most likely to form a stable dication with He.

Na<sup>+</sup> is already closed-shell, so Na<sup>+</sup> → Na<sup>2+</sup> is very unfavourable. Therefore, Na is least likely to form a dication with He.

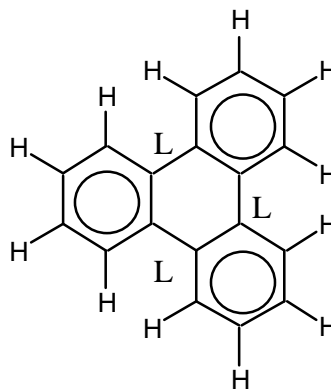
### PROBLEM 5.

- a). The structures are shown in b). below.

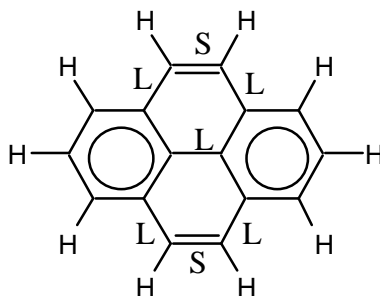
b).



Phenanthrene



Triphenylene



Pyrene

- c). Phenanthrene possesses two aromatic rings out of three (67%). Triphenylene has three aromatic rings out of four (75%). Pyrene has two aromatic rings out of four (50%). Therefore, triphenylene is the most aromatic of these PAHs; pyrene is the least aromatic.
- d). Phenanthrene possesses 2 aromatic rings for 14 C atoms (1:7). Triphenylene has 3 aromatic rings for 18 C atoms (1:6). Pyrene has 2 aromatic rings for 16 C atoms (1:8). Triphenylene is still the most aromatic of these PAHs, with pyrene still the least aromatic.
- e). (i) Average bond order =  $4/3$ . In any canonical form, one of every three C-C bonds must be a double bond, while two are single. Alternatively (see resonance structure below) two of every three C-C bonds have  $3/2$  bond order, while one out of three is formally single: again, an average order of  $4/3$  results.
- (ii) Bond order in benzene =  $3/2$ . Benzene's C-C bonds have more double-bond character than graphite: therefore graphite's bonds are longer.
- (iii) Only one in every three of graphite's rings is aromatic in any given canonical form. However, there is one ring per two C atoms in graphite, versus one ring per six C atoms in benzene. By this token, therefore, graphite and benzene are equally aromatic on a per-carbon-atom basis. (If larger  $\pi$ -delocalized systems are also considered, for example 10-electron systems, then graphite is more aromatic because such systems cannot feature in benzene's resonance stabilization).

## PROBLEM 6.

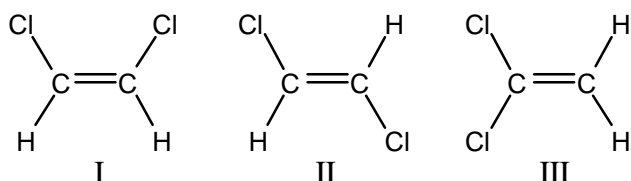
- The six isomers of  $C_4H_8$  are 1-butene, *cis*-2-butene, *trans*-2-butene, methyl propene, cyclobutane, and methyl cyclopropane.
- A, B, C, and D, decolourize bromine in the absence of light: therefore this process is bromine addition to an alkene: therefore A–D are the four alkenes, and E and F are the two cycloalkanes.
- Methyl cyclopropane possesses a dipole moment, while the dipole moment of cyclobutane is zero. Therefore, the boiling point of methyl cyclopropane will be higher than that of cyclobutane. Since  $bpt(E) > bpt(F)$ , E is methyl cyclopropane and F is cyclobutane.
- Hydrogenation of 1-butene, or of either isomer of 2-butene, yields n-butane. This accounts for the same product arising from hydrogenation of A, B, and C. The "odd one out" is D, which must therefore be methyl propene.
- Bromine addition to *cis*-2-butene produces the meso form of 2,3 dibromopropane, while addition to *trans*-2-butene yields the R,R and S,S enantiomers. This

accounts for the observation that B and C produce stereoisomeric products with bromine. By elimination (the deductive process, NOT the organic reaction mechanism!), A is 1-butene.

- *Cis*-2-butene should have a higher boiling point than *trans*-2-butene by virtue of the latter's zero dipole moment. Since  $\text{bpt}(\text{C}) > \text{bpt}(\text{B})$ , C is *cis*-2-butene and B is *trans*-2-butene.

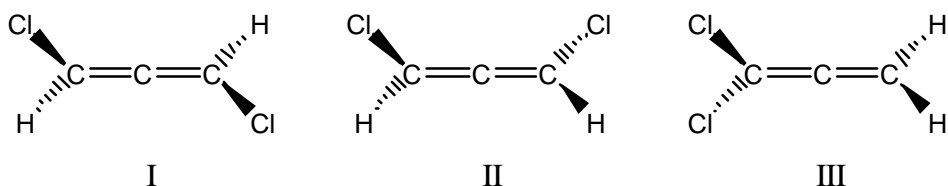
## PROBLEM 7.

- a). Three isomers:



I and II are geometric isomers.

- b).



I and II are optical isomers.

- c). Geometric isomers arise if  $n = \text{even}$ . Optical isomerism requires  $n = \text{odd}$ .

This distinction arises from the planarity of even- $n$  structures, which must therefore all possess a plane of symmetry and which therefore must all be superimposable upon their mirror images. Odd- $n$  structures aren't planar because the two terminal  $\text{C}=\text{C}$  bonds have  $\pi$  clouds which are orthogonal to each other: these structures will not possess planes of symmetry and can therefore possess non-superimposable mirror images (which is the true basis of optical isomerism).

## PROBLEM 8.

- a). The ion at  $m/z$  82 must be  $^{12}\text{C}^{35}\text{Cl}^{35}\text{Cl}$ . The absence of  $m/z$  83 requires an absence of  $^{13}\text{C}$  in the sample.

The ion at  $m/z$  28 must therefore be  $^{12}\text{C}^{12}\text{C}^2\text{H}^2\text{H}$ . The absence of  $m/z$  27 requires an absence of  $^1\text{H}$ .

Therefore, the ion at  $m/z$  75 must be  $^{35}\text{Cl}^{12}\text{C}_3^2\text{H}_2$ , and  $m/z$  77 is the  $^{37}\text{Cl}$ -isotopomer of this species.

b).  $I(m/z\ 77) = 0.6\ I(m/z\ 75)$

$$\therefore n(^{37}\text{Cl}) = 0.6\ n(^{35}\text{Cl})$$

$$\therefore \%(^{37}\text{Cl}) = [0.6/(1+0.6)] \times 100\% = 37.5\%$$

$$\therefore \%(^{35}\text{Cl}) = 62.5\%$$

There are three isotopomers of dichloropropadiene:

$$\%[\text{C}_3\text{D}_2(^{35}\text{Cl})_2] = (62.5\%)^2 = 39.06\%$$

$$\%[\text{C}_3\text{D}_2^{35}\text{Cl}^{37}\text{Cl}] = 2 \times 62.5\% \times 37.5\% = 46.88\%$$

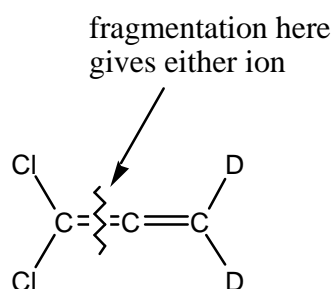
$$\%[\text{C}_3\text{D}_2(^{37}\text{Cl})_2] = (37.5\%)^2 = 14.06\%$$

c). 1 mole corresponds to:

$$0.3906\ \text{mole} \times 110.0\ \text{g mol}^{-1} + 0.4688\ \text{mole} \times 112.0\ \text{g mol}^{-1} + 0.1406\ \text{mole} \times 114.0\ \text{g mol}^{-1}$$

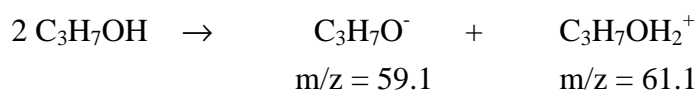
i.e., a molar mass of  $111.50\ \text{g mol}^{-1}$ .

d).  $\text{CCl}_2^+$  and  $\text{CCD}_2^+$  can only arise if the dichloropropadiene structure is



e). The peak at  $m/z = 242$  in positive ion detection mode is due to the species  $(\text{C}_4\text{H}_9)_4\text{N}^+$  ( $\text{C}_{16}\text{H}_{36}\text{N} = 242.4\ \text{amu}$ ) which is the only positive species in solution. In negative ion detection mode, peaks due to  $^{79}\text{Br}^-$  and  $^{81}\text{Br}^-$  are observed. The natural abundances of  $^{79}\text{Br}$  and  $^{81}\text{Br}$  are 50.7% and 49.3% respectively, so these two peaks are essentially of equal height.

f). These spectra are consistent with the self ionisation:



## PROBLEM 9.

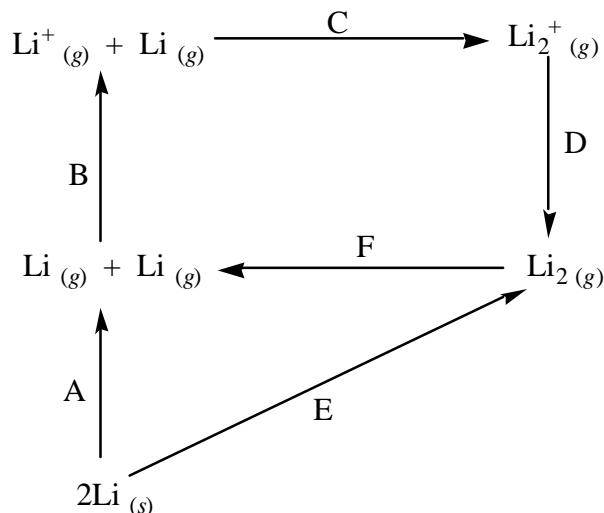
a). We can construct a thermochemical cycle where the known quantities are

$$A = 2 \Delta H^\circ_f(\text{Li}_{(g)}) = 318.8 \text{ kJ mol}^{-1}$$

$$B = \text{IE}(\text{Li}_{(g)}) = 520.3 \text{ kJ mol}^{-1}$$

$$C = -D^\circ(\text{Li}_2^+_{(g)}) = -129.8 \text{ kJ mol}^{-1}$$

$$D = -\text{IE}(\text{Li}_2_{(g)}) = -493.3 \text{ kJ mol}^{-1}$$



and the unknowns are

$$E = A + B + C + D = \Delta H^\circ_f(\text{Li}_2_{(g)})$$

$$\text{and } F = A - E = D^\circ(\text{Li}_2_{(g)}).$$

Thus, we obtain  $\Delta H^\circ_f(\text{Li}_2_{(g)}) = 216.0 \text{ kJ mol}^{-1}$  and  $D^\circ(\text{Li}_2_{(g)}) = 102.8 \text{ kJ mol}^{-1}$ .

- b). The number of moles of Li in the sample is  $(122.045 \text{ g} / 6.9410 \text{ g mol}^{-1}) = 17.583 \text{ moles}$ .

We can calculate the expected pressure if only  $\text{Li}_{(g)}$  is present, from  $PV = nRT$ :

$$P = nRT / V$$

$$\text{i.e. } P = 17.583 \text{ mol} \times 8.31441 \text{ J K}^{-1} \text{ mol}^{-1} \times 610.25 \text{ K} / (5.9474 \times 10^5 \text{ m}^3),$$

$$\text{yielding } P_{\text{expected}} = 0.15000 \text{ Pa (i.e. } 1.1251 \times 10^{-3} \text{ Torr)}.$$

Now, from the equilibrium reaction



we can see that 2 moles of  $\text{Li}_{(g)}$  produce 1 mole of  $\text{Li}_2_{(g)}$ , and so the dilithium partial pressure must equal the difference between the 'expected' pressure for atomic lithium vapour and the observed total pressure:

$$P(\text{Li}_2_{(g)}) = 1.1251 \times 10^{-3} \text{ Torr} - 9.462 \times 10^{-4} \text{ Torr} = 1.789 \times 10^{-4} \text{ Torr}.$$

$$\text{Similarly, } P(\text{Li}_{(g)}) = P_{\text{total}} - P(\text{Li}_2_{(g)}) = 9.462 \times 10^{-4} - 1.789 \times 10^{-4} \text{ Torr}$$

$$\text{i.e. } P(\text{Li}_{(g)}) = 7.673 \times 10^{-4} \text{ Torr}.$$

To determine  $K_c$ , we must convert partial pressures into concentrations. Manipulation of  $PV = nRT$  and of the various conversion constants indicates that, at 610.25 K, we can convert from Torr to mol L<sup>-1</sup> by multiplying by  $2.6276 \times 10^{-5}$  mol L<sup>-1</sup> Torr<sup>-1</sup>, yielding  $[\text{Li}_{2(g)}] = 4.701 \times 10^{-9}$  mol L<sup>-1</sup> and  $[\text{Li}_{(g)}] = 2.016 \times 10^{-8}$  mol L<sup>-1</sup>. Now, with  $K_c$  defined as

$$K_c = \frac{[\text{Li}_{2(g)}]}{[\text{Li}_{(g)}]^2}$$

we obtain a value of  $K_c = 1.156 \times 10^7$ .

- c). In this reaction chamber, moles Li = 265.384 g / 6.9410 g mol<sup>-1</sup> = 38.234 moles. We can determine that not all of the lithium is in the vapour phase:

If all Li<sub>(s)</sub> were converted to Li<sub>2(g)</sub>, then there would be 19.117 moles Li<sub>2(g)</sub> in a volume of  $5.9474 \times 10^8$  litres, corresponding to  $[\text{Li}_{2(g)}] = 3.2143 \times 10^{-8}$  mol L<sup>-1</sup>, or a total pressure of  $1.2233 \times 10^{-3}$  Torr. This is higher than the observed pressure; furthermore, since much of the lithium vapour will be atomic rather than diatomic, the total pressure should be significantly higher than  $1.2233 \times 10^{-3}$  Torr if all the lithium is vaporized. We can conclude, since the pressure has stabilized, that the vapour is in equilibrium with solid or liquid lithium: thus the observed pressure corresponds to the vapour pressure of lithium. The vapour pressure of dilithium can be defined as the partial pressure of Li<sub>2(g)</sub> in the gas phase under these conditions.

We can solve this from  $K_c$ , by substituting in  $[\text{Li}_{(g)}] + [\text{Li}_{2(g)}] = 2.7472 \times 10^{-8}$  mol L<sup>-1</sup> (from the observed pressure, and using the Torr → mol L<sup>-1</sup> conversion factor found in b)), from which we find  $[\text{Li}_{2(g)}] = 5.553 \times 10^{-9}$  mol L<sup>-1</sup>, corresponding to  $P_{\text{vap}}(\text{Li}_{2(g)}) = 2.113 \times 10^{-4}$  Torr at 610.25 K.

- d). First, we need to determine the energy necessary to accelerate the Enterprise to half lightspeed. The kinetic energy is  $E = mv^2 / 2$ , and with  $m = 3.586 \times 10^6$  kg and  $v = 1.49896 \times 10^8$  m s<sup>-1</sup>, we find  $E = 4.0286 \times 10^{19}$  kJ. Since the bond enthalpy of Li<sub>2(g)</sub> is 102.8 kJ mol<sup>-1</sup> (determined in a)), we require  $3.919 \times 10^{17}$  moles of dilithium – i.e.,  $5.44 \times 10^{15}$  kg of dilithium! (To be pedantic, we would need even more lithium than this because of the equilibrium between gaseous lithium and dilithium ...)
- e). The calculations in d) indicate that dilithium is not so efficacious a propellant as some researchers have suggested.<sup>†</sup> However, diberyllium would be even worse:

<sup>†</sup> With regard to the continued use of dilithium as the fuel of choice for 24th-century starships, we can only assume that 24th century replicator technology is sufficiently advanced to produce very large quantities of dilithium out of nothingness!



MO theory shows that  $\text{Li}_{2(g)}$  has a bond order of 1, while  $\text{Be}_{2(g)}$  has no net bonding character.

### PROBLEM 10.

- a). In a 100 g sample:

40.02 g is C: this is equivalent to  $(40.02/12.011) = 3.332$  moles of C atoms

6.75 g is H: equivalent to  $(6.75/1.00797) = 6.697$  moles of H atoms

53.23 g is O: equivalent to  $(53.23/15.9994) = 3.327$  moles of O

Ratio (C:H:O) = 1.001 : 2.013: 1, therefore the empirical formula is  $\text{CH}_2\text{O}$ .

- b).  $\Delta T_f = K_f M$ , where  $\Delta T_f$  is the freezing-point depression and  $M$  is the molality of the solution. First step is to determine the solution's molality:

$$\Delta T_f = 6.60 - 2.02 = + 4.58 \text{ }^\circ\text{C}$$

$$M = \Delta T_f / K_f, \text{ so } M = 0.229 \text{ mol kg}^{-1}.$$

Next step is to determine the solvent mass:

$$\text{Mass of solution} = \text{density} \times \text{vol} = 0.777 \text{ g mL}^{-1} \times 500 \text{ mL} \times 10^{-3} \text{ kg g}^{-1} = 0.3885 \text{ kg}$$

$$\text{Mass of solute} = \text{density} \times \text{vol} = 10.44 \text{ g (or } 0.01044 \text{ kg)}$$

$$\text{Mass of solvent} = 0.3885 - 0.01044 \text{ kg} = 0.3781 \text{ kg}$$

Molality is defined as the moles of solute divided by the mass of solvent, so:

$$\text{moles (X)} = 0.229 \text{ mol kg}^{-1} \times 0.3781 \text{ kg} = 8.66 \times 10^{-2} \text{ moles}$$

Mass (X) divided by moles (X) yields the molar mass:

$$M_r(\text{X}) = 10.44 \text{ g} / 8.66 \times 10^{-2} \text{ moles} = 120.6 \text{ g mol}^{-1}.$$

Now, using the molar mass of the 'formula unit'  $\text{CH}_2\text{O}$  as  $30.03 \text{ g mol}^{-1}$ , we obtain a formula for X of  $(\text{CH}_2\text{O})_{4.02}$ , i.e.  $\text{C}_4\text{H}_8\text{O}_4$ .

- c). Solution to this problem is largely analogous to that for b): the chief difference is that, in a polar solvent such as water, ionization might be expected. This possibility (of dissociation into ions) necessitates the use of the formula  $\Delta T_f = i K_f M$ , where the factor  $i$  indicates the mean number of dissociated fragments produced per solute molecule.

$$\Delta T_f = 0.0 - 3.54 = + 3.54 \text{ }^\circ\text{C}$$

$$i M = \Delta T_f / K_f = 3.54 / 1.86 = 1.903 \text{ mol kg}^{-1}.$$

$$\text{Mass of solvent} = (500 \text{ mL} \times 1.005 \text{ g mL}^{-1}) - (50 \text{ mL} \times 1.044 \text{ g mL}^{-1}) = 450.3 \text{ g}$$

Using  $M_r(\mathbf{X})$  obtained in b), we determine that 50 mL of  $\mathbf{X}$  is equivalent to 0.433 moles.

$$M = 0.433 \text{ moles} / 0.4503 \text{ kg} = 0.961 \text{ mol kg}^{-1}.$$

We can now evaluate the 'dissociation factor'  $i$ :

$$i = 1.903/0.961 = 1.980.$$

Thus, the dissociation of  $\mathbf{X}$  into two fragments appears virtually quantitative in aqueous solution. Alternatively, if we assume that  $i = 1$ , we can say that the molar mass of  $\mathbf{X}$  obtained by this method is  $120.6 \text{ g mol}^{-1} / 1.980 = 60.9 \text{ g mol}^{-1}$ .

- d). First, calculate the number of moles of hydroxide consumed by this reaction:

$$\text{Moles (OH}^{-}) = 1.247 \text{ mol L}^{-1} \times 33.60 \times 10^{-3} \text{ L} = 4.190 \times 10^{-2} \text{ moles}.$$

Now, since the reaction is monitored by pH, we can assume that this is in some sense an acid-base titration. Therefore, the number of moles of  $\text{OH}^{-}$  have reacted with an equal quantity of  $\text{H}^{+}$ , yielding water. (This argument is necessary to help determine the mass of solvent):

$$\text{Mass of solution} = \text{vol.} \times \text{density} = 58.50 \text{ mL} \times 1.003 \text{ g mL}^{-1} = 58.68 \text{ g}$$

$$\text{Mass of solute} = (\text{mass of } \mathbf{Y}^{i-}) + (\text{mass of } \text{Na}^{+})$$

$$\text{Mass of } \mathbf{Y}^{i-} = \text{mass}(\mathbf{X}) - \text{molar mass}(\text{H}^{+}) \times \text{moles}(\text{OH}^{-})$$

$$= (25.00 \text{ mL} \times 1.044 \text{ g mL}^{-1} \times 0.1^{*}) - 1.00797 \text{ g mol}^{-1} \times 0.0419 \text{ moles} = 2.57 \text{ g}$$

$$\text{Mass of } \text{Na}^{+} = 22.990 \times 0.0419 \text{ moles} = 0.96 \text{ g}$$

$$\text{So mass of solvent} = 58.68 \text{ g} - (2.57 \text{ g} + 0.96 \text{ g}) = 55.15 \text{ g}.$$

Now, using  $iM = \Delta T_f / K_f$ , we obtain:

$$iM = 2.78 \text{ }^{\circ}\text{C} / 1.86 \text{ }^{\circ}\text{C kg mol}^{-1} = 1.495 \text{ mol kg}^{-1}.$$

The parameter  $iM$  represents the number of moles of dissolved species per kg of water. These dissolved species are  $\text{Na}^{+}$  and  $\mathbf{Y}^{i-}$ . By multiplying through by the mass of solvent, we obtain

$$\text{moles}(\text{Na}^{+}) + \text{moles}(\mathbf{Y}^{i-}) = 1.495 \text{ mol kg}^{-1} \times 5.515 \times 10^{-2} \text{ kg} = 8.24 \times 10^{-2} \text{ moles}.$$

We have already determined  $\text{moles}(\text{Na}^{+}) = \text{moles}(\text{OH}^{-})$  consumed, so

$$\text{moles}(\mathbf{Y}^{i-}) = 8.24 \times 10^{-2} \text{ moles} - 4.19 \times 10^{-2} \text{ moles} = 4.05 \times 10^{-2} \text{ moles}.$$

Since  $\text{moles}(\mathbf{Y}^{i-}):(\text{Na}^{+}) = 1:1.03$ , we determine from the freezing-point analysis that the salt formed has the formula  $\text{Na}^{+}\mathbf{Y}^{i-}$ . By comparing the mass of  $\mathbf{Y}^{i-}$  (found

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\* 0.1 = dilution factor [50 mL  $\mathbf{X}$  diluted to 500 mL, in c)]

above) with moles ( $\text{Y}^{i-}$ ), we obtain  $\text{Mr}(\text{Y}^{i-}) = 64.4 \text{ g mol}^{-1}$  which compares with  $\text{Mr}(\text{C}_2\text{H}_3\text{O}_2^-) = 59.0 \text{ g mol}^{-1}$ .

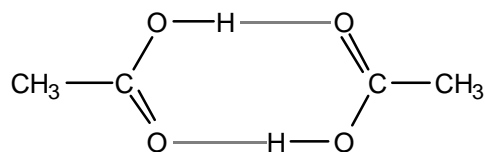
We can conclude that the salt formed is  $\text{Na}^+\text{C}_2\text{H}_3\text{O}_2^-$ .

Note that if, as suggested from b), the formula of **X** is  $\text{C}_4\text{H}_8\text{O}_4$ , there should be  $(25.00 \text{ mL} \times 1.044 \text{ g mL}^{-1} \times 0.1 / 120.6 \text{ g mol}^{-1} = ) 2.16 \times 10^{-2}$  moles of **X** present. Therefore, conversion of  $\text{C}_4\text{H}_8\text{O}_4$  into  $2(\text{C}_2\text{H}_3\text{O}_2^-)$  is essentially quantitative.

- e). The results of b) and c) appear in disagreement: cyclohexane suggests a molecular mass twice that obtained when water is the solvent. This could be resolved if **X** were to dissociate fully into two ions in aqueous solution: so perhaps **X** is a strong acid. However, strong acids are relatively rare in organic chemistry. Furthermore, we would not expect a strong acid to dissolve readily in a nonpolar solvent such as cyclohexane! The results of d) suggest a further problem: both of the 'dissociation products' of **X**, in aqueous solution, are apparently converted into  $\text{C}_2\text{H}_3\text{O}_2^-$ . How is this possible, if the two products are oppositely-charged ions?

An alternative explanation, and that which offers a better account of the chemistry occurring, is that the 'dissociated form' of **X** in  $\text{H}_2\text{O}$ , in part c), is a neutral species which is capable of reacting as an acid (as in d)). The calculated molar mass of this "dissociated neutral" species is  $60.9 \text{ g mol}^{-1}$ , which compares with  $60.1 \text{ g mol}^{-1}$  expected for  $\text{C}_2\text{H}_4\text{O}_2$ . There are few isomers of  $\text{C}_2\text{H}_4\text{O}_2$ , and the one which is most capable of acting as an acid is acetic acid (ethanoic acid),  $\text{CH}_3\text{COOH}$ .

So why does **X** apparently give 2 molecules of acetic acid in aqueous solution? This is best answered by considering that **X** doesn't dissociate in aqueous solution: rather, it dimerizes in cyclohexane. The hydrogen-bonded acetic acid dimer



is symmetrical and therefore non-polar, and therefore soluble in a non-polar solvent such as cyclohexane.

## PROBLEM 11.

- a). The free-energy change is obtained using  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ .

$$\Delta H^\circ = \Delta H_f^\circ(\text{H}) + \Delta H_f^\circ(\text{HD}) - \Delta H_f^\circ(\text{H}_2) - \Delta H_f^\circ(\text{D}) = -3.43 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = S^\circ(\text{H}) + S^\circ(\text{HD}) - S^\circ(\text{H}_2) - S^\circ(\text{D}) = +4.48 \text{ J mol}^{-1} \text{ K}^{-1}$$

so at 20 K,  $\Delta G^\circ = -3.52 \text{ kJ mol}^{-1}$ ; at 1000 K,  $\Delta G^\circ = -7.91 \text{ kJ mol}^{-1}$ .

The reaction is spontaneous in the forward direction at both temperatures. [In fact, since  $\Delta H^\circ$  is negative and  $\Delta S^\circ$  is positive, the forward reaction should be spontaneous at all temperatures.]

- b).  $\Delta H^\circ$  is negative in the forward direction: thus the bond strength of HD exceeds that of  $H_2$ . This is in accordance with the general trend, mentioned above, for light-isotope species to have slightly weaker bonds.

$\Delta S^\circ$  is positive in the forward direction, indicating that the products are less ordered than the reactants. The increase in disorder can be understood as arising from the possibility of forming either of two identical HD molecules (involving one or other of the two identical H atoms) from the one possible  $H_2$  molecule.

- c). The conversion of HD to  $D_2$  should be associated with a negative enthalpy change, since the bond strength of  $D_2$  should exceed that of HD (heavier isotopes give stronger bonds). The entropy change in the forward direction will also be negative, since (by analogy with the arguments raised above) HD is more disordered than  $D_2$ . Assuming the magnitudes of  $\Delta H^\circ$  and  $\Delta S^\circ$  are equal to those in a) [i.e.  $\Delta H^\circ = -3.43 \text{ kJ mol}^{-1}$ ;  $\Delta S^\circ = -4.48 \text{ J mol}^{-1} \text{ K}^{-1}$ ], we get

$$\Delta G^\circ = -3.34 \text{ kJ mol}^{-1} \text{ at } 20 \text{ K}, \Delta G^\circ = +1.05 \text{ kJ mol}^{-1} \text{ at } 1000 \text{ K}.$$

Thus the forward reaction is spontaneous at 20 K, but the reverse reaction becomes spontaneous at 1000 K.

- d). I). Since equilibrium (1) always lies towards the right hand side regardless of temperature, it is plain that atomic D cannot be the most abundant form of deuterium. Intuition would suggest that HD will predominate over  $D_2$  if the overall deuterium abundance is low, but a more rigorous examination is possible:

If the equilibrium (2) is reversed, then in combination with (1) this yields



or, with cancellations,



The free-energy change for this equilibrium is  $\Delta G^\circ(3) = \Delta G^\circ(1) - \Delta G^\circ(2)$ ; from the calculations in a) and c), we can estimate this to be  $\Delta G^\circ(3) = -0.18 \text{ kJ mol}^{-1}$ . Since  $\Delta G^\circ(3)$  is negative, the equilibrium must lie towards the right-hand side: therefore HD will indeed predominate over  $D_2$ .

- ii). The above argument also applies to the case where  $n(D) = n(H)$ , so HD will still predominate over  $D_2$ . Also, since equilibrium (3) lies towards the right-hand side, HD will also be the dominant form of hydrogen.

**PROBLEM 12.**

- a). Neutral helium has 2 electrons; a 'hydrogen-like' species has only one electron. Therefore, the species in question is  $\text{He}^+$ .
- b). The hydrogen spectrum obeys the relation

$$\Delta E = R_H \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

and so, in the present case, the  $\text{He}^+$  lines should obey

$$\Delta E = R_{\text{He}^+} \left( \frac{1}{4^2} - \frac{1}{n_f^2} \right)$$

which, with  $\Delta E = h\nu = hc / \lambda$ , may be rearranged to yield

$$R_{\text{He}^+} = (hc / \lambda) \left( \frac{1}{4^2} - \frac{1}{n_f^2} \right)^{-1}.$$

We must now attempt to fit the spectrum to such a relation. Assume that the longest wavelength observed, 6558 Å (which is the least energetic transition) corresponds to  $n_f = 5$ ; we obtain

$\lambda$	$n_f$	" $R_{\text{He}^+}$ "
$6.558 \times 10^{-7}$	5	$1.35 \times 10^{-17} \text{ J}$
$5.410 \times 10^{-7}$	6	$1.06 \times 10^{-17} \text{ J}$
$4.858 \times 10^{-7}$	7	$0.97 \times 10^{-17} \text{ J}$
$4.540 \times 10^{-7}$	8	$0.93 \times 10^{-17} \text{ J}$
$4.338 \times 10^{-7}$	9	$0.91 \times 10^{-17} \text{ J}$

If the assignment is correct, all transitions should yield the same  $R_{\text{He}^+}$  value. Clearly, this is not the case: we must try again.

If we choose  $n_f = 6$  for the 6558 Å transition, we get

$\lambda$	$n_f$	" $R_{\text{He}^+}$ "
$6.558 \times 10^{-7}$	6	$8.72 \times 10^{-18} \text{ J}$
$5.410 \times 10^{-7}$	7	$8.72 \times 10^{-18} \text{ J}$
$4.858 \times 10^{-7}$	8	$8.72 \times 10^{-18} \text{ J}$
$4.540 \times 10^{-7}$	9	$8.72 \times 10^{-18} \text{ J}$
$4.338 \times 10^{-7}$	10	$8.72 \times 10^{-18} \text{ J}$

This is the correct assignment, as is evident from the constancy of the  $R_{\text{He}^+}$  value obtained.

- c).  $\text{IE}(\text{He}^+)$  is equal to  $R_{\text{He}^+}$ . To convert this into electronvolts, multiply by  $6.02205 \times 10^{23} \text{ mol}^{-1}$  and divide by  $96486 \text{ J mol}^{-1} \text{ eV}^{-1}$ :  $\text{IE}(\text{He}^+) = 54.44 \text{ eV}$ .

- d).  $\text{IE}(\text{He}^+) / \text{IE}(\text{He}) = 2.180$ , so  $\text{IE}(\text{He}) = 24.97 \text{ eV}$ .

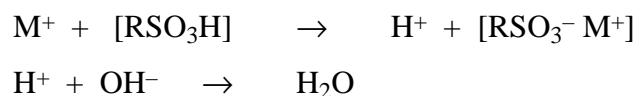
Thus  $\text{AE}(\text{He}^{2+}) = 79.41 \text{ eV} \equiv 1.272 \times 10^{-17} \text{ J}$ .

We can calculate the frequency,  $\nu = E/h = 1.920 \times 10^{16} \text{ s}^{-1}$ , and the wavelength,  $\lambda = c/\nu = 15.61 \text{ nm}$ , of the least energetic photon capable of the double-ionization. This is clearly a much shorter wavelength than the visible spectrum ( $300 \text{ nm} < \lambda < 700 \text{ nm}$ ): the sun isn't a hot enough 'black body' to produce many such photons, and most would be absorbed by the atmosphere before they reached the surface.

### PROBLEM 13.

- a). The student is essentially seeking to determine the molar mass of each sample,  $M_r(\text{MX})$ , by exchanging  $\text{M}^+$  with  $\text{H}^+$  from the ion-exchange column and by determining the quantity of  $\text{H}^+$  by titration.

Reactions involved are:



- b). Analysis of results:

moles  $\text{M}^+$  in 0.5 g = moles  $\text{OH}^- \times (250 \text{ mL} / 50 \text{ mL}) \times (100 \text{ mL} / 40 \text{ mL})$   
 = titre volume  $\times 0.0326 \text{ mol L}^{-1} \times 5 \times 2.5$

$M_r(\text{MX}) = \text{sample mass (0.5 g)} / \text{moles } \text{M}^+ \text{ in 0.5 g}$

This yields the following:

Sample	$M_r / \text{g mol}^{-1}$	Possible MX
A	58.01	NaCl(58.44), KF(58.10)
B	41.88	LiCl(42.39), NaF(41.99)
C	165.81	KI(166.00), RbBr(165.37), CsCl(168.36)
D	57.88	NaCl(58.44), KF(58.10)
E	119.13	KBr(119.00), RbCl(120.92)
F	42.09	LiCl(42.39), NaF(41.99)
KBr	119.71	KBr(119.00), RbCl(120.92)

A problem should be evident with the above results: some aspect of the experimental technique is apparently too inaccurate to identify the salts

unambiguously. For example, if all the samples are indeed different, and if the sample labelled 'KBr' is indeed KBr, then sample E must be RbCl. The molar mass of RbCl is significantly above that of KBr, yet sample E has the lower  $M_r$  according to the titration results. Note that the near-coincidences in molar mass for two (or even three) alkali halides precludes positive identification of A, B, C, D, or F.

- c). Watchglasses: Lithium salts are very hygroscopic, so leaving a small amount of (e.g.) 'B' and 'F' on adjacent watchglasses should allow identification of the lithium chloride: it'll form a puddle in a short time (unless the laboratory's atmosphere is very dry).

Litmus paper: Fluoride ion is the conjugate base of a weak acid (HF), so fluoride salts form alkaline solutions. Thus, litmus should identify a dilute solution of either 'B' or 'F' as NaF, and 'A' or 'D' as KF.

Acidified persulfate + starch: Persulfate oxidizes  $I^-$  to  $I_2$ , which forms a dark blue complex with starch solution. Thus, if 'C' is KI, it will give a deep blue starch complex. Persulfate will also oxidize  $Cl^-$  or  $Br^-$ , but these won't give the characteristic indication with starch: so this reagent won't distinguish RbBr and CsCl. (However, since the student was able to identify 'C' using the techniques listed, it implies that 'C' was indeed KI).

There are no tests here for NaCl: by elimination, whichever of 'A' and 'D' does not turn litmus blue is the NaCl.

- d). The property which precludes unambiguous identification on the basis of ion exchange is the occurrence of near-coincidences in the molar masses of different alkali halides MX. This arises because these compounds are uni-univalent, and also because the alkali metals are only two atomic numbers higher than the preceding halogen atoms: thus, subtracting a filled shell from a metal (e.g.  $K \rightarrow Na$ ) and adding a filled shell to a halogen (e.g.  $F \rightarrow Cl$ ) yields a compound having a molar mass nearly identical to the initial compound.

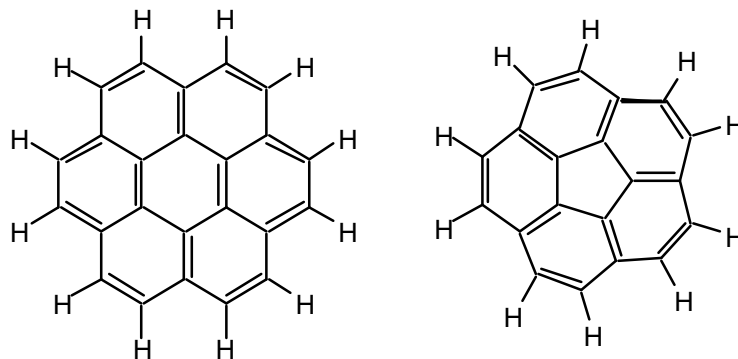
Alkaline earth halides won't have this problem (as a general rule), provided both halogen atoms X are the same: subtracting a filled shell from M (e.g.  $Ca \rightarrow Mg$ ) and adding a filled shell to each X (eg  $F \rightarrow Cl$ ) gives quite different molar masses (78.08 and 95.21 g mol<sup>-1</sup> respectively, for CaF<sub>2</sub> and MgCl<sub>2</sub>).

## PROBLEM 14.

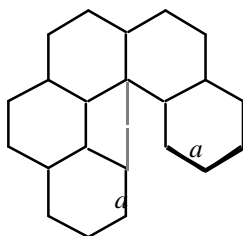
- a). Cubane appears to possess six rings, corresponding to the six faces of a cube.

- b).  $m = 2(n + 1 - r - d)$ . Cursory inspection of a few simple examples (methane, ethene, ethyne, benzene) should suffice to demonstrate this.
- c). For  $n = 8$ ,  $r = 6$ ,  $d = 0$ , a value for  $m = 6$  is returned (i.e.  $C_8H_6$ ). However, cubane is clearly  $C_8H_8$ .
- d). Coronene:  $n = 24$ ,  $r = 7$ ,  $d = 12$ , yielding  $m = 12$  (i.e.  $C_{24}H_{12}$ )  
 Corannulene:  $n = 20$ ,  $r = 6$ ,  $d = 10$ , yielding  $m = 10$  (i.e.  $C_{20}H_{10}$ ).

These values are consistent with the expected structures:



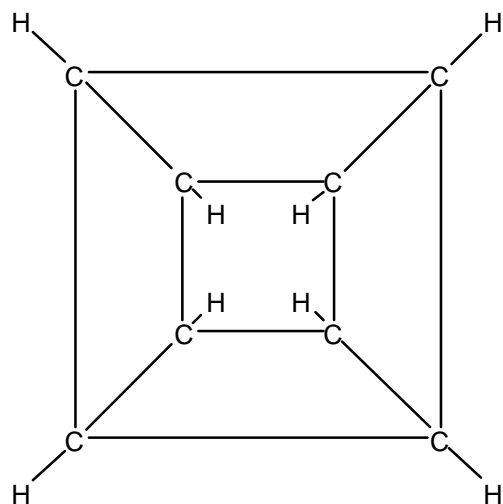
- e). Corannulene ( $C_{20}H_{10}$ ) is not flat. If you consider the bonds which radiate out from the central pentagon as 'spokes', then the preferred angle between two spokes is  $60^\circ$  (as dictated by the geometry of a regular hexagon). However, a 'ring' of five regular hexagons



can only subtend an angle of  $300^\circ$ : five hexagons are insufficient to complete the ring in planar space. Joining the sides labelled 'a' achieves closure of the corannulene skeleton, but makes the overall molecule somewhat bowl-shaped.

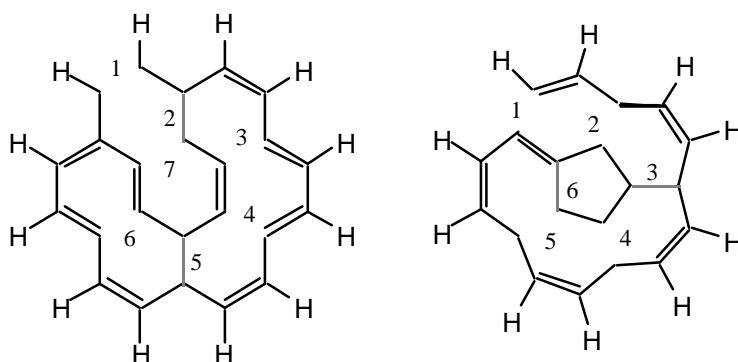
- f). Flattened cubane:



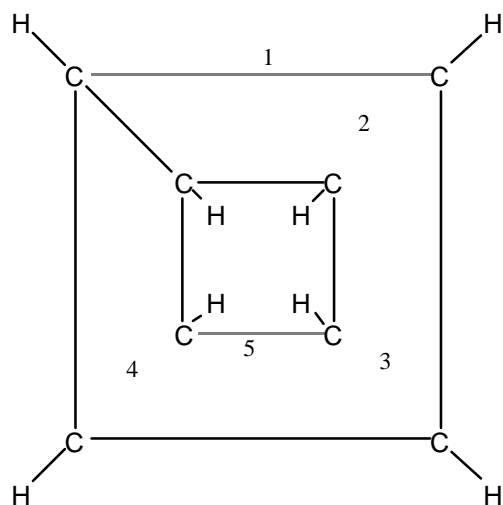


Cubane, drawn in this manner, can be seen to contain five rings. Using  $r = 5$  yields  $C_8H_8$ , in agreement with b) but in dispute with a).

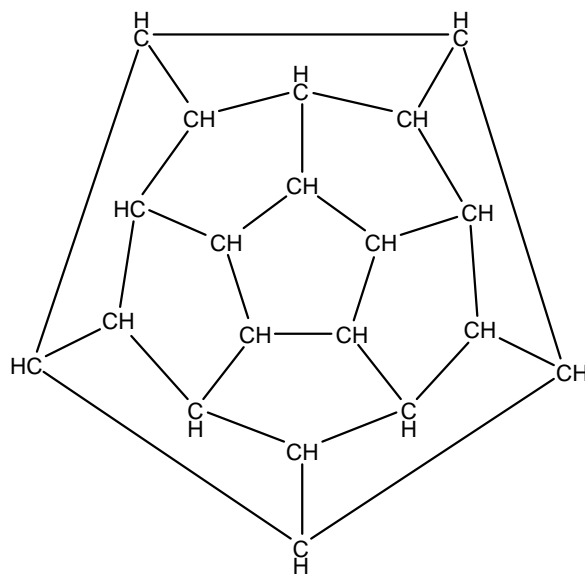
- g). Seven carbon-carbon bonds can be broken in coronene; six in corannulene. The number of bonds which may be broken without fragmenting the molecule is equal to the number of rings.



- h). Five bonds can be broken in cubane. Therefore cubane has five rings, in agreement with b) and f) but in disagreement with a).



- i). Dodecahedrane features 11 rings. This yields the correct chemical formula of  $C_{20}H_{20}$  upon implementation of  $m = 2(n + 1 - r - d)$ .



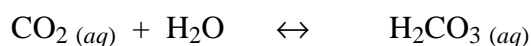
- j). Sixty C atoms, each with 3 nearest neighbours, yields 90 C-C bonds ( $60 \times 3$  yields double the number – this effectively counts each bond twice). Each C atom has a valence requirement for 4 bonds – so one bond to each C must be double. Therefore  $d = 30$  (again, each bond has two ends!). From the formula, we know that  $n = 60$  (C atoms) and  $m = 0$  (H atoms), so  $r$  (rings) must be 31.

If 12 rings are pentagons, then 19 rings must be hexagons. However, by analogy with the other cage structures (cubane and dodecahedrane), or by inspection of a soccerball, it can be seen that  $C_{60}$  possesses 32 faces (in a geometric sense), and that 20 of these faces are hexagons. One of the faces on the  $C_{60}$  surface does not correspond to a 'true ring', but any assignment of either a pentagon or a hexagon as the 'illusory' ring is quite arbitrary. We *can't* state unambiguously how many pentagonal or hexagonal rings are present!

### PROBLEM 15.

- a).  $CO_2(g) \rightleftharpoons CO_2(aq)$  (1)  
 $CO_2(aq) + H_2O \rightleftharpoons HCO_3^-(aq) + H^+(aq)$  (2)  
 $HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$  (3)

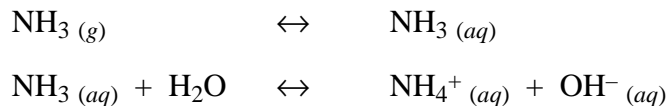
Note that an additional equilibrium



can be introduced to account for the separate existence of dissolved  $CO_2$  and aqueous carbonic acid, but such an equilibrium is not strictly necessary to explain the reaction chemistry of carbonate in water.

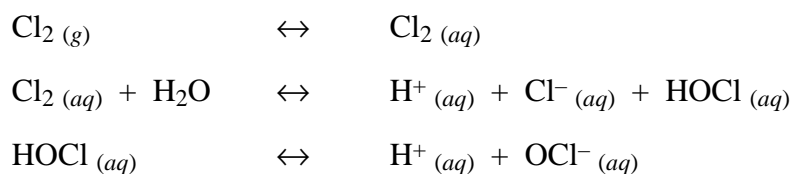
Since equilibrium will be established between the left and right hand side of each reaction, and since we are starting from  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}$ , the resulting solution will clearly be acidic.

- b).  $\text{NH}_3$  is a basic gas:



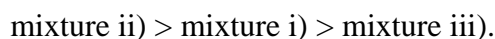
so an acid-base reaction will be established, pulling the equilibria (2) and (3) towards the right hand side. This will increase the tendency for atmospheric  $\text{CO}_2$  to dissolve.

$\text{Cl}_2$  is an acidic gas:



The increase in  $[\text{H}^+]$  engendered by these reactions will drive the equilibria (2) and (3) back towards the left hand side. This will decrease the tendency for atmospheric  $\text{CO}_2$  to dissolve.

Thus the tendency for  $\text{CO}_2$  to dissolve is:



- c). Acetate,  $\text{CH}_3\text{COO}^-$ , is the conjugate base of a weak acid:



The sodium acetate solution is significantly alkaline, and will pull each of the  $\text{CO}_2$  equilibria towards the right hand side.

The hydrochloric acid solution will drive the  $\text{CO}_2$  equilibria back towards the left hand side.

Thus the tendency for  $\text{CO}_2$  to dissolve is:



- d). The concentration of aqueous  $\text{CO}_2$  is given by Henry's law:

$$\begin{aligned} [\text{CO}_2(aq)] &= K_H P(\text{CO}_2) = 3.39 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1} \times 3.5 \times 10^{-4} \text{ atm} \\ &= 1.187 \times 10^{-5} \text{ mol L}^{-1}. \end{aligned}$$

It will be helpful to convert  $K_b$  values to  $K_a$ , using  $K_a = K_w / K_b$  at 25 °C:

$$K_a(\text{CO}_2(aq)) = 4.46 \times 10^{-7}$$

$$K_a(\text{HCO}_3^- \text{ (aq)}) = 4.67 \times 10^{-11}.$$

These  $K_a$  values are defined as:

$$K_a(\text{CO}_2 \text{ (aq)}) = 4.46 \times 10^{-7} = \frac{[\text{HCO}_3^-] [\text{H}^+]}{[\text{CO}_2 \text{ (aq)}]}$$

$$K_a(\text{HCO}_3^- \text{ (aq)}) = 4.67 \times 10^{-11} = \frac{[\text{CO}_3^{2-}] [\text{H}^+]}{[\text{HCO}_3^-]}$$

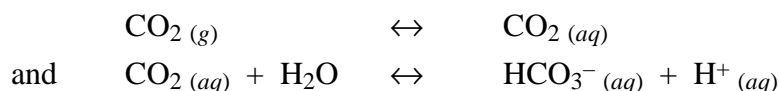
Since  $K_a(\text{CO}_2 \text{ (aq)}) \gg K_a(\text{HCO}_3^- \text{ (aq)})$ , we assume that in acidic solution only the first deprotonation equilibrium is significant (we can test this, once we've found  $[\text{H}^+]$ ). Therefore,

$$[\text{H}^+] = [\text{HCO}_3^-] = (4.46 \times 10^{-7} \times 1.187 \times 10^{-5})^{0.5} = 2.30 \times 10^{-6} \text{ mol L}^{-1}.$$

i.e. pH = 5.64.

Now, using  $[\text{H}^+] = [\text{HCO}_3^-] = 2.30 \times 10^{-6} \text{ mol L}^{-1}$ , we can see  $[\text{CO}_3^{2-}] \sim 4.67 \times 10^{-11} \text{ mol L}^{-1}$ . Thus, the degree of dissociation of  $\text{HCO}_3^-$  to  $\text{H}^+$  and  $\text{CO}_3^{2-}$  is very slight, and our assumption (that the second deprotonation equilibrium is insignificant in this case) is correct.

- e). It should be intuitively apparent that 1 atm of  $\text{CO}_2 \text{ (g)}$  will produce a substantially more acidic solution than will 350 ppm  $\text{CO}_2 \text{ (g)}$ : thus, for reasons analogous to those presented in d), we need consider only the equilibria



in solving this problem.

$$[\text{CO}_2 \text{ (aq)}] = K_H P(\text{CO}_2) = 3.39 \times 10^{-2} \text{ mol L}^{-1},$$

$$\text{and } [\text{H}^+] = [\text{HCO}_3^-] = (K_a [\text{CO}_2 \text{ (aq)}])^{0.5} = 1.23 \times 10^{-4} \text{ mol L}^{-1}$$

i.e. pH = 3.91.

- f). This is a weak (diprotic) acid / strong base titration.

We need, first, to determine the total  $[\text{CO}_2 \text{ (aq)}]$ :

$$\text{Total } [\text{CO}_2 \text{ (aq)}] = [\text{CO}_2 \text{ (aq)}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

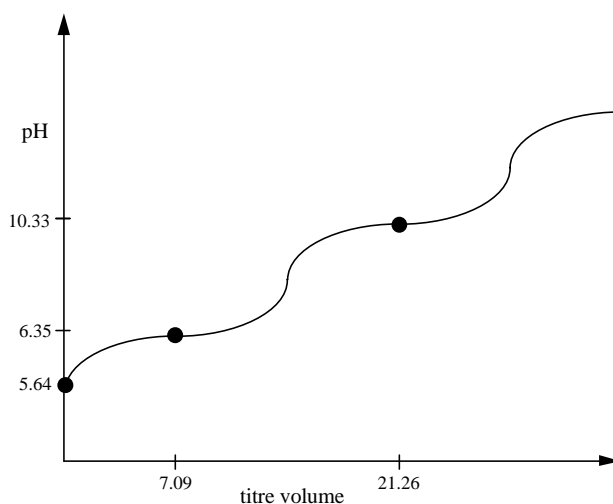
$$= (1.187 \times 10^{-5}) + (2.30 \times 10^{-6}) + (4.67 \times 10^{-11}) \text{ mol L}^{-1} = 1.417 \times 10^{-5} \text{ mol L}^{-1},$$

and so the 100 mL aliquot contains  $1.417 \times 10^{-6}$  moles of the weak diprotic acid  $\text{CO}_2 \text{ (aq)}$  and its assorted conjugate bases. This will require  $2.834 \times 10^{-6}$  moles of  $\text{OH}^-$  for complete neutralization, i.e. 28.34 mL of  $1.00 \times 10^{-4} \text{ mol L}^{-1}$  NaOH.

At the start of the titration, pH = 5.64 from d).

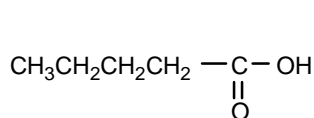
At 7.1 mL (the first half-equivalence point),  $\text{pH} = \text{p}K_{\text{a}}(\text{CO}_2(\text{aq})) = 6.35$

At 21.2 mL (the half-equivalence point for the second deprotonation),  $\text{pH} = \text{p}K_{\text{a}}(\text{HCO}_3^-) = 10.33$ .

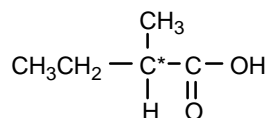


### PROBLEM 16.

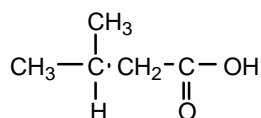
a). There are four different structural isomers:



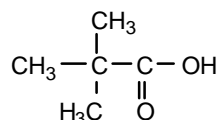
pentanoic acid



2-methylbutanoic acid



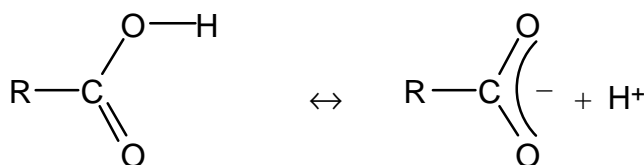
3-methylbutanoic acid



2,2-dimethylpropanoic acid

2-methylbutanoic acid will be optically active.

b). Acidity involves dissociation to form a carboxylate anion:



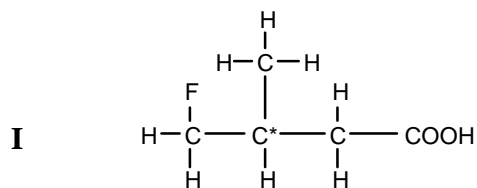
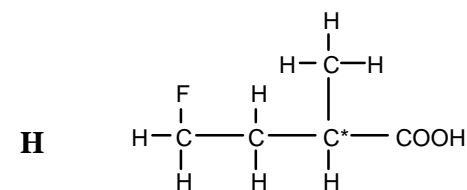
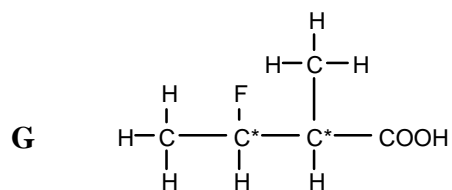
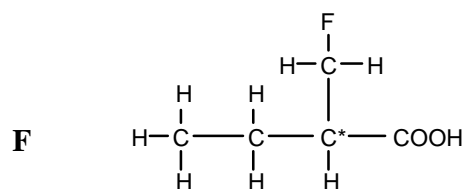
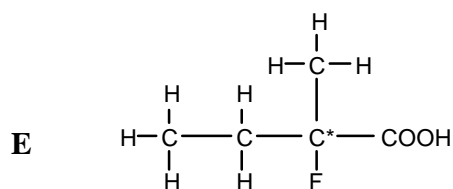
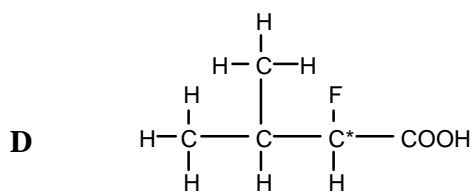
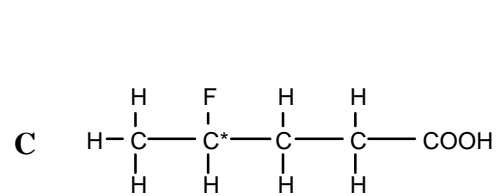
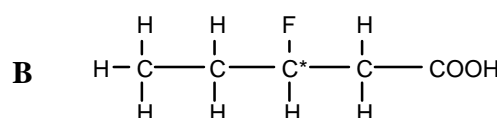
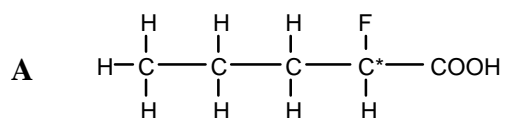
The position of the equilibrium thus depends on the stability of the anion  $\text{RCOO}^-$ . Since alkyl groups are inductive donors of electron density, the more branched structures will have the lower  $K_{\text{a}}$  values. Expected order of  $K_{\text{a}}$  (highest to lowest):

pentanoic acid (no branching on alkyl chain)

- 3-methylbutanoic acid (methyl sidechain on  $\beta$  carbon; weakly inductively destabilized)
- 2-methylbutanoic acid (methyl sidechain on  $\alpha$  carbon; more inductively destabilized)
- 2,2-dimethylpropanoic acid (two methyl sidechains on  $\alpha$  carbon; most inductively destabilized)

We can also compare these with the literature values (i.e., are the above arguments valid?). In the acid order given above, pKa values are 4.76, 4.76, (not known), 5.04, essentially in agreement with the results expected from the inductive effect.

c). There are 9 structural isomers of this type (several others are not optically active):

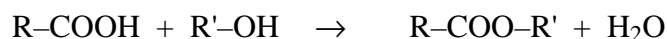


Fluorine is inductively electron withdrawing, and so proximity of the fluorine atom to the carboxylate group will stabilize the conjugate base (and increase the acid's strength).

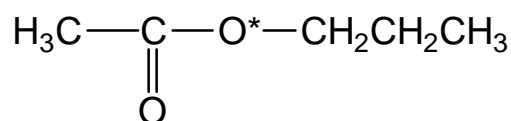
The most acidic species will be **A**, which has the fluorine  $\alpha$  to the carboxylic acid (maximum stabilization by F) and has no alkyl sidechains (minimum destabilization by methyl groups).

The least acidic of the optically-active species is **H**, which has the fluorine  $\gamma$  to the COOH group (minimum inductive donation from F to COO<sup>-</sup>) and which also has a methyl group  $\alpha$  to the COOH (maximum inductive withdrawing from COO<sup>-</sup>).

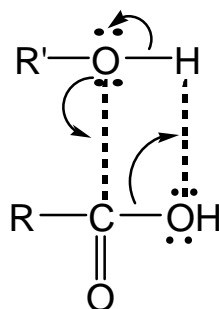
- d). This reaction produces an ester:



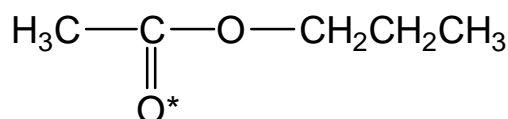
- e). The labelled ester is:



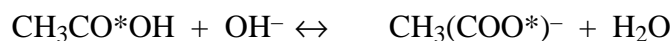
The reaction occurs as nucleophilic attack of the carboxyl carbon:



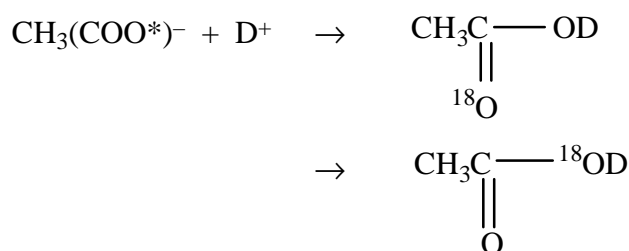
- f). i). The expected product is



ii) When ethanoic acid is added to the NaOH solution, an acid-base equilibrium is established:



The ethanoate anion has two equivalent oxygens. When the solution is re-acidified, the label is scrambled:



with the two isotopomers formed in equal amounts (provided that the ethanoic acid / hydroxide system had sufficient time to attain equilibrium). The former isotopomer will yield the same product as i); the latter will give unlabelled propyl ethanoate and labelled water (or, to be more precise, labelled HOD).

### PROBLEM 17.

- a). The volume of a sphere is  $V = (4/3) \pi r^3$ .

$$r = 3.5 \times 10^{-10} \text{ m, so } V = 1.796 \times 10^{-28} \text{ m}^3.$$

Now for the pressure:  $PV = nRT$ , so  $P = nRT / V$ .

$$n = 1 \text{ atom} = (6.02205 \times 10^{23})^{-1} = 1.661 \times 10^{-24} \text{ moles.}$$

$$\text{so } P = 2.2907 \times 10^4 \text{ kPa (i.e. 229 atmospheres)}$$

- b). First, we need the number of moles of  $C_{60}$  in 1 gram:

$$M_r(C_{60}) = 60 \times 12.011 = 720.66 \text{ g mol}^{-1}$$

$$\text{so } 1 \text{ g} \equiv 1.388 \times 10^{-3} \text{ moles.}$$

Now, we need the number of moles of  $^3\text{He}$  from 1 gram of  $C_{60}$ :

$$n = PV / RT \quad (P = 1.00 \times 10^5 \text{ Pa, } T = 298 \text{ K})$$

$$\text{so } n(^3\text{He}) = 1.00 \times 10^5 \text{ Pa} \times 1.15 \times 10^{-13} \text{ m}^3 / (8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K})$$

$$n(^3\text{He}) = 4.642 \times 10^{-12} \text{ moles / gram } C_{60}.$$

[so only one in every  $2.99 \times 10^8$  molecules of  $C_{60}$  contains a  $^3\text{He}$  atom!] We shall denote the fraction of  $C_{60}$  molecules containing  $^3\text{He}$ :  $f(^3\text{He}) = 3.34 \times 10^{-9}$ .

This corresponds to an effective mean partial pressure:

$$P_{\text{mean}}(^3\text{He}) = P(\text{He}@C_{60}) \times f(^3\text{He}) = 7.66 \times 10^{-5} \text{ kPa.}$$

Similarly for  $^4\text{He}$ , we obtain

$$n(^4\text{He}) = 8.436 \times 10^{-9} \text{ moles / gram } C_{60}, (f(^4\text{He}) = 6.08 \times 10^{-6}) \text{ and}$$

$$P_{\text{mean}}(^4\text{He}) = 0.139 \text{ kPa.}$$

- c).  $P_{\text{atm}} = 1.00 \times 10^2 \text{ kPa.}$

The atmospheric partial pressure of  $^4\text{He}$  equals total pressure  $\times$  mole fraction( $^4\text{He}$ ):

$$P(^4\text{He})_{\text{atm}} = 1.00 \times 10^2 \text{ kPa} \times 5.24 \times 10^{-6} = 5.24 \times 10^{-4} \text{ kPa.}$$

The  $^4\text{He}$  partial pressure in Earth's atmosphere is thus more than two orders of magnitude below that in the helium sample. The chemical interaction between  $^4\text{He}$  and  $C_{60}$  is essentially nonexistent, and so cannot provide a driving force

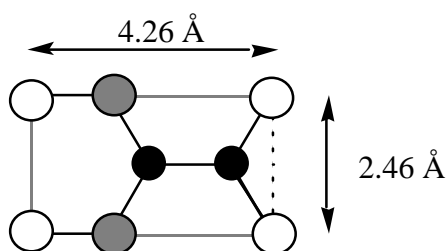


towards helium capture by  $C_{60}$ : it is difficult to understand how the mean  $^4\text{He}$  pressure within  $C_{60}$  could exceed the  $^4\text{He}$  partial pressure in the ambient atmosphere. Thus, the  $^4\text{He}$  content of the sample does not appear to support a terrestrial-atmosphere origin. [The question leaves unmentioned the possibility that Earth's atmospheric pressure was several hundred times higher at some earlier time: with the same helium content, i.e. mole fraction, a terrestrial origin for the caged helium would then be feasible. However, this is not a likely scenario!]

- d). The fullerene sample's  $^3\text{He}/^4\text{He}$  ratio is  $5.50 \times 10^{-4}:1$ , i.e. more than two orders of magnitude higher than the terrestrial atmospheric value. [Therefore, the  $^3\text{He}$  partial pressure in the fullerene sample exceeds the current terrestrial atmospheric value by a factor of  $1.12 \times 10^5$ !] The helium abundance ratio is definitely not in agreement with a terrestrial atmosphere origin for the caged helium in the fullerene. The implication is that the  $\text{He}@C_{60}$  was pre-existing within the meteorite, and survived the impact.

[As an aside, it is currently thought that the  $\text{He}@C_{60}$  within the meteorite is not only extraterrestrial in origin, but extrasolar as well: there are no environments in the solar system with a high enough helium pressure that don't also have very high pressures of  $\text{H}_2$  or other gases which inhibit fullerene formation. The best candidates (refer *Science* 272 (1996) 249) for the source of the  $\text{He}@C_{60}$  are a class of helium- and carbon-rich, hydrogen-poor red giant stars, whose outer envelopes are known to contain soot particles and which are all at least hundreds of light years distant ...]

- e). i). To determine the fullerene's surface area, we need to define a two-dimensional graphitic unit cell:



The unit cell has sides of length  $(r(\text{C}-\text{C}) \times [2 + 2\sin(30^\circ)])$  and  $(r(\text{C}-\text{C}) \times 2\cos(30^\circ))$ , respectively: thus the area of this unit cell is  $1.048 \times 10^{-19} \text{ m}^2$ .

The unit cell contains:

- 2 complete C atoms (shown in black)
- 2 half C atoms (grey)
- 4 quarter C atoms (white)
- i.e., 4 complete C atoms in total.

Therefore there is one complete C atom per  $2.62 \times 10^{-20} \text{ m}^2$ ; and, since there are  $5 \times 10^9$  C atoms, the total surface area of the fullerene is

$$A = 1.31 \times 10^{-10} \text{ m}^2.$$

The area of a sphere is  $A = 4 \pi r^2$ , so the fullerene has a radius of  $3.23 \times 10^{-6} \text{ m}$ .

The volume of a sphere is  $V = (4/3) \pi r^3$ , so  $V = 1.409 \times 10^{-16} \text{ m}^3$ .

ii). The fullerene's carbon shell has a density  $r_C = \text{mass} / V$ :

$$\text{mass} = 5.0 \times 10^9 \text{ atoms} \times 12.011 \text{ g mol}^{-1} / (6.02205 \times 10^{23} \text{ atom mol}^{-1})$$

$$\text{mass} = 9.97 \times 10^{-14} \text{ g};$$

$$\text{so } r_C = 708 \text{ g m}^{-3}.$$

The fullerene's inner helium 'atmosphere' has a density:

$$r_{\text{He}} = (P_{\text{He}} / P_{\text{atm}}) \times (M_r(\text{He}) / V_{\text{mol}}),$$

where  $V_{\text{mol}}$  is the molar volume at STP (i.e.  $2.2414 \times 10^{-2} \text{ m}^3$ ),

$$\text{so } r_{\text{He}} = 214 \text{ g m}^{-3}.$$

The total density of the fullerene is  $r_{\text{tot}} = r_C + r_{\text{He}} = 922 \text{ g m}^{-3}$ .

iii). The density of air is

$$r_{\text{air}} = M_r(\text{air}) / V_{\text{mol}} = 1294 \text{ g m}^{-3}.$$

iv). The helium-filled fullerene is less dense than air: a lighter-than-air solid!  
[Or, if you wish, a molecular helium balloon.]

## PROBLEM 18.

- a). If we denote the initial activity as  $I_0$  (i.e.  $7.0 \times 10^7 \text{ Bq mL}^{-1}$  in each case), and  $I_t$  as the activity after a time  $t$  has elapsed, then  $I_t$  is defined as  $I_t = I_0 e^{-(\ln 2 \ t / t_{1/2})}$  or  $I_t = I_0 2^{-(t / t_{1/2})}$

It will be helpful to convert all  $t_{1/2}$  values into minutes:

$$t_{1/2}({}^{67}\text{Ga}) = 78.25 \text{ hr} \times 60 \text{ min hr}^{-1} = 4.695 \times 10^3 \text{ min}$$

$$t_{1/2}({}^{68}\text{Ge}) = 287 \text{ days} \times 24 \text{ hr day}^{-1} \times 60 \text{ min hr}^{-1} = 4.133 \times 10^5 \text{ min}.$$

We can now determine i)  $I_t$ , and ii)  $I_t$  after dilution [the latter quantity is (1 / 2500) of the former]:

nuclide	$I_t$ (Bq mL <sup>-1</sup> )	$I_t$ after dilution (Bq mL <sup>-1</sup> )

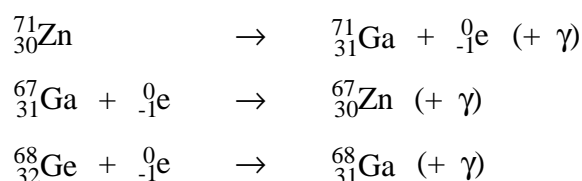
$^{71}\text{Zn}$	12100	4.83
$^{67}\text{Ga}$	$6.97 \times 10^7$	$2.79 \times 10^4$
$^{68}\text{Ge}$	$6.9996 \times 10^7$	$2.80 \times 10^4$

- b).  $^{71}\text{Zn}$  has too short a half-life to remain active for long: after 30 minutes, almost all of the activity has ceased. The count rate, especially after dilution into the patient's blood volume, is too low to give a reliable measurement. Furthermore, such a short half-life means that the nuclide needs to be synthesized for each patient: it has negligible storage time!

$^{68}\text{Ge}$  has the opposite problem: it's still almost as active after 30 minutes, and with a half-life of almost a year will remain active over a very long time. If the nuclide is retained within the patient, this means that the patient is being subjected to an unacceptably high dose of radiation over this period, with consequent dangers of cellular damage etc.

$^{67}\text{Ga}$  has a lifetime which is sufficiently long for convenience, but sufficiently short that a reliable measurement (of blood volume) can be made using a comparatively small dose of radioactive material.

c).



- d). i). The radiopharmaceutical initially contains  $(1.025 \times 10^{-2} \text{ g} / 69.72 \text{ g mol}^{-1} =) 1.47 \times 10^{-4} \text{ moles Ga}$ , and therefore contains  $(1.47 \times 10^{-4} \times 5.0 \times 10^{-7} =) 7.35 \times 10^{-11} \text{ moles of } ^{67}\text{Ga}$  (i.e.  $4.43 \times 10^{13}$  atoms of this nuclide).

For radioactive decay, first-order kinetics gives

$$\text{Rate} = I_t = k n_t(^{67}\text{Ga}),$$

(where  $I_t$  is in Becquerels and  $n_t(^{67}\text{Ga})$  is the number of atoms of  $^{67}\text{Ga}$  present at time  $t$ ),

and  $k = \ln(2) / t_{1/2}$ , where  $t_{1/2} = 78.25 \text{ hr} = 2.817 \times 10^5 \text{ s}$ .

Thus,  $k = 2.461 \times 10^{-6} \text{ s}^{-1}$  and  $I_0 = 1.09 \times 10^8 \text{ Bq}$  (in 100 mL at  $t = 0$ ).

In the 1 mL dose at  $t = 8 \text{ hr}$ ,

$$I_t = I_0 2^{-(t/t_{1/2})} \times V_{\text{dose}} / V_{\text{total}} = 1.09 \times 10^8 \text{ Bq} \times 2^{-(8/78.25)} \times 1/100$$

$$I_t = 1.015 \times 10^6 \text{ Bq}.$$

- ii). The residual activity of the 1 mL dose after a further hour would be

$$I_t = 1.015 \times 10^6 \text{ Bq} \times 2^{-(1/78.25)} = 1.006 \times 10^6 \text{ Bq}.$$

Comparison of this activity, with that observed for the 1 mL blood sample, yields the dilution factor:

$$\text{Dilution factor} = 1.006 \times 10^6 / 105.6 = 9531.$$

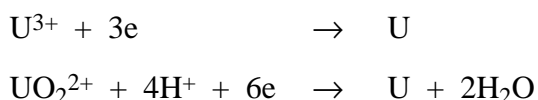
The patient's blood volume is thus 9.53 litres.

### PROBLEM 19.

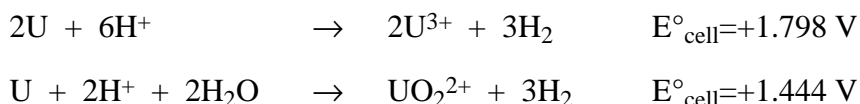
- a). Metallic uranium has an oxidation state of zero, by definition. Oxidation states for the other species: U(III) [ $\text{U}^{3+}$ ]; U(IV) [ $\text{U}^{4+}$ ]; U(V) [ $\text{UO}_2^+$ ]; U(VI) [ $\text{UO}_2^{2+}$ ].
- b). The conditions described are standard conditions, so we can use standard reduction potentials to determine in which directions the reactions are spontaneous. We must also consider the reduction step:



Two half-reactions involve metallic U:

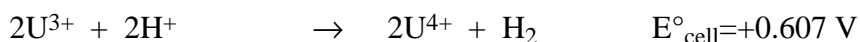


these will form the starting points for oxidation of the uranium:

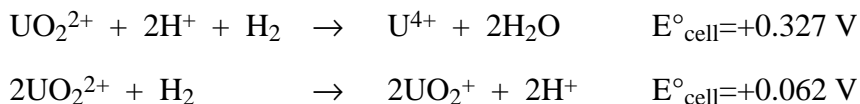


Regardless of which of these processes is favoured, neither of the 'primary products',  $\text{U}^{3+}$  or  $\text{UO}_2^{2+}$ , is the ultimate product.

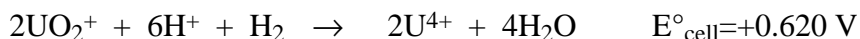
U(III) is spontaneously oxidized to U(IV):



while U(VI) is spontaneously reduced to either U(IV) or U(V):

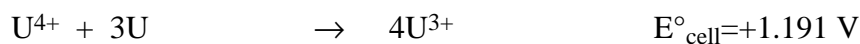


and U(V) is also spontaneously reduced to U(IV):



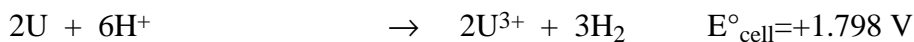
Since  $\text{U}^{4+}$  is the only species which cannot spontaneously react with  $\text{H}^+$  or  $\text{H}_2$ , this is the species which will ultimately predominate in aqueous solutions under these conditions.

[A codicil to the above is that, while metallic U is still present, the process



is favourable, but can only occur until the U is exhausted, after which time U(III) will be oxidized to U(IV) as above.]

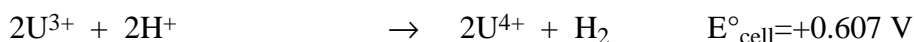
- c). Since conditions are standard except for  $[\text{H}^+] = 1.0 \times 10^{-6} \text{ mol L}^{-1}$ , we can use a simplified form of the Nernst equation as follows, for the relevant equations:



$$E_{\text{cell}} = E^\circ_{\text{cell}} - (RT / 6F) \ln([\text{H}^+]^{-6}) = +1.444 \text{ V}$$



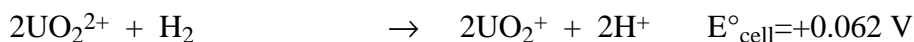
$$E_{\text{cell}} = E^\circ_{\text{cell}} - (RT / 6F) \ln([\text{H}^+]^{-2}) = +1.326 \text{ V}$$



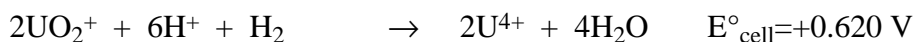
$$E_{\text{cell}} = E^\circ_{\text{cell}} - (RT / 2F) \ln([\text{H}^+]^{-2}) = 0.253 \text{ V}$$



$$E_{\text{cell}} = E^\circ_{\text{cell}} - (RT / 2F) \ln([\text{H}^+]^{-2}) = -0.027 \text{ V}$$



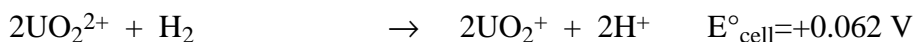
$$E_{\text{cell}} = E^\circ_{\text{cell}} - (RT / 2F) \ln([\text{H}^+]^2) = +0.293 \text{ V}$$



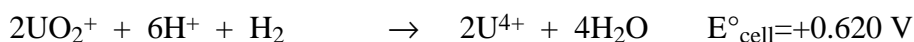
$$E_{\text{cell}} = E^\circ_{\text{cell}} - (RT / 2F) \ln([\text{H}^+]^{-6}) = -0.444 \text{ V}$$

All of the above processes have positive  $E^\circ_{\text{cell}}$  values for reaction as written in the forward direction, and so all are spontaneous in this direction at pH = 0. In contrast,  $\text{U(VI)} \rightarrow \text{U(IV)}$  and  $\text{U(V)} \rightarrow \text{U(IV)}$  are spontaneous in the *reverse* direction at pH = 6 (as indicated by the negative  $E_{\text{cell}}$  values): U(IV) is now oxidized to U(V) or U(VI). Since U(VI) is now the only oxidation state which will not react spontaneously with either  $\text{H}^+$  or  $\text{H}_2$  under these conditions, the dominant species will be  $\text{UO}_2^{2+}$ .

- d). To solve this, we need to consider only those reactions in which  $\text{UO}_2^+$  appears:



$$E_{\text{cell}} = E^\circ_{\text{cell}} - (RT / 2F) \ln([\text{H}^+]^2 P(\text{H}_2)^{-2})$$



$$E_{\text{cell}} = E^\circ_{\text{cell}} - (RT / 2F) \ln([\text{H}^+]^{-6} P(\text{H}_2)^{-2})$$

At the threshold conditions,  $E_{\text{cell}} = 0$ , which corresponds to the following cases:

$$[\text{H}^+] = \{P(\text{H}_2)^2 e^{(2FE^\circ_{\text{cell}} / RT)}\}^{1/2} \text{ for } \text{U(VI)} \leftrightarrow \text{U(V)}, \text{ and}$$

$$[\text{H}^+] = \{e^{(-2FE^\circ_{\text{cell}} / RT)} / P(\text{H}_2)^2\}^{1/6} \text{ for } \text{U(IV)} \leftrightarrow \text{U(V)}.$$

These expressions yield threshold values of:

- i).  $[H^+] < 11.2 \text{ mol L}^{-1}$ , i.e.  $\text{pH} > -1$  for U(V) to be stable against U(VI), and  
 $[H^+] < 3.19 \times 10^{-4} \text{ mol L}^{-1}$ , i.e.  $\text{pH} > 3.50$  for U(V) stable versus U(IV).
- ii).  $[H^+] < 1.12 \times 10^{-5} \text{ mol L}^{-1}$ , i.e.  $\text{pH} > 4.95$  for U(V) stable against U(VI), and  
 $[H^+] < 3.19 \times 10^{-2} \text{ mol L}^{-1}$ , i.e.  $\text{pH} > 1.50$  for U(V) stable versus U(IV).

Thus  $\text{UO}_2^+$  is seen to be stable against other oxidation states over a pH range of 3.5 – 7 (we are considering only acidic or neutral solutions) under a standard hydrogen atmosphere, but is stable against oxidation to U(VI) only at pH values greater than 4.95.

The  $\text{H}_2$  partial pressure in the atmosphere is very low, so the latter conditions (ie ii)) correspond more closely to those encountered in typical terrestrial environments.  $\text{UO}_2^+$  isn't actually as stable as its standard cell potentials would suggest.

## PROBLEM 20.

- a). The colour is due to nitrogen dioxide,  $\text{NO}_2$ . Since air is 78%  $\text{N}_2$  and 21%  $\text{O}_2$ , oxygen is the limiting reagent: if there is complete conversion of  $\text{O}_2$  to  $\text{NO}_2$  (which is very unlikely), the nitrogen oxide concentration will be:

$$\begin{aligned} [\text{NO}_2] &= 0.21 \text{ (mole \% of } \text{O}_2) / 24.484 \text{ L mol}^{-1} \text{ (molar volume at } 25^\circ\text{C -} \\ &\text{both gases are liquids at STP!)} \\ &= 8.6 \times 10^{-3} \text{ mol L}^{-1} \end{aligned}$$

- b).  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ .
- c). i). Orders for NO and  $\text{O}_2$  can be found from those measurements in which one or other concentration is held approximately constant (i.e.  $[\text{NO}]$  is essentially constant in measurements #1, 2, & 3, while  $[\text{O}_2]$  is similar for #2, 4, and 5):

Order with respect to NO:

Measurements	$[\text{NO}]$ ratio	Initial rate ratio
#4 : #2	2.01	4.03
#4 : #5	4.02	15.9
#2 : #5	2.00	3.95

The rate is observed to vary as  $[\text{NO}]^2$ : therefore the reaction is second order in NO.

Order with respect to  $\text{O}_2$ :

Measurements	$[\text{O}_2]$ ratio	Initial rate ratio
#2 : #1	1.99	1.98

#2 : #3	3.85	3.65
#1 : #3	1.93	1.84

The rate varies essentially as  $[O_2]$ : the reaction is first order in  $O_2$ , and is therefore third order overall.

ii). The rate law is

$$\text{rate} = k[NO]^2 [O_2] \quad \text{so } k = \text{rate} / ([NO]^2 [O_2]).$$

The various measurements yield the following:

Measurement	$k$
#1	$7.063 \times 10^3 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$
#2	$7.154 \times 10^3 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$
#3	$7.159 \times 10^3 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$
#4	$7.117 \times 10^3 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$
#5	$7.165 \times 10^3 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$

Mean value:  $k = 7.13 \times 10^3 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ .

- d). i). Measurements #1, 2, & 3 feature essentially the same initial  $[NO]$ , with  $[O_2]$  varying substantially: the stoichiometric excess of  $[O_2]$  over  $[NO]$  is only  $7.2 \times 10^{-6} \text{ mol L}^{-1}$  for measurement #3, but  $3.67 \times 10^{-4} \text{ mol L}^{-1}$  for measurement #2. Thus, if the reaction has not gone to completion, then the  $A_\infty:[NO]_{\text{initial}}$  ratio should vary significantly: but for all of the first three measurements, the ratio of  $A_\infty:[NO]_{\text{initial}}$  is virtually constant. Therefore the reaction has gone to completion, or near enough.

ii). Beer's law defines absorbance:

$$A = \ln(I_0/I) = \epsilon c l,$$

where  $c = [NO_2] = [NO]_{\text{initial}}$  (since reaction has gone to completion, and since NO is the limiting reagent)

and  $l = 10 \text{ cm}$ .

Using measurement #1 as an example yields

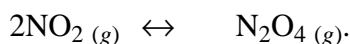
$$\epsilon = A_\infty / c l = 0.341 / (1.16 \times 10^{-4} \times 10)$$

$$= 294 \text{ L cm}^{-1} \text{ mol}^{-1}$$

- iii).  $NO_2$  is brown. Of the colours of the visible spectrum, this is closest to orange; thus, if brown is being transmitted, then the colour complement (i.e. blue) is being absorbed. This is consistent with peak absorption at about 400 nm.
- e). Compare the volume with PV:

V (mL)	PV (atm mL)
1000	2.49
500	2.45
200	2.36
100	2.25
50	2.12
20	1.92
10	1.78

PV is proportional to the number of moles of gas present in the container. Evidently, the number of moles of gas is decreasing as V decreases. This is due to the following equilibrium:



If we assume that the pressure at V = 1000 mL is due to NO<sub>2</sub> only (which is a fair initial approximation, since PV changes only slightly between 1000 and 200 mL), then we can determine P(NO<sub>2</sub>) and P(N<sub>2</sub>O<sub>4</sub>) for any other volume, since there is a conversion of 2 moles → 1 mole in going from left to right:

$$P(\text{N}_2\text{O}_4) = P(1000 \text{ mL}) \times (1000 / V) - P_{\text{tot}}$$

$$P(\text{NO}_2) = P_{\text{tot}} - P(\text{N}_2\text{O}_4).$$

For the measurement at 10 mL, for example,

$$P(\text{N}_2\text{O}_4) = 7.1 \times 10^{-2} \text{ atm}$$

$$P(\text{NO}_2) = 0.107 \text{ atm}$$

$$K_P = P(\text{N}_2\text{O}_4)/(P(\text{NO}_2)^2) = 6.20.$$

We can now use this value to test whether our hypothesis, that only NO<sub>2</sub> is present at V = 1000 mL, is correct. From  $P(\text{N}_2\text{O}_4) = 6.20 \times P(\text{NO}_2)^2$ , and assuming  $P(\text{N}_2\text{O}_4) \ll P(\text{NO}_2)$ , we get  $P(\text{N}_2\text{O}_4) = 3.84 \times 10^{-5} \text{ atm}$  (and, by subtraction from  $P_{\text{tot}}$ ,  $P(\text{NO}_2) = 2.45 \times 10^{-3} \text{ atm}$ ) at V = 1000 mL. This means we need to revise our equations for the partial pressures:

$$P(\text{N}_2\text{O}_4) = 2.53 \times 10^{-3} \text{ atm} \times (1000 / V) - P_{\text{tot}}$$

$$P(\text{NO}_2) = P_{\text{tot}} - P(\text{N}_2\text{O}_4),$$

where  $2.53 \times 10^{-3} \text{ atm}$  is  $2P(\text{N}_2\text{O}_4) + P(\text{NO}_2)$  at V = 1000 mL, i.e. the total pressure if all N<sub>2</sub>O<sub>4</sub> was converted to NO<sub>2</sub> at this volume.

We can now recalculate  $K_P$  from the V = 10 mL measurement. [Any other measurement would also serve for this purpose, but the lowest volume will have



the highest  $P(\text{N}_2\text{O}_4) : P(\text{NO}_2)$  ratio and thus the least uncertainty in  $K_P$ .] At  $V = 10 \text{ mL}$ , we now obtain

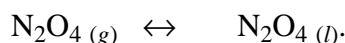
$$P(\text{N}_2\text{O}_4) = 7.5 \times 10^{-2} \text{ atm}$$

$$P(\text{NO}_2) = 0.103 \text{ atm}$$

$$K_P = P(\text{N}_2\text{O}_4)/(P(\text{NO}_2)^2) = 7.07.$$

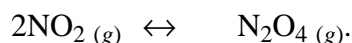
Using this revised value of  $K_P$ , for the  $V = 1000 \text{ mL}$  data, yields in turn  $P(\text{N}_2\text{O}_4) = 4.24 \times 10^{-5} \text{ atm}$  at  $1000 \text{ mL}$ . While this is somewhat higher than the value determined on the first iteration, it does not make any significant difference to the quantity  $2P(\text{N}_2\text{O}_4) + P(\text{NO}_2)$ : consequently we have arrived at a self-consistent solution, within the accuracy of the quoted measurements, of  $K_P = 7.07$ .

- f). The process responsible is the condensation of  $\text{N}_2\text{O}_4$  at sufficiently high pressure:



The pressure stabilizes because gaseous  $\text{N}_2\text{O}_4$  is in equilibrium with its liquid form, and so  $P(\text{N}_2\text{O}_4)$  cannot exceed the  $\text{N}_2\text{O}_4$  vapour pressure; equilibrium also continues to exist between  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$ , as governed by  $K_P$ , and since  $P(\text{N}_2\text{O}_4)$  is constrained,  $P(\text{NO}_2)$  is also fixed. The pressure will remain constant with continued compression [until the liquid itself begins to become compressed].

We can determine  $P(\text{N}_2\text{O}_4)$  and  $P(\text{NO}_2)$  from  $K_P$  and  $P_{\text{tot}}$ :



$$P(\text{NO}_2) = x \text{ atm}$$

$$P(\text{N}_2\text{O}_4) = (1.215 - x) \text{ atm}$$

$$K_P = 7.07 = (1.215 - x) / x^2$$

$$\Rightarrow 7.07x^2 + x - 1.215 = 0.$$

Solution of this quadratic yields  $P(\text{NO}_2) = x = 0.350 \text{ atm}$  and  $P(\text{N}_2\text{O}_4) = 0.865 \text{ atm}$  at  $V = 1 \text{ mL}$ .

The equilibrium constant for  $\text{N}_2\text{O}_4$  condensation is, by definition,  $K_P = P(\text{N}_2\text{O}_4)^{-1}$ . [The activity of pure  $\text{N}_2\text{O}_4 (l)$  is unity, and so does not appear in the equilibrium constant.] From  $P(\text{N}_2\text{O}_4) = 0.865 \text{ atm}$  in equilibrium with the liquid, we find:

$$K_P = 1.156.$$

## PROBLEM 21.

- a). The following values are obtained:

pH	$\alpha_{Y^{4-}}$	$[Y^{4-}] / \text{mol L}^{-1}$
----	-------------------	--------------------------------

2	$3.712 \times 10^{-14}$	$8.26 \times 10^{-16}$
6	$2.249 \times 10^{-6}$	$5.01 \times 10^{-8}$
10	0.3548	$7.90 \times 10^{-3}$

The anion concentrations are determined using  $C_T(\text{EDTA}) = 0.02226 \text{ mol L}^{-1}$  ( $M_r(\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8) = 292.25 \text{ g mol}^{-1}$ ).

- b). We need to determine the ratio  $[\text{MY}^{2-}] / [\text{M}^{2+}]$ , which (by the definition of the complex formation constant) has the value  $K_Y [\text{Y}^{4-}]$ . We can determine  $[\text{Y}^{4-}]$  from x determined in a). This yields values:

pH	$[\text{Y}^{4-}]$	$[\text{HgY}^{2-}] / [\text{Hg}^{2+}]$	$[\text{FeY}^{2-}] / [\text{Fe}^{2+}]$	$[\text{CaY}^{2-}] / [\text{Ca}^{2+}]$
2	$1.856 \times 10^{-16}$	$1.17 \times 10^6$	0.039	$9.28 \times 10^{-6}$
6	$1.1245 \times 10^{-8}$	$7.08 \times 10^{13}$	$2.36 \times 10^6$	562
10	$1.774 \times 10^{-3}$	$1.12 \times 10^{19}$	$3.73 \times 10^{11}$	$8.87 \times 10^7$

It can be seen that, at pH = 2, only  $\text{Hg}^{2+}$  forms a complex in essentially quantitative yield; at pH = 6, both  $\text{Hg}^{2+}$  and  $\text{Fe}^{2+}$  do so, while at pH = 10, all three metal ions form complexes with high efficiency.

- c). Since HCl is a strong acid, the equilibrium between  $\text{Hg}^{2+}$  and  $\text{Cl}^-$  should be pH-independent: we can calculate that  $[\text{HgCl}_4^{2-}] / [\text{Hg}^{2+}]$  will have a value of  $2.488 \times 10^{14}$  for  $[\text{Cl}^-] = 0.5 \text{ mol L}^{-1}$ . Using the  $[\text{HgY}^{2-}] / [\text{Hg}^{2+}]$  values obtained in b), we find

pH	$[\text{HgY}^{2-}] / [\text{Hg}^{2+}]$	$\%(\text{Hg}^{2+})$	$\%(\text{HgY}^{2-})$	$\%(\text{HgCl}_4^{2-})$
2	$1.17 \times 10^6$	$4 \times 10^{-13}$	$5 \times 10^{-7}$	> 99.9
6	$7.08 \times 10^{13}$	$3 \times 10^{-13}$	22.2	78.8
10	$1.12 \times 10^{19}$	$9 \times 10^{-18}$	> 99.9	$2.2 \times 10^{-3}$

- d). The results from b) indicate that, at pH = 2, the EDTA complexation of  $\text{Ca}^{2+}$  is negligible: we can presume that at pH = 2.6 this will still be the case, and so the EDTA is reacting only with  $\text{Hg}^{2+}$  at such a low pH. At pH = 10, the complexation of both  $\text{Hg}^{2+}$  and  $\text{Ca}^{2+}$  is essentially quantitative, and so at pH = 9.5 the titration tells us the total quantity of  $\text{Hg}^{2+}$  and  $\text{Ca}^{2+}$ . We must assume that EDTA does not significantly react with  $\text{Na}^+$ .

At a pH of 2.6, moles  $\text{Y}^{4-} = 5.391 \times 10^{-4}$  moles.

This is equal to moles ( $\text{Hg}^{2+}$ ) in 25 mL; so moles ( $\text{Hg}^{2+}$ ) in 500 mL =  $1.078 \times 10^{-4}$  moles. Since the atomic mass of Hg is  $200.59 \text{ g mol}^{-1}$ , this indicates a mass of mercury, within the sample, of 2.163 g.

At a pH of 9.5, moles  $\text{Y}^{4-} = 7.006 \times 10^{-4}$  moles.

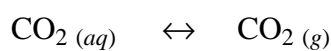
This is equal to moles ( $\text{Hg}^{2+} + \text{Ca}^{2+}$ ) in 10 mL; so moles ( $\text{Hg}^{2+} + \text{Ca}^{2+}$ ) in 500 mL =  $3.503 \times 10^{-2}$  moles, and therefore moles ( $\text{Ca}^{2+}$ ) in 500 mL =  $2.425 \times 10^{-2}$  moles. This corresponds to 0.972 g of calcium within the sample.

By subtraction, the mass of sodium in the sample (assuming no other contamination) is 2.083 g. Thus the sample's content is: Hg (41.45%), Na (39.92%), Ca (18.63%).

## PROBLEM 22.

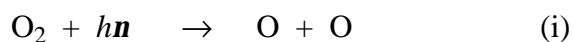
- Greenhouse gases warm the lower atmosphere, because some IR photons (originating from Earth's surface) which would otherwise escape from the atmosphere are absorbed and re-emitted; the re-emission is as likely to be back towards the surface as away from it, and so a warming of the lower atmosphere results.
- Greenhouse gases *cool* the upper atmosphere: because fewer IR photons manage to reach this altitude from the surface, less IR absorption occurs at 15 km than would otherwise be the case. Less absorption implies lower temperatures.

- The equilibria in question are

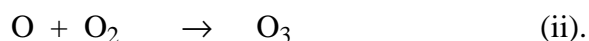


Both of these equilibria will move to the right as the temperature increases: thus the concentration of water vapour, and of  $\text{CO}_2$ , will increase with T. Since both of these species are greenhouse gases, there is a degree of positive feedback involved.

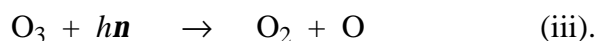
- In a pure oxygen atmosphere, photochemical production of ozone must involve oxygen photolysis:



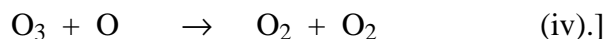
then



Photolysis also destroys ozone:



[Another possible process for ozone destruction is



- From the quoted enthalpies of formation (and that for  $\text{O}_2$ , which is zero by definition), we obtain enthalpies of reaction for (i) and (iii):

$$\Delta H^\circ_{(i)} = 498 \text{ kJ mol}^{-1} = 8.27 \times 10^{-19} \text{ J molecule}^{-1}$$

$$\Delta H^\circ_{(iii)} = 106 \text{ kJ mol}^{-1} = 1.76 \times 10^{-19} \text{ J molecule}^{-1}.$$

Now, using  $E = h\nu = hc/\lambda$  ( $h = 6.626 \times 10^{-34} \text{ J s}$ ;  $c = 2.9979 \times 10^8 \text{ m s}^{-1}$ ), we obtain

$$\lambda_{(i)} = 2.40 \times 10^{-7} \text{ m} = 240 \text{ nm}$$

$$\lambda_{(iii)} = 1.129 \times 10^{-6} \text{ m} = 1129 \text{ nm}.$$

These are the longest-wavelength photons possessing sufficient energy to photolyze  $\text{O}_2$  and  $\text{O}_3$ , respectively [in practice, the efficient photolysis of ozone requires shorter wavelengths than the value suggested, because production of ground-state products is symmetry-forbidden; but that's beyond the scope of this question.]

- f). All three of these equilibria involve the formation of a bond of some sort in going from left to right, so the equilibria will lie more to the left at high temperature and more to the right at low temperature.
- g). Three hypotheses can be rejected as follows:
- i). The notion that Northern hemisphere levels of CFC abundance have lagged behind Southern hemisphere levels is counterintuitive: most industrialization, and most CFC release, is in the North. [In fact, the CFC concentrations in the lower atmosphere are fairly similar over the whole globe: they're mixed pretty thoroughly.]
  - iii). While it's likely that an increase in water vapour would increase the probability of PSC formation, there's no suggestion in the 'information supplied above' that increased transport of water vapour to the Arctic stratosphere (rather than to the lower atmosphere) is occurring.
  - iv). The effect of increasing greenhouse gas concentrations (and they are still increasing!) is to *decrease* the amount of IR reaching the stratosphere. Besides, even though near-infra-red photons possess more energy than the  $\text{O}_2$ -O bond strength, they don't actually photolyse ozone.

Hypothesis ii) is the answer which makes the most sense - greenhouse gases will warm the lower atmosphere at the expense of the upper atmosphere. [That's not to say, however, that this mechanism is the true cause - natural chemical systems have a tendency to always be more complex than we expect!]

**PROBLEM 23.**

Since C = 65.2%      H = 8.75%       $\Rightarrow$       O = 26.05%

This corresponds to an empirical formula of  $C_{10}H_{16}O_3$ .

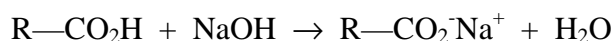
The relative molecular mass of this molecule is

$$(10 \times 12.01 + 16 \times 1.008 + 3 \times 16.00) = 120.1 + 16.13 + 48 = 184.13$$

Now we are told that the molecular mass of **Q** is in the vicinity of 200 so it follows that the empirical formula of **Q** is the same as the molecular formula.



Next the problem tells us that **Q** is acidic and we can infer that it might contain  $CO_2H$  groups. If this is so there can only be one group since there are 3 oxygens in total and a  $CO_2H$  group requires 2. This proposal would lead us to believe that **Q** is monoprotic. That is to say 1 mole of **Q** would react with 1 mole of NaOH:



Now  $43.7 \text{ mg} \equiv \frac{43.7}{1000} \text{ g}$  of **Q** react with 23.7 mL of 0.0100 M NaOH.

This is equivalent to  $\frac{23.7}{1000} \times 0.0100$  moles of NaOH

So if  $\frac{43.7}{1000} \text{ g}$  of **Q** reacts with  $\frac{23.7}{1000} \times 0.0100$  moles of NaOH

$$\frac{43.7}{1000} \times \frac{1000}{23.7 \times 0.01} \text{ g Q reacts with 1 mole of NaOH.}$$

*i.e.* 184.3 g of **Q** reacts with 1 mole of NaOH.

This proves 1 mole of **Q** reacts with 1 mole of NaOH and hence we conclude **Q** is a monoprotic acid of the type  $R-CO_2H$ .

Next we need to address the remaining oxygen in  $C_{10}H_{16}O_3$  (or  $C_9H_{15}O-CO_2H$ )

This could be    an ether                       $R-O-R$

                         an alcohol                 $R-O-H$

                         a ketone                       $\begin{array}{c} R-C=O \\ | \\ R \end{array}$

                         or an aldehyde             $\begin{array}{c} R \\ \diagdown \\ C=O \\ | \\ H \end{array}$

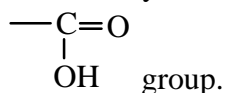
and at this point we cannot choose between these possibilities.

To proceed further we need to look at the double bond equivalents (DBE's) in **Q**.

Recall that for $C_aH_bO_c$ $DBE = \frac{(2a + 2) - b}{2}$
--

In the case of **Q**,  $DBE = \frac{(20 + 2) - 16}{2} = \frac{22 - 16}{2} = 3$

Now clearly **two** (2) of these DBE have yet to be explained but **one** (1) is in the

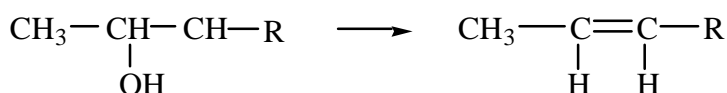


Next we look at the Chemistry of the problem



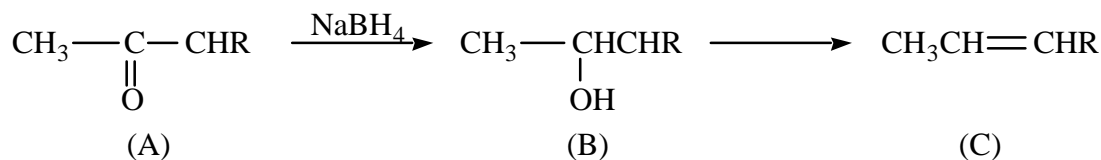
**C** is an alkene which suggests **B** is an alcohol, since **B** loses water when heated with  $H^+$ .

Furthermore since **C** shows a methyl group attached to a double bond we might expect the chemistry to reflect



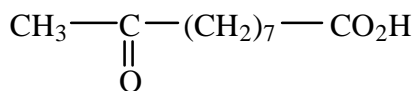
If this were correct and so far it looks very promising **A** must have been a ketone

*i.e.*



You are expected to know that aldehydes and ketones are reduced with  $NaBH_4$  to give  $1^\circ$  and  $2^\circ$  alcohols respectively.

Now if **A** contains a ketone group as well as a carboxylic acid we could think of **A** as follows



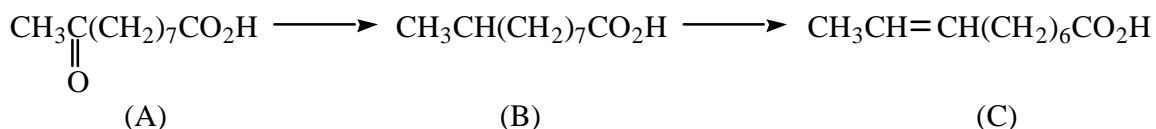
which now accounts for 2 of the double bond equivalents. One (1) in the carboxylic acid and one (1) in the ketone.

This means that in **Q** there is one DBE left to be accounted for and since **Q** reacts with hydrogen it means that the remaining functionality must be a double bond.

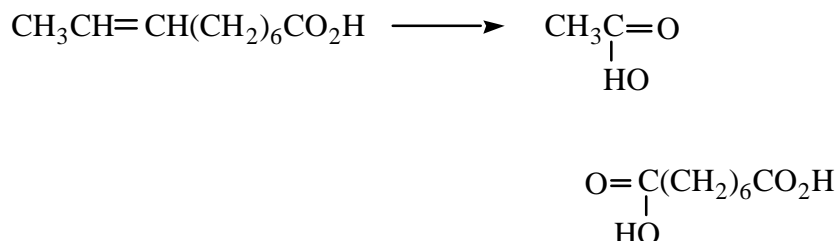
You are expected to know that carbon-carbon double bonds add hydrogen.

The outstanding problem is to know where to place the double bond in **Q** and this becomes evident in the last part of the problem.

We already suspect in principle that



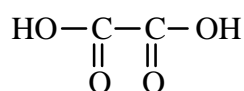
and our hypothesis is confirmed since **C** cleaves with ozone and an oxidant to yield acetic acid and a straight chain dicarboxylic acid



This uniquely defines **C** and hence we are certain of **A**.

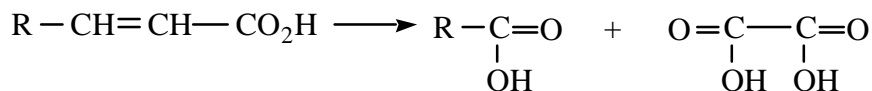
**Q** we are now certain is simply a molecule which contains a ketone (as does **A**), a carboxylic acid (as does **A**) and a double bond.

But **Q** on ozonolysis and oxidation affords

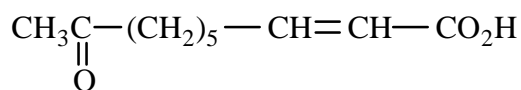


together with **E**.

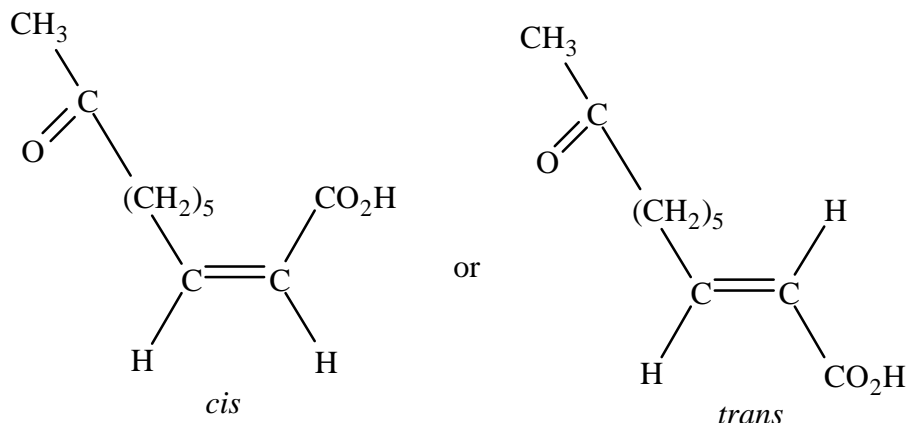
It turns out that we don't need to worry about **E** because the small fragment can only come from a molecule of the general type



This uniquely defines **Q** as



The only problem remains in the *cis/trans* isomerisation of the double bond



and this can't be decided on the information given.

Key Points to Aid Study.

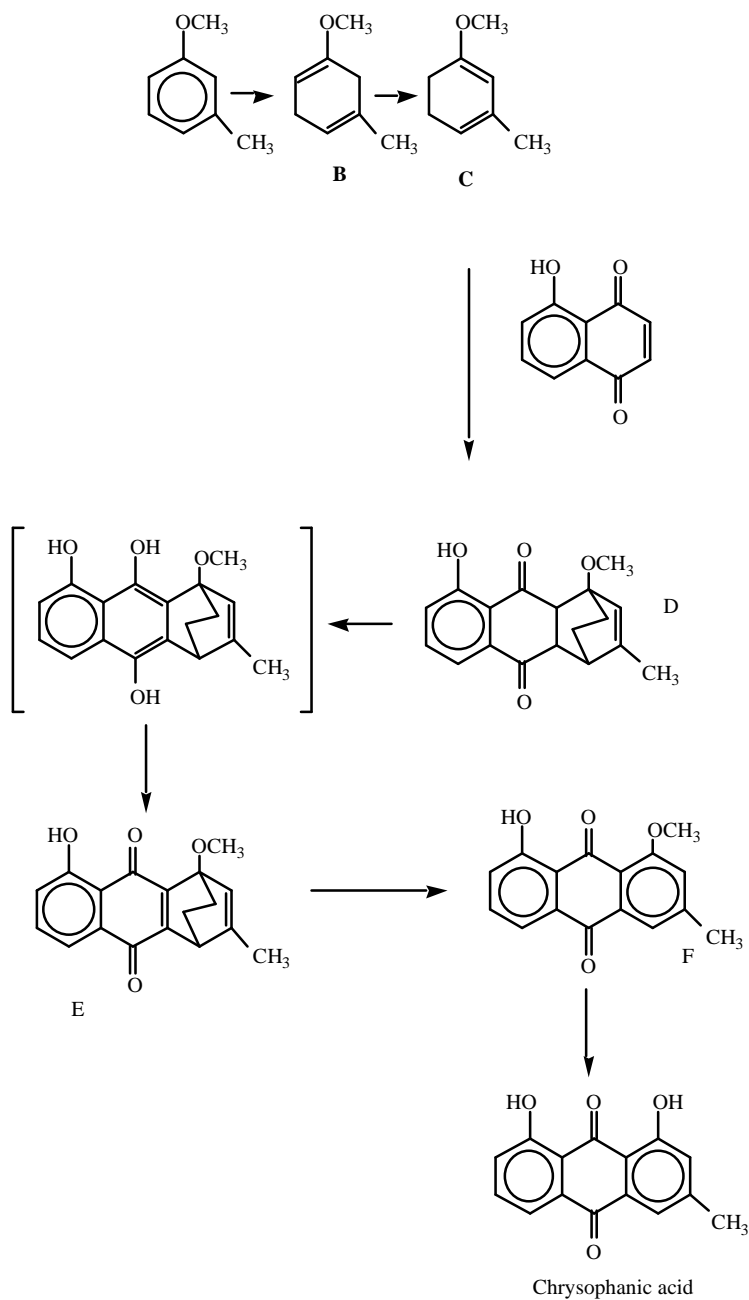
- Degrees of unsaturation (also known as "double bond equivalents").
- Functional groups.
- Reduction.

Ozonolysis with both oxidative and reductive work ups especially for molecules which contain more functionality than simply double bonds.



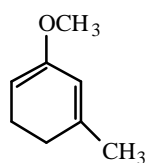
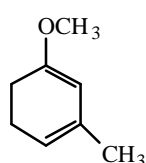
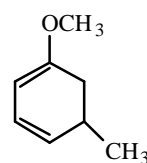
# PROBLEM 24.

The total solution to the question is as follows



## Notes on the solution

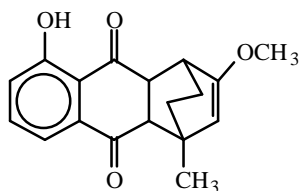
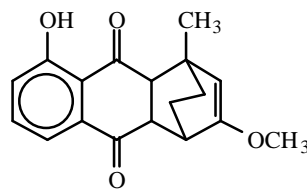
- Compound B is the expected Birch reduction product.
- C being a conjugated isomer of B could be any of the structures C-1, C-2, C-3

**C-1****C-2****C-3**

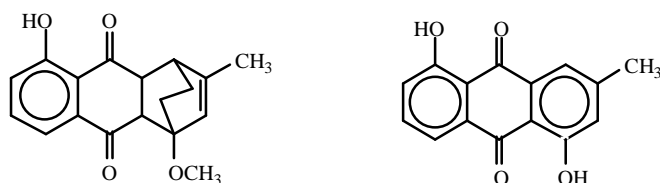
Of these three structures only two, C-1 and C-2 fit the NMR data. Hence C-3 is discarded at this stage at least as far as the final answer is concerned.

- c). Any three Diels Alder products derived from C-1 to C-3 would be acceptable as an answer to part three since they will all contain an intramolecularly bonded hydroxyl. Whilst this is relatively easy to answer the unique solution to the problem requires more thought.

Distinguishing between C-1 and C-2 as the correct answer for C is not possible at this stage of the problem. At the end however it becomes clear that answers which have been generated through either D-1 or D-11, that is the cycloadducts of C-1 are not acceptable since they will not be demethylated with BCl<sub>3</sub>. This reagent at least at -100 is selective for cleaving methyl ethers *peri* to a carbonyl; in this regard it is more selective than BBr<sub>3</sub>. The full solution, shown above, is worked through for the correct isomer C.

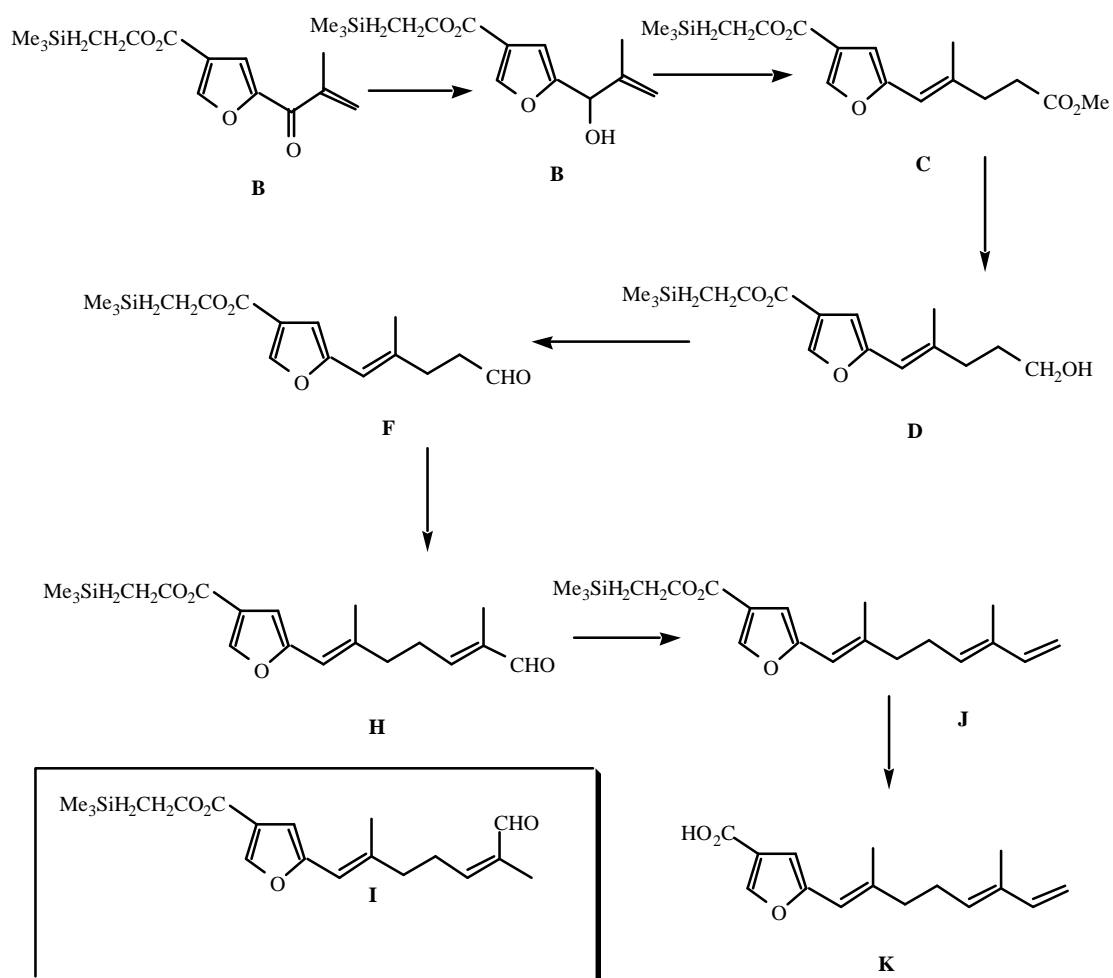
**D-1****D-11**

However even here there is the possibility of another outcome but not one which can yield chrysophanic acid. The regiochemistry of the cycloaddition shown above is in fact the one found in practice but the Diels Alder reaction could have proceeded to give the alternative isomer as shown below. This would not lead to chrysophanic acid and since this structure was given in the question the student can deduce the answer. However it is worth pointing out that as a synthesis this is not truly unambiguous and could not have been used as a proof of the structure of chrysophanic acid. Given this information it is possible to answer Question d) which really addresses the regiochemistry of the cycloaddition of C-2 and the 5-hydroxynaphthalene-1,4-dione

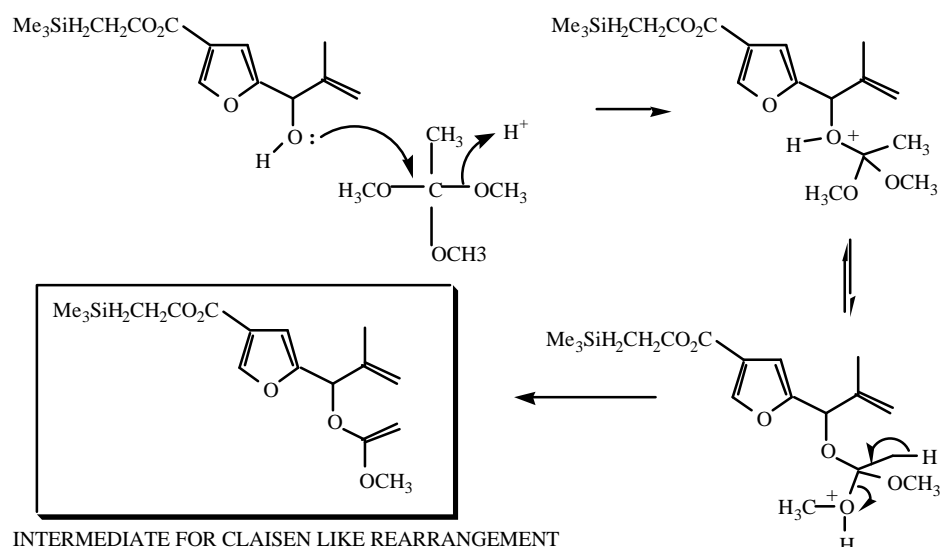


Key Points to Aid Study

- Birch reduction or aromatics - no mechanism required.
- Diels-Alder reaction - regiochemistry or the direction of addition.
- Broad concept of nmr. No coupling details are required but rather an appreciation of the information simple NMR data can give the practising chemist.
- Enolisation of ketones.
- Oxidation of phenols to quinones.
- $\text{BCl}_3$  as a selective demethylating agent which demethylates only ethers which are peri to a carbonyl. i.e. to be effective it needs two oxygens, that of the carbonyl and that of the methoxy group to chelate to the boron.
- The strategy to solve road map problems.

**PROBLEM 25.**Notes on the Solution

At first sight this problem seems very difficult. However the problem is rich in information and tests an understanding of reactions together with a knowledge of simple oxidations, reductions and esterifications. The most difficult part of the problem is setting up the conversion of B to C.



There is no need to have this depth of mechanistic chemistry as the problem gives in its introduction a significant clue as to how this chemistry must work in overall terms.

The oxidation with pyridinium chlorochromate is noteworthy in as much that under anhydrous conditions the primary alcohol is oxidised only to the aldehyde and NOT the carboxylic acid. The reductants hold no special significance and do not need to be learned as special reagents. They simply achieve selective reductions and the nature of these are outlined in the problem.

The conversion of C to D must involve reduction of the methyl ester since D still contains silicon. Had the trimethylsilylethyl ester been reduced the silicon would have been removed. This is a nice challenge for the student to work out and requires no advanced knowledge of the different ester reactivities - it simply follows from the elemental composition.

Finally it is worth noting that this problem uses the symbolism for a Wittig reagent, ie a structure with a formal double bond rather than the more frequently used dipolar structure for the ylid. It is worth noting that reagent G effectively allows one to extend the chain length of an aldehyde.

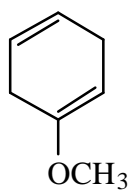
#### Key Points to Aid Study

- Claisen like rearrangements- students may care to look at the rearrangement of the allyl ethers of phenols as another example.
- Oxidation and reduction.
- Esterification with simple and complex alcohols.
- Wittig reactions.
- E/Z isomerism and notation.
- Degree of unsaturation (also known as double bond equivalents)

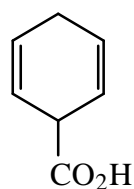
# PROBLEM 26.

## REDUCTIONS

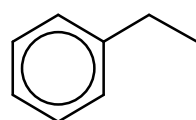
(i)



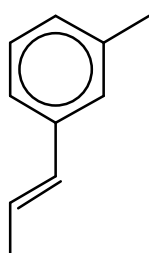
(ii)



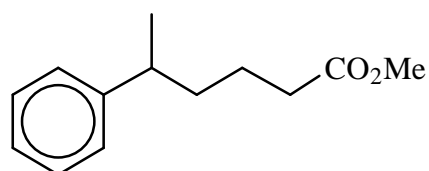
(iii)



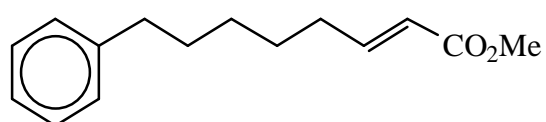
(iv)



(v)

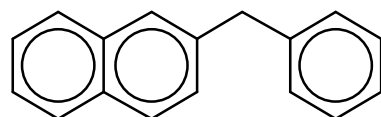


(vi)

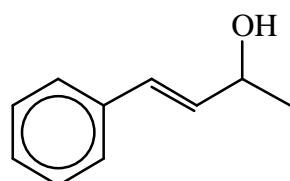


(Note: XS reductant may reduce the polarised alkene)

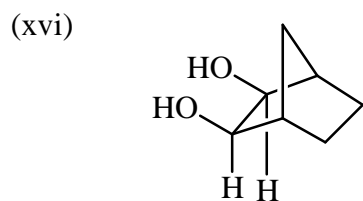
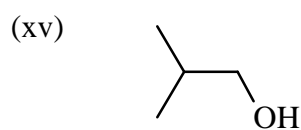
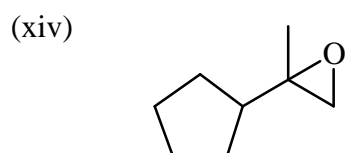
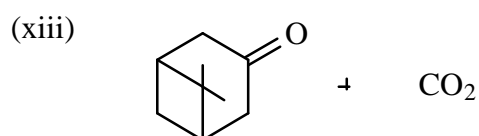
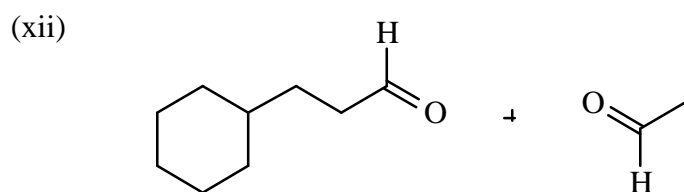
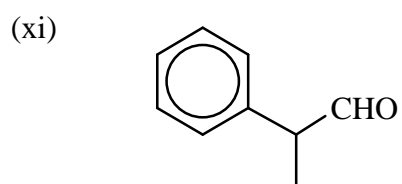
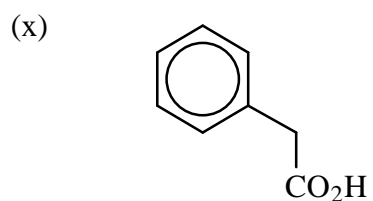
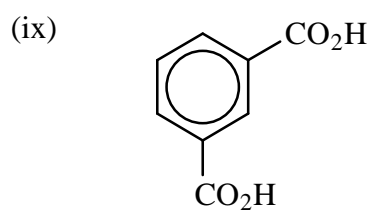
(vii)



(viii)

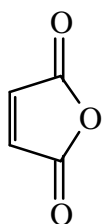


# **OXIDATIONS**



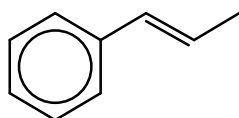
# OTHER REACTIONS

(xvii)

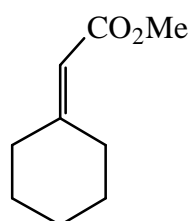


(xviii) No reaction except at extreme temperatures

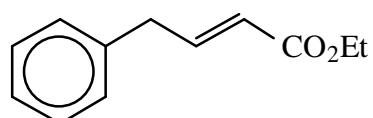
(xix)



(xx)

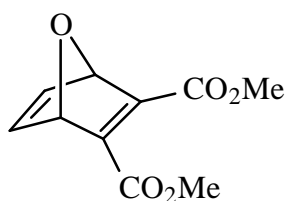


(xxi)

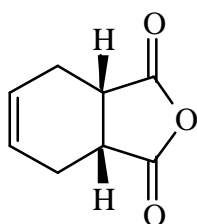


Students should be aware that the outcome of a Wittig reaction *i.e.* *cis/trans* isomer may vary with reaction conditions, and reaction/reagent structure.

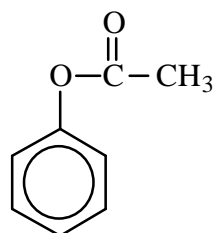
(xxii)



(xxiii)

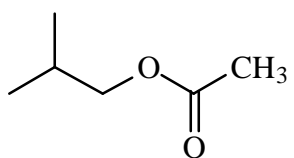


(xxiv)

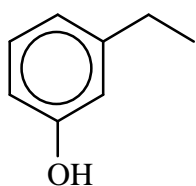




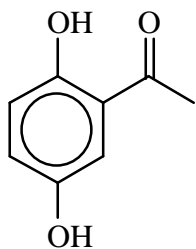
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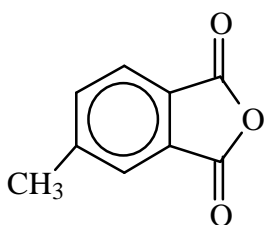
(xxvi)



(xxvii)



(xxviii)





**PREPARATORY PROBLEMS**

**AND**

**WORKED SOLUTIONS**

**ERRATA**

Melbourne, Australia July 5 – 14, 1998

The Royal Australian Chemical Institute