1 Molecules and molecular structures: an overview

1.1 (a) Draw Lewis structures for the molecules PH_3 and PF_3, making sure that in your structures you have accounted for all the valence electrons. Show that in each structure there is no formal charge on the phosphorus atom, and that the oxidation number of the phosphorus in PF_3 is +3.

(b) Draw two alternative Lewis structures for the molecule POF_3: one in which there is a double bond between the phosphorus and the oxygen, and one in which there is a P–O single bond. For each structure, determine the formal charge on both the oxygen and the phosphorus atoms. Assuming that the oxidation number of the oxygen is −2, determine the oxidation number of the phosphorus. Has the octet been expanded for phosphorus in either of your structures?

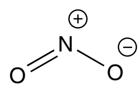
(c) For the hypothetical molecule PO_2F, draw three alternative Lewis structures: one with two doubly-bonded oxygen atoms, one with one doubly-bonded oxygen, and one with only single bonds to oxygen. For all three structures, determine the formal charges on the phosphorus and each of the oxygen atoms.

(d) The species $[PO_3]^{3-}$ is usually referred to as the phosphite anion. For this species, determine the oxidation number of the phosphorus and draw a Lewis structure, indicating any formal charges.

Protonation of this anion gives the phosphonate anion, $[HPO_3]^{2-}$, which has approximately tetrahedral coordination at phosphorus. The hydrogen is attached to the phosphorus and the three oxygen atoms occupy equivalent positions. Draw possible Lewis structures for this anion, and explain whether or not they are consistent with its known geometry. Explain how the concept of resonance can be helpful in describing the bonding on this anion.

1.2 (a) Determine the oxidation number of nitrogen in NO_2.

(b) NO_2 is known to be a free radical (i.e. it has an unpaired electron) and to adopt a bent geometry. One possible representation of the bonding in NO_2 is shown below: indicate in the usual way the location of the electrons in this molecule, and verify that the formal charges shown are correct.

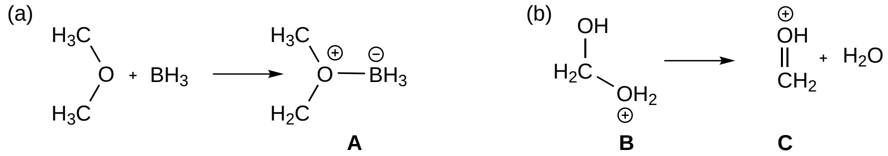


(c) Experimental data indicates that NO_2 has a dipole moment which lies in the plane of the molecule and bisects the O–N–O angle. Explain why the structure shown above is *not* consistent with these data.

(d) Use the concept of resonance structures to give an explanation for the direction of the observed dipole in NO_2.

(e) Draw two alternative Lewis structures for carbon monoxide: one in which there is a triple bond and one in which there is a double bond. Determine if there are any formal charges on the atoms. Experimentally it is found that this molecule has a small dipole moment, with the carbon being $\delta-$. How can this observation be reconciled with your Lewis structures?

1.3 Explain how the formal charges on the oxygen and boron arise in the product **A** of reaction (a), and how the formal charges on the oxygen arise in reactant **B** and product **C** of reaction (b), shown below.



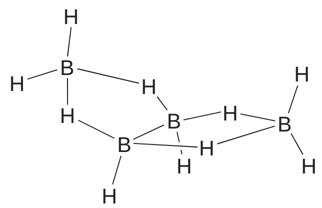
1.4 Assuming that there is no charge on the sulfur atom, use the approach described in section 1.1.2 on page 5 to determine the number of lone pairs on the sulfur in the following molecules: (a) SF_2, (b) SF_4, (c) SF_6, (d) SO_3.

1.5 Determine the oxidation state of oxygen in the following compounds: (a) Li_2O, (b) Na_2O_2, (c) KO_2, (d) MgO, (e) $Ba(O_3)_2$.

1.6 Determine the oxidation state of phosphorus in the following compounds or ions: (a) PCl_3, (b) PF_5, (c) P_2O_5, (d) PO_4^{3-}.

1.7 Determine the oxidation state of chromium in the following compounds or ions: (a) CrF_6, (b) $CrCl_4^-$, (c) CrO_4^{3-}, (d) $Cr_2O_7^{2-}$.

1.8 The boron hydride with formula B_4H_{10} is often drawn as

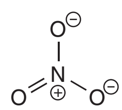


(a) If each line represents a conventional bond in which two electrons are shared between two atoms, how many electrons are indicated by this structure?

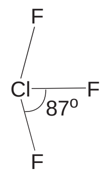
(b) Assuming that each boron contributes three electrons, and each hydrogen contributes one, how many valence electrons are there in B_4H_{10}?

(c) How can you reconcile your answers to (a) and (b)?

1.9 Use the VSEPR model to predict approximate structures for the following species: (i) BH_3, (ii) BH_4^-, (iii) H_3O^+, (iv) CH_5^-, (v) PCl_5, (vi) PCl_4^+, (vii) PCl_6^-,(viii) NO_3^- (structure given below). (Hint: for the charged species, first work out the number of electrons in the valence shell ignoring the charge, and then reduce this total by one for a positive overall charge, or increase it by one for an overall negative charge).



1.10 ClF_3 is a highly reactive but nevertheless well-characterized volatile liquid used (among other things) to produce UF_6 in the processing of nuclear fuels. It has the following T-shaped structure



(a) Use the VSEPR theory to show that the structure of ClF_3 can be expected to be based on a trigonal bipyramid.

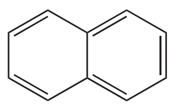
(b) The T-shaped structure can be considered to be a distorted trigonal bipyramid in which two 'equatorial' positions are occupied by lone pairs. Draw a diagram to illustrate this, and suggest why the bond angle in ClF_3 is not 90° as it would be in a regular trigonal bipyramid.

1.11 Explain why, at normal pressures and temperatures, $MgCl_2$ is a solid, SiO_2 is a solid, CO_2 is a gas and Ar is a gas.

1.12 What is the distinction between a *molecular* solid and an *ionic* solid? Account for the following observations:

(a) Solid $PbBr_2$ does not conduct electricity, but when molten the salt is a good conductor.

(b) Neither solid naphthalene nor molten naphthalene conduct electricity.



naphthalene

(c) Metallic gold, both when solid and molten, conducts electricity.

1.13 As we go down Group 18, the noble gases, the atoms become more polarizable. Explain what you understand by this statement. Also explain how this trend in polarizability can be used to explain the observation that the boiling points of the liquefied noble gases increase as you go down the group.

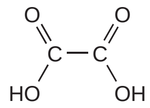
1.14 Explain the following trends in the boiling points of the following two sets of hydrides:

set (a)	boiling point / °C	set (b)	boiling point / °C
H_2O	100.0	CH_4	−161.5
H_2S	−59.6	NH_3	−33.3
H_2Se	−41.3	H_2O	100.0
H_2Te	−2		

1.15 What types of intermolecular forces are present in the following molecules: (a) butane C_4H_{10}; (b) CH_3F; (c) CH_3OH; (d) CF_4?

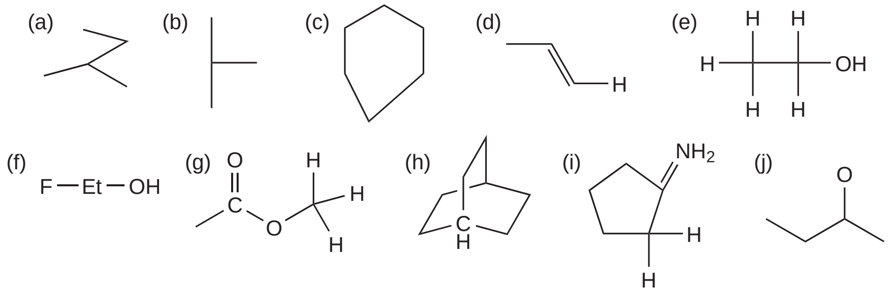
1.16 In the gas phase, ethanoic acid is thought to exist as a dimer, held together by *two* hydrogen bonds. Suggest a structure for the dimer.

In the solid, oxalic acid, $(COOH)_2$, forms extended chains, also held together by hydrogen bonds. Sketch a likely structure for such a chain.

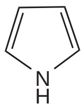


oxalic acid

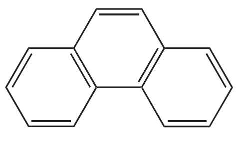
1.17 The following framework structures are poorly drawn or simply implausible. Point out the errors in each, and re-draw them correctly.



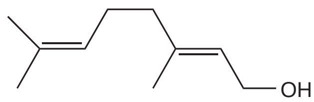
1.18 Find the molecular formula (i.e. $C_aH_b\ldots$) of each of the following framework structures:



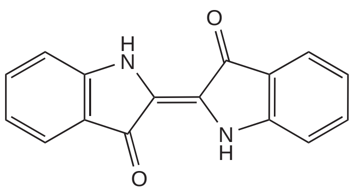
pyrrole



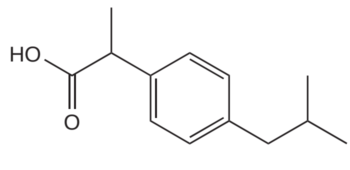
phenanthrene



geraniol



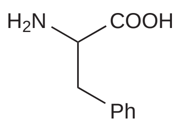
indigo



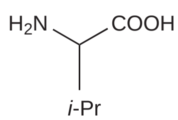
ibuprofen

1.19 Draw framework structures of the following molecules:

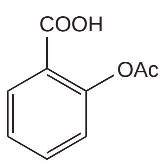
t-BuOH	*i*-PrOEt	EtOAc	EtAc
n-BuCl	AcOH	PhMe	PhH
Ac_2O	EtCN	Et_2O	*n*-PrNHAc



(Phenylalanine)



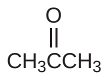
(Valine)

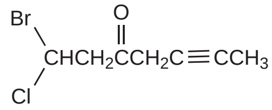


(Aspirin)

1.20 Draw framework structures of the following molecules:

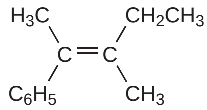
(a) $CH_3CH_2CH_2NHCH_2CH_3$

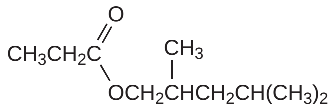
(b) 

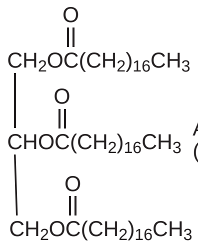
(c) 

(d) $HOCH_2CH_2CO_2Me$

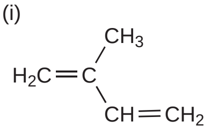
(e) $(CH_3)_3CNH_2$

(f) 

(g) 

(h) 

A triacyl glycerol
(a component of saturated fat)

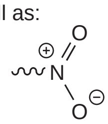
(i) 

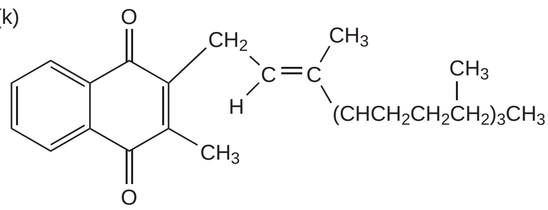
Isoprene
(a component of natural rubber)

(j) $C(CH_2ONO_2)_4$

PETN
(an extremely powerful explosive)

Hint: the nitro groups can be written simply as -NO_2, or drawn out in full as:



(k) 

Vitamin K_1

1.21 Calculate the concentration, in moles m^{-3} and molecules m^{-3}, of nitrogen gas at a pressure of 0.1 atmospheres and a temperature of 298 K. You may assume that the gas behaves ideally. (1 atmosphere is 1.013×10^5 N m^{-2})

1.22 What pressure will one mole of an ideal gas exert at 298 K if it is confined to a volume of (i) 1 m^3, (ii) 1 dm^3, and (iii) 1 cm^3?

1.23 A container of volume 100 cm^3 contains 1.0×10^{-4} moles of H_2 and 2.0×10^{-4} moles of N_2, such that the total pressure is 0.1 atmospheres. Calculate the mole fraction and partial pressure of each species. Also, calculate the temperature of the mixture.