SECTION 5

STRUCTURAL FORMULAE

Structural formulae of molecules and ions give more information than simple chemical formulae. Lewis structures show which atoms are bonded to which using the letter symbols for the atoms, and the arrangement of the valence electrons forming the bonds. A line represents a two-electron bond. Lewis structures are like words of chemical language and are found in all chemical literature. It is essential that you can write Lewis structures for molecules and ions assuming knowledge of which atoms are bonded to which. This section gives simple rules which allow you to do this. It also introduces you to the concept of the shape of molecules.

Structural formula: A chemical formula which shows the groupings of atoms in a compound.

Lewis structures (defined in *section 4*) of discrete molecules and ions are an essential part of the chemical language. They are used to show details of structure and of chemical reactions. The ability to write Lewis structures for basic molecules and ions is an essential skill for chemists. The following rules require knowledge only of the number of valence electrons of an atom of each element, and the arrangement of the nuclei, i.e. which atoms are joined or bonded together.

Rules for Drawing Lewis Structures

(a) Determine the total number of valence electrons in the molecule or ion by adding together the numbers of valence electrons of each atom, and if an anion, by adding the overall charge of the ion, and if a cation, by subtracting the overall charge of the ion.

(b) Place the atoms in their relative positions.

(c) Draw a line representing a single bond containing two electrons between joined atoms.

(d) Distribute the remaining electrons evenly in pairs on the outer atoms so these have up to eight electrons (except for hydrogen which has two). Any still not used after this should be placed on the central atom.

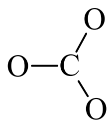
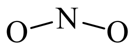
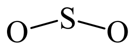
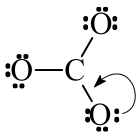
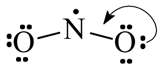
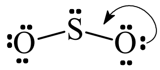
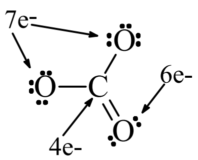
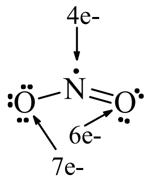
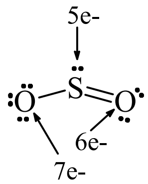
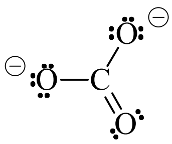
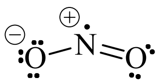
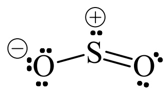
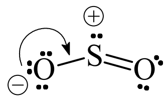
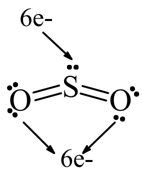
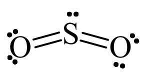
(e) If the central atom is now surrounded by fewer than eight electrons, move sufficient non-bonding pairs from outer atoms other than halogens to between joined atoms, thus making them bonding, to bring the number on the central atom up to a maximum of eight.

(f) Count the number of electrons "owned" by each atom assuming bonding electrons are shared evenly. To evaluate the **formal charge** at that atom compare the result with the number of valence electrons of the neutral atom. Show only non-zero charges.

(g) For central atoms from the third row or later rows of the periodic table, move further non-bonding pairs to bonding positions to lower the positive formal charge on the central atom to one or zero.

Formal Charge: The electric charge of an atom in a molecule or ion assuming perfect covalent bonding. [e.g. in NH_4^+, N "owns" four electrons and has the formal charge +1 as an N atom has five valence electrons.]

Examples:

Rule	CO_3^{2-}	NO_2	SO_2
a	C O 4 + 3 x 6 + 2 = 24	N O 5 + 2 x 6 = 17	S O 6 + 2 x 6 = 18
B, c			
D, e			
E, f			
f			 structure 1
g			   structure 2

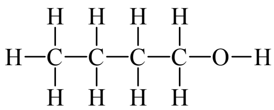
Examples of the application of the rules for drawing Lewis structures

In the case of CO_3^{2-} and NO_2 above each C-O and both N-O bonds are identical although a single Lewis structure might suggest otherwise. The problem can be overcome by writing the three possible Lewis structures for CO_3^{2-}, or the two possible Lewis structures for NO_2 and drawing a double headed arrow, ↔, between them. Each individual Lewis structure for a molecule or ion is called a **resonance structure**, and the true structure of the molecule or ion is a composite of these called the **resonance hybrid**. (See benzene, *page 6-5*)

Of course, many molecules or ions do not have a "central atom". Organic molecules with more than one C are obvious examples. Provided the structure is known, (i.e. which atoms are bonded to which), extending the rules with common sense will work. [e.g. C_2H_2, H-C-C-H, put pairs on C atoms evenly, and move both pairs to between C atoms to make a triple bond.

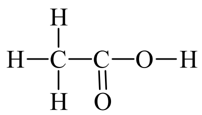
]

Condensed structures. The information provided by a Lewis structure can frequently also be provided by a modified or condensed form which is easily understood once some basic ideas are mastered. Often the non-bonding electron pairs are not shown. In many organic compounds (compounds of carbon), chains of carbon atoms joined together are present. Thus butan-1-ol, for which the complete Lewis structure is



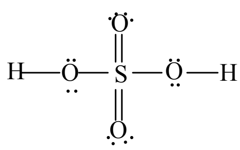
can be represented as $CH_3CH_2CH_2CH_2OH$, where atoms joined to a carbon are shown on its right before the adjoining atom is given. Butan-2-ol is $CH_3CH_2CH(OH)CH_3$.

Ethanoic acid:



is written as CH_3COOH or CH_3CO_2H. A degree of condensation appropriate for the required information can be chosen. See *section 6* for further condensation of the carbon skeleton of organic compounds.

The structure of sulfuric acid:



may be written as $(HO)_2SO_2$, which is much more meaningful than the more usual representation (H_2SO_4) in that it shows that the H's are joined to oxygen.

Familiarity with these types of formulae comes with practice and experience based on the electron structure and valency of the atoms of the elements.

Molecular shape. The **shape** of a simple molecule or ion describes the relative positions of the nuclei of the atoms in the molecule. H_2O is described as bent because the H-O-H atoms do lie on a straight line. NH_3 is described as trigonal pyramid because the N atom is above the plane of the three H's which are at the corners of an equilateral triangle. CH_4 is described as tetrahedral because the C atom is in the middle and surrounded tetrahedrally by the four H atoms. BF_3 is trigonal planar, because the boron atom is in the centre of an equilateral triangle with fluorines at each corner. CO_2 and C_2H_2 are linear the O-C-O atoms and H-C-C-H atoms lying in straight lines. It is difficult to give a simple description of shape of more complex molecules such as butanol, ethanoic acid and sulfuric acid above. However we can describe the arrangement of the atoms around a single atom. Thus in butanol above, each C atom is surrounded tetrahedrally by four other atoms. In ethanoic acid the carbon atom bonded to two O's and a C is in the centre in an equilateral triangle, the other carbon atom being tetrahedrally surrounded by the three H's and one C.

Valence-shell electron pair repulsion (VSEPR) theory: A theory which gives a simple rationale of shape (reason for the particular arrangement or shape). The "groups" of electrons (i.e. a non-bonding electron pair, a bonding pair, the four electrons of a double bond, the six electrons of a triple bond) around the central atom (as shown in the Lewis structure) keep as far away from each other as possible. [e.g. NH_3 is a trigonal pyramid - there are four pairs of electrons tetrahedrally around the N, but the shape description only involves the atoms; H_2O is bent - there are four pairs of electrons tetrahedrally around the O; the carbonate ion, CO_3^{2-}, is a planar triangle; sulfur dioxide, SO_2 is bent. In sulfuric acid the S is tetrahedrally surrounded by four O's, and the H-O-S atoms do not lie on a straight line.]

EXERCISES

Draw Lewis structures for the following species. Unless otherwise stated the first element in the formula is central and bonded individually to the other atoms. Remember to show non-zero formal charge.

1. Tetrafluoromethane, CF_4
2. Ammonia, NH_3
3. Sulfur trioxide, SO_3
4. sulfite anion, SO_3^{2-}
5. Nitrate anion, NO_3^-
6. Nitrite anion, NO_2^-
7. Ammonium cation, NH_4^+
8. Nitrous oxide, N_2O, (one N central, linear)

Draw the full Lewis structures of the compounds of condensed structures:

9. HCHO
10. $CH_3CH_2CH_2Cl$
11. CH_3COCH_3
12. CH_3CHCH_2
13. $CH_3CH_2OOCH_3$
14. CH_3COOCH_3
15. $CH_3CHBrCH_2CH_3$
16. $HOCH_2CH_2CHO$
17. $FCH_2CH_2CCl(OH)CH_2OH$
18. $CH_2ICH_2CH_2COCCCH(NH_2)CH_3$