Unit 7

Answers: Chemical Bonding

Quick checks

1 b Nitrogen is $2s^2\,2p^3$: its three 2p electrons sit one in each p orbital (Hund's rule), so it has three unpaired electrons and makes three bonds. Its five outer electrons include a 2s pair, which stays as a lone pair.

2 c A donor needs a lone pair. Ammonia's nitrogen has one. H^+ and BF_3 are acceptors (they have empty orbitals), and methane's carbon has no lone pair: all four of its pairs are shared.

3 b 1 mol NH_3 has 4 mol of atoms (1 N and 3 H in each molecule): $4 \times 6.022 \times 10^{23}$. 1 g of H_2 is 0.5 mol of molecules, 1 mol of atoms; 1 mol O_2 is 2 mol of atoms; 12 g of carbon is 1 mol of atoms.

4 b That is Avogadro's law. Their masses differ (CO_2 molecules are 22 times heavier than H_2), and so do their numbers of atoms: each CO_2 has 3 atoms, each H_2 only 2.

5 b $M(SO_2) = 32 + 2 \times 16 = 64$, and VD $= \frac{M}{2} = 32$. (64 is the molecular mass, not the vapor density.)

1 a. **c** N≡N is a triple bond. Two atoms are joined by only one σ bond; the other two bonds are π bonds.

1 b. **d** A π bond is the sideways overlap of two parallel p orbitals. The other three are head-on overlaps, which give σ bonds.

1 c. **c** In NH_4^+ the nitrogen of ammonia gives its lone pair to an H^+ ion. The others have only ordinary covalent bonds.

1 d. **c** 1 mol of any gas fills 22.4 L at STP, so 2 mol fill $2 \times 22.4 = 44.8$ L. (64 is the mass of 2 mol O_2 in grams.)

2 a. Noble gas atoms already have a full outer shell, a duplet (helium) or an octet (the others), which is a very stable, low-energy arrangement. They have no unpaired electrons to share and don't easily gain or lose electrons, so they have little to gain by bonding. Other atoms bond precisely to reach such a full shell.

2 b. A σ bond is formed by head-on overlap along the axis between the nuclei: the overlap is large and the shared pair lies directly between the two nuclei, attracted strongly by both. A π bond is formed by sideways overlap of parallel p orbitals: the overlap is smaller and lies above and below the axis, farther from the line between the nuclei. Less overlap means a weaker bond (C=C adds only about 267 kJ/mol to the 347 of C–C).

2 c. An electric current needs charged particles that can move: free electrons (in metals) or free ions (in molten or dissolved ionic compounds). Covalent compounds are made of neutral molecules, with their electrons held in bonds, and give no ions in the liquid or in water, so there is nothing to carry the current.

2 d. A coordinate bond differs from an ordinary covalent bond only in where its electrons came from. Once it has formed, it is a pair of electrons shared between nitrogen and hydrogen, exactly like the other three N–H bonds. So all four have the same length and strength, and the ion is a regular tetrahedron; the arrow only records the bond's history.

2 e. Organic compounds are covalent: they are made of molecules held to one another by weak forces of attraction, so little heat is needed to separate them, and they melt and boil at low temperatures (ethanol boils at 78 °C). Common salt is ionic: each ion is held by strong electrostatic attraction to the oppositely charged ions all round it, in every direction through the crystal, so a lot of heat is needed (NaCl melts at 801 °C).

2 f. One mole of any gas contains the same number of molecules, 6.022×10^{23}. By Avogadro's law, equal numbers of molecules of any gases occupy equal volumes at the same temperature and pressure. So one mole of every gas occupies the same volume at STP: 22.4 L.

3 i. The six differences are in the table at the end of Why a π bond is weaker than a σ bond. Any four for full marks:

- σ: head-on (axial) overlap, on the axis between the nuclei; π: sideways (lateral) overlap of parallel p orbitals, above and below the axis.
- σ: s–s, s–p or p–p; π: p–p only.
- σ is stronger; π is weaker.
- σ can exist alone; π forms only after a σ bond. The atoms can rotate about a σ bond, not about a π bond.

3 ii. As in the table in 7.2:

- Covalent: each atom gives one electron to the shared pair, so each needs an unpaired electron; shown A–B (H–H, CH_4, H_2O).
- Coordinate: both electrons come from one atom, the donor with a lone pair, to an acceptor with an empty orbital; shown A→B ($H_3N \rightarrow H^+$ in NH_4^+, H_3O^+, O_3, SO_3).

4 a. A **covalent bond** is a bond formed between two atoms by the mutual sharing of a pair of electrons, each atom giving one electron.
Chlorine (2, 8, 7) is $3s^2\ 3p^5$: one of its 3p orbitals holds a single, unpaired electron. When two chlorine atoms meet, their half-filled 3p orbitals overlap head-on along the axis joining the nuclei, and the two electrons, with opposite spins, pair up in the overlap. This is a single covalent bond, a **σ bond (p–p)**. Each atom now has three lone pairs and one shared pair: an octet.

Dot-and-cross diagram: two overlapping circles, Cl and Cl; one dot and one cross in the overlap; three pairs of dots round the first atom and three pairs of crosses round the second (as in the first diagram of Figure 7.1). Structural formula Cl–Cl.

4 b. Any five:

- They are usually gases, liquids or soft solids at room temperature.
- They have low melting and boiling points, because the forces between molecules are weak.
- They don't conduct electricity, since they have no free ions or electrons.
- Most are insoluble in water but soluble in organic solvents such as kerosene or alcohol.
- Their reactions are slow, because bonds must be broken and remade.
- Their bonds are directional, so their molecules have definite shapes and can show isomerism.

4 c. A **σ bond** is a covalent bond formed by the head-on (axial) overlap of two orbitals along the axis joining the nuclei. A **π bond** is a covalent bond formed by the sideways (lateral) overlap of two parallel p orbitals, above and below that axis.

- s–s: two spheres overlapping on the axis (H_2).
- s–p: a sphere overlapping one lobe of a p orbital pointing at it (HCl).
- p–p head-on: two p orbitals pointing at each other, overlapping on the axis (Cl_2).
- π: two upright p orbitals side by side, overlapping above and below the axis, with no overlap on it.

The diagrams are as in Figure 7.5. A π bond forms only between atoms already joined by a σ bond: a double bond is 1 σ + 1 π, a triple bond 1 σ + 2 π.

4 d. Nitrogen is $1s^2\ 2s^2\ 2p^3$, with one electron in each of its three 2p orbitals, p_x, p_y and p_z, which point at right angles to each other. When two N atoms approach along the x axis:

- the two p_x orbitals overlap head-on: **one σ bond**;
- the two p_y orbitals, now parallel, overlap sideways above and below the axis: **one π bond**;
- the two p_z orbitals overlap sideways in front and behind: **a second π bond**.

So N≡N is a triple bond, 1 σ + 2 π, with six shared electrons. Each N keeps its 2s pair as a lone pair and has an octet. The triple bond is very strong (945 kJ/mol), so nitrogen is unreactive.

4 e. A **coordinate covalent (dative) bond** is a covalent bond in which both electrons of the shared pair are given by one atom.
Conditions: one atom (the **donor**) must have a lone pair in its outer shell; the other (the **acceptor**) must have an empty orbital, two electrons short of a stable duplet or octet.
In water, oxygen has two lone pairs. A hydrogen ion, H^+, has an empty 1s orbital. Oxygen shares one of its lone pairs with H^+: $H_2O + H^+ \rightarrow H_3O^+$. Oxygen keeps its octet (three shared pairs and one lone pair), the new hydrogen gets a duplet, and the ion carries the charge +1. The diagram is as in Figure 7.7.

4 f.

- **Ozone:** O=O→O. The first two oxygens share two pairs (a double bond); the middle oxygen gives one of its lone pairs to the third oxygen (a coordinate bond). The molecule is bent.
- **Sulphur trioxide:** one oxygen is joined by a double bond, S=O, and sulphur gives a lone pair each to the other two oxygens, S→O and S→O, in a flat triangle.

Every atom has an octet, as in Figure 7.8. (The real molecules are resonance hybrids, with all their bonds alike, but these are the structures to draw.)

4 g.

i. **Avogadro number:** the number of particles in one mole of a substance, 6.022×10^{23}.

ii. **Gram atom:** the atomic mass of an element expressed in grams; it contains 6.022×10^{23} atoms (1 gram atom of carbon = 12 g).

iii. **Gram mole (gram molecule):** the molecular mass of a substance expressed in grams; it contains 6.022×10^{23} molecules (1 gram mole of water = 18 g).

iv. **Molar volume (gram molecular volume):** the volume occupied by one mole of any gas at STP, 22.4 L.

4 h. **Avogadro's law:** equal volumes of all gases, at the same temperature and pressure, contain equal numbers of molecules.
Vapor density is the ratio of the mass of a volume of a gas to the mass of the same volume of hydrogen, at the same temperature and pressure:

$$= \frac{V}{V}$$

By Avogadro's law, the two volumes contain the same number of molecules, n:

$$= \frac{n \times}{n \times 2} = \frac{}{2}$$

since the molecular mass of hydrogen, H_2, is 2. So **molecular mass = 2 × vapor density**.

4 i. By experiment, 1 volume of hydrogen + 1 volume of chlorine → 2 volumes of hydrogen chloride (same temperature and pressure).
By Avogadro's law, if 1 volume holds n molecules: n molecules of hydrogen + n molecules of chlorine → $2n$ molecules of hydrogen chloride. So 1 molecule of hydrogen gives 2 molecules of hydrogen chloride.
Every molecule of hydrogen chloride contains at least one atom of hydrogen, so 2 molecules contain at least 2 hydrogen atoms, and these came from 1 molecule of hydrogen. A hydrogen molecule therefore has (at least) **two atoms**: H_2.

5 a. $M = 44$ g/mol; $n = 4.4 \div 44 =$ **0.1 mol**; molecules $= 0.1 \times 6.022 \times 10^{23} =$ **6.022×10^{22}**.

5 b. $n = 3.011 \times 10^{23} \div 6.022 \times 10^{23} = 0.5$ mol; $M(SO_2) = 32 + 32 = 64$ g/mol.
Mass $= 0.5 \times 64 =$ **32 g**.

5 c. $n = 2.24 \div 22.4 = 0.1$ mol. Mass $= 0.1 \times 16 =$ **1.6 g**. Molecules $= 0.1 \times 6.022 \times 10^{23} =$ **6.022×10^{22}**.

5 d. $M = 2 + 32 + 64 = 98$ g/mol; $n = 4.9 \div 98 = 0.05$ mol; molecules $=$ $0.05 \times 6.022 \times 10^{23} = 3.011 \times 10^{22}$.
Hydrogen: $2 \times 3.011 \times 10^{22} =$ **6.022×10^{22} atoms**; sulphur: **3.011×10^{22} atoms**; oxygen: $4 \times 3.011 \times 10^{22} =$ **1.204×10^{23} atoms**.

5 e.

$$\frac{18}{6.022 \times 10^{23}} = 2.99 \times 10^{-23}$$

About 2.99×10^{-23} g.

5 f. Molecular mass $= 2 \times 8.5 =$ **17**. $n = 34 \div 17 = 2$ mol; volume $= 2 \times 22.4 =$ **44.8 L**. It could be **ammonia**, NH_3 $(14 + 3 = 17)$.

5 g. $n = 0.56 \div 22.4 = 0.025$ mol; $M = 1.1 \div 0.025 =$ **44 g/mol**; VD $= 44 \div 2 =$ **22**.

5 h. Nitrogen: $40 \times ½ =$ **20 L**; hydrogen: $40 \times ⅔ =$ **60 L**.
At STP, 40 L of NH_3 is $40 \div 22.4 = 1.786$ mol; mass $= 1.786 \times 17 =$ **30.4 g**.

5 i. $n(\text{Mg}) = 6 \div 24 = 0.25$ mol. The equation gives 1 mol H_2 per mol Mg, so 0.25 mol H_2 $= 0.25 \times 22.4 =$ **5.6 L at STP**.

5 j. In a gas the molecules are tiny compared with the empty space between them (at STP they fill less than a thousandth of the volume), so their size hardly affects the volume. At the same temperature every molecule has the same average kinetic energy and adds the same push to the pressure, so equal volumes at the same temperature and pressure hold **equal numbers** of molecules, whatever their size or mass (Avogadro's law). Mass does differ: each oxygen molecule (32) is 16 times heavier than a hydrogen molecule (2), so the liter of oxygen is **16 times heavier** (1.43 g against 0.09 g at STP), with the same number of molecules.