Unit 7

Chemical Bonding

This unit online, with its interactives:
science-playground.com/s/10a7

Boil a pot of water for dal and the water turns to steam at 100 °C. But the steam is still water: every molecule is still one oxygen atom holding two hydrogen atoms. To pull those atoms apart you would need a flame of well over 2,000 °C. So there are two very different holds in a glass of water: a weak one between the molecules, which a kitchen stove breaks, and a strong one inside each molecule, which it can't. The strong one is a **covalent bond**: a pair of electrons shared by two atoms.

In this unit you will see how a covalent bond forms when two atoms' electron clouds overlap, why that gives two kinds of bond, sigma and pi, and why covalent compounds melt and boil so much lower than salts. You will meet a bond in which one atom gives both electrons (it holds together the ammonium in your fertilizer and the ozone high above Nepal), and then the chemist's way of counting atoms you can never see: the mole, and Avogadro's law for gases.

Why atoms bond

Of all the elements, only the noble gases (helium, neon, argon and the rest) are found in nature as single atoms. Every other atom joins others: oxygen as O_2, sodium and chlorine as salt, carbon in a chain. Atoms join because a bonded group of atoms has **less energy** than the same atoms apart, and anything left to itself settles into its lowest energy, as a ball rolls to the bottom of a bowl. The noble gases already have the lowest energy they can: their outer shell is full, with 2 electrons (helium) or 8 (the others).

Other atoms reach a full outer shell, a **duplet** or an **octet**, in one of two ways:

- **Transferring electrons.** A metal atom, which holds its outer electrons loosely, gives them to a non-metal atom, which pulls on electrons strongly. The two become oppositely charged ions held by their attraction: an **electrovalent (ionic) bond**, as in sodium chloride, Na^+Cl^-.
- **Sharing electrons.** Two non-metal atoms both pull strongly on electrons; neither will let go of its own. Instead each puts one electron into a pair that both atoms share: a **covalent bond**.

Which happens depends on how differently the two atoms pull on electrons, their **electronegativity** (Unit 6). A common rule of thumb: if the two electronegativities differ by more than about 1.7, the bond is mostly ionic (sodium 0.93 and chlorine 3.16 differ by 2.23); if they differ by less, it is covalent. It is a guide, not a sharp line: hydrogen fluoride differs by 1.78 and is still a covalent molecule.

7.1 Covalent bond

Formation

A **covalent bond** is the bond formed between two atoms by the **mutual sharing of a pair of electrons**, each atom giving one electron to the pair. The shared pair counts for both atoms, so each can reach a duplet or an octet. Covalent bonds usually form between non-metal atoms: of the same element (H_2, Cl_2, O_2, N_2) or of different elements (HCl, H_2O, CO_2, CH_4).

What the shared pair does

Why should sharing two electrons hold two atoms together? Take two hydrogen atoms, each a proton with one electron round it. Far apart, they don't notice each other. As they come closer, each proton starts to pull on the **other** atom's electron as well as its own, and the two electron clouds begin to overlap. The two electrons then spend much of their time **between** the two nuclei, where each electron is attracted by both protons at once. That attraction, of both nuclei for the shared pair between them, is the bond.

The atoms can't come too close, though: the two protons repel each other, and very close up the repulsion wins. So there is one distance at which the energy is lowest. Two hydrogen atoms settle there, 74 pm (picometers; 1 pm = 10^{-12} m) apart.

The distance between the nuclei of two bonded atoms is the **bond length**, and the energy needed to break one mole of the bonds (to pull the atoms apart again) is the **bond energy**. For H–H they are 74 pm and 436 kJ/mol. The same energy is given out when the bond forms, which is why hydrogen burns so fiercely: making new, stronger bonds gives out more energy than breaking the old ones takes.

Overlap of orbitals

You know from Unit 6 that electrons live in **orbitals**, each holding at most two electrons, and two electrons in the same orbital must spin in opposite directions. A covalent bond is formed when a **half-filled orbital** of one atom (holding one electron) overlaps a half-filled orbital of the other, and the two electrons, with opposite spins,

c. What are σ and π bonds? With diagrams, show how a σ bond can form from s–s, s–p and p–p overlap, and how a π bond forms.

d. Explain the formation of a nitrogen molecule in terms of σ and π bonds.

e. What is a coordinate covalent bond? What conditions are needed for it to form? Explain its formation in the hydronium ion with a diagram.

f. Draw the structures of ozone and sulphur trioxide, showing the coordinate bonds.

g. Define (i) Avogadro number, (ii) gram atom, (iii) gram mole, (iv) molar volume.

h. State Avogadro's law. Using it, show that molecular mass = 2 × vapor density.

i. Use Avogadro's law to show that a molecule of hydrogen has two atoms.

5. Numerical problems

(Atomic masses: H = 1, C = 12, N = 14, O = 16, Na = 23, Mg = 24, S = 32, Cl = 35.5, Ca = 40. $N_A = 6.022 \times 10^{23}$; molar volume at STP = 22.4 L.)

a. Find the number of moles and of molecules in 4.4 g of carbon dioxide.

b. Find the mass of 3.011×10^{23} molecules of sulphur dioxide, SO_2.

c. Find the mass and the number of molecules of 2.24 L of methane, CH_4, at STP.

d. How many atoms of each element are there in 4.9 g of sulphuric acid, H_2SO_4?

e. Find the mass of one molecule of water.

f. A gas has a vapor density of 8.5. Find its molecular mass, and the volume of 34 g of it at STP. Which gas could it be?

g. 0.56 L of a gas at STP weighs 1.1 g. Find its molar mass and its vapor density.

h. Ammonia is made by $N_2 + 3H_2 \rightarrow 2NH_3$. What volumes of nitrogen and hydrogen are needed to make 40 L of ammonia, all at the same temperature and pressure? What mass of ammonia is that, if the volume was measured at STP?

i. How many liters of hydrogen at STP are given off when 6 g of magnesium reacts with excess hydrochloric acid? $Mg + 2HCl \rightarrow MgCl_2 + H_2$

j. **Think:** Mingma says, "A liter of hydrogen and a liter of oxygen at the same temperature and pressure must hold different numbers of molecules, because oxygen molecules are 16 times heavier and much bigger." Explain what is wrong, and find how much heavier the liter of oxygen is.

Found a mistake? Please tell us.

Exercise

1. Choose the correct option

a. The number of σ and π bonds in a nitrogen molecule, N_2, is:

- **a** 3 σ
- **b** 2 σ and 1 π
- **c** 1 σ and 2 π
- **d** 3 π

b. Which overlap gives a π bond?

- **a** s–s
- **b** s–p
- **c** p–p head-on
- **d** p–p sideways

c. Which of these contains a coordinate covalent bond?

- **a** CH_4
- **b** H_2O
- **c** NH_4^+
- **d** HCl

d. The volume of 2 moles of oxygen gas at STP is:

- **a** 11.2 L
- **b** 22.4 L
- **c** 44.8 L
- **d** 64 L

2. Give reasons

a. Noble gases rarely form compounds.

b. A π bond is weaker than a σ bond.

c. Covalent compounds are poor conductors of electricity.

d. In the ammonium ion all four N–H bonds are identical, though one of them is a coordinate bond.

e. Organic compounds have lower melting and boiling points than inorganic compounds such as common salt.

f. The molar volume of every gas at STP is the same.

3. Differentiate between

i. Sigma bond and pi bond

ii. Covalent bond and coordinate covalent bond

4. Answer the following questions

a. What is a covalent bond? Explain its formation in a chlorine molecule by orbital overlap, and draw its dot-and-cross diagram.

b. Write any five characteristics of covalent compounds.

pair up in the region where the orbitals overlap. The more the orbitals overlap, the stronger the bond.

This tells you how many covalent bonds an atom can make: one for each half-filled orbital, that is, each **unpaired electron** in its outer shell. That number is its **covalency**.

Atom	Outer configuration	Unpaired electrons	Covalency	Example
hydrogen	$1s^1$	1	1	H–H
chlorine	$3s^2\ 3p^5$ (↑↓ ↑↓ ↑)	1	1	H–Cl
oxygen	$2s^2\ 2p^4$ (↑↓ ↑ ↑)	2	2	H–O–H
nitrogen	$2s^2\ 2p^3$ (↑ ↑ ↑)	3	3	NH_3, N≡N
carbon	$2s^2\ 2p^2$ (↑ ↑ and an empty 2p)	2, but 4 in compounds	4	CH_4

Carbon is the odd one. In its ground state it has only two unpaired electrons, yet it almost always makes four bonds. When carbon bonds, one of its 2s electrons moves up into the empty 2p orbital, leaving four unpaired electrons, and the energy of two extra bonds more than pays for the move. (Why the four bonds of methane then come out exactly alike, 109.5° apart, is explained in Grade 11 chemistry by hybridization.)

Showing covalent bonds

Bonds are shown in two ways. A **dot-and-cross diagram** (an electron dot or Lewis structure) shows every outer electron, one atom's as dots and the other's as crosses, with the shared pairs where the shells overlap. Pairs that belong to one atom alone are **lone pairs**. A **structural formula** shows each shared pair as a line: one line for a **single bond** (one shared pair), two for a **double bond** (two pairs), three for a **triple bond** (three pairs).

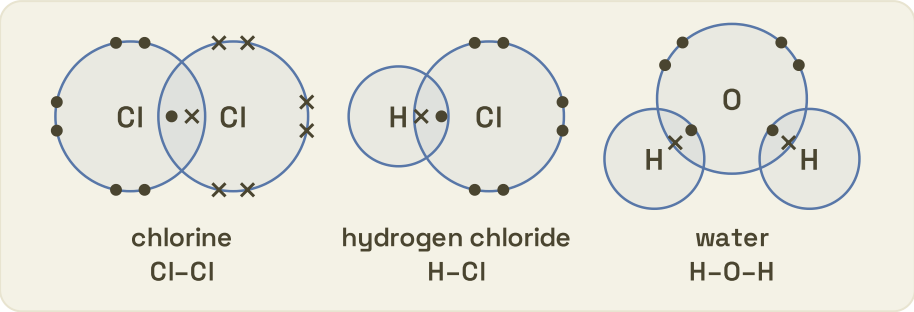


Figure 7.1 *Three molecules with single bonds. In chlorine each atom shares one electron with the other and keeps three lone pairs: both reach an octet. In hydrogen chloride, hydrogen reaches a duplet. In water, oxygen shares one pair with each hydrogen; its two lone pairs push the hydrogens together, so the molecule is bent at 104.5°.*

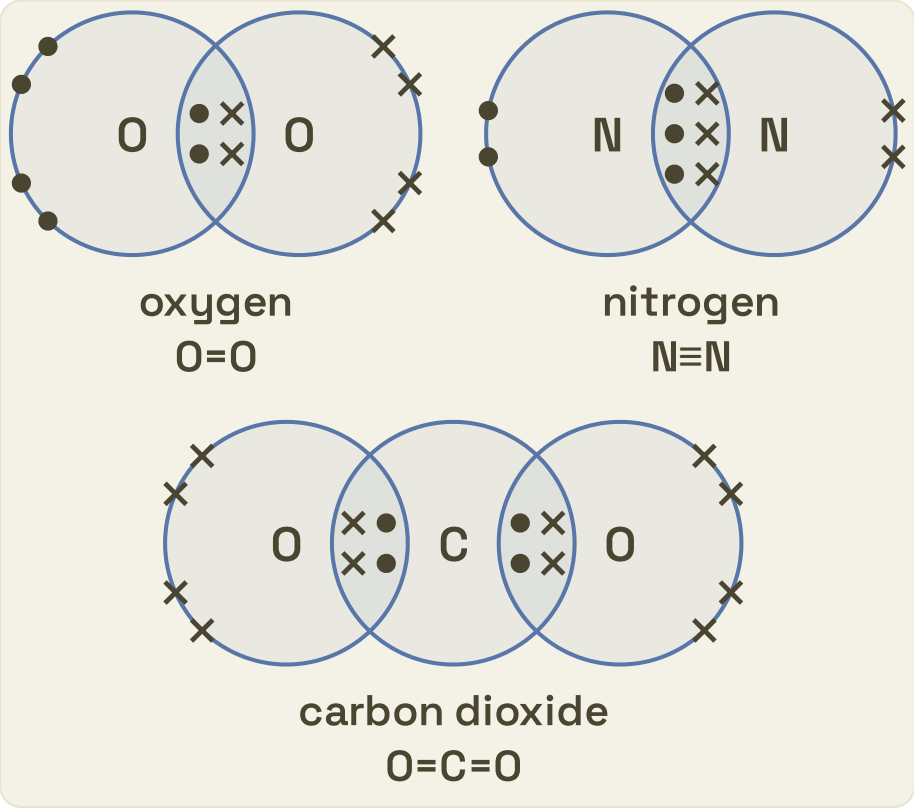


Figure 7.2 *Double and triple bonds. Two oxygen atoms share two pairs (O=O); two nitrogen atoms share three (N≡N). In carbon dioxide, carbon shares two pairs with each oxygen: two double bonds, O=C=O, a straight molecule.*

Check 4

At the same temperature and pressure, 1 L of hydrogen and 1 L of carbon dioxide have:

a the same mass
b the same number of molecules
c the same number of atoms
d the same density

Check 5

The vapor density of sulphur dioxide, SO_2, is:

a 16
b 32
c 64
d 128

IN SHORT

- A **covalent bond** is a pair of electrons shared by two atoms, each giving one; it forms when half-filled orbitals overlap, and an atom makes one bond for each unpaired electron (its **covalency**). Single, double and triple bonds share one, two and three pairs.
- **Covalent compounds** (H_2O, CH_4, NH_3, CO_2, HCl) are mostly gases, liquids or soft solids with low melting and boiling points, don't conduct, mostly don't dissolve in water, react slowly and have definite shapes. Organic compounds melt and boil lower than ionic inorganic ones for this reason.
- A **σ bond** is a head-on overlap on the axis (s–s, s–p, p–p); a **π bond** is a sideways overlap of parallel p orbitals, above and below the axis, weaker and formed only after a σ bond. Single = 1 σ; double = 1 σ + 1 π; triple = 1 σ + 2 π.
- In a **coordinate covalent (dative) bond** both electrons come from one atom (donor, with a lone pair) to another (acceptor, with an empty orbital), shown A → B. Examples: NH_4^+, H_3O^+, O_3 (O=O → O), SO_3 (one S=O, two S → O). Once formed, it is like any covalent bond.
- **Avogadro number** $N_A = 6.022 \times 10^{23}$. A **gram atom** is the atomic mass in grams; a **gram mole** the molecular mass in grams; each holds N_A particles. **Molar volume:** 1 mol of any gas fills 22.4 L at STP.
- $n = m \div M = N \div N_A = V \div 22.4$ L (gas at STP).
- **Avogadro's law:** equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules; $\frac{V_1}{n_1} = \frac{V_2}{n_2}$. It gives the molar volume, the atomicity of gases, **molecular mass = 2 × vapor density**, and the volumes of gases in reactions.

WORKED EXAMPLE

From vapor density

The vapor density of a gas is 22. Find its molecular mass and the volume that 11 g of it fills at STP.

Answer

Molecular mass $= 2 \times \text{VD} = 2 \times 22 =$ **44**.
$n = \frac{11}{44} = 0.25$ mol, so volume $= 0.25 \times 22.4 =$ **5.6 L at STP**. (It could be carbon dioxide, or propane, C_3H_8: both are 44.)

WORKED EXAMPLE

Burning methane

What volume of oxygen is needed to burn 10 L of methane completely, and what volume of carbon dioxide forms? All volumes are measured at the same temperature and pressure.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Answer

By Avogadro's law the volumes are in the ratio of the numbers in the equation, $CH_4 : O_2 : CO_2 = 1 : 2 : 1$.
Oxygen $= 2 \times 10 =$ **20 L**; carbon dioxide = **10 L**. (The water condenses to a liquid at room temperature, so it isn't counted as a gas volume.)

WORKED EXAMPLE

Carbon dioxide from limestone

How many liters of carbon dioxide at STP are produced when 50 g of calcium carbonate is heated strongly? (Ca = 40, C = 12, O = 16)

$$CaCO_3 \rightarrow CaO + CO_2$$

Answer

$M(CaCO_3) = 40 + 12 + 3 \times 16 = 100$ g/mol, so 50 g is 0.5 mol.
The equation gives 1 mol CO_2 for each mole of $CaCO_3$: 0.5 mol $CO_2 = 0.5 \times 22.4 =$ **11.2 L at STP**.

WORKED EXAMPLE

Counting to eight

Show that every atom in carbon dioxide has an octet, and find how many lone pairs the molecule has.

Answer

Carbon has 4 outer electrons and each oxygen 6: $4 + 6 + 6 = 16$ electrons in all, or 8 pairs.

- Carbon shares two pairs with each oxygen: 4 shared pairs round carbon = **8 electrons**.
- Each oxygen shares two pairs with carbon (4 electrons) and keeps two lone pairs (4 electrons): **8 electrons**.

Pairs: 4 shared + 2 lone pairs on each oxygen $= 4 + 4 = 8$ pairs, all 16 electrons accounted for. **The molecule has 4 lone pairs**, all on the oxygens.

Check 1

Why does nitrogen form three covalent bonds with hydrogen in ammonia, NH_3?

a. nitrogen has three electrons in its outer shell
b. nitrogen has three unpaired electrons in its outer shell
c. nitrogen has three shells
d. hydrogen has three electrons to share

CAREFUL

A shared pair is not always shared equally

When the two atoms are the same (H–H, Cl–Cl), the pair is shared equally: a **non-polar** covalent bond. When one atom is more electronegative, it pulls the pair closer: a **polar** covalent bond. In H–Cl the chlorine end is slightly negative (δ−) and the hydrogen end slightly positive (δ+); the same is true of O–H in water, which is why water dissolves salt and sugar so well. It is still a covalent bond: the electrons are shared, not handed over.

A STORY FROM SCIENCE

Lewis, Langmuir and Pauling

In 1916 the American chemist Gilbert N. Lewis suggested that two atoms could be held together by **sharing a pair of electrons**, and drew the dots that we still call Lewis structures. Irving Langmuir took up the idea and named it the **covalent** bond in 1919. Why a shared pair should hold atoms together was explained only in 1927, when Walter Heitler and Fritz London worked out the hydrogen molecule with the new quantum mechanics. Linus Pauling then built the whole picture of overlapping orbitals, sigma and pi bonds, and electronegativity, in his book *The Nature of the Chemical Bond* (1939), and won the Nobel Prize in Chemistry in 1954.

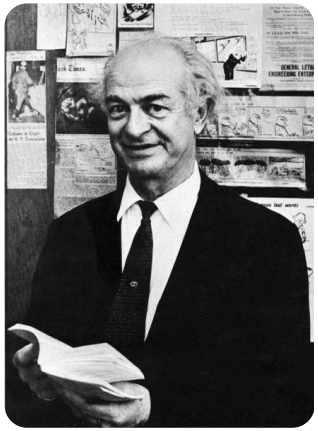


Figure 7.3 *Linus Pauling in 1964. Electronegativity and the sigma and pi picture of bonds are both largely his.*

Photo: Unknown author, Public domain

Examples of covalent compounds

Compounds whose atoms are held together by covalent bonds are **covalent compounds**. Most compounds of non-metals with each other are covalent, and so are almost all organic compounds.

3. Molecular mass and vapor density. The **vapor density** (VD) of a gas is how many times heavier a volume of it is than the same volume of hydrogen at the same temperature and pressure:

$$\text{VD} = \frac{\text{mass of a volume of the gas}}{\text{mass of the same volume of hydrogen}}$$

By Avogadro's law, the two volumes hold the same number of molecules, say n. So

$$\text{VD} = \frac{n \times \text{mass of one gas molecule}}{n \times \text{mass of one hydrogen molecule}} = \frac{\text{molecular mass of the gas}}{\text{molecular mass of hydrogen}} = \frac{M}{2}$$

since hydrogen is H_2, molecular mass 2. Therefore

$$\text{molecular mass} = 2 \times \text{vapor density}$$

A gas's vapor density can be found by weighing a flask of it; this gives its molecular mass.

4. Volumes in gas reactions. In a balanced equation for gases, the numbers in front of the formulas give the ratio of their **volumes**, as well as of their molecules and moles (at the same temperature and pressure). For making ammonia,

$$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$$

1 volume of nitrogen and 3 volumes of hydrogen give 2 volumes of ammonia.

WORKED EXAMPLE

Filling a balloon

A balloon holds 0.50 mol of helium and has a volume of 12 L. 0.25 mol more helium is added, at the same temperature and pressure. What is its new volume?

Answer

$n_1 = 0.50$ mol, $V_1 = 12$ L, $n_2 = 0.50 + 0.25 = 0.75$ mol. By Avogadro's law,

$$V_2 = \frac{V_1 n_2}{n_1} = \frac{12 \times 0.75}{0.50} = 18 \text{ L}$$

18 L. Half as much gas again, half as much volume again.

Why it is true. By the kinetic theory Grade 9, the molecules of a gas are tiny compared with the spaces between them, and at the same temperature the molecules of every gas have the same average kinetic energy. A heavy molecule moves more slowly than a light one, but it hits the wall harder, and the two effects cancel: each molecule adds the same push to the pressure. So the same number of molecules, in the same space at the same temperature, gives the same pressure, whatever the gas.

A STORY FROM SCIENCE

Avogadro's forgotten idea

Avogadro (1776–1856) was a lawyer turned physics professor in Turin. His idea had a second, bolder part: the smallest particle of hydrogen or oxygen gas is not a single atom but **two atoms joined**, a molecule. That was the only way 2 volumes of hydrogen and 1 of oxygen could make 2 volumes of steam. John Dalton, the great atomic theorist, rejected it: he believed atoms of the same element repel each other, so H_2 seemed impossible. For almost fifty years chemists couldn't agree on atomic masses: some wrote water HO, others H_2O. In 1860, four years after Avogadro's death, Stanislao Cannizzaro handed out a pamphlet at the first international chemistry conference, in Karlsruhe, showing that Avogadro's law settled all of it. Within a few years every chemist used it, and Mendeleev built his periodic table on the atomic masses it gave.

Applications of Avogadro's law

1. Molar volume. One mole of any gas contains the same number of molecules, N_A, so by Avogadro's law one mole of any gas fills the same volume at the same temperature and pressure: **22.4 L at STP**.

2. The atomicity of gases. The **atomicity** of an element is the number of atoms in one of its molecules. Hydrogen and chlorine react:

	hydrogen	+ chlorine	→ hydrogen chloride
by experiment	1 volume	1 volume	2 volumes
by Avogadro's law	n molecules	n molecules	2n molecules
for one	1 molecule	1 molecule	2 molecules

One molecule of hydrogen gives two molecules of hydrogen chloride. Each HCl molecule contains at least one hydrogen atom, so one molecule of hydrogen must contain at least **two** atoms: hydrogen is $\mathbf{H_2}$. The same reasoning shows chlorine is Cl_2, and the 2 : 1 : 2 volumes of hydrogen, oxygen and steam show oxygen is O_2.

Compound	Formula	Bonds	Where you meet it
water	H_2O	two O–H	everywhere
methane	CH_4	four C–H	biogas, about half to three quarters of it
ammonia	NH_3	three N–H	fertilizer factories, the smell of urine left standing
carbon dioxide	CO_2	two C=O	breath, soda drinks, burning
hydrogen chloride	HCl	one H–Cl	dissolved in water, hydrochloric acid (in your stomach)
ethanol	C_2H_5OH	C–C, C–H, C–O, O–H	spirit, hand sanitizer
glucose	$C_6H_{12}O_6$	many single bonds	blood sugar, fruit
urea	$CO(NH_2)_2$	C=O, C–N, N–H	the white fertilizer sold all over Nepal

Most covalent substances are made of separate **molecules**, small groups of atoms bonded together, held to other molecules only weakly. A few are **giant covalent** (network) solids, in which covalent bonds run through the whole crystal, with no separate molecules: diamond and graphite (carbon), and quartz, SiO_2, the mineral of sand.



Figure 7.4 *A natural diamond crystal (left) and a lump of graphite (right). Both are pure carbon held by covalent bonds through the whole crystal, so neither has molecules of its own. Graphite stays solid until about 3,600 °C.*

Photo: Robert M. Lavinsky / Robert M. Lavinsky, CC BY-SA 3.0

Characteristics of covalent compounds

A covalent molecule is held together inside by strong bonds, but one molecule holds the next only by weak forces of attraction between molecules (the intermolecular forces of Going Further). Almost every property of covalent compounds follows from that.

1. **Physical state.** Many are gases (CH_4, CO_2, NH_3) or liquids (water, ethanol, petrol) at room temperature; the solids are usually soft (wax, sugar, naphthalene). Ionic compounds are hard crystalline solids.
2. **Low melting and boiling points.** Melting or boiling a molecular substance only separates its molecules, against weak forces; the covalent bonds inside them are not broken. So covalent compounds melt and boil far lower than ionic ones, whose ions are held by strong attraction in every direction through the crystal (methane melts at −182 °C, sodium chloride at 801 °C).
3. **Poor conductors of electricity.** They contain no ions and no free electrons, so neither the solid, the liquid nor a solution in water conducts (sugar water doesn't light a bulb), while a molten salt or salt water does. Exceptions: graphite conducts, and a few polar molecules such as HCl react with water to form ions, so hydrochloric acid conducts.
4. **Solubility.** Most are insoluble in water but dissolve in organic solvents such as kerosene, alcohol or benzene: oil and wax don't dissolve in water but do in petrol. **Like dissolves like**: non-polar substances mix with non-polar ones. Polar covalent compounds that can attract water molecules, such as sugar, ethanol, ammonia and HCl, do dissolve in water. Most ionic compounds dissolve in water but not in kerosene.
5. **Slow reactions.** Reactions of ionic compounds in solution are almost instant, because their ions are already free. Reactions of covalent compounds need bonds to be broken and remade, so they are often slow: cooking takes time.
6. **Fixed shapes.** A covalent bond points in a definite direction, from one atom to the other (an ion pulls equally all round), so covalent molecules have definite shapes (water bent, methane tetrahedral, CO_2 straight). That is also why the same atoms can be joined in different ways to give different compounds, **isomers**, which you meet in Unit 9.

Most organic compounds are covalent and most of the familiar inorganic compounds (salts, metal oxides) are ionic, so **organic compounds melt and boil lower than inorganic ones**:

WORKED EXAMPLE

From liters to grams

Find the mass of 5.6 L of ammonia at STP. (N = 14, H = 1)

Answer

$n = \frac{5.6}{22.4} = 0.25$ mol; $M = 14 + 3 = 17$ g/mol.
Mass $= 0.25 \times 17 =$ **4.25 g**.

WORKED EXAMPLE

Which gas is it?

1.6 g of a gas occupies 1.12 L at STP. Find its molar mass, and suggest what gas it could be.

Answer

$n = \frac{1.12}{22.4} = 0.05$ mol.

$$M = \frac{m}{n} = \frac{1.6}{0.05} = 32 \text{ g/mol}$$

32 g/mol: it could be oxygen, O_2 ($2 \times 16 = 32$).

7.4 Avogadro's law

Statement

In 1808 the French chemist Joseph Louis Gay-Lussac found that gases react in simple whole-number ratios **by volume**: 2 liters of hydrogen burn with exactly 1 liter of oxygen to give 2 liters of steam, and 1 liter of hydrogen with 1 liter of chlorine gives 2 liters of hydrogen chloride. In 1811 the Italian scientist Amedeo Avogadro explained why:

Avogadro's law: equal volumes of all gases, at the same temperature and pressure, contain equal numbers of molecules.

So at a fixed temperature and pressure the volume of a gas is directly proportional to the number of its molecules, and so to its number of moles:

$$V \propto n \quad \text{or} \quad \frac{V}{n} = k \quad \text{so} \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

(at constant temperature and pressure). Twice the moles, twice the volume.

Check 3

Which contains the largest number of atoms?

a 1 g of hydrogen gas, H_2
b 1 mol of ammonia, NH_3
c 1 mol of oxygen gas, O_2
d 12 g of carbon

Gas	Molar mass	Density at STP	Volume of 1 mol
hydrogen, H_2	2.016 g/mol	0.0899 g/L	2.016 ÷ 0.0899 = 22.4 L
nitrogen, N_2	28.01 g/mol	1.2506 g/L	22.4 L
oxygen, O_2	32.00 g/mol	1.429 g/L	22.4 L
carbon dioxide, CO_2	44.01 g/mol	1.977 g/L	22.3 L

The volumes agree although the gases' masses differ 22 times: the volume of a gas depends on how many molecules it has, not what they are. (Carbon dioxide comes out a little less because it is a real gas whose molecules attract each other: real and ideal gases.) The reason is Avogadro's law, in 7.4.

For a gas at STP,

$$n = \frac{V}{22.4\ \text{L}}$$

So the mole links four things: mass, number of particles and, for a gas, volume.

$$n = \frac{m}{M} = \frac{N}{N_\text{A}} = \frac{V\ (\text{at STP})}{22.4\ \text{L}}$$

WORKED EXAMPLE

From grams to liters

What volume does 11 g of carbon dioxide occupy at STP, and how many molecules does it contain? (C = 12, O = 16)

Answer

$M = 44$ g/mol, so $n = \frac{11}{44} = 0.25$ mol.
Volume at STP $= 0.25 \times 22.4 =$ **5.6 L**.
Molecules $= 0.25 \times 6.022 \times 10^{23} =$ **1.51×10^{23}**.

Organic (covalent)	Melts at	Boils at	Inorganic (ionic)	Melts at	Boils at
methane	−182 °C	−162 °C	sodium chloride	801 °C	1,413 °C
ethanol	−114 °C	78 °C	calcium chloride	772 °C	1,935 °C
ethanoic acid	17 °C	118 °C	calcium oxide (quicklime)	2,613 °C	2,850 °C
naphthalene	80 °C	218 °C	magnesium oxide	2,852 °C	3,600 °C
candle wax	about 60 °C	above 370 °C	aluminium oxide	2,072 °C	2,977 °C

CAREFUL

It is the bonding, not "organic"

The rule is really about **molecular covalent** substances against **ionic** ones. Water, ammonia and carbon dioxide are inorganic, but they are covalent molecules and melt and boil low too. Quartz and diamond are covalent but giant: quartz melts at about 1,700 °C, and graphite stays solid to about 3,600 °C, hotter than any salt. In an exam, "organic compounds have low melting and boiling points because they are covalent" is the expected answer.

Types of covalent bond: sigma and pi

Two orbitals can overlap in two different ways, and they give two kinds of covalent bond.

Sigma (σ) bond. When two orbitals overlap **end to end, along the axis** joining the two nuclei (head-on or axial overlap), they form a **sigma bond**. The shared pair spends its time on that axis, between the nuclei. Any orbitals can do it:

- **s–s overlap:** two s orbitals, as in H_2;
- **s–p overlap:** an s and a p orbital, as in H–Cl (hydrogen's 1s and chlorine's 3p);
- **p–p overlap (head-on):** two p orbitals pointing at each other, as in Cl–Cl.

Pi (π) bond. Two p orbitals that lie **parallel** to each other, side by side, can overlap **sideways** (lateral overlap). Their overlap is in two parts, **above and below** the axis, with none on the axis itself. This is a **pi bond**.

A π bond never forms alone. Two atoms are always joined first by one σ bond, and only then can their other, parallel p orbitals overlap sideways. So:

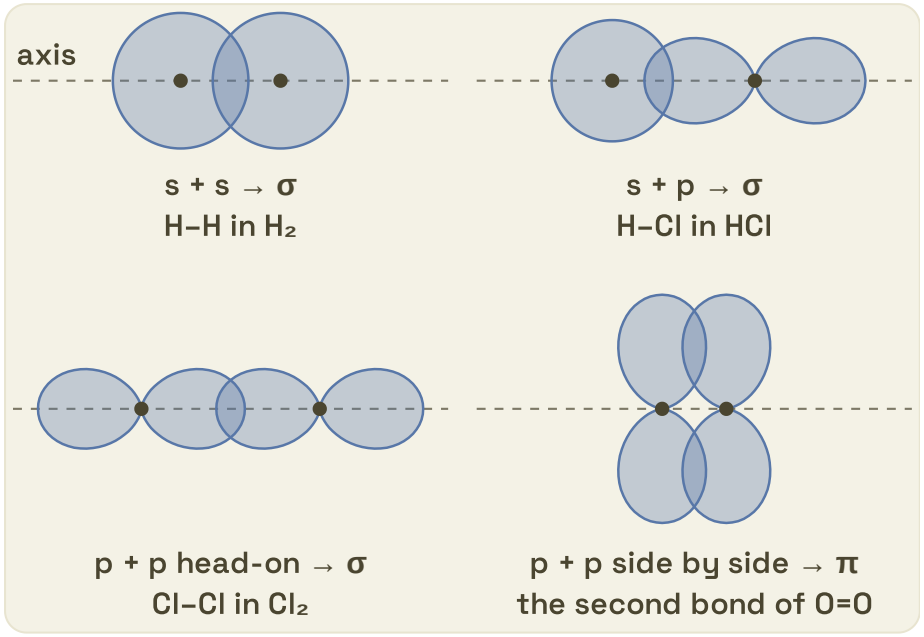


Figure 7.5 How σ and π bonds form. Where two orbitals overlap the color is darker: that is where the shared pair is found. In the three σ bonds the overlap lies on the dashed axis between the nuclei. In the π bond, two parallel p orbitals overlap above and below the axis, and not on it.

Bond	Made of	Example
single	1 σ	H–H, H–Cl, C–H
double	1 σ + 1 π	O=O, C=C in ethene
triple	1 σ + 2 π	N≡N, C≡C in ethyne

Take nitrogen. Each N atom has three half-filled p orbitals, at right angles to each other: p_x, p_y and p_z. The two p_x orbitals point at each other along the axis and overlap head-on: one σ bond. The p_y orbitals are then parallel, side by side, and overlap above and below: one π bond. The p_z orbitals, parallel too, overlap in front and behind: a second π bond. So N≡N is one σ bond and two π bonds, and its six shared electrons fill the space round the axis. It is one of the strongest bonds there is (945 kJ/mol), which is why the nitrogen that makes up 78% of the air hardly reacts.

Why a π bond is weaker than a σ bond

A head-on overlap is large, and the shared pair sits right between the two nuclei, where both pull on it hardest. A sideways overlap is smaller and off the axis. So a π bond is weaker. Compare bond energies:

WORKED EXAMPLE

Gram atoms of sodium

How many gram atoms and how many atoms are there in 46 g of sodium? (Na = 23)

Answer

Number of gram atoms = $\frac{46}{23}$ = **2 gram atoms**.

Number of atoms = $2 \times 6.022 \times 10^{23}$ = **1.204×10^{24} atoms**.

WORKED EXAMPLE

Molecules and atoms in water

For 9 g of water, find (a) the number of moles, (b) the number of molecules, (c) the number of hydrogen atoms. (H = 1, O = 16)

Answer

Molar mass of $H_2O = 2 \times 1 + 16 = 18$ g/mol.

a. $n = \frac{9}{18}$ = **0.5 mol**.

b. $N = 0.5 \times 6.022 \times 10^{23}$ = **3.011×10^{23} molecules**.

c. Each molecule has 2 H atoms: $2 \times 3.011 \times 10^{23}$ = **6.022×10^{23} hydrogen atoms**, a whole gram atom of hydrogen, 1 g, as it should be: 9 g of water contains 1 g of hydrogen.

WORKED EXAMPLE

The mass of one molecule

Find the mass of one molecule of carbon dioxide. (C = 12, O = 16)

Answer

$M = 12 + 2 \times 16 = 44$ g/mol: 6.022×10^{23} molecules weigh 44 g.

$$\text{mass of one molecule} = \frac{44}{6.022 \times 10^{23}} = 7.31 \times 10^{-23}\ \text{g}$$

7.31×10^{-23} g. No balance could ever weigh it; the mole lets us work it out.

Element	Atomic mass	1 gram atom	Atoms in it
hydrogen	1	1 g	6.022×10^{23}
carbon	12	12 g	6.022×10^{23}
sodium	23	23 g	6.022×10^{23}
iron	56	56 g	6.022×10^{23}

$$\text{number of gram atoms} = \frac{\text{mass in grams}}{\text{atomic mass}}$$

Gram mole

The molecular mass of a substance expressed in grams is its **gram molecular mass**, one **gram molecule** or **gram mole** of it. One gram mole of any substance contains 6.022×10^{23} molecules.

This leads to the general unit. A **mole** (symbol **mol**) is the amount of a substance that contains 6.022×10^{23} particles, whether atoms, molecules or ions. (Since 2019 this is the mole's exact definition: $6.022\,140\,76 \times 10^{23}$ particles.) One mole of a substance has a mass equal to its atomic or molecular mass in grams: its **molar mass**, M, in g/mol. A gram atom is a mole of atoms; a gram mole is a mole of molecules.

$$n = \frac{m}{M} \qquad N = n \times N_{\mathrm{A}}$$

where n is the number of moles, m the mass in grams, M the molar mass in g/mol and N the number of particles.

CAREFUL

Say what you are counting

"One mole of oxygen" is unclear. One gram atom of oxygen, O, is 16 g; one gram mole of oxygen gas, O_2, is 32 g, and it contains twice as many atoms as molecules. Always write the formula: 1 mol O_2.

Molar volume

A mole of a gas has a definite volume at a given temperature and pressure. At STP (0 °C and 1 atm, the STP of Nepal's books and exams, Grade 9 Optional Science), the volume of one mole of **any** gas is **22.4 L**. (At IUPAC's newer standard, 0 °C and 1 bar, it is 22.7 L; use 22.4 L unless a question says otherwise.) This is the **molar volume**, or **gram molecular volume**: the volume occupied by one gram mole of any gas at STP.

You can check it from measured densities at STP:

Bond	Bond energy	Bond length
C–C (1 σ)	347 kJ/mol	154 pm
C=C (1 σ + 1 π)	614 kJ/mol	134 pm
C≡C (1 σ + 2 π)	839 kJ/mol	120 pm

Adding a π bond to C–C adds only $614 - 347 = 267$ kJ/mol, less than the 347 of the σ bond. That is why alkenes and alkynes react at their π bonds and alkanes don't (Unit 9's addition reactions). Each extra bond also pulls the atoms closer together.

A σ bond lets the two atoms turn about it, like a wheel on an axle: the overlap stays the same as they turn. A π bond doesn't: turning one atom would twist its p orbital out of line with the other's and break the overlap. That is why a double bond holds a molecule flat and rigid (you can turn the models in Unit 9's Bonds and shapes).

Sigma (σ) bond	Pi (π) bond
Formed by head-on (axial) overlap of orbitals.	Formed by sideways (lateral) overlap of parallel p orbitals.
s–s, s–p or p–p orbitals can form it.	Only p–p (or d) orbitals can form it.
Overlap is large, on the axis between the nuclei.	Overlap is smaller, above and below the axis.
Stronger.	Weaker.
Can exist alone (every single bond).	Forms only after a σ bond between the same atoms.
The atoms can rotate about it.	No rotation about it.

WORKED EXAMPLE

Counting σ and π bonds

How many σ and π bonds are there in (a) carbon dioxide, O=C=O, and (b) hydrogen cyanide, H–C≡N?

Answer

Every bond line between two atoms has exactly one σ bond; the second and third lines are π.

a. Two double bonds: each is 1 σ + 1 π. **2 σ and 2 π.**
b. H–C is 1 σ; C≡N is 1 σ + 2 π. **2 σ and 2 π.**

DID YOU KNOW?

Oxygen sticks to a magnet

The dot-and-cross picture of O_2 pairs up every electron. But liquid oxygen is pulled into the gap between a strong magnet's poles: it is **paramagnetic** 🕮 Grade 10, and that needs unpaired electrons. A better theory of bonding, the molecular orbital theory you meet in Grade 11, explains it: O_2 really has two unpaired electrons, in two half-filled π orbitals. It is still a double bond. For your exams, O=O with one σ and one π is right.

7.2 Coordinate covalent bonds

Formation

In an ordinary covalent bond, each atom gives one electron to the shared pair. But a shared pair can also come entirely from **one** atom. A bond formed by sharing a pair of electrons that **both come from the same atom** is a **coordinate covalent bond** (also written co-ordinate, and called a **dative bond**).

- The atom that gives the pair is the **donor**. It must have a **lone pair** in its outer shell.
- The atom that receives it is the **acceptor**. It must have room for two more electrons: an empty orbital, so that it is two electrons short of a duplet or octet.

A coordinate bond is shown by an **arrow from the donor to the acceptor**, A → B (or as a line, once you know which atom gave the pair).

The best-known example is the **ammonium ion**. In ammonia, NH_3, nitrogen has an octet: three shared pairs and one lone pair. A hydrogen ion, H^+, is a hydrogen atom that has lost its electron: it has an empty 1s orbital. When ammonia meets an acid, the nitrogen's lone pair is shared with H^+:

$$NH_3 + H^+ \rightarrow NH_4^+$$

Once it has formed, a coordinate bond is **exactly like** any other covalent bond: a shared pair of electrons between two atoms. In NH_4^+ all four N–H bonds are identical, the same length and strength, with the four hydrogens at the corners of a tetrahedron, 109.5° apart. Nobody could tell which hydrogen came last. The arrow only records where the pair came from.

DID YOU KNOW?

Why a charcoal heater can kill

Carbon monoxide has a lone pair on its carbon atom, and it gives that pair to the iron atom in your blood's hemoglobin, in a coordinate bond: Fe ← CO. Hemoglobin holds CO about 200 to 250 times more tightly than the oxygen it is meant to carry, so even a little CO in the air steadily stops the blood carrying oxygen. CO has no color and no smell. Every winter, people in Nepal die in their sleep beside a charcoal stove or heater burning in a closed room. Never sleep with a fire burning in a room without fresh air.

Check 2

Which of these can act as the donor in a coordinate bond?

a H^+
b BF_3
c NH_3
d CH_4

7.3 Mole concept

Counting by weighing

Atoms are far too small and far too many to count one by one: a single drop of water holds more than a thousand billion billion molecules. Chemists count them the way a shopkeeper counts coins, by weighing. If you know what one atom weighs, you know how many are in a heap.

The trick is to weigh atoms in grams in batches of a fixed, enormous number. That number is the **Avogadro number** (Avogadro constant), N_A:

$$N_A = 6.022 \times 10^{23}$$

It was chosen so that this many atoms of an element weigh, in grams, exactly as much as the element's atomic mass. Twelve grams of carbon (atomic mass 12) holds 6.022×10^{23} carbon atoms; 16 g of oxygen atoms (atomic mass 16) holds the same number. (Going Further shows how big that number is, and how it was measured.)

Gram atom

The atomic mass of an element expressed in grams is its **gram atomic mass**, or one **gram atom** of it. One gram atom of any element contains 6.022×10^{23} atoms.

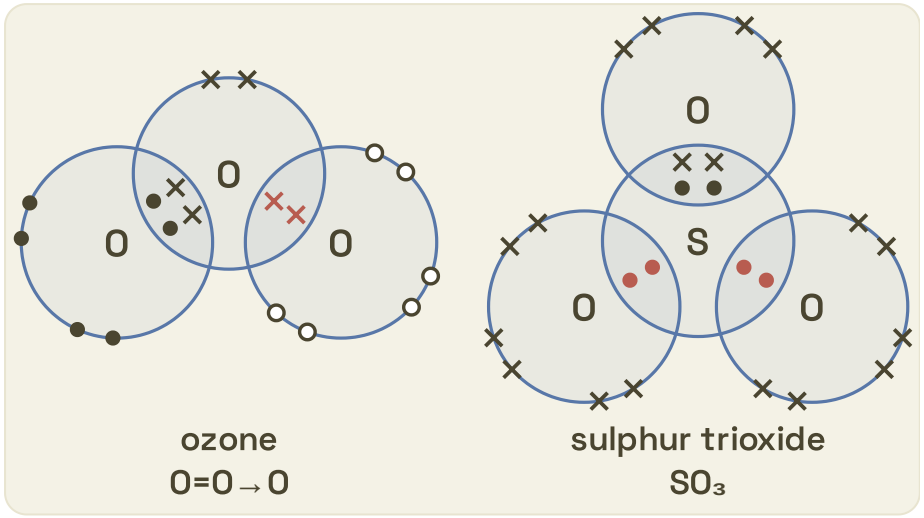


Figure 7.8 *Ozone and sulphur trioxide as they are usually drawn. The red pairs are coordinate bonds: in ozone the middle atom (crosses) gives a lone pair to the third oxygen (rings); in SO_3 sulphur (dots) gives a pair each to two of its oxygens. Count round any atom: eight.*

CAREFUL

Ozone and SO_3 are really resonance hybrids

Measurements don't quite fit the drawings. In ozone both O–O bonds are the same length, 128 pm, between a single bond (148 pm) and a double bond (121 pm); in SO_3 all three S–O bonds are the same, 142 pm, and the molecule is a flat triangle. The double bond isn't in one place: the real molecule is a blend (a **resonance hybrid**) of the drawings with the double bond in each possible position. Grade 11 chemistry explains this. For your exams, draw O_3 as O=O → O and SO_3 with one S=O and two S → O, as above.

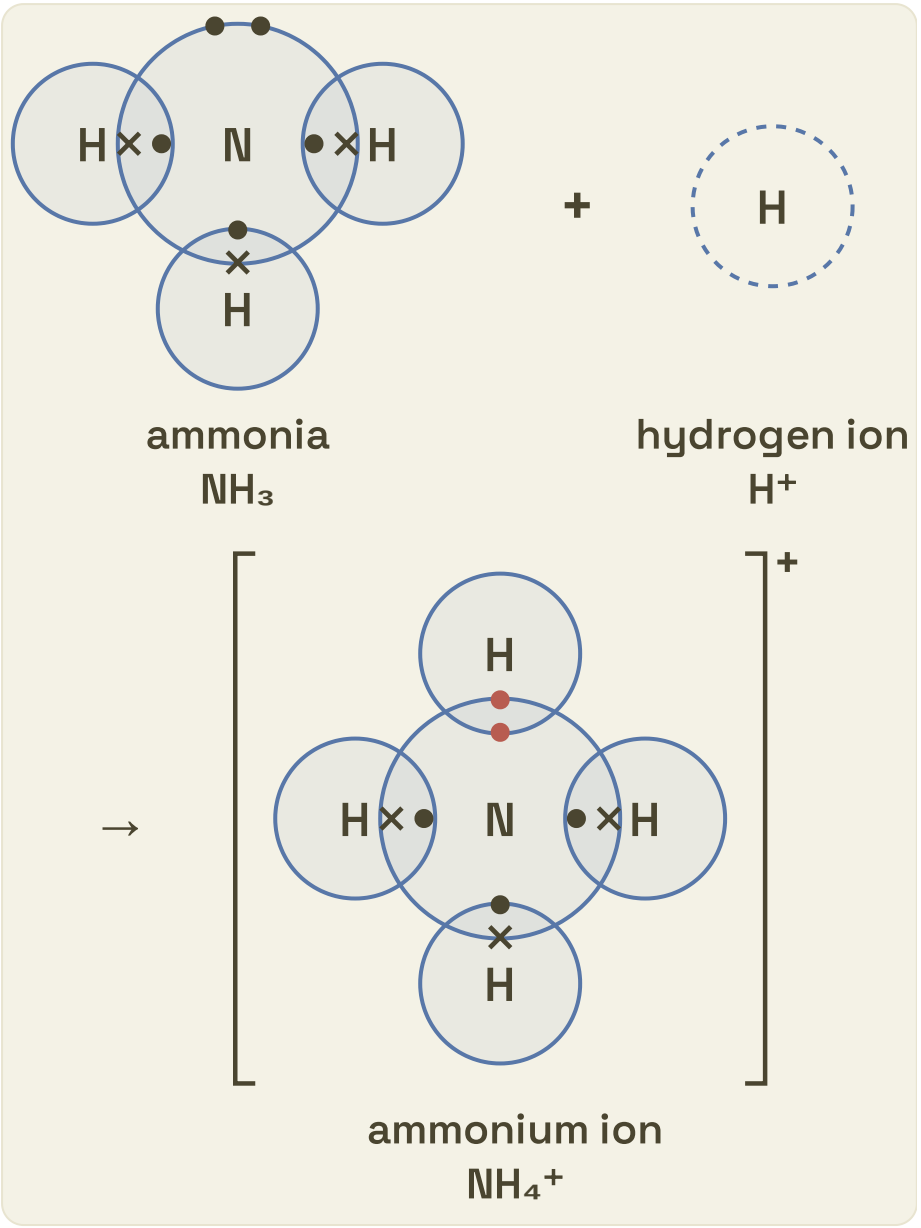


Figure 7.6 *Ammonia and a hydrogen ion make the ammonium ion. The hydrogen ion brings no electron (its shell is dashed); nitrogen's lone pair (red) becomes the shared pair of a coordinate bond, so nitrogen keeps its octet and the new hydrogen gets a duplet. The ion keeps the hydrogen ion's charge, +1.*

Covalent bond	Coordinate covalent bond
Each atom gives one electron to the shared pair.	Both electrons of the shared pair come from one atom.
Each atom needs an unpaired electron.	The donor needs a lone pair; the acceptor an empty orbital.
Shown by a line, A–B.	Shown by an arrow from donor to acceptor, A → B.
Examples: H_2, Cl_2, H_2O, CH_4.	Examples: NH_4^+, H_3O^+, O_3, SO_3.

Examples of coordinate covalent compounds

Hydronium ion, H_3O^+. An acid such as HCl, dissolved in water, gives H^+ ions. A bare H^+ never stays free in water: it is grabbed at once by a lone pair of a water molecule's oxygen, $H_2O + H^+ \rightarrow H_3O^+$. So the "$H^+$" of every acid is really H_3O^+, as Grade 9 Optional Science's Arrhenius theory mentions.

Ammonium compounds. Every ammonium salt, ammonium chloride (NH_4Cl, *nausadar*, used in soldering and dry cells), ammonium sulphate and DAP, the di-ammonium phosphate that Nepal's farmers use as fertilizer, contains NH_4^+ ions, each with one coordinate bond.

Ozone, O_3. Ozone, the gas whose layer in the stratosphere shields us from the Sun's ultraviolet rays Grade 9, has three oxygen atoms. As usually drawn, the first two share two pairs, a double bond, and the middle atom then gives one of its lone pairs to the third oxygen, which has six electrons and needs two more: O=O→O.

Sulphur trioxide, SO_3. In the contact process for making sulphuric acid, sulphur dioxide is turned into sulphur trioxide, which with water gives the acid: $SO_3 + H_2O \rightarrow H_2SO_4$. As usually drawn, sulphur makes one double bond with one oxygen, and gives each of the other two oxygens one of its pairs: two coordinate bonds.

Other examples. A molecule with a lone pair can give it to one with an empty orbital: ammonia gives its lone pair to boron trifluoride (boron has only six outer electrons), $H_3N \rightarrow BF_3$. Carbon monoxide, C≡O, has two ordinary shared pairs and one pair given by oxygen to carbon.

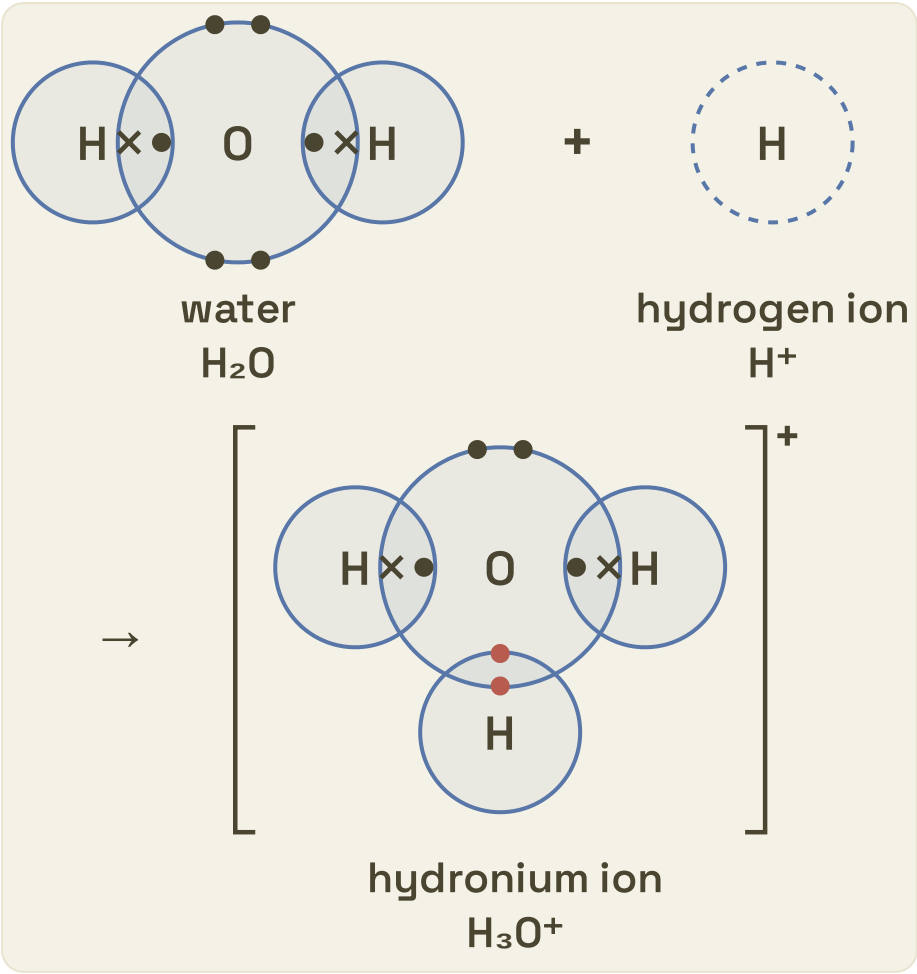


Figure 7.7 *Water and a hydrogen ion make the hydronium ion. One of oxygen's two lone pairs (red) is shared with H^+; oxygen keeps one lone pair. (Water is drawn flat here; the real molecule is bent, and H_3O^+ is a low pyramid.)*