3 Chemical bonding

This topic introduces the different ways by which chemical bonding occurs and the effect this can have on physical properties.

3.2 Covalent bonding and co-ordinate (dative covalent) bonding ☐

COVALENT BONDING

3 Chemical bonding

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	Learning outcomes Candidates should be able to:
3.2 Covalent bonding and co-ordinate (dative covalent) bonding including shapes of simple molecules	a) describe, including the use of 'dot-and-cross' diagrams: (i) covalent bonding, in molecules such as hydrogen, oxygen, chlorine, hydrogen chloride, carbon dioxide, methane, ethene (ii) co-ordinate (dative covalent) bonding, such as in the formation of the ammonium ion and in the Al_2Cl_6 molecule b) describe covalent bonding in terms of orbital overlap, giving σ and π bonds, including the concept of hybridisation to form sp, sp^2 and sp^3 orbitals (see also Section 14.3) c) explain the shapes of, and bond angles in, molecules by using the qualitative model of electron-pair repulsion (including lone pairs), using as simple examples: BF_3 (trigonal), CO_2 (linear), CH_4 (tetrahedral), NH_3 (pyramidal), H_2O (non-linear), SF_6 (octahedral), PF_5 (trigonal bipyramidal) d) predict the shapes of, and bond angles in, molecules and ions analogous to those specified in 3.2(b) (see also Section 14.3)

CHEMICAL BONDING

When two or more atoms form a chemical compound, the atoms are held together in a characteristic arrangement by attractive forces.

The chemical bond is the force of attraction between any two atoms in a compound. The attraction is the force that overcomes the repulsion of the positively charged nuclei of the two atoms.

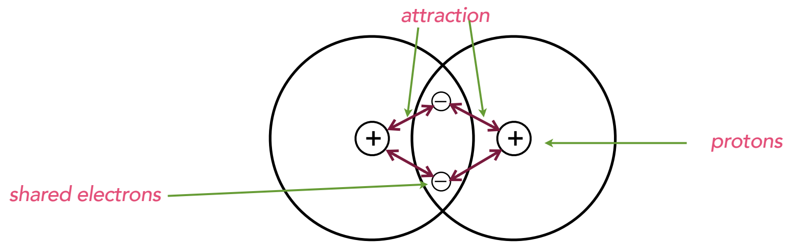
Interactions involving valence electrons are responsible for the chemical bond. We shall focus our attention on these electrons and the electron arrangement of atoms both before and after bond formation.

COVALENT BONDING

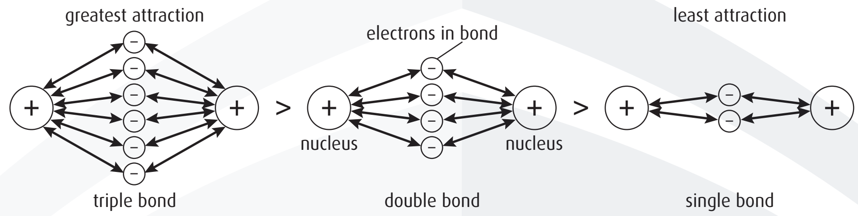
When electrons are shared rather than transferred, the shared electron pair is referred to as a covalent bond.

Covalent bonds tend to form between atoms with similar tendencies to gain or lose electrons. The most obvious examples are the diatomic molecules H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2.

COVALENT BONDING



A covalent bond is the electrostatic force of attraction between the positively charged nuclei of both atoms and their shared pair(s) of electrons.



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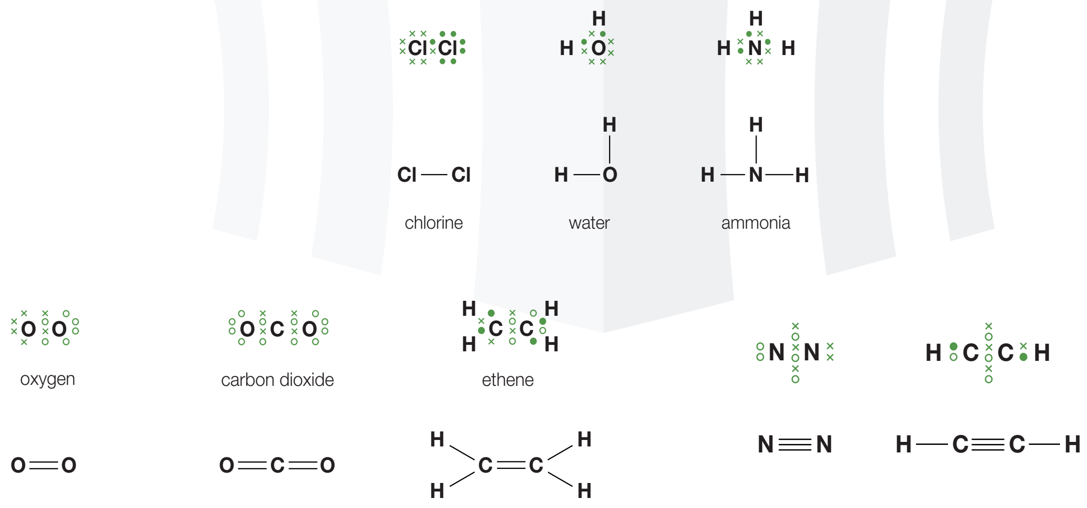
'DOT – AND – CROSS' DIAGRAMS



4

COVALENT BONDING

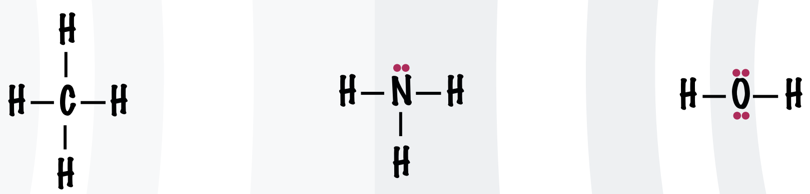
The bond is the force of attraction between the pair of electrons and the two positive nuclei of the atoms.

This increased negative charge in the centre holds the two positively charged nuclei together, thus forming the bond.

Depending on the number of electrons involved, the bonding is classified as single double and triple.

H—H H—Cl O=O N≡N

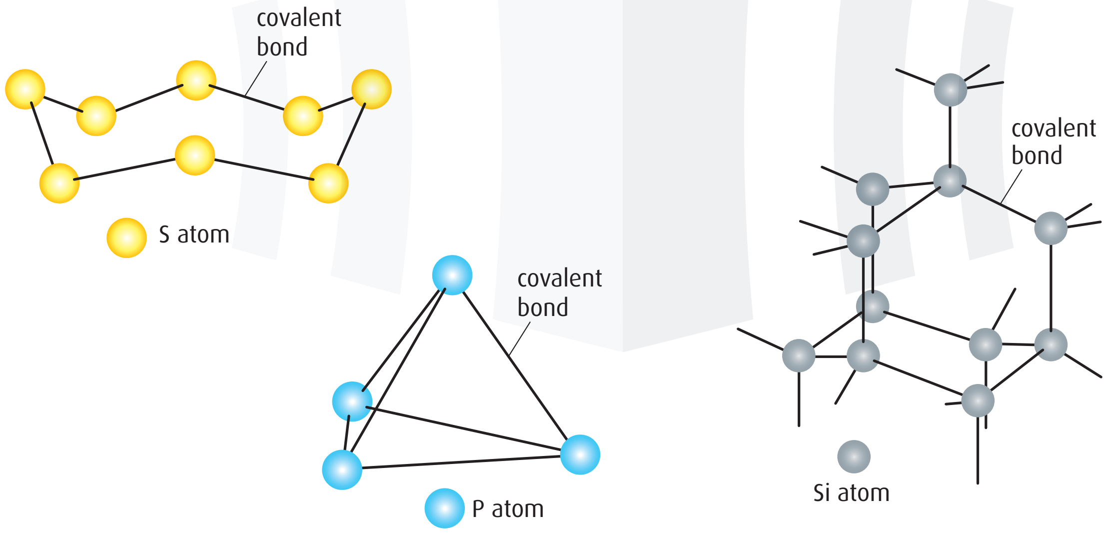
COVALENT COMPOUNDS



SKILL CHECK 1

Draw dot and cross diagrams of PCl_3, N_2, CS_2, C_2H_4, NH_3, H_2O_2, N_2H_4, SO_3

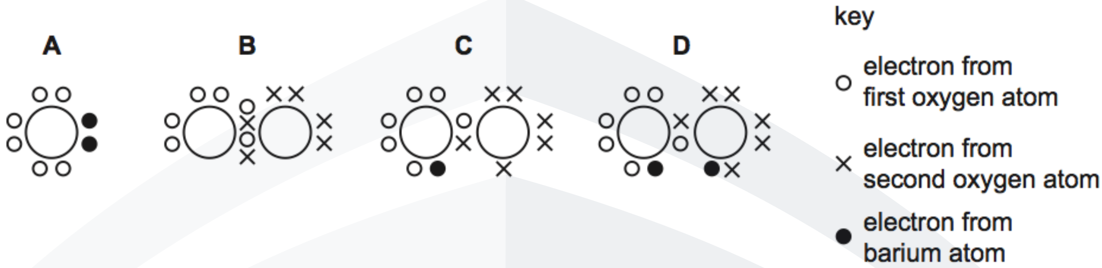
EXAMPLES OF MOLECULES



SKILL CHECK 2

When barium metal burns in oxygen, the ionic compound barium peroxide, BaO_2, is formed.

Which dot-and-cross diagram represents the electronic structure of the peroxide anion in BaO_2?



9

SKILL CHECK 3

Dicarbon monoxide, C_2O, is found in dust clouds in space. Analysis of it shows that the sequence of atoms in this molecules is C-C-O. All bonds are double bonds and there are no unpaired electrons.

How many lone pairs of electrons are present in a molecule of C_2O?

A 1　　B 2　　C 3　　D 4

10

COVALENT BONDING

Atoms share electrons to get the nearest noble gas electronic configuration

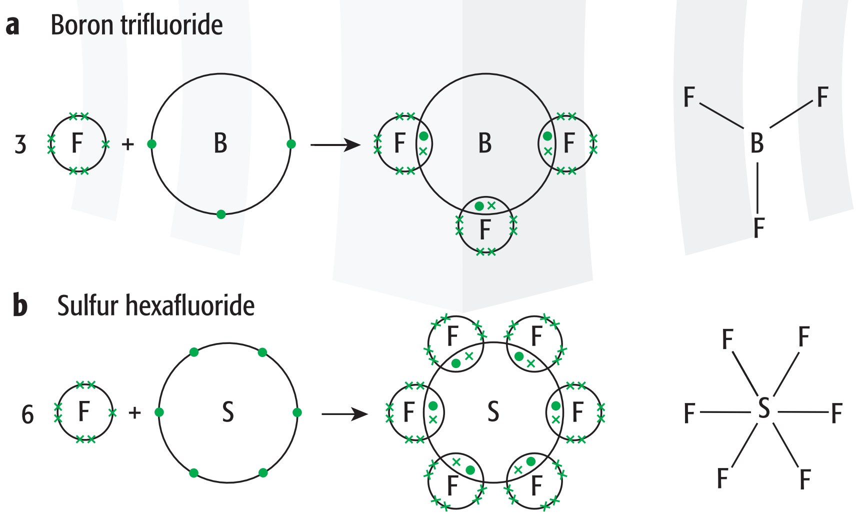
Some don't achieve an "octet" as they haven't got enough electrons
e.g. Al in $AlCl_3$

Others share only some — if they share all they will exceed their "octet"
e.g. NH_3 and H_2O

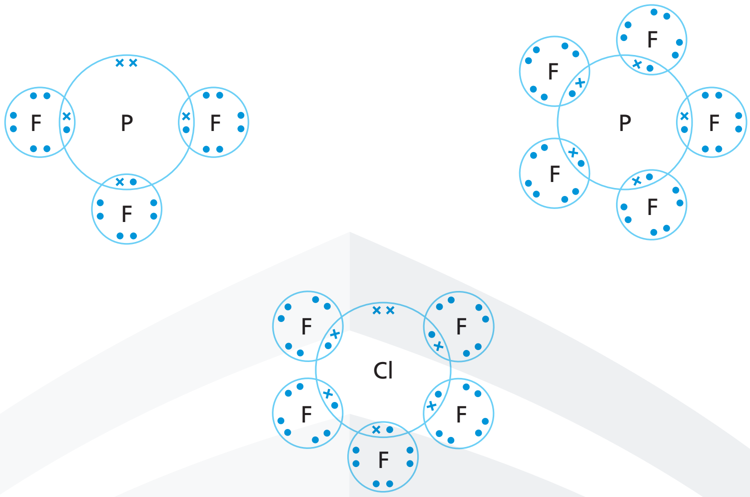
Atoms of elements in the 3rd period onwards can exceed their "octet" if they wish as they are not restricted to eight electrons in their "outer shell"
e.g. PCl_5 , SO_2 , SO_3 and SF_6

Only in period 2 are the elements restricted to form an octet. However, in period 3, more an 8 electrons can be taken in the outermost shell due to the s, p and d orbitals which take up 2, 6 and 10 electrons respectively.

DEFYING OCTET



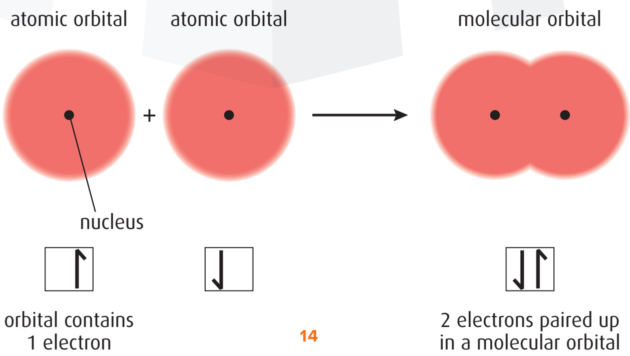
DEFYING OCTET



MOLECULAR ORBITALS

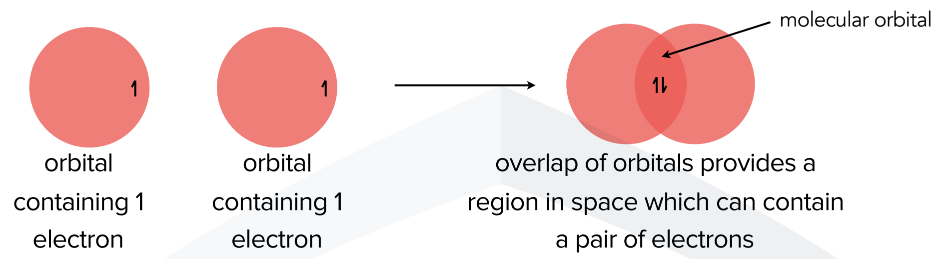
Covalent bonding is brought about by the atomic orbitals of each atom overlapping with each other, coalescing and forming a molecular orbital.

Only individually filled orbitals take part in such bonding, so that the resultant molecular orbital has only two electrons. In the molecular orbital the two electrons circulate around and are attracted to two nuclei of the two bonded atoms.



ORBITAL OVERLAP

Covalent bonds are formed when orbitals, each containing one electron, overlap. This forms a region in space where an electron pair can be found; new molecular orbitals are formed.



The space that these shared electrons move within is called a molecular orbital. A molecular orbital is made when two atomic orbitals overlap.

15

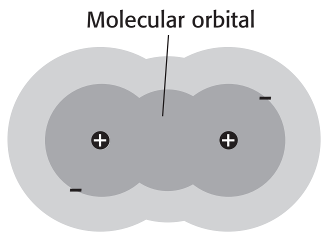
SIGMA BONDS

A Sigma bond (σ bond) is formed when orbitals overlap head-on in a covalent bond.

In a sigma bond, the electron density is concentrated in the orbital overlap volume between the two nuclei.

A sigma bond can be rotated without breaking the bond.

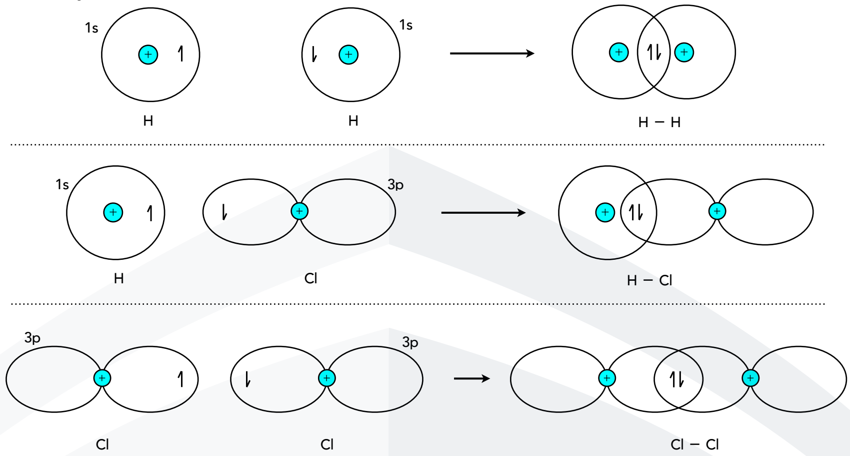
The region where the the two orbitals overlap is the molecular orbital which contains electrons of the sigma bond.



16

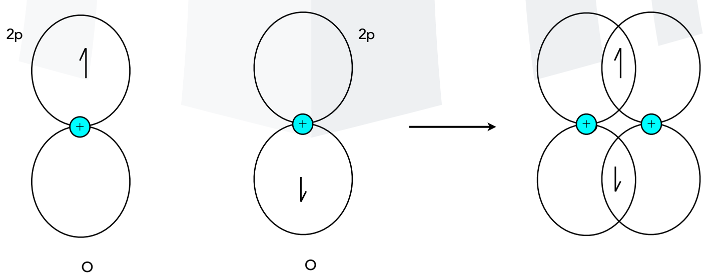
SIGMA BONDS

Sigma bonds can form by overlap of two s-orbitals, and s-orbital and p-orbital or two p-orbitals.

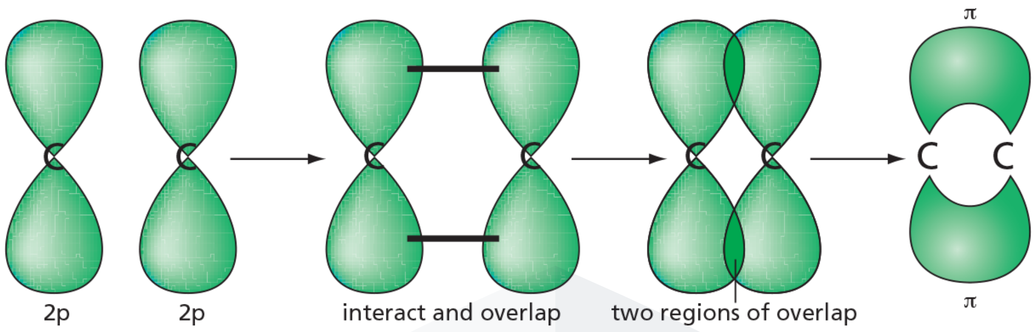


PI BONDS

A pi bond (π bond) is formed when orbitals overlap sideways in a covalent bond. Pi bonds are found in molecules with double and triple bonds.



PI BONDS

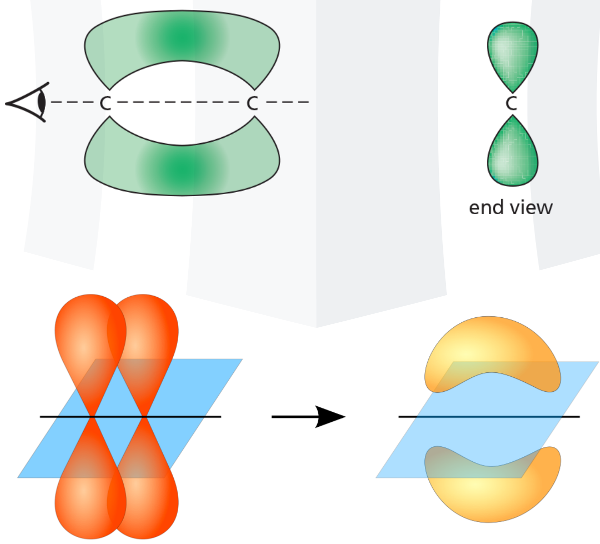


A single π bond is drawn as two electron clouds, one arising from each lobe of the p orbitals.

The two clouds of electrons in a π bond represent one bond consisting of a total of two electrons.

19

PI BONDS



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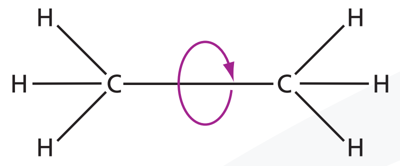
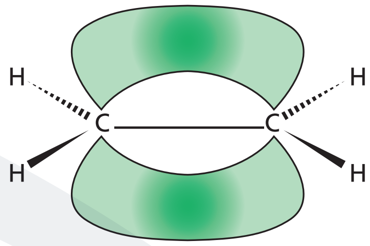
PI BONDS

In a pi bond, the electron density is concentrated in the orbital overlap volumes above and below the line joining the two nuclei.

A pi bond cannot be rotated with out breaking the bond.



rotation possible around
the single bond



no rotation possible

SKILL CHECK 4

What is always involved in a carbon-carbon π bond?

A a shared pair of electrons

B a sideways overlap of p orbitals

C delocalized electrons

DOUBLE BONDS

A double bond consists of one sigma bond and one pi bond, for example the C=C double bond in ethene and the O=O double bond in oxygen.

A typical triple bond, for example in nitrogen, consists of one sigma bond and two pi bonds in two mutually perpendicular planes.

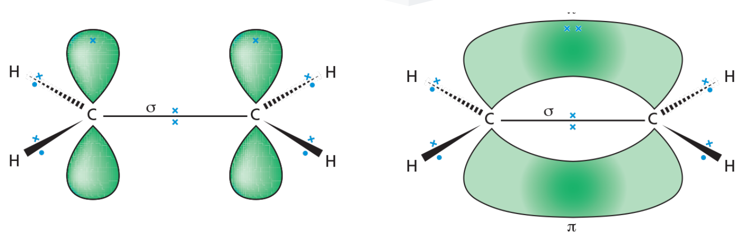
Pi bonds are weaker than sigma bonds.

MULTIPLE BONDS - ETHENE

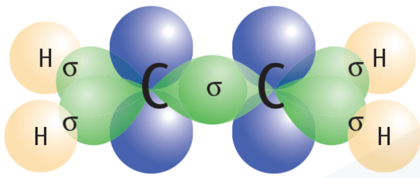
An example of a pi bond is the C ═ C bond in ethene. This bond consists of two parts.

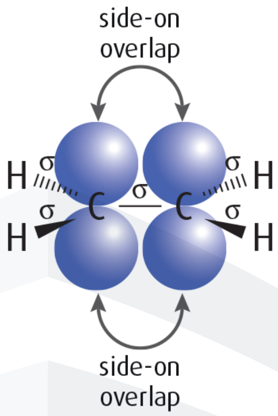
One part consists of two p orbitals of carbon overlapping in a sigma bond.

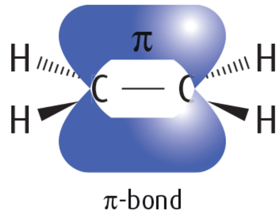
In the other part of the bond, two p orbitals overlap in a pi bond



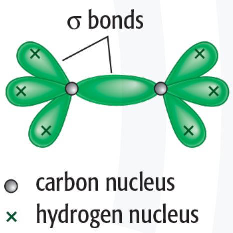
MULTIPLE BONDS - ETHENE

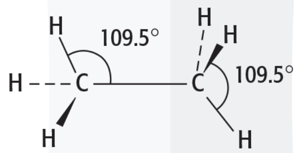


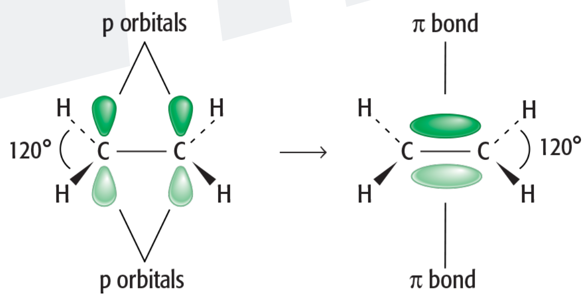




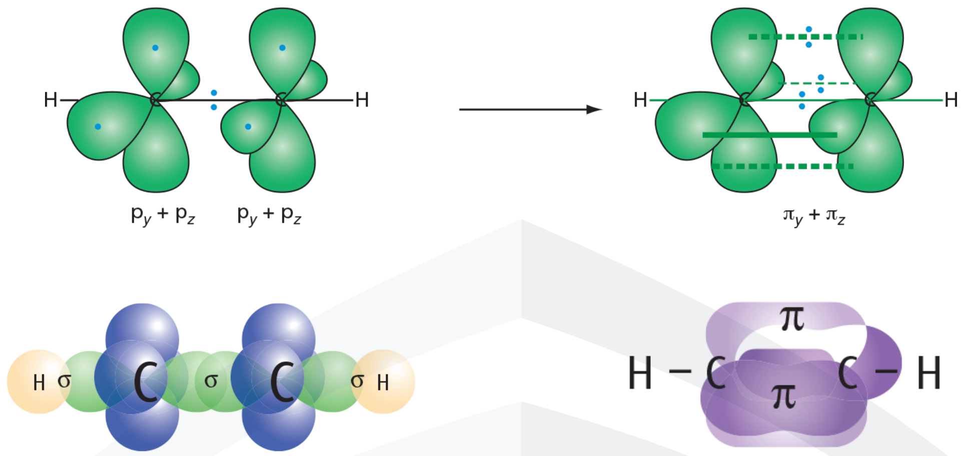
ETHANE AND ETHENE



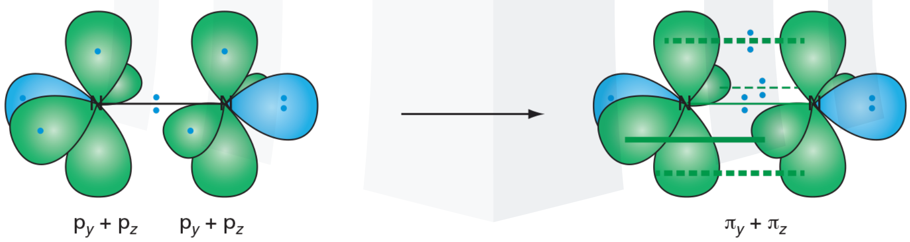




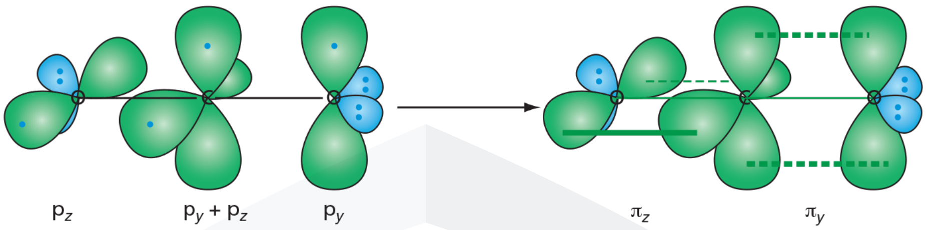
TRIPLE BOND - ETHYNE



TRIPLE BOND - NITROGEN



TWO DOUBLES - CARBON DIOXIDE



SKILL CHECK 5

Which statements about covalent bonds are correct?

A A triple bond consists of one π bond and two σ bonds.

B The electron density is a σ bond is highest along the axis between the two bonded atoms.

C A π bond restricts rotation about the σ bond axis.

DATIVE COVALENT BONDING

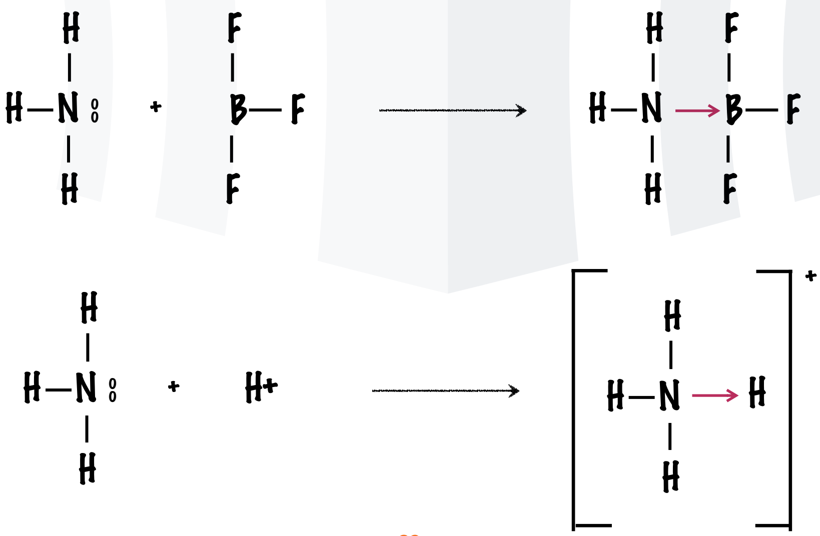
A dative covalent bond (or coordinate covalent bond) is a covalent bond between two atoms in which the shared electrons are contributed by only one of the atoms.

e.g. Boron trifluoride & ammonia NH_3BF_3

Boron has an incomplete shell in BF_3 and can accept/share a pair of electrons donated by ammonia.

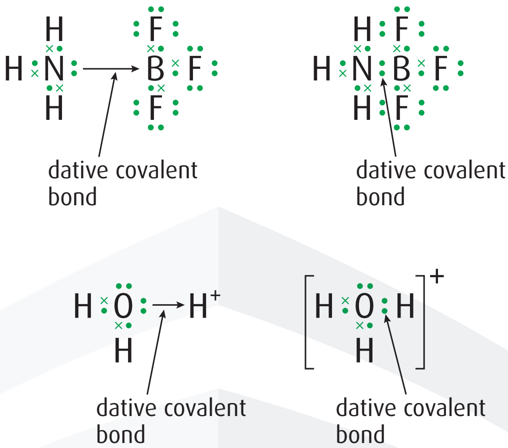
31

DATIVE COVALENT BONDING



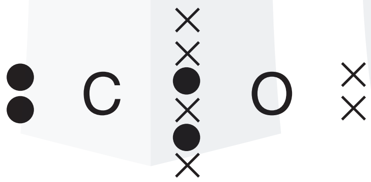
32

DATIVE COVALENT BONDING



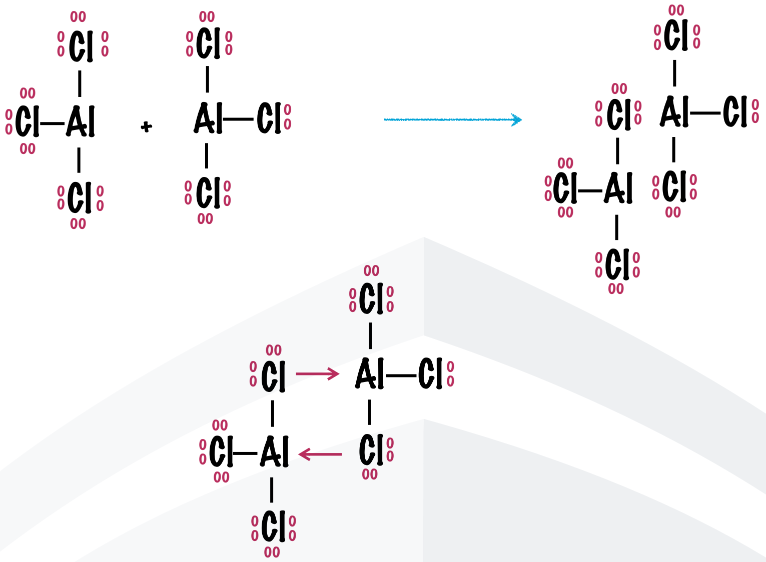
33

DATIVE COVALENT BONDING

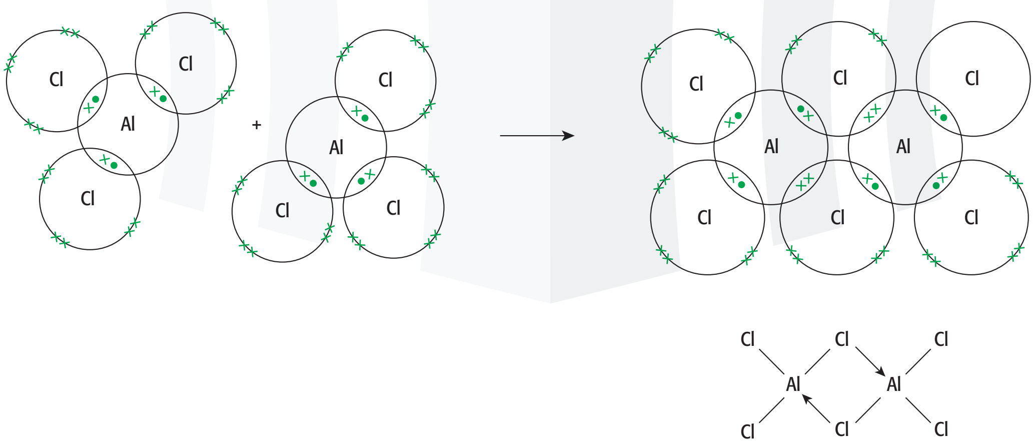


34

AL_2CL_6



AL_2CL_6



DATIVE COVALENT BONDING

A dative covalent bond differs from covalent bond only in its formation

Both electrons of the shared pair are provided by one species (donor) and it shares the electrons with the acceptor

Donor species will have lone pairs in their outer shells

Acceptor species will be short of their "octet" or maximum.

Chemists call it a dative covalent bond because the word dative means 'giving' and one atom gives both the electrons to make the bond. Once formed, there is no difference between a dative bond and any other covalent bond.

BOND ENERGY

The strength of a covalent bond is measured by the bond energy.

The bond energy is the amount of energy required to break a covalent bond, per mole of bonds. The greater the bond energy, the stronger the bond.

Very large bond energies can make molecules unreactive. The nitrogen molecule (N_2) is unreactive because of the very large N≡N bond energy of 944 KJ mol^{-1}.

BOND ENERGY

Bond forming releases energy, and is therefore exothermic.

Bond breaking requires energy, and is therefore endothermic. For the same two atoms, triple bonds are stronger than double bonds which in turn are stronger than single bonds.

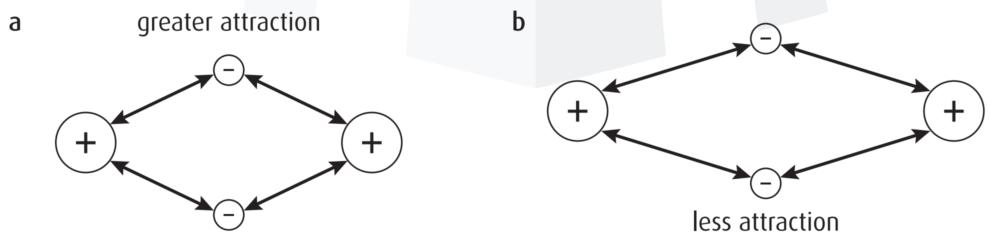
C – C	350
C = C	610
C ≡ C	840

39

BOND LENGTH

The covalent bond length is the distance between the nuclei of the two atoms linked by one or more covalent bonds

For the same two atoms, triple bonds are shorter than double bonds which in turn are shorter than single bonds.



40