

FORCES OF ATTRACTION

2.1. INTERMOLECULAR VERSUS INTRAMOLECULAR BONDS

Intermolecular attractions are attractions between one molecule and a neighbouring molecule. The forces of attraction which hold an individual molecule together (for example, the covalent bonds) are known as **intramolecular** attractions. These two words are so confusingly similar that it is safer to abandon one of them and never use it. (Clark 2004)

The forces of attraction between particles are:

- Ionic Bonds
- Covalent Bonds
- Hydrogen Bonds
- Metallic Bonds
- van der Waals forces

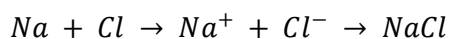
2.2. TYPES OF BONDS

2.2.1. IONIC BOND

An **ionic bond** is a type of chemical bond that involves a metal and a nonmetal ion (or polyatomic ions such as ammonium) through electrostatic attraction. In short, it is a bond formed by the attraction between two oppositely charged ions. The metal donates one or more electrons, forming a positively charged ion or cation with a stable electron configuration. These electrons then enter the non metal, causing it to form a negatively charged ion or anion which also has a stable electron configuration. The electrostatic attraction between the oppositely charged ions causes them to come together and form a bond. (Wikipedia, 2010)

For example, common table salt is sodium chloride. When sodium (Na) and chlorine (Cl) are combined, the sodium atoms each lose an electron, forming cations (Na^+), and the

chlorine atoms each gain an electron to form anions (Cl^-). These ions are then attracted to each other in a 1:1 ratio to form sodium chloride (NaCl). **(Wikipedia, 2010)**



The removal of electrons from the atoms is endothermic and causes the ions to have a higher energy. There may also be energy changes associated with breaking of existing bonds or the addition of more than one electron to form anions. However, the attraction of the ions to each other lowers their energy. **(Wikipedia, 2010)**

Ionic bonding will occur only if the overall energy change for the reaction is favourable – when the bonded atoms have a lower energy than the free ones. The larger the resulting energy change the stronger the bond. The low electronegativity of metals and high electronegativity of non-metals means that the energy change of the reaction is most favorable when metals lose electrons and non-metals gain electrons. **(Wikipedia, 2010)**

Pure ionic bonding is not known to exist. All ionic compounds have a degree of covalent bonding. The larger the difference in electronegativity between two atoms, the more ionic the bond. Ionic compounds conduct electricity when molten or in solution. They generally have a high melting point and tend to be soluble in water. **(Wikipedia, 2010)**

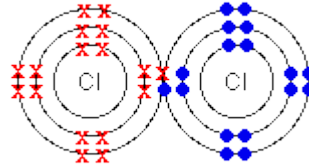
2.2.2. COVALENT COMPOUNDS

2.2.2.1. THE IMPORTANCE OF NOBLE GAS STRUCTURES

At a simple level (like GCSE) a lot of importance is attached to the electronic structures of noble gases like neon or argon which have eight electrons in their outer energy levels (or two in the case of helium). These noble gas structures are thought of as being in some way a "desirable" thing for an atom to have. You may well have been left with the strong impression that when other atoms react, they try to achieve noble gas structures. As well as achieving noble gas structures by transferring electrons from one atom to another as in ionic bonding, it is also possible for atoms to reach these stable structures by sharing electrons to give covalent bonds. **(Clark, 2004)**

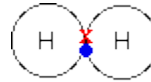
2.2.2.2. CHLORINE

For example, two chlorine atoms could both achieve stable structures by sharing their single unpaired electron as in the diagram. (Clark, 2004)



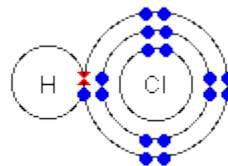
The fact that one chlorine has been drawn with electrons marked as crosses and the other as dots is simply to show where all the electrons come from. In reality there is no difference between them. The two chlorine atoms are said to be joined by a covalent bond. The reason that the two chlorine atoms stick together is that the shared pair of electrons is attracted to the nucleus of both chlorine atoms. (Clark, 2004)

2.2.2.3. HYDROGEN



Hydrogen atoms only need two electrons in their outer level to reach the noble gas structure of helium. Once again, the covalent bond holds the two atoms together because the pair of electrons is attracted to both nuclei. (Clark, 2004)

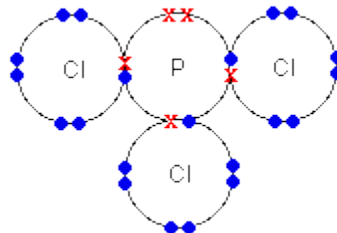
2.2.2.4. HYDROGEN CHLORIDE



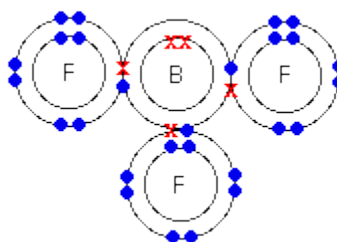
The hydrogen has a helium structure, and the chlorine an argon structure.

2.2.2.5. PHOSPHOROUS TRI-CHLORIDE

Even with a more complicated molecule like PCl_3 , there's no problem. In this case, only the outer electrons are shown for simplicity. Each atom in this structure has inner layers of electrons of 2,8. Again, everything present has a noble gas structure. (Clark, 2004)



2.2.2.6. BORON TRI-FLUORIDE

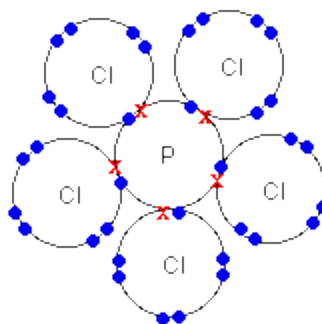


A boron atom only has 3 electrons in its outer level, and there is no possibility of it reaching a noble gas structure by simple sharing of electrons. Is this a problem? No. The boron has formed the maximum number of bonds that it can in the circumstances, and this is a perfectly valid structure. (Clark, 2004)

Energy is released whenever a covalent bond is formed. Because energy is being lost from the system, it becomes more stable after every covalent bond is made. It follows, therefore, that an atom will tend to make as many covalent bonds as possible. In the case of boron in BF_3 , three bonds is the maximum possible because boron only has 3 electrons to share. (Clark, 2004)

2.2.2.7. PHOSPHORUS PENTA-CHLORIDE

In the case of phosphorus 5 covalent bonds are possible - as in PCl_5 . Phosphorus forms two chlorides - PCl_3 and PCl_5 . When phosphorus burns in chlorine both are formed - the majority product depending on how much chlorine is available. We've already looked at the structure of PCl_3 . The diagram of PCl_5 (like the previous diagram of PCl_3) shows only the outer electrons. (Clark, 2004)



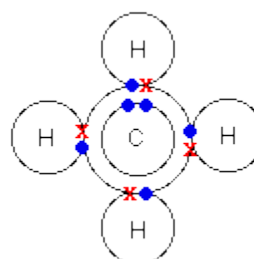
Notice that the phosphorus now has 5 pairs of electrons in the outer level - certainly not a noble gas structure. You would have been content to draw PCl_3 at GCSE, but PCl_5 would have looked very worrying. **(Clark, 2004)**

Why does phosphorus sometimes break away from a noble gas structure and form five bonds? In order to answer that question, we need to explore territory beyond the limits of current A'level syllabuses. Don't be put off by this! It isn't particularly difficult, and is extremely useful if you are going to understand the bonding in some important organic compounds. **(Clark, 2004)**

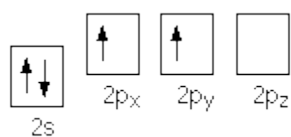
The bonding in methane, CH_4

What is wrong with the dots-and-crosses picture of bonding in methane?

We are starting with methane because it is the simplest case which illustrates the sort of processes involved. You will remember that the dots-and-crossed picture of methane looks like this. **(Clark, 2004)**

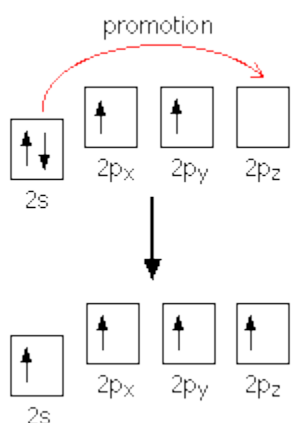


There is a serious mis-match between this structure and the modern electronic structure of carbon, $1s^2 2s^2 2p_x^1 2p_y^1$. The modern structure shows that there are only 2



unpaired electrons for hydrogens to share with, instead of the 4 which the simple view requires. You can see this more readily using the electrons-in-boxes notation. Only the 2-level electrons are shown. The $1s^2$ electrons are too deep inside the atom to be involved in bonding. The only electrons directly available for sharing are the 2p electrons. Why then isn't methane CH_2 ? (Clark, 2004)

Promotion of an electron

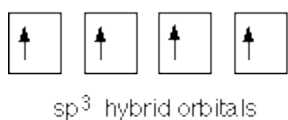


When bonds are formed, energy is released and the system becomes more stable. If carbon forms 4 bonds rather than 2, twice as much energy is released and so the resulting molecule becomes even more stable. There is only a small energy gap between the 2s and 2p orbitals, and so it pays the carbon to provide a small amount of energy to promote an electron from the 2s to the empty 2p to give 4 unpaired electrons. The extra energy released when the bonds form more than compensates for the initial input. The carbon atom is now said to be in an *excited state*. (Clark, 2004)

atom is now said to be in an *excited state*. (Clark, 2004)

Now that we've got 4 unpaired electrons ready for bonding, another problem arises. In methane all the carbon-hydrogen bonds are identical, but our electrons are in two different kinds of orbitals. You aren't going to get four identical bonds unless you start from four identical orbitals. (Clark, 2004)

Hybridisation



The electrons rearrange themselves again in a process called hybridisation. This reorganises the electrons into four identical hybrid orbitals called sp^3 hybrids (because they are made from one s orbital and three p orbitals). You should

read " sp^3 " as "s p three" - not as "s p cubed". (Clark, 2004)

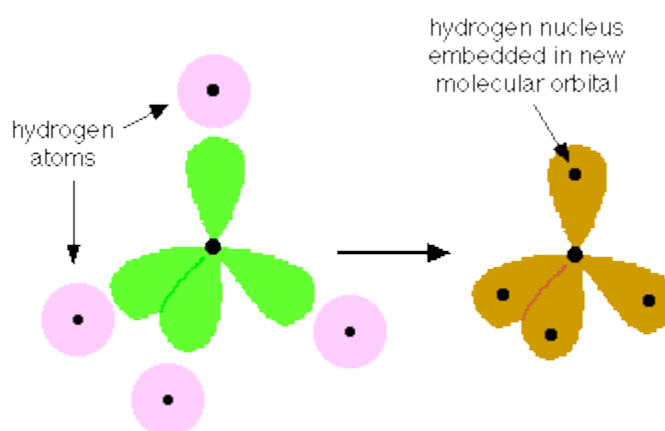
sp^3 hybrid orbitals look a bit like half a p orbital, and they arrange themselves in space so that they are as far apart as possible. You



can picture the nucleus as being at the centre of a tetrahedron (a triangularly based pyramid) with the orbitals pointing to the corners. For clarity, the nucleus is drawn far larger than it really is. (Clark, 2004)

What happens when the bonds are formed?

Remember that hydrogen's electron is in a 1s orbital - a spherically symmetric region of space surrounding the nucleus where there is some fixed chance (say 95%) of finding the electron. When a covalent bond is formed, the atomic orbitals (the orbitals in the individual atoms) merge to produce a new molecular orbital which contains the electron pair which creates the bond. (Clark, 2004)



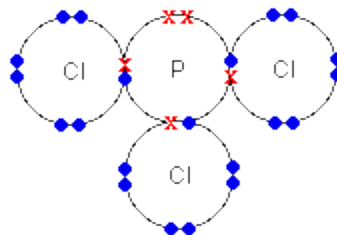
Four molecular orbitals are formed, looking rather like the original sp^3 hybrids, but with a hydrogen nucleus embedded in each lobe. Each orbital holds the 2 electrons that we've previously drawn as a dot and a cross. (Clark, 2004)

The principles involved - promotion of electrons if necessary, then hybridisation, followed by the formation of molecular orbitals - can be applied to any covalently-bound molecule. (Clark, 2004)

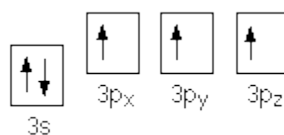
The bonding in the phosphorus chlorides, PCl_3 and PCl_5

What's wrong with the simple view of PCl_3 ?

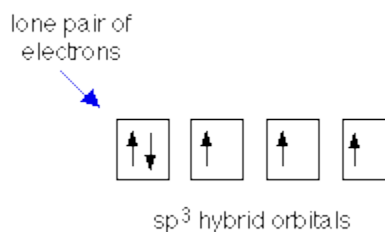
This diagram only shows the outer (bonding) electrons.



Nothing is wrong with this! (Although it doesn't account for the shape of the molecule properly.) If you were going to take a more modern look at it, the argument would go like this: Phosphorus has the electronic structure $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$. If we look only at the outer electrons as "electrons-in-boxes": **(Clark, 2004)**



There are 3 unpaired electrons that can be used to form bonds with 3 chlorine atoms. The four 3-level orbitals hybridise to produce 4 equivalent sp^3 hybrids just like in carbon - except that one of these hybrid orbitals contains a lone pair of electrons. **(Clark, 2004)**

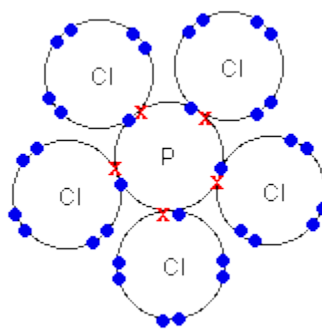


Each of the 3 chlorines then forms a covalent bond by merging the atomic orbital containing its unpaired electron with one of the phosphorus unpaired electrons to make 3 molecular orbitals. **(Clark, 2004)**

You might wonder whether all this is worth the bother! Probably not! It *is* worth it with PCl_5 , though. **(Clark, 2004)**

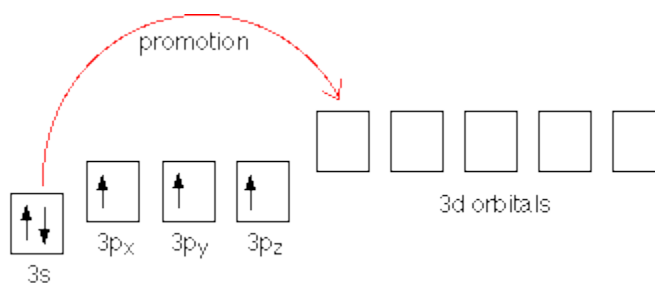
What's wrong with the simple view of PCl_5 ?

You will remember that the dots-and-crosses picture of PCl_5 looks awkward because the phosphorus doesn't end up with a noble gas structure. This diagram also shows only the outer electrons. **(Clark, 2004)**

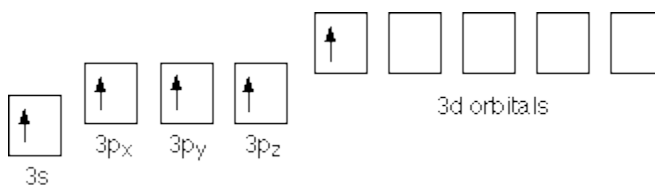


In this case, a more modern view makes things look better by abandoning any pretence of worrying about noble gas structures. **(Clark, 2004)**

If the phosphorus is going to form PCl_5 it has first to generate 5 unpaired electrons. It does this by promoting one of the electrons in the 3s orbital to the next available higher energy orbital. Which higher energy orbital? It uses one of the 3d orbitals. You might have expected it to use the 4s orbital because this is the orbital that fills before the 3d when atoms are being built from scratch. Not so! Apart from when you are building the atoms in the first place, the 3d always counts as the lower energy orbital. **(Clark, 2004)**



This leaves the phosphorus with this arrangement of its electrons:



The 3-level electrons now rearrange (hybridise) themselves to give 5 hybrid orbitals, all of equal energy. They would be called sp^3d hybrids because that's what they are made from. **(Clark, 2004)**



sp³d hybrid orbitals

The electrons in each of these orbitals would then share space with electrons from five chlorines to make five new molecular orbitals - and hence five covalent bonds. Why does phosphorus form these extra two bonds? It puts in an amount of energy to promote an electron, which is more than paid back when the new bonds form. Put simply, it is energetically profitable for the phosphorus to form the extra bonds. The advantage of thinking of it in this way is that it completely ignores the question of whether you've got a noble gas structure, and so you don't worry about it. (Clark, 2004)

A non-existent compound - NCl₅

Nitrogen is in the same Group of the Periodic Table as phosphorus, and you might expect it to form a similar range of compounds. In fact, it doesn't. For example, the compound NCl₃ exists, but there is no such thing as NCl₅. Nitrogen is 1s²2s²2p_x¹2p_y¹2p_z¹. The reason that NCl₅ doesn't exist is that in order to form five bonds, the nitrogen would have to promote one of its 2s electrons. The problem is that there aren't any 2d orbitals to promote an electron into - and the energy gap to the next level (the 3s) is far too great. In this case, then, the energy released when the extra bonds are made *isn't* enough to compensate for the energy needed to promote an electron - and so that promotion doesn't happen. Atoms will form as many bonds as possible provided it is energetically profitable. (Clark, 2004)

2.2.3. METALLIC BONDS

2.2.3.1. METALLIC BONDING IN SODIUM

Metals tend to have high melting points and boiling points suggesting strong bonds between the atoms. Even a metal like sodium (melting point 97.8°C) melts at a considerably higher temperature than the element (neon) which precedes it in the Periodic Table. (Clark, 2004)

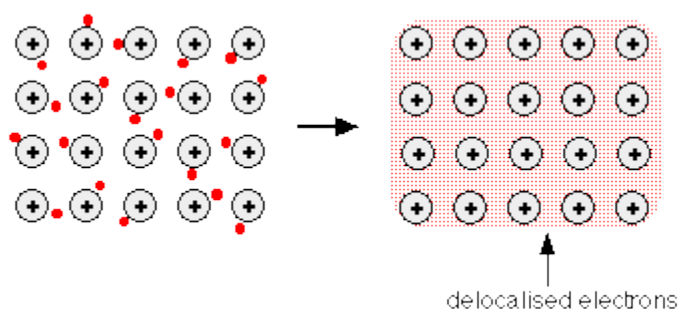
Sodium has the electronic structure 1s²2s²2p⁶3s¹. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the

corresponding electron on a neighbouring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed. (Clark, 2004)

The difference, however, is that each sodium atom is being touched by eight other sodium atoms - and the sharing occurs between the central atom and the 3s orbitals on all of the eight other atoms. And each of these eight is in turn being touched by eight sodium atoms, which in turn are touched by eight atoms - and so on and so on, until you have taken in all the atoms in that lump of sodium. (Clark, 2004)

All of the 3s orbitals on all of the atoms overlap to give a vast number of molecular orbitals which extend over the whole piece of metal. There have to be huge numbers of molecular orbitals, of course, because any orbital can only hold two electrons. (Clark, 2004)

The electrons can move freely within these molecular orbitals, and so each electron becomes detached from its parent atom. The electrons are said to be *delocalised*. The metal is held together by the strong forces of attraction between the positive nuclei and the delocalised electrons. (Clark, 2004)



This is sometimes described as "an array of positive ions in a sea of electrons".

If you are going to use this view, beware! Is a metal made up of atoms or ions? It is made of *atoms*. (Clark, 2004)

Each positive centre in the diagram represents all the rest of the atom apart from the outer electron, but that electron hasn't been lost - it may no longer have an attachment to a particular atom, but it's still there in the structure. Sodium metal is therefore written as Na - *not* Na⁺. (Clark, 2004)

2.2.3.2. METALLIC BONDING IN MAGNESIUM

If you work through the same argument with magnesium, you end up with stronger bonds and so a higher melting point. Magnesium has the outer electronic structure $3s^2$. Both of these electrons become delocalised, so the "sea" has twice the electron density as it does in sodium. The remaining "ions" also have twice the charge (if you are going to use this particular view of the metal bond) and so there will be more attraction between "ions" and "sea". (Clark, 2004)

More realistically, each magnesium atom has one more proton in the nucleus than a sodium atom has, and so not only will there be a greater number of delocalised electrons, but there will also be a greater attraction for them. Magnesium atoms have a slightly smaller radius than sodium atoms, and so the delocalised electrons are closer to the nuclei. Each magnesium atom also has twelve near neighbours rather than sodium's eight. Both of these factors increase the strength of the bond still further. (Clark, 2004)

2.2.3.3. METALLIC BONDING IN TRANSITION ELEMENTS

Transition metals tend to have particularly high melting points and boiling points. The reason is that they can involve the 3d electrons in the delocalisation as well as the 4s. The more electrons you can involve, the stronger the attractions tend to be. (Clark, 2004)

2.2.3.4. THE METALLIC BOND IN MOLTEN METALS

In a molten metal, the metallic bond is still present, although the ordered structure has been broken down. The metallic bond isn't fully broken until the metal boils. That means that boiling point is actually a better guide to the strength of the metallic bond than melting point is. On melting, the bond is loosened, not broken. (Clark, 2004)

2.3. VALENCE SHELL ELECTRON REPULSION THEORY (VSEPR)

Valence shell electron pair repulsion (VSEPR) theory is a model in chemistry used to predict the shape of individual molecules based upon the extent of electron-pair electrostatic repulsion. It is also named Gillespie-Nyholm theory after its two main

developers. The acronym "VSEPR" is sometimes pronounced "vesper" for ease of pronunciation. **(Wikipedia, 2010)**

The premise of VSEPR is that the valence electron pairs surrounding an atom mutually repel each other, and will therefore adopt an arrangement that minimizes this repulsion, thus determining the molecular geometry. The number of electron pairs surrounding an atom, both bonding and nonbonding, is called its **steric number**. **(Wikipedia, 2010)**

VSEPR theory is usually compared and contrasted with valence bond theory, which addresses molecular shape through orbitals that are energetically accessible for bonding. Valence bond theory concerns itself with the formation of sigma and pi bonds. Molecular orbital theory is another model for understanding how atoms and electrons are assembled into molecules and polyatomic ions. **(Wikipedia, 2010)**

VSEPR theory has long been criticized for not being quantitative, and therefore limited to the generation of "crude", even though structurally accurate, molecular geometries of covalent molecules. However, molecular mechanics force fields based on VSEPR have also been developed. **(Wikipedia, 2010)**

2.3.1. DESCRIPTION

VSEPR theory mainly involves predicting the layout of electron pairs surrounding one or more central atoms in a molecule, which are bonded to two or more other atoms. The geometry of these central atoms in turn determines the geometry of the larger whole. The number of electron pairs in the valence shell of a central atom is determined by drawing the Lewis structure of the molecule, expanded to show all lone pairs of electrons, alongside protruding and projecting bonds. Where two or more resonance structures can depict a molecule, the VSEPR model is applicable to any such structure. For the purposes of VSEPR theory, the multiple electron pairs in a multiple bond are treated as though they were a single "pair". **(Wikipedia, 2010)**

These electron pairs are assumed to lie on the surface of a sphere centered on the central atom, and since they are negatively charged, tend to occupy positions that minimizes their mutual electrostatic repulsions by maximising the distance between

them. The number of electron pairs therefore determines the overall geometry that they will adopt. **(Wikipedia, 2010)**

For example, when there are two electron pairs surrounding the central atom, their mutual repulsion is minimal when they lie at opposite poles of the sphere. Therefore, the central atom is predicted to adopt a *linear* geometry. If there are 3 electron pairs surrounding the central atom, their repulsion is minimized by placing them at the vertices of a triangle centered on the atom. Therefore, the predicted geometry is *trigonal*. Similarly, for 4 electron pairs, the optimal arrangement is tetrahedral. **(Wikipedia, 2010)**

This overall geometry is further refined by distinguishing between *bonding* and *nonbonding* electron pairs. A bonding electron pair is involved in a sigma bond with an adjacent atom, and, being shared with that other atom, lies farther away from the central atom than does a nonbonding pair (lone pair), which is held close to the central atom by its positively-charged nucleus. Therefore, the repulsion caused by the lone pair is greater than the repulsion caused by the bonding pair. As such, when the overall geometry has two sets of positions that experience different degrees of repulsion, the lone pair(s) will tend to occupy the positions that experience less repulsion. In other words, the lone pair-lone pair (lp-lp) repulsion is considered to be stronger than the lone pair-bonding pair (lp-bp) repulsion, which in turn is stronger than the bonding pair-bonding pair (bp-bp) repulsion. Hence, the weaker bp-bp repulsion is preferred over the lp-lp or lp-bp repulsion. **(Wikipedia, 2010)**

This distinction becomes important when the overall geometry has two or more non-equivalent positions. For example, when there are 5 electron pairs surrounding the central atom, the optimal arrangement is a trigonal bipyramid. In this geometry, two positions lie at 180° angles to each other and 90° angles to the other 3 adjacent positions, whereas the other 3 positions lie at 120° to each other and at 90° to the first two positions. The first two positions therefore experience more repulsion than the last three positions. Hence, when there are one or more lone pairs, the lone pairs will tend to occupy the last three positions first. **(Wikipedia, 2010)**

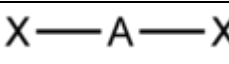
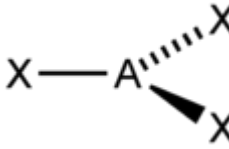
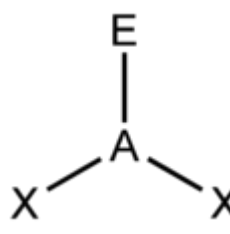
The difference between lone pairs and bonding pairs may also be used to rationalize deviations from idealized geometries. For example, the H₂O molecule has four electron pairs in its valence shell: two lone pairs and two bond pairs. The four



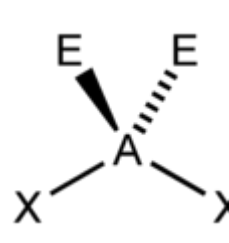
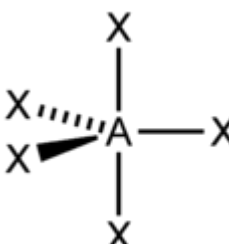

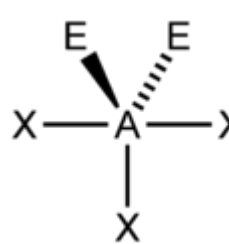

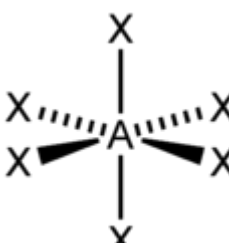

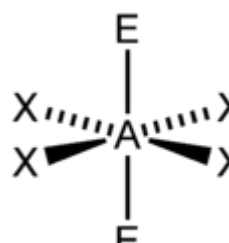
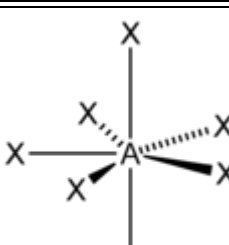
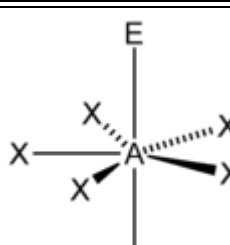
electron pairs are spread so as to point roughly towards the apices of a tetrahedron. However, the bond angle between the two O-H bonds is only 104.5° , rather than the 109.5° of a regular tetrahedron, because the two lone pairs (whose density or probability envelopes lie closer to the oxygen nucleus) exert a greater mutual repulsion than the two bond pairs. (Wikipedia, 2010)





2.3.2. THE AXE METHOD

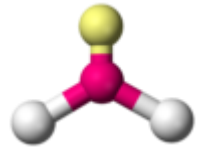
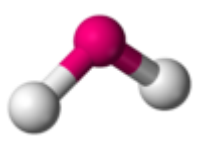
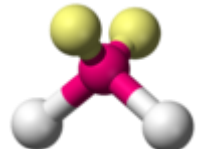
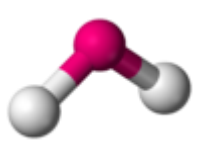
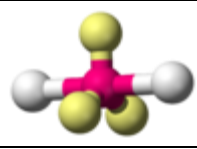
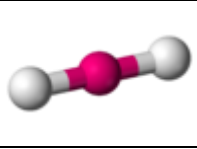
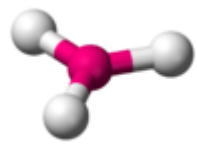
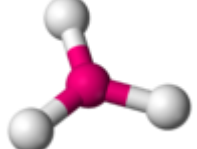
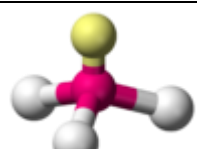
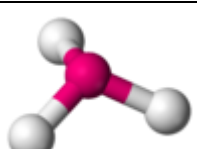
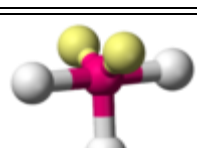
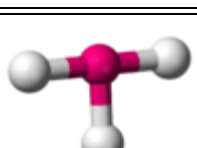
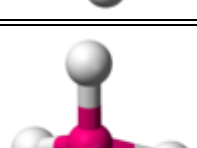
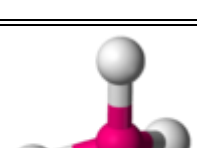
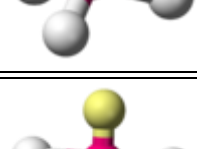
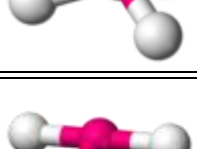
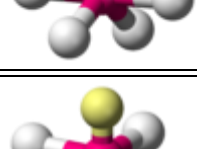
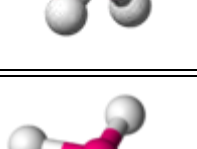
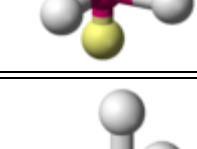
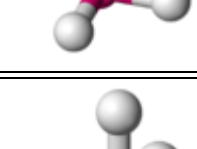
The "AXE method" of electron counting is commonly used when applying the VSEPR theory. The *A* represents the central atom and always has an implied subscript one. The *X* represents the number of sigma bonds between the central atoms and outside atoms. Multiple covalent bonds (double, triple, etc) count as one *X*. The *E* represents the number of lone electron *pairs* surrounding the central atom. The sum of *X* and *E*, known as the steric number, is also associated with the total number of hybridized orbitals used by valence bond theory. (Wikipedia, 2010)

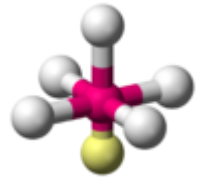
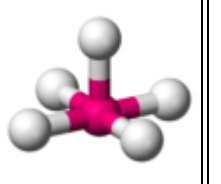
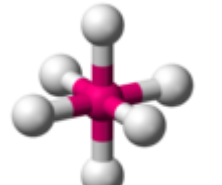
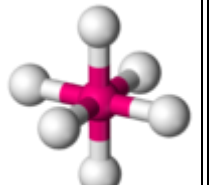
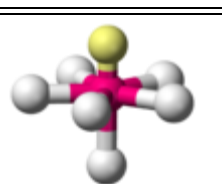
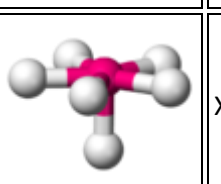
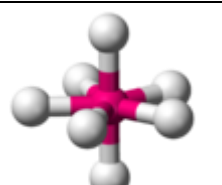
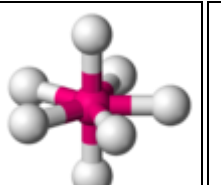
Based on the steric number and distribution of *X*'s and *E*'s, VSEPR theory makes the predictions in the following tables. Note that the geometries are named according to the atomic positions only and not the electron arrangement. For example the description of AX_2E_1 as bent means that AX_2 is a bent molecule without reference to the lone pair, although the lone pair helps to determine the geometry. (Wikipedia, 2010)

Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs
2	 Linear			
3	 Trigonal planar	 Bent		

4	 <p>Tetrahedral</p>	 <p>Trigonal pyramid</p>	 <p>Bent</p>	
5	 <p>Trigonal bipyramid</p>	 <p>Seesaw</p>	 <p>T-shaped</p>	 <p>Linear</p>
6	 <p>Octahedral</p>	 <p>Square pyramid</p>	 <p>Square planar</p>	
7	 <p>Pentagonal bipyramid</p>	 <p>Pentagonal pyramid</p>		
8	<p>Square antiprismatic</p>			

Molecule Type	Shape	Electron arrangement [†]	Geometry [‡]	Examples
AX_1E_n	Diatomic			HF, O ₂
AX_2E_0	Linear			BeCl ₂ , HgCl ₂ , CO ₂

AX_2E_1	Bent			NO_2^-, SO_2, O_3
AX_2E_2	Bent			H_2O, OF_2
AX_2E_3	Linear			XeF_2, I_3^-
AX_3E_0	Trigonal planar			$BF_3, CO_3^{2-}, NO_3^-, SO_3$
AX_3E_1	Trigonal pyramidal			NH_3, PCl_3
AX_3E_2	T-shaped			ClF_3, BrF_3
AX_4E_0	Tetrahedral			$CH_4, PO_4^{3-}, SO_4^{2-}, ClO_4^-$
AX_4E_1	Seesaw			SF_4
AX_4E_2	Square planar			XeF_4
AX_5E_0	Trigonal bipyramidal			PCl_5

AX_5E_1	Square pyramidal			ClF_5, BrF_5
AX_6E_0	Octahedral			SF_6
AX_6E_1	Pentagonal pyramidal			$XeOF_5^-, IOF_5^{2-}$ [7]
AX_7E_0	Pentagonal bipyramidal			IF_7
AX_8E_0	Square antiprismatic			XeF_2-8

When the substituent (X) atoms are not all the same, the geometry is still approximately valid, but the bond angles may be slightly different from the ones where all the outside atoms are the same. For example, the double-bond carbons in alkenes like C_2H_4 are AX_3E_0 , but the bond angles are not all exactly 120° . Similarly, $SOCl_2$ is AX_3E_1 , but because the X substituents are not identical, the XAX angles are not all equal. (Wikipedia, 2010)

2.3.3. EXCEPTIONS

There are groups of compounds where VSEPR fails to predict the correct geometry.

2.3.3.1. TRANSITION METAL COMPOUNDS

Many transition metal compounds do not have geometries explained by VSEPR which can be ascribed to there being no lone pairs in the valence shell and the interaction of core *d* electrons with the ligands. The structure of some of these compounds, including metal hydrides and alkyl complexes such as hexamethyltungsten, can be predicted correctly using the VALBOND theory, which is based on *sd* hybrid orbitals and the 3-

center-4-electron bonding model. Crystal field theory is another theory that can often predict the geometry of coordination complexes. **(Wikipedia, 2010)**

2.3.3.2. GROUP 2 HALIDES

The gas phase structures of the triatomic halides of the heavier members of group 2, (i.e. calcium, strontium and barium halides, MX_2), are not linear as predicted but are bent, (approximate X-M-X angles: CaF_2 , 145° ; SrF_2 , 120° ; BaF_2 , 108° ; SrCl_2 , 130° ; BaCl_2 , 115° ; BaBr_2 , 115° ; BaI_2 , 105°). It has been proposed by Gillespie that this is caused by interaction of the ligands with the electron core of the metal atom, polarising it so that the inner shell is not spherically symmetric, thus influencing the molecular geometry. **(Wikipedia, 2010)**

2.3.3.3. SOME AX_2E_2 MOLECULES

One example is molecular lithium oxide, Li_2O , which is linear rather than being bent, and this has been ascribed to the bonding being essentially ionic leading to strong repulsion between the lithium atoms. **(Wikipedia, 2010)**

Another example is $\text{O}(\text{SiH}_3)_2$ with an Si-O-Si angle of 144.1° which compares to the angles in Cl_2O (110.9°), $(\text{CH}_3)_2\text{O}$ (111.7°) and $\text{N}(\text{CH}_3)_3$ (110.9°). Gillespie's rationalisation is that the localisation of the lone pairs, and therefore their ability to repel other electron pairs, is greatest when the ligand has an electronegativity similar to, or greater than, the central atom. When the central atom is more electronegative, as in $\text{O}(\text{SiH}_3)_2$, the lone pairs are less well localised, have a weaker repulsive effect and this combined with the stronger ligand-ligand repulsion ($-\text{SiH}_3$ is a relatively large ligand compared to the examples above) gives the larger than expected Si-O-Si bond angle. **(Wikipedia, 2010)**

2.3.3.4. SOME AX_6E_1 MOLECULES

Some AX_6E_1 molecules, e.g. the Te(IV) and Bi(III) anions, TeCl_6^{2-} , TeBr_6^{2-} , BiCl_6^{3-} , BiBr_6^{3-} and BiI_6^{3-} , are regular octahedra and the lone pair does not affect the geometry. One rationalization is that steric crowding of the ligands allows no room for the non-bonding lone pair; another rationalization is the inert pair effect. **(Wikipedia, 2010)**

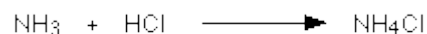
2.3.4. PROBLEMS & SOLUTIONS

2.4. COORDINATE (DATIVE COVALENT)

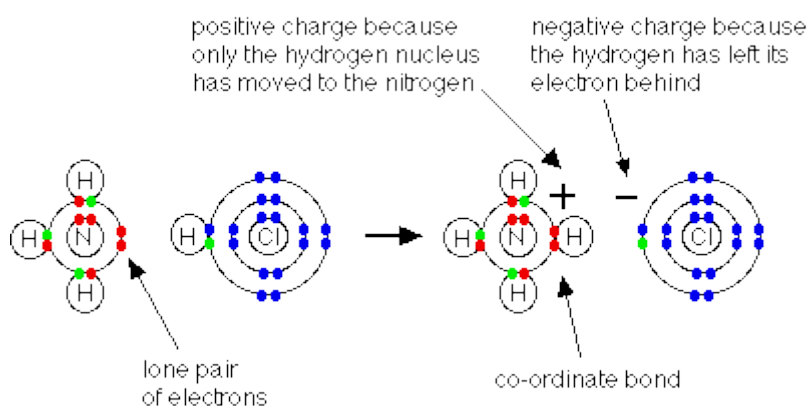
A covalent bond is formed by two atoms sharing a pair of electrons. The atoms are held together because the electron pair is attracted by both of the nuclei. In the formation of a simple covalent bond, each atom supplies one electron to the bond - but that doesn't have to be the case. A co-ordinate bond (also called a dative covalent bond) is a covalent bond (a shared pair of electrons) in which both electrons come from the same atom. For the rest of this page, we shall use the term co-ordinate bond - but if you prefer to call it a dative covalent bond, that's not a problem!

2.4.1. THE REACTION BETWEEN AMMONIA AND HYDROGEN CHLORIDE

If these colourless gases are allowed to mix, a thick white smoke of solid ammonium chloride is formed.



Ammonium ions, NH_4^+ , are formed by the transfer of a hydrogen ion from the hydrogen chloride to the lone pair of electrons on the ammonia molecule.

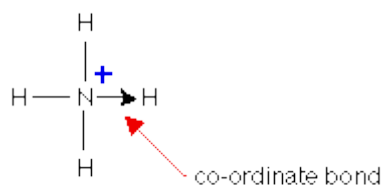


When the ammonium ion, NH_4^+ , is formed, the fourth hydrogen is attached by a dative covalent bond, because only the hydrogen's nucleus is transferred from the chlorine to the nitrogen. The hydrogen's electron is left behind on the chlorine to form a negative chloride ion.

Once the ammonium ion has been formed it is impossible to tell any difference between the dative covalent and the ordinary covalent bonds. Although the electrons are shown differently in the diagram, there is no difference between them in reality.

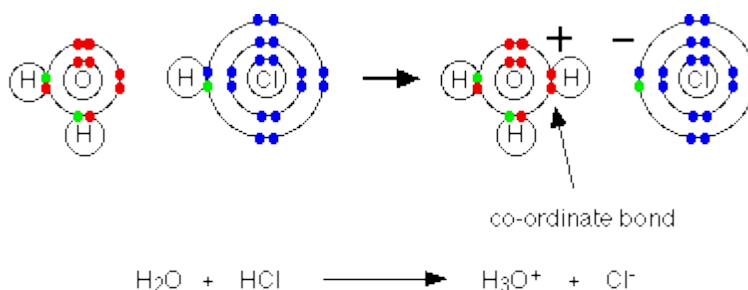
2.4.1.1. REPRESENTING CO-ORDINATE BONDS

In simple diagrams, a co-ordinate bond is shown by an arrow. The arrow points from the atom donating the lone pair to the atom accepting it.



2.4.1.2. DISSOLVING HYDROGEN CHLORIDE IN WATER TO MAKE HYDROCHLORIC ACID

Something similar happens. A hydrogen ion (H^+) is transferred from the chlorine to one of the lone pairs on the oxygen atom.



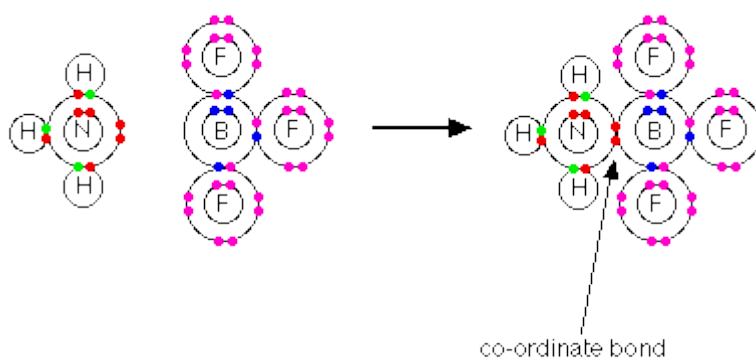
The H_3O^+ ion is variously called the hydroxonium ion, the hydronium ion or the oxonium ion. In an introductory chemistry course (such as GCSE), whenever you have talked about hydrogen ions (for example in acids), you have actually been talking about the hydroxonium ion. A raw hydrogen ion is simply a proton, and is far too reactive to exist on its own in a test tube.

If you write the hydrogen ion as $H^+_{(aq)}$, the " $_{(aq)}$ " represents the water molecule that the hydrogen ion is attached to. When it reacts with something (an alkali, for example), the

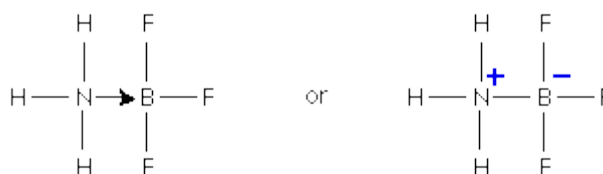
hydrogen ion simply becomes detached from the water molecule again. Note that once the co-ordinate bond has been set up, all the hydrogens attached to the oxygen are exactly equivalent. When a hydrogen ion breaks away again, it could be any of the three.

2.4.2. THE REACTION BETWEEN AMMONIA AND BORON TRIFLUORIDE

If you have recently read the page on covalent bonding, you may remember boron trifluoride as a compound which doesn't have a noble gas structure around the boron atom. The boron only has 3 pairs of electrons in its bonding level, whereas there would be room for 4 pairs. BF_3 is described as being *electron deficient*. The lone pair on the nitrogen of an ammonia molecule can be used to overcome that deficiency, and a compound is formed involving a co-ordinate bond.



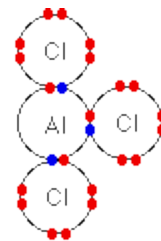
Using lines to represent the bonds, this could be drawn more simply as:



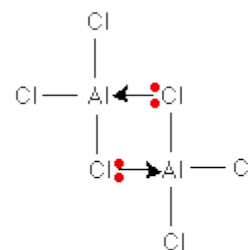
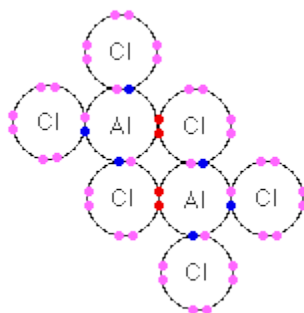
The second diagram shows another way that you might find co-ordinate bonds drawn. The nitrogen end of the bond has become positive because the electron pair has moved away from the nitrogen towards the boron - which has therefore become negative. We shan't use this method again - it's more confusing than just using an arrow.

2.4.3. THE STRUCTURE OF ALUMINIUM CHLORIDE

Aluminium chloride sublimes (turns straight from a solid to a gas) at about 180°C. If it simply contained ions it would have a very high melting and boiling point because of the strong attractions between the positive and negative ions. The implication is that when it sublimes at this relatively low temperature, it must be covalent. The dots-and-crosses diagram shows only the outer electrons. AlCl₃, like BF₃, is electron deficient. There is likely to be a similarity, because aluminium and boron are in the same group of the Periodic Table, as are fluorine and chlorine.



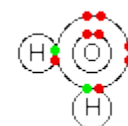
Measurements of the relative formula mass of aluminium chloride show that its formula in the vapour at the sublimation temperature is not AlCl₃, but Al₂Cl₆. It exists as a dimer (two molecules joined together). The bonding between the two molecules is co-ordinate, using lone pairs on the chlorine atoms. Each chlorine atom has 3 lone pairs, but only the two important ones are shown in the line diagram.



Energy is released when the two co-ordinate bonds are formed, and so the dimer is more stable than two separate AlCl₃ molecules.

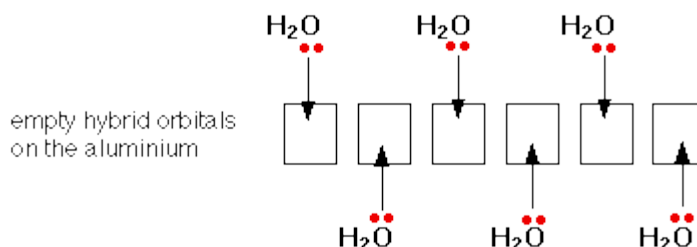
2.4.4. THE BONDING IN HYDRATED METAL IONS

Water molecules are strongly attracted to ions in solution - the water molecules clustering around the positive or negative ions. In many cases, the attractions are so great that formal bonds are made, and this is true of almost all positive metal ions. Ions with water molecules attached are described as **hydrated ions**. Although aluminium chloride is covalent, when it dissolves in water, ions are produced. Six water molecules bond to the aluminium to give an ion with the formula Al(H₂O)₆³⁺. It's called the hexaaquaaluminium ion - which translates as six ("hexa") water molecules ("aqua") wrapped around an aluminium ion. The bonding in this (and the similar

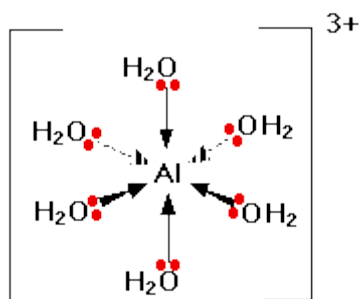


ions formed by the great majority of other metals) is co-ordinate (dative covalent) using lone pairs on the water molecules.

Aluminium is $1s^2 2s^2 2p^6 3s^2 3p_x^1$. When it forms an Al^{3+} ion it loses the 3-level electrons to leave $1s^2 2s^2 2p^6$. That means that all the 3-level orbitals are now empty. The aluminium re-organises (hybridises) six of these (the 3s, three 3p, and two 3d) to produce six new orbitals all with the same energy. These six hybrid orbitals accept lone pairs from six water molecules. You might wonder why it chooses to use six orbitals rather than four or eight or whatever. Six is the maximum number of water molecules it is possible to fit around an aluminium ion (and most other metal ions). By making the maximum number of bonds, it releases most energy and so becomes most energetically stable.



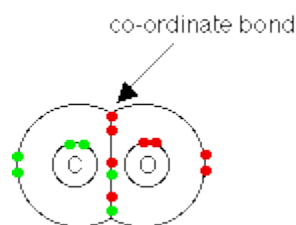
Only one lone pair is shown on each water molecule. The other lone pair is pointing away from the aluminium and so isn't involved in the bonding. The resulting ion looks like this:



Because of the movement of electrons towards the centre of the ion, the 3+ charge is no longer located entirely on the aluminium, but is now spread over the whole of the ion.

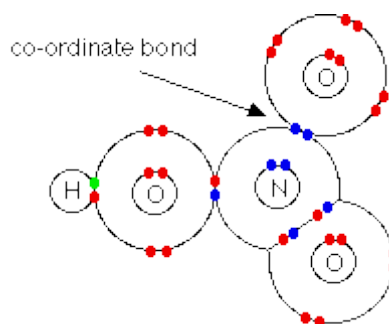
2.4.5. CARBON MONOXIDE

Carbon monoxide (CO) can be thought of as having two ordinary covalent bonds between the carbon and the oxygen plus a co-ordinate bond using a lone pair on the oxygen atom.



2.4.6. NITRIC ACID

In this case, one of the oxygen atoms can be thought of as attaching to the nitrogen via a co-ordinate bond using the lone pair on the nitrogen atom.



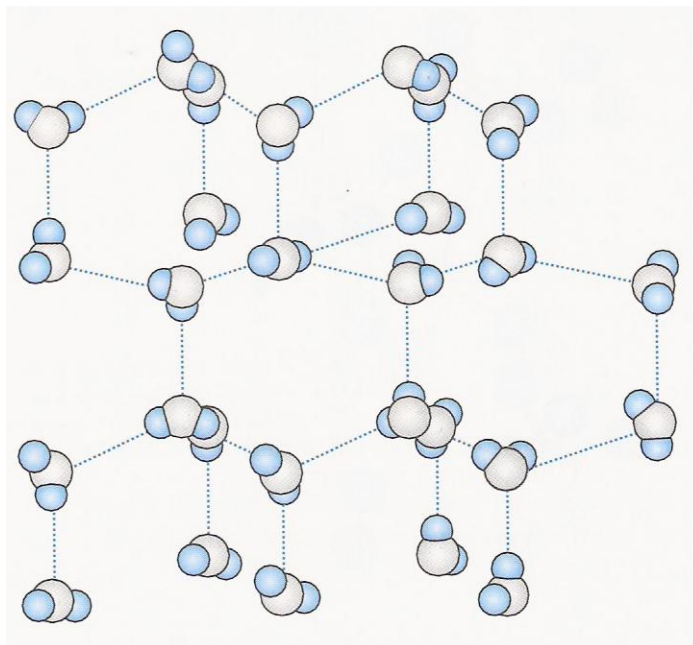
In fact this structure is misleading because it suggests that the two oxygen atoms on the right-hand side of the diagram are joined to the nitrogen in different ways. Both bonds are actually identical in length and strength, and so the arrangement of the electrons must be identical. There is no way of showing this using a dots-and-crosses picture. The bonding involves delocalisation.

2.11. LATTICE STRUCTURES

2.11.1. SIMPLE MOLECULAR

Iodine, I₂, molecules are packed in layers and held by weak van der waals forces. Treated earlier.

2.11.2. HYDROGEN BONDING



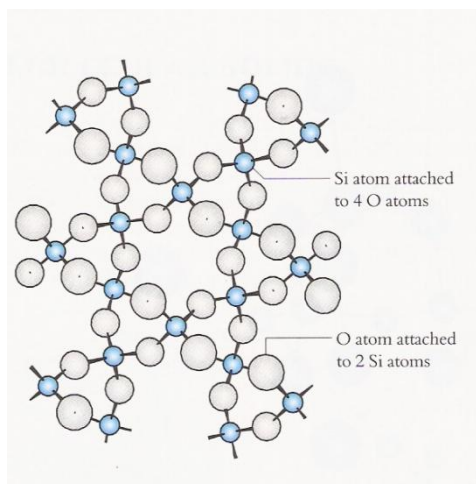
Water is one substance that is less dense as a solid than it is as a liquid. The water molecules line up in such a way as to maximize the amount of hydrogen bonding between them. This leaves a tremendous amount of space in the lattice structure hence the low density, melting point -0°C . In ice each water molecule is held by hydrogen bonds. Each oxygen atom is surrounded tetrahedrally by four hydrogen atoms, two covalently bonded. The density of most substances decrease when they are warmed, the density increases as more hydrogen bonds are broken because the molecules continue to come closer together. As the temperature rises above 4°C the density of water gradually decreases.

The hydrogen bond strength in ice is 21 kJ mol^{-1} of water molecules. The heat required to melt ice at 0°C is only 5.9 kJ mol^{-1} . These figures show that less than 30% of the H – bonds are broken when ice melts. This means that considerable hydrogen bonding remain in liquid water. Because of H – bonding water has a high boiling point, latent heat of fusion, vaporization, heat capacity, surface tension, etc.

2.11.3. GIANT MOLECULAR

Giant molecular or infinite covalent compound consist in the solid state a lattice work of atoms joined together by covalent bonds e.g. silicon dioxide (silica). SiO_2 (empirical formula) or better by $(\text{SiO}_2)_n$. The Si – O bonds about each silicon atom are tetrahedrally distributed and each oxygen atom is bonded to two other silicon atoms. SiO_2 has a very

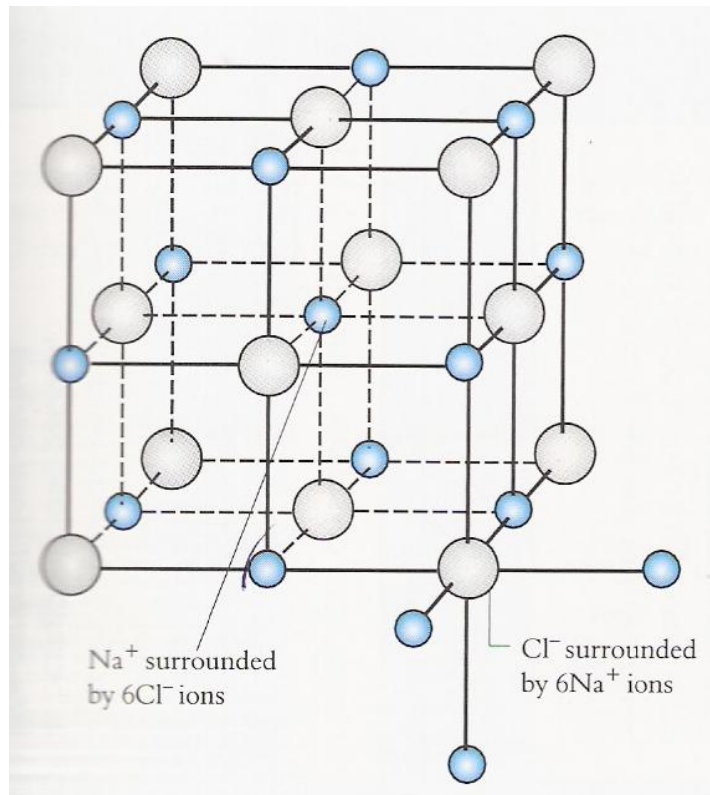
high melting (1410 °C) and boiling (2355 °C) temperature. Silicon is used in semi – conductors. First ionization energy 789 K J mol⁻¹.



2.11.4. GIANT IONIC

Ionic compound composed of ions of opposite charges, held together by electrostatic (Coulombs) forces. A positively charged ion (cation) forms when an atom loses one or more electrons and a negatively charged ion (anion) forms when an atom accepts electrons. Special stability results when an atom, by either losing or gaining electrons as the outermost shell of a noble gas atom. The tendency of atoms of elements in Group I and II achieve an octet by losing electrons to form cations, and atoms of elements in Group (VI) and (VII) achieve an octet by gaining electrons to form anions. Reactions of metallic elements of the left side of the periodic table with the non – metallic elements on the right side transfer just enough electrons to form ions with complete octet.

The melting point and boiling point temperatures of ionic compounds are high, owing to the strong force of electrostatic attraction between the ions in the crystal. Ionic compounds also conduct electricity when molten or in solution. The best arrangement of ions in a structure is one that has the lowest energy and allows the greatest number of contacts between oppositely charged ions without charge. Sodium chloride has a face centred – cubic closed – packed lattice of chloride ions (radius 0.131 nm), which is exchanged to accommodate sodium ions (radius 0.098 nm) in the lattice anions. There are 6 Na⁺ ions surrounding each Cl⁻ ion; the coordination number of chlorine is 6. Similarly there are 6 Cl⁻ ions surrounding each Na⁺ ion: the coordination number of Na is 6. The structure below shows 6 : 6 coordination:



2.11.5. GIANT ATOMIC

Diamond has a macromolecular structure; it is very hard and is an allotrope of carbon. Each carbon atom is tetrahedrally bonded by sp^3 hybrid bonds to four other carbon atoms and forms an interlocking crystal structure. The exceptional strength of the C – C bond (350 kJ mol^{-1}) and the covalently interlocking crystal structure accounts for the physical properties of diamond. Because of its hardness it is used for drilling, cutting, grinding and in bearings. Graphite is another allotrope of carbon and it is a *layered* structure. Within each layer, every carbon atom is bonded to three sp^2 hybrid orbitals. A network of coplanar hexagons is formed. Between layers the distance is 0.335 nm and is held by weak van der Waals forces of attraction. Because this force is weak it allows layers to slip and slide over each other which is account for the property of graphite being a lubricant, etc. The unhybridized p – electron form a delocalized cloud of electrons similar to the metallic. These electrons are mobile and graphite therefore conducts electricity and appears slimy. Graphite is composed entirely of planes of trigonal carbon atoms joined in a honeycomb pattern. The bond angle is 120° and the melting point is 3652°C .

2.12. REFERENCES

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