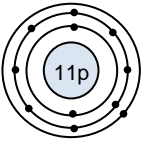
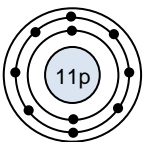
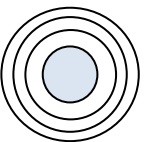
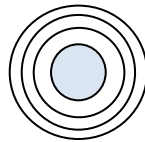
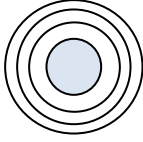
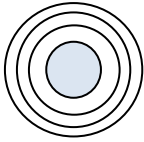
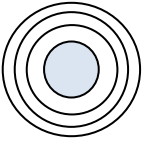
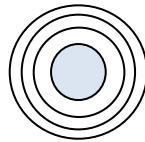
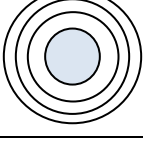
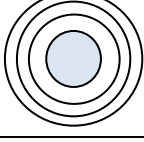
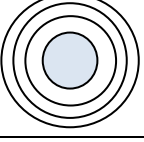
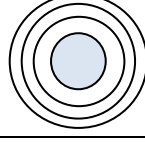
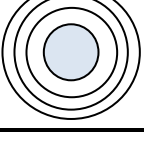
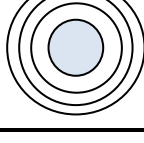
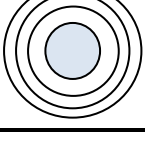
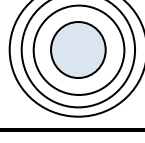


CHEMICAL BOND

Chemical bond = a force which holds atoms in a compound together; valence electrons participate in it.

Electron dot symbols (used for *s* and *p* elements): valence electrons are represented by dots around the symbol of the atom, e.g. boron (group III.A) has three valence electrons: $\cdot\dot{\text{B}}\cdot$.

1. Fill the table with electron dot symbols and Bohr's models of the following atoms: magnesium, neon, chlorine, oxygen, fluorine, aluminium and argon. The one for sodium has been done for you.

1	2	3	4	5	6	1	2	3	4	5	6
Na		Na·	I	Na		O					
Mg						F					
Ne						Al					
Cl						Ar					

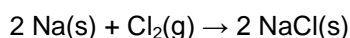
2. Write down the most common oxidation number to each of the elements from the table above to the next column (column 4).
3. Make a dot electron diagram (to column 5) and write down the full electron arrangement (to column 6) for the ions with the charges corresponding to the most common oxidation numbers.
4. Compare the Bohr's models in column 6 and make a conclusion:
When atoms form ions they either or electrons in order to achieve stable electronic configurations similar to the next higher or lower in the periodic table.
5. What are the charges of the ions made from the following atoms: Se, Rb, Ba, N, Sr, Te, P?

Electronegativity = the ability of a bonded atom to attract the bonding electrons.

- includes both ionization energy and electron affinity

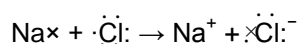
IONIC BOND

When sodium metal is brought into contact with chlorine gas, Cl_2 , a violent reaction occurs.



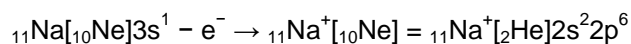
The product of this reaction is sodium chloride NaCl , a substance composed of Na^+ and Cl^- ions.

The formation of Na^+ from Na and Cl^- from Cl_2 indicates that an electron has been lost by a sodium atom and gained by a chlorine atom. Using **dot-cross diagrams** - it means that valence electrons of one atom are represented by dots and those of the second atom as crosses - (and showing a chlorine atom rather than the Cl_2 molecule) we can represent this reaction as follows:

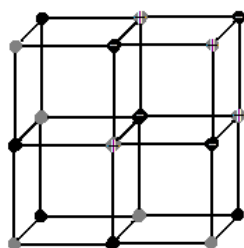


“The atoms lose or gain electrons in order to achieve a stable noble gas configuration.”

Or in other words: they lose or gain electrons in order to have eight electrons in their last shell.



These ions (Na^+ and Cl^-) are arranged throughout the solid NaCl in a regular three-dimensional array, as shown in the Figure 1.



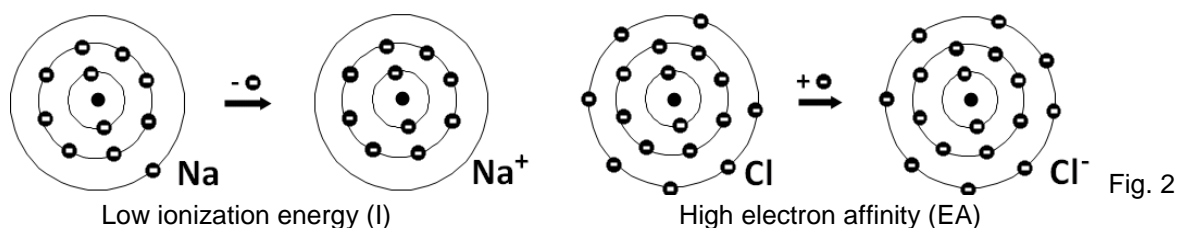
grey spheres ... sodium ions Na^+
black spheres ... chloride ions Cl^-

Fig.1

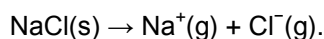
Energetics of the formation of an ionic bond

The formation of ionic compounds requires an atom with a low **ionization energy** that easily loses an e^- to form a positive ion (usually metals from IA and IIA groups) and an atom with a high **electron affinity** that easily accepts an e^- to form a negative ion (usually non-metals from VIA or VIIA groups).

The electronegativity difference of the bonded atoms is usually > 1.7 .



Much of the stability of NaCl results from the packing of the oppositely charged Na^+ and Cl^- ions together as shown in the Fig.1. A measure of just how much stabilization from the packing is given by the **lattice energy**. This quantity is the energy required for 1 mol of the solid substance to be separated completely into ions far removed from one another. We can write the process as:



To get the picture of this process, imagine that the lattice shown in the Fig.1 expands from within, so that the spaces between the ions grow larger and larger, until the ions are very far apart. The energy



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that would be required for that to occur for a lattice containing 1 mol of Na^+ and 1 mol of Cl^- ions is the lattice energy.

6. Write the dot and cross diagrams for the following ionic compounds:



COVALENT BOND

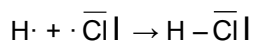
- bonded atoms electrons in order to achieve the nearest noble gas configuration
- the electronegativity difference of bonded atoms < 1.7

7. Consider the following molecules and use their dot and cross diagrams to find out whether and how their atoms achieve stable noble gas configuration:



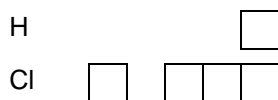
The covalent bond may be expressed also by:

- structural **electronic formula** – electron pairs are represented by dashes



- **box diagrams** of valence electrons

The electrons forming a pair have an opposite spin.



8. Make the electronic formula and the box diagram for H_2S , CH_4 , NH_3 , Cl_2 , H_2O .

Multiple bonds - atoms share more than one electron pair

double bond: $O_2: \overline{O} = \overline{O}$ triple bond: $N_2: \overline{N} \equiv \overline{N}$



9. Make the electronic formulae and box diagrams for: CO_2 and C_2H_2 .

Orbitals and bonding theory

σ -bond

When two hydrogen atoms approach each other their 1s orbitals overlap when their nuclei are close enough. The chance of finding an electron between the nuclei is increased. This kind of bond is called σ -bond. The electron density is highest the nuclei. This is typical for bonds.



s-s overlap

10. Suggest other possible overlaps leading to the formation of the σ -bond.

π -bond

When two atoms are close together their p orbitals may overlap broadside on and give rise to two regions of increased electron density and the plane of the nuclei. The resulting bond is called π -bond.



p_z - p_z overlap

11. Suggest other possible overlaps leading to the formation of the π -bond.

A double bond consists of one σ -bond and one π -bond, a triple bond consists of one σ -bond and two π -bonds.

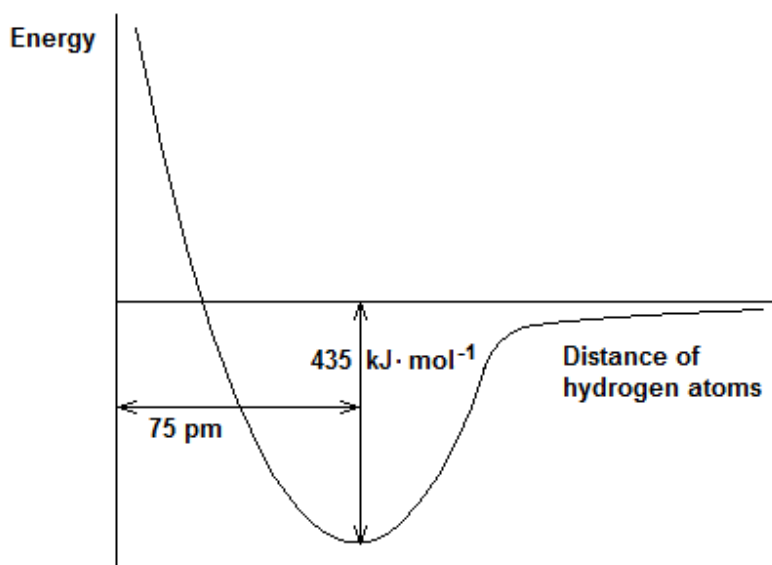
1. Although there are two regions with higher electron density it is only one bond.
2. π -bond is *weaker/stronger* than σ -bond because the regions with increased electron density and that's why a double bond is *weaker /stronger* than two σ -bonds.
3. A double bond is resistant to twisting because as one end of the molecule is rotated relative to the other, the broadside overlap of the two p orbitals is decreased, the bond is weakened and the energy of the molecule rises.

12. Draw the box diagrams to show what orbitals take part on bonding in H_2 , Cl_2 , HI , O_2 , N_2 .

Bond properties

- **Bond** = average distance between the nuclei held together by the bond.
- **Bond** = the energy needed to break the bond to produce neutral atoms. When the bond is formed, energy is released. The energy of the molecule depends on the distance between the nuclei.

Molecular potential energy curve for H_2 molecule



atoms approach → lowering of energy, minimum of energy corresponds to the equilibrium bond length

further approaching → increasing of energy because of the repulsion between positive nuclei

Examples of some bond energies:

Bond	Bond energy ($\text{kJ}\cdot\text{mol}^{-1}$)	Bond	Bond energy ($\text{kJ}\cdot\text{mol}^{-1}$)
F-F	158	H-H	436
Cl-Cl	243	H-O	460
Br-Br	193	H-Cl	432
I-I	151	C-H	413

13. Put the halogens in order with respect to the stability of their molecules.
14. Calculate the energy needed to break all the bonds in 1 mole of:
- a. HCl b. H_2O c. CH_4
15. Calculate the energy needed to break all the bonds in:
- a. 1 g of CH_4 b. 10 g of Br_2 c. 0.9 g of H_2O
16. Calculate the number of hydrogen molecules which may be broken using the energy of 100 kJ.
17. Compare and explain the relationship between the length and the energy of the carbon – carbon bond.

	Bond energy ($\text{kJ}\cdot\text{mol}^{-1}$)	Bond length (μm)
C-C	348	154
C=C	614	134
C \equiv C	839	120

18. The following table gives some data on carbon halide bonds:

Bond	Bond length / μm	Electronegativity difference
C-F	132	1.5
C-Cl	177	0.5
C-Br	194	0.3
C-I	214	0.0

- a. Why does the bond length increase with decreasing electronegativity difference?
- b. State another factor which would cause the bond length to increase along the series C-F, C-Cl, C-Br, C-I.
- c. Predict how the bond energy would vary along the series C-F, C-Cl, C-Br, C-I.
- **Bond angle** = the angle between the lines connecting an atom to its two neighbours.

Molecular shape

Valence shell electron pair repulsion (VSEPR) theory:

- shapes of polyatomic molecules are a result of the valence electron repulsions
- the shapes depend on the number of electron pairs (both bonding and lone) around the central atom of the molecule
- the most stable shape - electron pairs are as far from each other as possible

Central atoms surrounded by bond pairs only

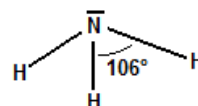
Number of pairs	Example	Shape
2	BeH ₂	
3	BF ₃	
4	CH ₄	
5	PCl ₅	
6	SF ₆	

Central atoms with lone electron pairs:

NH₃ has four electron pairs around the central atom ⇒ tetrahedron with one corner occupied by a lone electron pair

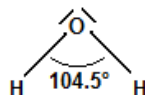
Lone electron pair is closer to the nitrogen atom, it squeezes the other three pairs closer to each other ⇒ decreasing of the bonding angle to 106°.

The shape is called a



H₂O has four electron pairs around the oxygen atom \Rightarrow tetrahedron with two corners occupied by lone electron pairs. The bonding angle is then even smaller = 104.5°

The molecule is called



19. Predict the shapes of the following molecules: H₂S, AlCl₃, PH₃, SiF₄, BeCl₂, AsBr₅, BF₃, SO₂

Multiple bonding

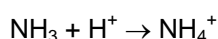
Single shared pair of electrons leads to the formation of a bond, two shared electron pairs form a bond and three electron pairs form a bond.

With an increasing number of shared electrons the length of the bond *decreases/increases* and its stability *decreases/increases*.

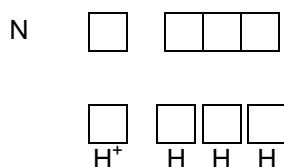
The effect of multiple bonding on shape:

1. A multiple bond is treated as though it were a single electron pair. The molecule of CO₂ is that's why linear O=C=O.
2. A double or triple bond is rigid to twisting.

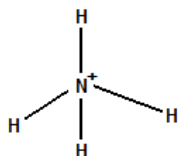
Coordinate covalent bond (dative bond)



20. Suggest a way how these two particles: NH₃ and H⁺ may form a bond to form NH₄⁺.



This bond is formed when one atom (donor) contributes a lone electron pair to a covalent bond. This electron pair is accepted by an atom with an empty orbital (acceptor).



Nitrogen has a lone electron pair and H⁺ ion has an empty orbital. Nitrogen is a and hydrogen ion an of an electron pair.

Once formed all the bonds in NH₄⁺ are equal.

21. Use the box diagram to show the bonding between:

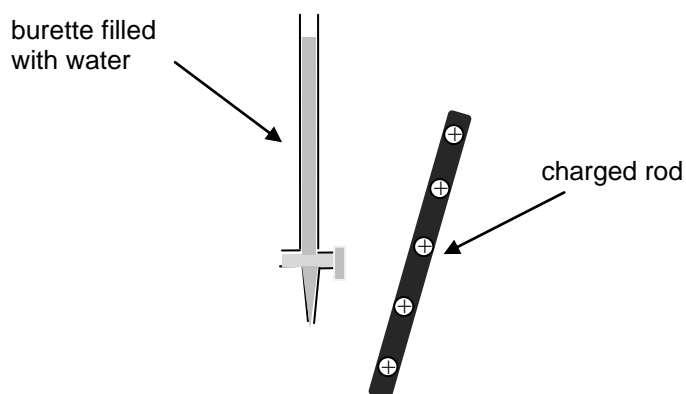
- H^+ and H_2O in H_3O^+
- F^- and boron trifluoride in BF_4^-
- ammonia and boron trifluoride

Polar molecules

Experiment:

You are shown an experiment where a positively charged rod approaches a weak stream of water.

Draw the stream of water to the picture



Explanation:

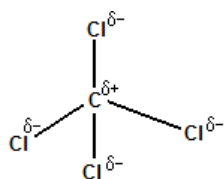
1. Draw the structural formula of water showing its shape.
2. What are the electronegativities of oxygen and hydrogen?
3. Are the bonding electrons shared equally between oxygen and hydrogen?
4. Where is the highest probability of finding them?
5. Is there an even distribution of bonding electrons in the molecule of water?
6. What part of the water molecule tends to be slightly negatively charged?
7. What part is positive?
8. If the rod in the experiment is positively charged what part of the water molecule is attracted to it?
9. What happens if we use a negatively charged rod in the same experiment?

Such molecules possessing negative and positive ends (poles) are called molecules. They have so-called dipole.

Two conditions must be met so that a molecule is polar:

1. The electronegativity difference of the bonded atoms > 0.4 , which means that the bonds are polar.
2. The bonds must be arranged asymmetrically around the central atom.

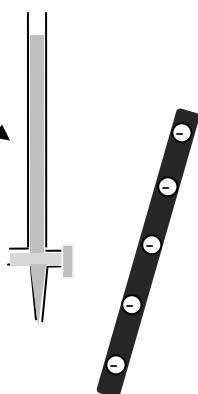
That means that molecules with polar bonds do not have to be polar. They are not polar when the bonds are symmetrically distributed around the central atoms, their dipoles then cancel each other out as in e.g. tetrachloromethane:



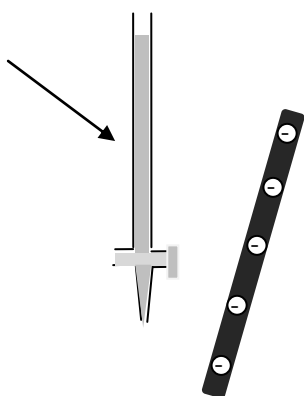
22. State which of these molecules are polar: CO_2 , NO_2 , HBr , PCl_3 , BF_3 , C_6H_6 , CS_2

23. Show how the liquids in the pictures below are affected by the charged rods.

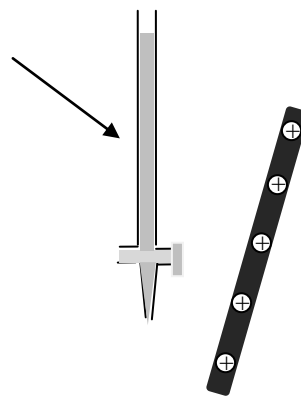
burette filled
with benzene



burette filled
with liquid
ammonia



burette filled
with liquid
ammonia



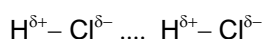
Intermolecular forces

Boiling and melting points of molecular substances are affected by intermolecular forces = forces molecules. The stronger intermolecular forces the *higher/lower* the boiling and melting points.

1. permanent dipole – dipole interactions

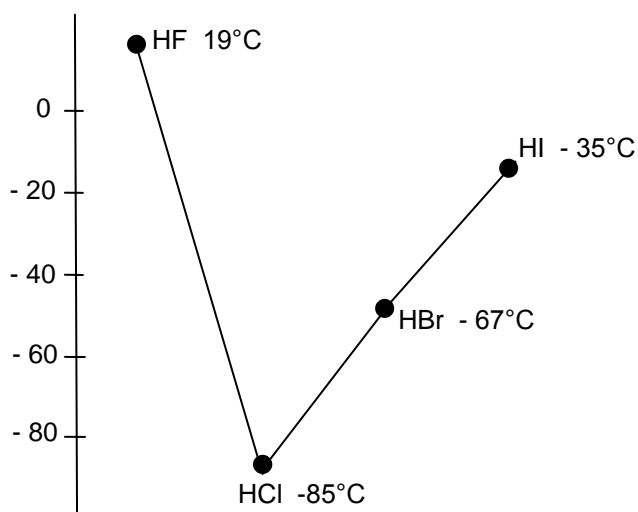
are forces much weaker than a covalent bond.

This is caused by permanent dipoles of polar molecules, e.g. between HCl molecules.



24. Compare the electronegativity differences in HCl and in HBr. Is there stronger dipole-dipole attraction between HCl molecules or between HBr molecules?

25. See the graph below and state which of these two substances: HCl and HBr has a higher boiling point.



..... has a higher boiling point which means that the molecules of are attracted together *more/less* strongly than the molecules of

This is caused by another type of forces:

2. Van der Waals' forces

The distribution of electrons in a molecule is never perfectly symmetrical – electrons move randomly within a molecule. It may happen that on one side of the molecule there is a higher electron density (This side is then slightly) and on the other side there is a electron density (This side is slightly) The molecule then possesses a dipole ($\text{A}^{\delta+} - \text{B}^{\delta-}$).



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However, as the electrons in the molecule move the dipole may change in a short time ($A^{\delta-} - B^{\delta+}$).

That's why the dipole is called dipole. Once a dipole is formed in one molecule it induces dipoles in the neighbouring molecules:



The molecules are then attracted to each other due to this dipole-dipole attractions. Such interactions are called Van der Waals' forces. Their strength depends on the total number of in the molecule. This is the reason why HBr has a higher boiling point than HCl.

26. Explain how a dipole of one molecule may induce a dipole in the neighbouring molecule.

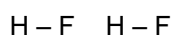
27. Find some other series of molecular substances where the boiling point increases with increasing number of electrons in a molecule (increasing size of molecules).

-
-
-

28. See the graph with the boiling points of hydrogen halides and state what is exceptional there:

3. Hydrogen bonding (hydrogen bridges)

When a very electronegative element (F, O, N) is bonded to a hydrogen atom, the hydrogen electron is drawn to the more electronegative atom. A hydrogen atom has almost no electrons and its almost empty orbital forms a strong interaction with a lone electron pair of another molecule. This interaction is about ten times weaker than a covalent bond and about the same strength as van der Waals forces. It causes e.g. the unusually high boiling point of water.



29. In which of the following compounds will hydrogen bonding occur:

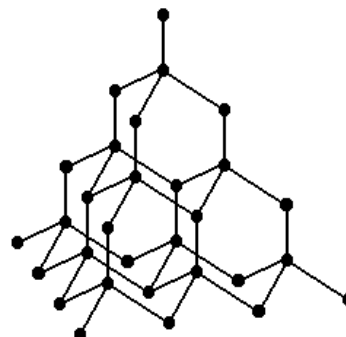
- | | |
|-----------------|----------------|
| a. $C_2H_5NH_2$ | d. CH_3OH |
| b. CH_3I | e. CF_4 |
| c. H_2SO_4 | f. CH_3OCH_3 |

THE STRUCTURE AND PROPERTIES

1. Giant molecular (covalent) structures

The structure of diamond

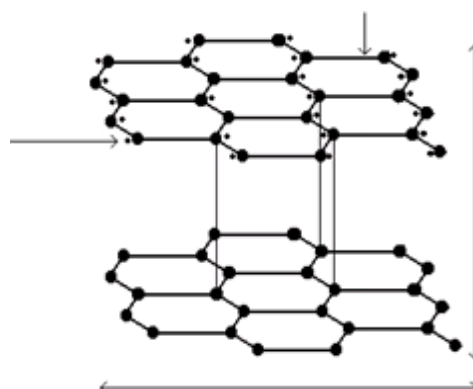
Every carbon atom can be imagined to be at the centre of a regular surrounded by other carbon atoms at the corners of the tetrahedron. Because there are strong bonds that are *difficult/easy* to break between carbon atoms, diamond is very *hard/soft*, *brittle/rigid*, has *low/high* melting and boiling point. As all the valence electrons contribute to the bonding, they *cannot/can* move freely and so diamond *does not conduct/conducts* electricity.



2. Layer structure

The structure of graphite

Carbon atoms are hexagonally arranged in flat, parallel Each carbon atom is bonded to other atoms in its layer by bonding. Three carbon electrons form three σ/π bonds, the fourth one is called electron. It may move throughout the whole layer and cause the electrical and colour of graphite.



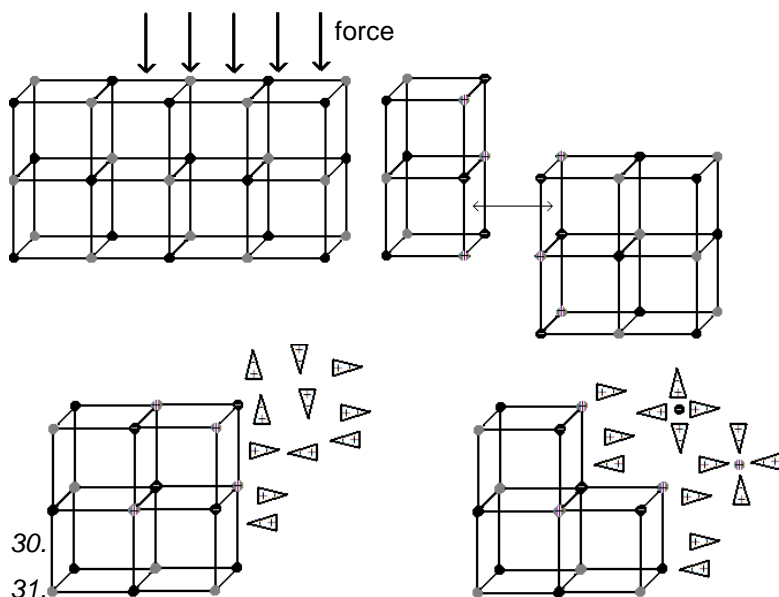
There are weak forces between the layers \Rightarrow the distance between the layers is *longer/shorter* than C-C bond length. The layers can slide over each other easily and it is used in in pencils. Graphite is *hard/soft* and is also used as a lubricant.

3. Giant ionic structures

The structure of NaCl

There are regularly arranged positive and negative ions. They hold together due strong electrostatic interactions (..... bond).

Properties: *hard/soft* and *rigid/brittle*, involatile, with *low/high* melting and boiling point, good electric conductors when or in a, non-conductors when, soluble in *polar/non-polar* solvents, insoluble in *polar/non-polar* solvents. When they dissolve in a solvent, their ions are said to be (solvation). In the case of water they are (hydration). It is an interaction between the ions and solvent molecules



30. What properties or processes are shown in the pictures above? Describe them.

4. Simple molecular structures

Non-metals and their compounds are usually composed of simple molecules (.....,,). The atoms in the molecules are held together by a strong bond. But the separate molecules are attracted to each other by weak forces or by bonding. Solid molecular substances form crystals

Properties: *soft/hard, high/low* melting and boiling point, *do not conduct/conduct* electricity, non-polar molecules are insoluble or almost insoluble in water, they are *insoluble/soluble* in non-polar solvents.

31. What types of bonding would you expect in the Ne, H₂O, CH₄, CO₂, Si, CaCl₂, NaF lattices?

32. Consider the following types of crystalline solids:

A ionic

B giant molecular

C composed of monoatomic molecules

D composed of molecules containing small number of atoms

Select the letter A-D for the structure most likely to show the following properties:

a. a solid which melts at -250°C

b. a solid with a very high boiling point which doesn't conduct when liquid

c. a hard, brittle solid which easily cleaves

d. a substance which boils at -50°C and decomposes at high temperatures

(Chemistry in Context)



INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

33. Discuss and explain the following:

- The ionic nature of MgCl_2 is greater than that of AlCl_3 which is greater than that of SiCl_4 .
- Silicon(IV) oxide is a solid at room temperature which does not melt until 1973 K, whereas CO_2 (m.p. = 217 K) is a gas at room temperature.
- CaO and NaCl have a very similar arrangement of ions yet CaO melts at 2973 K whereas NaCl melts at 1074 K.
- Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is much more soluble in water than in benzene but cyclohexane (C_6H_6) is much more soluble in benzene than in water.

(Chemistry in Context)

Revision questions:

- Let's consider the following substances: PF_3 , N_2 , O_2 , NaBr , H_2S , Na_2O , CO_2 , CaF_2 , F_2 , CaO , CH_4 .
 - Classify the bonds in the substances as ionic, covalent non-polar and covalent polar.
 - Show the transfer of electrons in the ionic compounds using dot and cross formulae.
 - Show how the electrons are shared in the covalent molecules using Lewis (electronic) formulae and box diagrams. Show which bonds are σ and which bonds are π .
 - Which of the molecules containing polar bonds are polar?
- Give the shapes of the following molecules: PCl_5 , SF_6 , SnCl_2 , BF_3 , BeCl_2 .
- Calculate the overall energy needed to break all the bonds in:
 - 5 moles of H_2O $E(\text{H-O}) = 463 \text{ kJ}\cdot\text{mol}^{-1}$
 - 400 g of HBr $E(\text{H-Br}) = 366 \text{ kJ}\cdot\text{mol}^{-1}$
- Show the hydrogen bonding between the molecules of:
 - HF
 - H_2O
 - NH_3
- Which of the following molecules may form hydrogen bonding: ethanol $\text{C}_2\text{H}_5\text{OH}$, ethanoic acid CH_3COOH , methane CH_4 , hydrogen peroxide H_2O_2 ?
- Explain the terms: ionization energy, electron affinity, lattice energy, dative bonding, van der Waals forces.