In Figure 2- 26 it is seen that the cations are placed in the octahedral holes in the anionic lattice. Thus the cations each have six anion neighbours. From geometrical considerations the radius of the octahedral holes be calculated from the radius of the anions according to equation (2- 4).

$$r_{octahedral\ holes} = 0.414 \cdot r_{anion} \tag{2- 4}$$

When the r_+/r_- ration is between 0.225 and 0.414 the structure is tetrahedral. In this case the cations are relatively small compared to the anions. Thus they fit into the tetrahedral holes of the anion structure. This is sketched for a zinc sulphide lattice in Figure 2- 27.
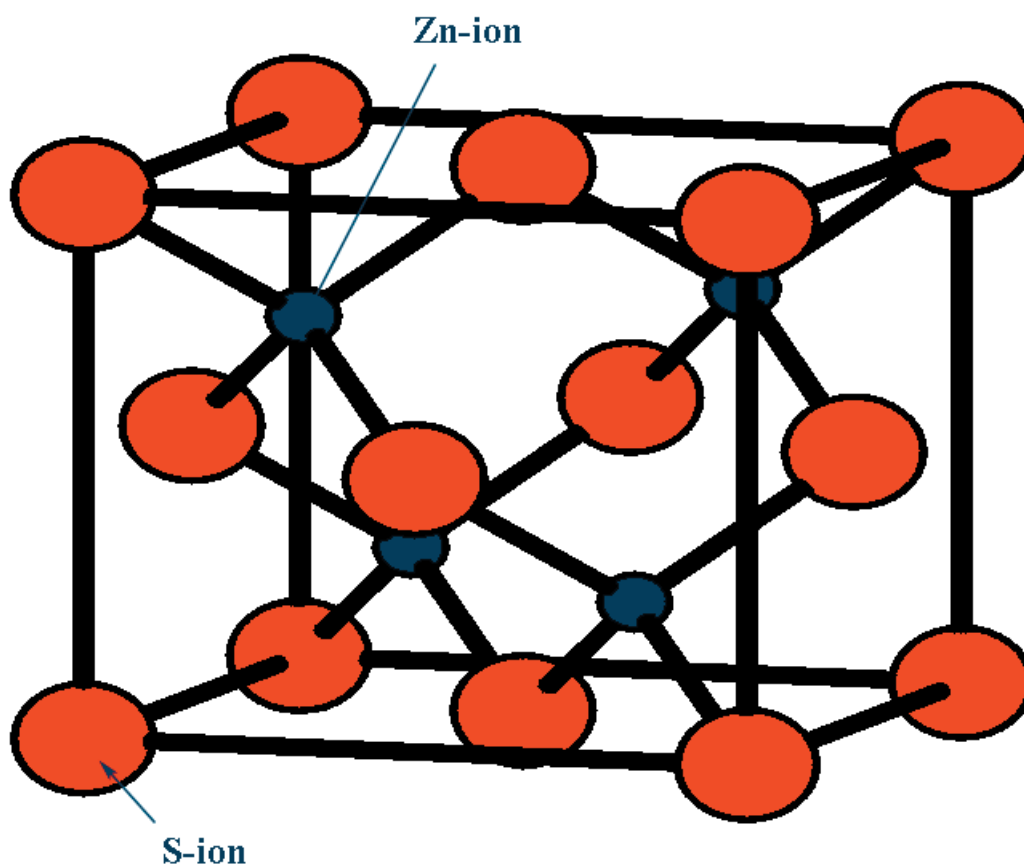

Figure 2- 27: Tetrahedral structure for an ionic compound

Ionic compound with a r_+/r_- ration in the interval 0.225 – 0.414. The cations are placed in the tetrahedral holes of the anion structure. Thus each cation touches four anions. Zinc sulphide (ZnS) is an example of an ionic compound with tetrahedral structure.

The anions are arranged in a cubic close packed system and the cations are located in the tetrahedral holes of this structure. Thus each cation has four anion neighbours. From geometrical considerations the radius of the tetrahedral holes can be calculated from the radius of the anions according to equation (2- 5).

$$r_{tetrahedral\ holes} = 0.225 \cdot r_{anion} \tag{2- 5}$$

By looking at the equations (2- 4) and (2- 5) you can see why it is at the r_+/r_- rations of 0.225 and 0.414 (according to Table 2- 4 on page 89) that we have the lower limits for the tetrahedral and octahedral structures respectively.

2.4.3 Energy calculations in ionic compounds

In the previous section we saw how ionic compound often are arranged in different lattice structures depending on the ration between the cation radius and the anion radius. In this section we are going to look at the *lattice energy* in an ionic compound and how you can calculate the total change in energy when for example lithium metal and fluor gas reacts into solid lithium fluoride. Based on this specific compound we will see how a combination of different terms such as the lattice energy, ionization energy and sublimation energy can lead us to calculate a specific energy term.

Example 2- R:

Energy calculations for lithium fluoride (LiF)

What is the total change in energy when lithium metal reacts with fluor gas and forms solid lithium fluoride?

$$Li(s) + \tfrac{1}{2}F_2(g) \rightarrow LiF(s)$$
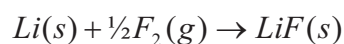
The energy changes are sketched in Figure 2- 28. We are looking at the case where 1 mole of lithium atoms reacts with a ½ mole of fluor gas molecules and 1 mole of solid lithium fluoride is formed.
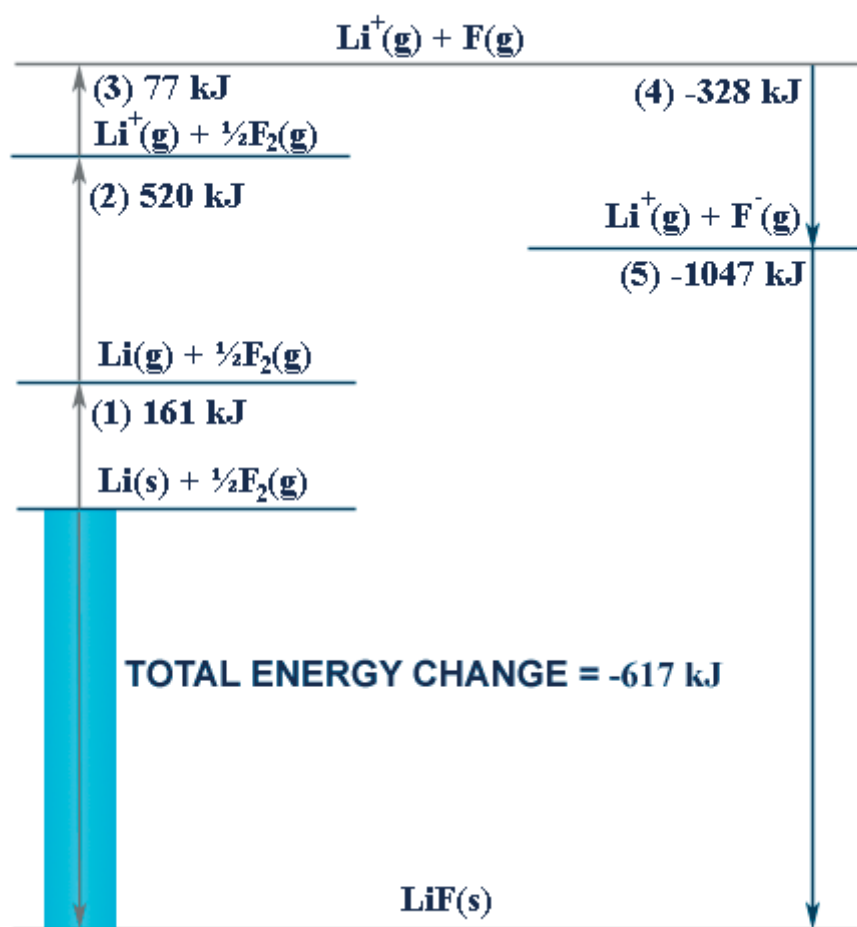

Figure 2- 28: Energy diagram for the formation of lithium fluoride
The arrows pointing upwards indicate that energy has to be supplied in order to make the reaction occur. The arrows pointing downwards indicate that energy is released when the reaction occurs. 1 mole of solid lithium fluoride is formed.

The single steps are explained below:

The first step is to sublimate the lithium metal into lithium gas. The sublimation enthalpy is 161 kJ/mole. Thus 161 kJ are required.

The second step is to get the lithium gas atom ionized. The ionization energy for lithium is 520 kJ/mole. Thus 520 kJ are required.

The third step is to break the covalent F-F bonds in order to get single fluor atoms. It requires 154 kJ/mole to break the bonds and since a half mole of bonds are to be broken, 77 kJ are required.

The forth step is to let the fluor atom each adopt an electron. The energy change here is thus the electron affinity for fluor which is -328 kJ/mole. Thus 328 kJ are released.

The fifth step is to let the lithium ions and the fluoride react and form solid lithium fluoride. The energy change here corresponds to the lattice energy for LiF which is 1047 kJ/mole. Thus when 1 mole of LiF is formed from the gaseous ions, 1047 kJ will be released.

The total change in energy can thus be determined by summing up the energies in the five steps.

$$Total\ energy\ change = (161 + 520 + 77 + (-328) + (-1047))kJ = \underline{\underline{-617kJ}}$$

Thus 617 kJ are released when 1 mole of LiF(s) is formed from 1 mole of Li(s) and ½ mole of F_2(g)

By setting up an energy diagram as in Figure 2- 28 you are able to calculate different energy terms when the other terms are known. Many of the terms can be looked up in tables in the literature and educational textbooks.

2.5 Summing up on chapter 2

In this chapter we have been looking at three types of chemical bonds; covalent bond, ionic bonds and metallic bonds. The bonds are described by using different models and theory which introduce the molecular orbitals. These molecular orbitals are formed from atomic orbitals which we heard about in chapter 1.

In the section *2.2 Covalent bonds* we first introduced some considerations about energy changes associated with formation of chemical bonds. We concluded that in order for a chemical bond to be formed the total energy between the two atoms must have a minimum at a certain distance between the atoms. This distance is thus the length of the covalent bond. Molecular orbital theory could be used in the explanation of why some atoms join and form molecules while others do not. Here we introduced the bond orbitals and the anti-bond orbitals. By use of the molecular orbital theory we were able to predict bond orders. Thus we can predict whether a bond is a single, double or triple bond. In order to talk about the arrangement of the different atoms inside a molecule or composite ion we learned to write down the Lewis structure. This Lewis structure could also tells about the bond order and the placement of the electrons groups (lone pairs bond electron pairs) around the central atom in a molecule or composite ion. Such information is useful when the VSEPR theory is to be applied. The VSEPR theory tells us that the electron groups around an atom will be placed as far apart as possible. Thus the VSEPR theory is a tool that helps us to predict the actual geometry of a molecule or composite ion. However the VSEPR theory tells nothing about where the different electron groups precisely are located or to put it another way; in which orbitals are the electron groups hosted? In

order to answer this question we have to use the orbital hybridization theory. From this theory we know that atomic orbitals transform or "melt" into molecular hybrid orbitals with the "right" orientation in space according the VSEPR theory. The type of hybridization depends on how many electron groups that surround the central atom.

The bond electrons in covalent bond are very "locked" in the hybrid orbitals which gives very poor electrical conductance. This is in contrast to the bonds in metals. These bonds can be described by an *electron sea model* that tells us that the valence electrons freely can move around in the metal structure. The band theory tells us that the valence electrons move around in empty anti-bond orbitals that all lie very close in energy to the bond orbitals. The free movement of electrons in metals explain the very high electrical and thermal conductivity of metals. Metal atoms are arranged in different lattice structures. We saw how knowledge about the lattice structure and atomic radius can lead to calculation of the density of a metal.

Ionic bonds are described as well. The transition from covalent over polar covalent to ionic bonds is very fluent and depends on the difference in electronegativity between the atoms. The covalent bonds consist of sharing an electron pair and ionic bonds are electrostatic interactions between a cation and an anion. Solid ionic compounds are often arranged in lattice structures with many similarities with the lattice structures that we saw for the metallic compounds. The type of lattice structure for solid ionic compound depends on the ration between the radius of the cation and anion.

3. Reactions kinetics

Central for the applications of chemistry in practise is the understanding of chemical reaction kinetics. We will in this chapter begin with the fundamental understanding of the chemical reaction and how to write the chemical stoichiometric equation followed by a deeper presentation of the chemical reaction kinetics.

3.1 The chemical reaction

A chemical reaction is defined by the products and reactants taking part of the reaction. First when all products and reactants are known from e.g. experiments it becomes possible to set up the chemical stoichiometric equation in order to make sure that there are an equal number of atoms on each side of the reaction arrow. Thus, the stoichiometry must be fulfilled.

There are certain principles when a stoichiometric equation is to be set up. A reaction scheme is a symbolic way to represent a chemical reaction. A reaction scheme must express as much right information as possible. It is often advantageous to write a reaction scheme by the following bullets:
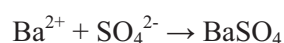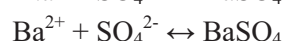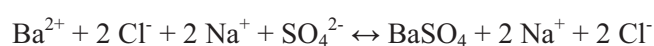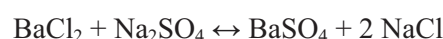
- Reactants are written on the left side and products on the right side.
- The species are written on the form that they are in before and after the chemical reaction.
- Only species that participate in the reaction are included.
- As term for the reaction a double arrow ↔ is used as there is in principle and equilibrium. Is this equilibrium displaced to the right a single arrow may be used → and similarly ← may be used if the reaction is displaced to the left. In the last case no reaction exists.

Example 3- A:
Reaction equation for precipitation of BaSO₄

Write the reaction scheme for precipitation of barium sulphate ($BaSO_4$) by addition of barium chloride ($BaCl_2$) to a aqueous solution of sodium sulphate (Na_2SO_4):

Following the general rules one achieves:

$$BaCl_2 + Na_2SO_4 \leftrightarrow BaSO_4 + 2\ NaCl$$

$$Ba^{2+} + 2\ Cl^- + 2\ Na^+ + SO_4^{2-} \leftrightarrow BaSO_4 + 2\ Na^+ + 2\ Cl^-$$
$$Ba^{2+} + SO_4^{2-} \leftrightarrow BaSO_4$$

$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$$

In which the last two lines is the correct way of writing as they fulfil all the above mentioned rules.

In all chemical reactions it is necessary to know the spontaneity of the reaction thereby indicating the willingness of the reaction to proceed all by itself. That a reaction is spontaneous does not necessarily mean that the reaction also is fast. This means that even if a reaction is spontaneous it may e.g. take many years before the amount of product is sufficient. Hence, it is essential to know something about the rate of reaction. The part of the chemistry is known as *chemical reaction kinetic*s and this is the subject for the following chapter.

Example 3- B:

Production of ammonia

The production of ammonia NH_3 is one of the most important chemical reactions and is used as e.g. fertiliser. Roughly 20 millions tonnes of ammonia is produced each year. The formation of ammonia may from a thermodynamically viewpoint be expressed as:

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$$
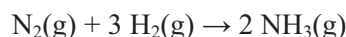
Does one however have N_2 and H_2 on gas form side by side at 25 ºC, no reaction will take place. This is caused by the fact that the rate of reaction is extremely slow at 25 ºC. One has to find other methods for producing NH_3 in practise. This illustrated that even if the reaction actually may proceed from a thermodynamic point of view and even if the stoichiometry fits it is not certain that the reaction actually will take place fast enough to exploit the reaction in practise. It is necessary in addition to know something about the rate of reaction.

3.2 Rate of reaction

We will introduce the term reaction velocity in this chapter. For a chemical reaction it is the concentration of reactants or products changing with time. For an arbitrary specie A with the concentration in moles/litres the rate of reaction may be expressed as:

$$\text{Rate of reaction} = \frac{\Delta[A]}{\Delta[t]} \rightarrow \frac{d[A]}{dt} \tag{3- 1}$$

Example 3- C:

Decomposition of nitrogen dioxid

In an experiment we begin by having a flask of gas filled with NO_2 at room temperature (25 ºC). At this temperature NO_2 is stabile, but if the gas is heated up to 300 ºC, it decompose to NO and O_2 following the following reaction scheme:

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

By measurement of the concentration of the three gases as function of time, the following data is obtained:

Time in seconds	Concentration of NO_2	Concentration of NO	Concentration of O_2
0	0,01	0	0
50	0,0079	0,0021	0,0011
100	0,0065	0,0035	0,0018
150	0,0055	0,0045	0,0023
200	0,0048	0,0052	0,0026
250	0,0043	0,0057	0,0029
300	0,0038	0,0062	0,0031
350	0,0034	0,0066	0,0033
400	0,0031	0,0069	0,0035

By applying equation (3-1) it becomes possible to determine the velocity, by which O_2 is formed. For instance is O_2 formed in the time interval 150 s → 200 s with the velocity:

$$\text{Rate of reaction (formation of } O_2) = \frac{\Delta[A]}{\Delta[t]} = \frac{(0,0029 mol/L - 0,0026 mol/L)}{(200s - 150s)} = 6.0 \cdot 10^{-6} \frac{mol}{L \cdot s}$$

while the velocity in the interval 350 s → 400 s is:

$$\text{Rate of reaction (formation of } O_2) = \frac{\Delta[A]}{\Delta[t]} = \frac{(0,0035 mol/L - 0,0033 mol/L)}{(400s - 350s)} = 4.0 \cdot 10^{-6} \frac{mol}{L \cdot s}$$

It is thereby worth noting that the rate of reaction is not a constant factor but actually decreases with time in this case.

Following the stoichiometric scheme for the conversion of NO_2 two molecules of NO_2 is converted each time one molecule of O_2 is formed. It is thereby easy to understand that the rate of reaction for the conversion of NO_2 must be given by the double of the velocity for the formation of O_2. hence, we may summarise the rate of reaction as follows:

Velocity for the use of NO_2 = Velocity for the formation of NO = 2 · Velocity for the formation of O_2

3.3 Rate expressions

So far we have only looked at irreversible reactions but as mentioned earlier all reactions are in principle reversible meaning that the reactions run in both directions. In the prior example with the decomposition of nitrogen dioxide the following reaction may also take place if there is excess O_2 available:

$$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$

Such contra dictionary reactions have naturally importance regarding the writing of the rate expressions. Typically, complications are avoided but neglecting the reversible reaction and thereby assume that the rate of reaction only depends on the concentration of the reactants. For the decomposition of nitrogen dioxide the rate expressions is written as:

$$\text{Rate of reaction} = k \cdot \left[NO_2 \right]^n \qquad \text{(3- 2)}$$

Such an expression describing how the rate of reaction depends on the concentration of reactant is called a rate expression. The proportionality constant k is called the rate constant and n is called the order of reaction which always must be determined from experimental data. The order of reaction may be positive as well as negative as well as an integer or e fraction. In general rate expressions are studied under conditions where n is either 0, 1 or 2, because there are analytical solutions for different time values t and values for the parameter k. When n is 0, the reaction is called a zero order reaction, while we have a first order and second order reaction when n is 1 or 2 respectively. The following things are worth noting concerning equation (3-2):

- Product concentration does not take part of the rate expressions because the rate of reaction is studied under conditions that do not contribute to the overall rate of reaction.
- The value of the order of reaction n must always be determined from experimental data and not be found from the reaction equation.

Example 3- D:

Order of reaction and rate expressions

For 1. order reactions, where *n* equals 1, the general rate expressions for the use of reactant A may be expressed as:

$$\text{Rate for the use of A} = -\frac{d[A]}{dt} = k \cdot [A]^n = k \cdot [A], \quad n = 1$$

This differential equation may be solve analytically and it may be shown that the concentration of reactant A depends on the initial concentration of A (symbolised by $[A]_0$), rate constant k and time t in the following manner:

$$[A] = [A]_0 \cdot \exp(-k \cdot t)$$

For 2. order reactions where the parameter *n* is 2 a similar expression for the use of reactant A is:

$$\text{Rate of reaction for the use of A} = -\frac{d[A]}{dt} = k \cdot [A]^n = k \cdot [A]^2, \quad n = 2$$

Analogously, one achieves by the solution of this differential equation for the concentration of A:

$$\frac{1}{[A]} = k \cdot t + \frac{1}{[A]_0}$$

For the cases where the order of reaction is zero the following expression is achieved:

$$\text{Rate of reaction for the use of A} = -\frac{d[A]}{dt} = k \cdot [A]^n = k, \quad n = 0$$

For a zeroth order reaction the rate of reaction is constant and does not depend of the concentration of reactant. By integration one achieves simply the following expression for the concentration of *A* as function of time, the parameter *k* as well as the initial concentration *[A]₀*:

$$[A] = -k \cdot t + [A]_0$$