

3.4 Chemical kinetics and catalysts

After the introduction of rate of reaction we have seen how a chemical reaction depends of other things than stoichiometry. It is thereby reasonable to assume that the temperature also plays a significant role for the cause and velocity of reaction. This combination is described by the Arrhenius-equation named after the Swedish chemist Svante Arrhenius due to his work on reaction kinetics in the 1880'ies. The Arrhenius-equation gives the connection between temperature, reaction constant and the concentration of reactant in the following manner:

$$\ln(k) = -\frac{E_a}{R} \frac{1}{T} + \ln(A) \quad (3- 3)$$

in which R is a universal constant called the gas constant and T is the temperature in Kelvin (absolute temperature). The parameter E_a is called the energy of activation. One can imagine that if a reaction should take place the reactants must collide and become products. This requires a certain amount of energy as there is a barrier to be overcome if the reactants should become products. The parameter E_a may be seen as the magnitude of this barrier. Does E_a have a large value it is difficult to make the products whereas it is easy to obtain the products if E_a has a small value. In the following example we shall look at a case where a value of E_a can be calculated using the Arrhenius-equation.

Please click the advert

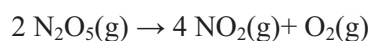


Read The Spanner online on oxygen.ie

Download free books at BookBooN.com

Example 3- E:*Energy of activation*

The following gas phase reaction has been studied under different conditions:



The rate constant k for a temperature of 30 °C is determined to be $7.3 \cdot 10^{-5} \text{ s}^{-1}$ and for a temperature of 60 °C determined to be $2.9 \cdot 10^{-3} \text{ s}^{-1}$. The value of E_a is to be determined.

We set-up the following expression on the basis of equation 3-3. For a temperature of 30 °C we have:

$$\ln(7.3 \cdot 10^{-5}) = -\frac{E_a}{R} \frac{1}{(273.15 + 30)} + \ln(A)$$

And for a temperature of 60 °C:

$$\ln(2.9 \cdot 10^{-3}) = -\frac{E_a}{R} \frac{1}{(273.15 + 60)} + \ln(A)$$

By subtracting the first expression from the last we obtain the equation:

$$\ln\left(\frac{2.9 \cdot 10^{-3}}{7.3 \cdot 10^{-5}}\right) = \frac{E_a}{8.314} \left(\frac{1}{(273.15 + 30)} - \frac{1}{(273.15 + 60)} \right) \Leftrightarrow E_a = 1.0 \cdot 10^5 \text{ J/mol}$$

Because the rate of reaction in general is highly affected by temperature one could believe that it was sufficient to either just turn up or turn down the temperature in order to let the desired reaction proceed as fast as possible. As well-known from many chemical processes e.g. from household cooking a number of reaction do run faster the higher temperature. Nevertheless one cannot always just increase the temperature. As an example, many of the vital functions in the human body are highly sensitive for changes in temperature. Further is it in addition often costly to increase the temperature industrially. Which other possibilities are there then? Catalysts are the solution to many problems in which it is necessary to increase the rate of reaction without having to increase the temperature. A catalyst is a chemical specie that makes a chemical reaction occur without being used itself in the reaction.

How do catalysts work? As mentioned earlier, it is required that reactants overcome a certain energy barrier before they can become products. One can imagine that what the catalyst does is to bring the height of the barrier down making it easier for the reaction to proceed. This means in other words that the rate of reaction is increased.

Catalysts are divided into tow classes; homogenous and heterogeneous. A homogenous catalyst is one that may be found in same type of phase as the species that the catalyst helps to react. A heterogeneous catalyst

exists on the contrary in another phase (typically in solid form) than the species that it helps to react. Heterogeneous catalyst often involves that reactants on gas form is adsorbed on the surface of the solid catalyst material. Homogenous catalysts exist typically in either liquid or gas phases and are commonly found in nature.

Example 3- F:*Enzymes – catalysts of nature*

Some of the most advanced homogenous catalysts are found in nature where they, in form of enzymes, help numerous processes vital for plants and life. Enzymes are large molecules with specific properties optimised typically on one chemical reaction. Enzymes are typically proteins and enzymes are used in many products in daily life as part of detergents, animal feed, industrial baking, dairy industries and more.

Enzymes are attractive to companies in the chemical industry as enzymes often tend to be less harmful to the environment than other types of catalysts. Unfortunately enzymes are sensitive molecules that often must have special temperatures and pH-conditions to function properly. You may find more information on enzymes at www.biosite.dk.

3.5 Kinetics of radioactive decay

We saw in section 1.1.1, how atoms with identical atom number but with different amount of neutrons are called isotopes. Likewise did we see that the combined number of protons and neutrons are called nucleons and that radioactive species decay under emission of different types of radiation. The rate of such decay is in principle similar to the rate of reaction for the transition of reactants to products in a chemical reaction. We imagine that for a specific time $t = 0$ we have an amount of specie with N_0 radioactive nuclei. It has been found that all nuclei have a specific probability of decaying within the next second. If this probability is e.g. 1/100 pr. second this means that on an average 1% of all nuclei decay each second. The number of radioactive nuclei is thereby a decreasing function with time and may formally be written as $N(t)$. The rate for the average number of decays pr. time is thereby defined analogously to equation (3-1) as:

$$\text{Rate of decay} = -\frac{\Delta N}{\Delta t} \rightarrow -\frac{dN}{dt} \quad (3-4)$$

in which the minus sign indicates that the number of radioactive nuclei is decreasing due to the decay. The fraction in equation (3-4) is called the activity and is denoted $A(t)$. The unit for the activity is s^{-1} as it indicates the number of decays pr. time but often the unit for radioactivity is called *Becquerel*. The probability that a certain nucleus decays within a certain time interval is denoted by the constant k called the constant of decay. Thereby equation (3-4) may be written as:

$$\text{Rate of decay} = -\frac{dN}{dt} = k \cdot N(t) = A(t) \quad (3-5)$$

By integration it may be shown that $N(t)$ depends of the constant of decay k , time t and the number of radioactive nuclei initially N_0 as:

$$N(t) = N_0 \cdot \exp(-k \cdot t) \quad (3-6)$$

3.5.1 Half-life

The half-life indicates how long it takes before the activity is decreased to half of the initial level. It is denoted by $t_{1/2}$ and given by:

$$t_{1/2} = \frac{\ln 2}{k} \quad (3-7)$$

The half-life for radioactive nuclei varies significantly from one species to another. E.g. has the Uranium-isotope ^{238}U a half-life of ca. 4.5 billion years whereas the bismuths isotope ^{214}Bi has a half-life of only roughly 20 minutes.

Is the half-life known it is possible to calculate a value for the decay constant k which thereby may be used in calculations of the activity and the number of radioactive nuclei to a given time.

Please click the advert

WHAT'S MISSING IN THIS EQUATION?

You could be one of our future talents

MAERSK INTERNATIONAL TECHNOLOGY & SCIENCE PROGRAMME

Are you about to graduate as an **engineer** or **geoscientist**? Or have you already graduated?
If so, there may be an exciting future for you with A.P. Moller - Maersk.



MAERSK

www.maersk.com/mitas

Example 3- G:*Radon in the cellar!*

Radon is a gas-specie that is formed by the solid radioactive element *radium* there is found all over in the earth in different amounts. Radon is radioactive and can be found in measurable amounts in our houses typically in the cellar. Radon penetrates into building primarily through the underground through cracks in the building fundament.

In a concrete cellar an activity from radon of 200 Becquerel from 1 m³ of air has been measured. If the cellar walls are isolated such that no new radon is added from the walls and floor the activity will decrease with time. As the half-life for radon-222 is 3.82 days the activity after this period will be 100 Becquerel. After further 3.82 days the activity will be 50 Becquerel.

We wish to determine how long it takes before the activity is decreased to 10 Becquerel. As we know the half-life we begin by calculating the decay constant k :

$$k = \frac{\ln 2}{3.82 \text{ dage}} = 0.181 \text{ dage}^{-1}$$

And hereby we achieve from equation (3- 6):

$$\begin{aligned} A(t) &= A_0 \cdot \exp(-k \cdot t) \Rightarrow \\ 10 \text{ Becquerel} &= 200 \text{ Becquerel} \cdot \exp(-0.181 \text{ dage}^{-1} \cdot t) \Rightarrow t = 16.6 \text{ dage} \end{aligned}$$

It thereby takes 16.6 days before the activity of radon is decreased to a value of 10 Becquerel.

Example 3- H:*Carbon-14 as a method to determine age*

A method to determine age on old items is the carbon-14 method that is based on the principles behind decay of the radioactive carbon-14 isotope. Items found in the Lascaux-caves in France have a rate of decay of ^{14}C nuclei of 2.25 pr. minute pr. gram carbon.

We wish to determine how old such items from the caves are. Half-life for ^{14}C is 5730 years. In living organisms 15.3 nuclei ^{14}C decay each minute pr. grams of carbon.

We exploit that decay, as earlier described, happens exponentially and that this may be expressed as:

$$\ln\left(\frac{A}{A_0}\right) = -k \cdot t,$$

where k can be expressed in terms of the half-life as:

$$k = \frac{\ln 2}{t_{1/2}}$$

We thereby arrive at:

$$\ln\left(\frac{2,25}{15,3}\right) = -\left(\frac{\ln 2}{5730 \text{ år}}\right) \cdot t \Leftrightarrow t = 15846 \text{ år}$$

The items found in the Lascaux-caves in France thereby has an approximate age of 15846 years.

3.6 Summing up on chapter 3

In this chapter we first saw how the chemical reaction equation must be written in terms of certain principles and rules; the stoichiometry must be fulfilled on both the right and the left side of the reaction arrow. We further saw through examples how reaction rate is a central term for the application of chemistry in practice. Expressions for rate of reactions were defined and we saw how rate of reaction not always is a constant parameter but often decreases with time. Further, the expression for the reaction rate was introduced with corresponding orders of reaction and rate constant. It was seen how the concentration of reactant clearly depended on the reaction order and expressions for 1., 2, and 0th order reactions was developed. The importance of temperature was highlighted via the introduction of the Arrhenius-equation with corresponding energy of activation. The term catalysts was briefly introduced by which it was described how catalysts may increase the rate of reaction (by lowering the energy of activation) of a chemical reaction without being consumed itself. Lastly, we saw how kinetics of radioactive decay in many ways is similar the kinetics for other chemical reactions. We looked at half-life and activity and via examples on how radioactive decay may be used to determine age of different old organic items.



www.job.oticon.dk

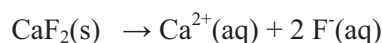
oticon
PEOPLE FIRST

4. Equilibrium

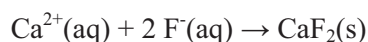
Solubility and equilibrium are closely connected and central terms in chemistry. In this section we shall look at equilibrium when solid species are dissolved in water. We will start by introducing basic terms as solubility and product of solubility.

4.1 Solubility equilibrium and solubility product

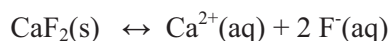
When a solid ionic compound is dissolved in water it is often assumed that the compound is completely separated into an anion and a cation. As example we look at the dissolution of solid calcium fluoride in water:



When CaF_2 are brought in contact with water there are initially no Ca^{2+} and F^{-} ions present. As the dissolution proceed the concentration of Ca^{2+} and F^{-} ions increase and with increasing concentration the probability that the opposite reaction occurs increases as well, being that the ions collide and once against forms solid CaF_2 following the reaction scheme below:



At last a dynamic equilibrium between the two reactions exist which is written as:



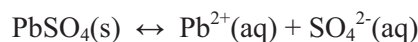
When the equilibrium occurs there is not more of the solid specie and the solution is said to be satisfied. We may write an equilibrium equation for this condition in the following manner:

$$K_{\text{sp}} = [\text{Ca}^{2+}] \cdot [\text{F}^{-}]^2$$

where $[\text{Ca}^{2+}]$ and $[\text{F}^{-}]$ are the concentrations of ions expressed in moles/L. The constant K_{sp} is called the *solubility constant* for the equilibrium. The reason that the solid specie CaF_2 is not included in the equilibrium expression is that solid species have an activity of 1. Solid species is thereby never included in equilibrium expressions even though it may seem strange that the amount of solid specie does not have any importance for the solution.

Example 4- A:*Calculation of solubility of PbSO₄*

We wish to calculate the solubility of lead sulphate PbSO₄ at 25 °C. At 25 °C PbSO₄ has a solubility constant of $1.3 \cdot 10^{-8} \text{ M}^2$. When solid PbSO₄ dissolves initially the system only contains PbSO₄(s) and H₂O but as time goes the solid specie will dissolve following the reaction scheme below:



Due to the equilibrium reaction scheme the equilibrium expression may be written as:

$$K_{\text{sp}} = [\text{Pb}^{2+}] \cdot [\text{SO}_4^{2-}]$$

To determine the solubility of PbSO₄ it is necessary first to find the equilibrium concentrations of Pb²⁺ and SO₄²⁻. This may be done by specifying the initial concentrations (prior to any dissolution of lead sulphate) followed by a definition of the changes that are needed in order to reach equilibrium. As we in this case do not know the solubility we assume that x moles/L of the solid specie is to be dissolved in order to reach equilibrium. The scheme of reaction indicates 1:1 stoichiometry which is why we have:



By substitution of the equilibrium concentrations into the expression for K_{sp} we achieve:

$$1.3 \cdot 10^{-8} \text{ M}^2 = K_{\text{sp}} = [\text{Pb}^{2+}] \cdot [\text{SO}_4^{2-}] = x \cdot x \Leftrightarrow x = \sqrt{K_{\text{sp}}}$$

By which we get $x = 1.1 \cdot 10^{-4} \text{ M}$. Thus, the solubility of lead sulphate PbSO₄ at 25 °C is $1.1 \cdot 10^{-4} \text{ moles/L}$.

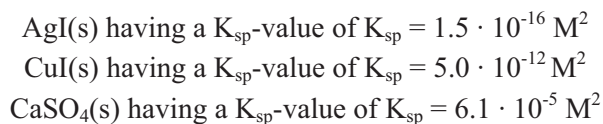
It is very important to distinguish between solubility of a solid specie and the product of solubility. Whereas the product of solubility is an equilibrium constant and thereby only has one value at a certain temperature, solubility is an equilibrium position which has an infinity of possible values at a given temperature depending on other factors such as the presence on foreign ions and more. The solubility product and the solubility of ions do also have different units which is why they cannot be readily compared.

4.1.1 Relative solubility

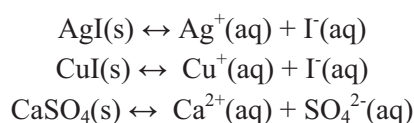
A solid species solubility constant K_{sp} gives important information about the species solubility. This is very convenient in a situation where only the solid specie is to be dissolved. K_{sp} values are often easy to find in literature. Are several solid species about to go into solution, the solubility product cannot be used in similar manner as earlier described. In principle one may imagine two situations, both of which we are going to look further into in the following examples. In one of the situations two or more solid species are about to go into solution where the solid species produce the same amount of ions. In the other situation there is likewise two or more different solid species but this time they produce a different amount of ions.

Example 4- B:*Relative solubility; first example*

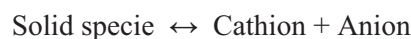
We wish to determine the order of solubility of three solid species. In other words we wish to investigate which of the three following species that are easiest to dissolve:



These three solid species give upon dissolution all two ions following the reaction schemes:



Or expressed more generally:



$$K_{\text{sp}} = [\text{Cathion}] \cdot [\text{Anion}]$$

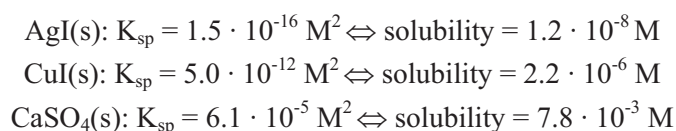
If we assume that the solubility of cation as well as anion is x moles/L at equilibrium we achieve:

$$\begin{aligned}[\text{Cathion}] &= x \text{ mol/l} \\ [\text{Anion}] &= x \text{ mol/l}\end{aligned}$$

And thereby by insertion in the expression for K_{sp} :

$$\begin{aligned}K_{\text{sp}} &= [\text{Cathion}] \cdot [\text{Anion}] = x^2 \Leftrightarrow \\ x &= K_{\text{sp}}^{1/2} = \text{solubility}\end{aligned}$$

Thus, from the K_{sp} -values from above:



CaSO_4 is thereby most dissolvable followed by CuI and lastly AgI . In that the number of ions for the three different ions are the same (all include 2 ions) the product of solubility have the units of (M^2). Therefore in this case you may determine the order of dissolubility just by looking at the sizes of the solubility products (K_{sp}).

Please note that this is only possible when the units for K_{sp} are similar.