IV. CHEMICAL KINETICS

INTRODUCTION

The aim of chemical kinetics is to predict the rates of chemical reactions and to understand the mechanisms of reaction. It is more difficult than the prediction of chemical equilibria, which are concerned only with the initial and final states and not with time or intermediate states.

Consider the reaction of the form:

\[ A + 2B \rightarrow 3C + D \]

A, B - substrates; C, D - products

in which the some instant the molar concentration of the participant J is \([J]\).

The instantaneous rate of consumption of one of the substrates at given time is \(- \frac{d[A]}{dt}\) or \(- \frac{d[B]}{dt}\). The rate of formation of one of the products C or D is given by the equation: \(\frac{d[C]}{dt}\) or \(\frac{d[D]}{dt}\).

Def.: The unique rate of reaction \(\nu\) is defined with the formula:

\[ \nu = \frac{1}{\nu_J} \frac{d[J]}{dt} \]

where \(\nu_J\) is the stochiometric number of substance J.

For example:

\[ \nu = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = \frac{d[D]}{dt} \]

The rate of reaction is often to be proportional to the concentrations of the reactants raised to a power. For example, the rate of a reaction may be found to be proportional to the molar concentrations of two reactants A and B, in which case we write:

\[ \nu = k[A][B] \]

where each concentration is raised to the first power. The coefficient \(k\) is called the rate constant for the reaction. The rate constant is independent of the concentrations but depends on the temperature. An experimentally determined equation of this kind is called the rate law of the reaction. The concentrations of all the species present in the overall chemical equation for the reaction at some time:

\[ \nu = f([A][B]) \]
the rate law of the reaction is to be determined experimentally, and cannot in general be inferred from the chemical equation for the reactions.

**THE ARRHENIUS PARAMETERS**

The rate constant of most reactions increase as the temperature is raised. It is found experimentally for many reactions that plot of \( \ln k \) against \( 1/T \) gives a straight line. This behaviour is normally expressed mathematically by introducing two parameters, one representing the intercept and the other the slope of the straight line, and writing the **Arrhenius equation**

\[
\ln k = \ln A - \frac{E_a}{RT}
\]

the parameter \( A \) is called the **pre-exponential factor**, the parameter \( E_a \) is called the **activation energy**. Collectively the two quantities are called the Arrhenius parameters.

**REACTION ORDER**

Many reactions are found to have rate laws of the form

\[
u = k [A]^a [B]^b \ldots
\]

the power to which the concentration of a species (a product or a reactant) is raised in the rate law of this kind is the order of the reaction with respect to that species. The overall order of the reaction is the sum of the individual orders, \( a + b + \ldots \).

**FIRST ORDER REACTIONS**

The first consideration in chemical kinetics is the influence of concentration on the reaction rate. The simplest case is the first-order reaction, in which the rate of reaction is experimentally found proportional to the concentration of the only one reacting substance. The situation is described mathematically as follows:

**Differential Rate Law:**

\[
\frac{d[A]}{dt} = -k[A]
\]

Chemists call the equation \( d[A]/dt = -k[A] \) a **first order rate law** because the rate is proportional to the **first power** of \([A]\). Integration of this ordinary differential equation is elementary, giving:

**Integrated Rate Law:**

\[
[A] = [A_0] \exp(-kt)
\]

A common way for a chemist to discover that a reaction follows first order kinetics is to plot the measured concentration versus the time on a semi-log plot. Namely, the concentration versus time data is fitted to the following equation:
**Data Analysis:**

\[
\ln([A]) = \ln([A_0]) - kt
\]

A plot of \(\ln([A])\) versus \(t\) is a straight line with slope \(-k\). Alternatively, a plot of rate versus \([A]\) is a straight line with slope \(-k\). From experimental data the rate constant can be found as a slope of the appropriate plot.

**SECOND ORDER REACTIONS**

Second Order Reactions are characterized by the property that their rate is proportional to the product of two reactant concentrations (or the square of one concentration). Suppose that \(2A \rightarrow \text{products}\) is second order in \(A\), or suppose that \(A + B \rightarrow \text{products}\) is first order in \(A\) and also first order in \(B\). Then the differential rate laws in these two cases are given by differential rate laws:

\[
\frac{d[A]}{dt} = -k[A]^2 \quad (\text{for } 2A \rightarrow \text{products})
\]

\[
\frac{d[A]}{dt} = -k[AB] \quad (\text{for } A + B \rightarrow \text{products})
\]

A chemist calls them **second order rate laws** because the rate is proportional to the product of two concentrations. By elementary integration of these differential equations integrated rate laws can be obtained:

\[
\frac{1}{[A]} - \frac{1}{[A]_0} = kt \quad (\text{for } 2A \rightarrow \text{products})
\]

\[
\left(\frac{1}{(a-b)}\right)\ln\left(\frac{(a-x)/(b-x)}{a/b}\right) = kt \quad (\text{for } A + B \rightarrow \text{products})
\]

where \(a\) and \(b\) are the initial concentrations of \(A\) and \(B\) (assuming \(a\) not equal to \(b\)), and \(x\) is the extent of reaction at time \(t\). Note that the latter can also be written:

\[
\frac{(a-x)/(b-x)}{a/b} = \exp\left[(a-b)kt\right]
\]

A common way for a chemist to discover that a reaction follows second order kinetics is to plot \(1/[A]\) versus the time in the former case, or \(\ln(b(a-x)/a(b-x))\) versus \(t\) in the latter case.

**Data Analysis:**

\[
1/[A] = 1/[A]_0 + kt
\]

A plot of \(1/[A]\) versus \(t\) is a straight line with slope \(k\).

**HALF-LIVES**

A useful indication of the rate of a first-order chemical reaction is the **half-life**, \(t_{1/2}\), of a substance, the time taken for the concentration of a reactant to fall to half its initial
value. The time for $[A]$ to decrease from $[A_0]$ to $\frac{1}{2}[A_0]$ in a first-order reaction is given by equation:

$$kt_{1/2} = -\ln \left( \frac{1}{2} \frac{[A_0]}{[A]} \right) = -\ln \frac{1}{2} = \ln 2$$

hence

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

the main point to note is that, for the first-order reaction, the half-life of the reactant is independent of its initial concentration.

For the second-order reaction:

$$t_{1/2} = \frac{1}{k[A_0]}$$
IV.A. INVERSION OF SUCROSE

INTRODUCTION

In this experiment the rate of reaction between sucrose and water catalyzed by hydrogen ion is followed by measuring the angle of rotation of polarized light passing through the solution. The reaction is:

\[ C_{12}H_{22}O_{11} \text{(sucrose)} + H_2O + H^+ \rightarrow C_6H_{12}O_6 \text{(fructose)} + C_6H_{12}O_6 \text{(glucose)} + H^+ \]

Sucrose is dextrorotatory, but the resulting mixture of glucose and fructose is slightly levorotatory because the levorotatory fructose has a greater molar rotation than the dextrorotatory glucose. As the sucrose is used up and the glucose-fructose mixture is formed, the angle of rotation to the right (as the observer looks in the direction opposite to that of the light propagation) becomes less and less, and finally the light is rotated to the left.

The experiment includes two parts. In the first part you will learn the properties of the polarized light from He-Ne laser, and in the second you will study the chemical kinetics of the hydrogen ion catalyzed inversion of sucrose.

WHAT DO YOU NEED TO KNOW

Classification of Polarization

Light in the form of a plane wave in space is said to be linearly polarized. Light is a transverse electromagnetic wave, but natural light is generally unpolarized, all planes of propagation being equally probable. If light is composed of two plane waves of equal amplitude by differing in phase by 90°, then the light is said to be circularly polarized. If two plane waves of differing amplitude are related in phase by 90°, or if the relative phase is other than 90° then the light is said to be elliptically polarized.

Linear Polarization

A plane electromagnetic wave is said to be linearly polarized. The transverse electric field wave is accompanied by a magnetic field wave as illustrated.
Circular Polarization

Circularly polarized light consists of two perpendicular electromagnetic plane waves of equal amplitude and 90° difference in phase. The light illustrated is right-circularly polarized.

If light is composed of two plane waves of equal amplitude by differing in phase by 90°, then the light is said to be circularly polarized. If you could see the tip of the electric field vector, it would appear to be moving in a circle as it approached you. If while looking at the source, the electric vector of the light coming toward you appears to be rotating clockwise, the light is said to be right-circularly polarized. If counterclockwise, then left-circularly polarized light.

The electric field vector makes one complete revolution as the light advances one wavelength toward you. Circularly polarized light may be produced by passing linearly polarized light through a quarter-wave plate at an angle of 45° to the optic axis of the plate.
Malus Law

Let $A$ be the amplitude of plane polarized light incident on a polarizer. Vibration direction of polarizer is inclined at angle $\theta$ to direction of polarization.

![Diagram]

The component of $A$, $A\cos \theta$ is transmitted and $A\sin \theta$ is blocked out.

Recall that the intensity is proportional to the square of amplitude, so that the intensity transmitted is:

$$I\Theta = I \cos^2 \Theta \to \text{Law of Malus}$$

where $I$ is the intensity of light incident on polarizer.

If unpolarized light $I_u$ falls on the polarizer, ideally only half of the light (i.e. $I_u/2$) is transmitted (the field of the incident wave has components parallel and perpendicular to the polarizing axis. The incident light is a random mix of both so each component is equal).

If a second polarizer is now placed in the beam, with vibration direction $\theta$ relative to the first polarizer, the intensity transmitted is thus

$$I\Theta = \frac{I_u \cos^2 \Theta}{2}$$

Note that the polarization direction of the light after passing the polarizer is identical to the polarizer orientation, however the intensity is reduced according to Malus law. When a polarized light passes an optically active substance the polarization direction changes, however the intensity remains unchanged.

Optically active compounds

Two compounds are called isomers if they have the same molecular formula but different chemical structures. Optical isomers are those in which two compounds have not only the same molecular formula but also identical bonding connections between the various atoms. A pair of optical isomers remain distinct from each other, however, because they are nonsuperimposable mirror images of each other. One optical isomer cannot be superimposed on the other, just as your left hand cannot be superimposed on your right hand. Compounds that exist as optical isomers are frequently referred to as chiral compounds, and each member of a pair of optical isomers is named an enantiomer. Molecules such as H$_2$O and CH$_4$, which
do not exist as nonsuperimposable pairs. are called *achiral*. A few examples of chiral compounds are presented in Figure 1.

Enantiomers have identical atoms and bonds, but the two different forms have different optical properties. If plane polarized light is passed through a solution of a chiral compound, the plane of polarization of the light is rotated either clockwise or counterclockwise. The extent of this rotation depends on the nature of the compound and the path length of the solution, as well as environmental factors such as temperature. Under the same conditions, enantiomers rotate light to the same extent, except that one rotates the plane of polarized light to the left and the other structure rotates it to the right.

Only chiral compounds rotate light in this way, and for this reason chiral compounds are often called *optically active compounds* (and achiral compounds are referred to as optically inactive). The reason chiral compounds rotate polarized light is complex and is fully explained only by a quantum mechanical treatment of the interaction of electromagnetic radiation with chiral compounds. One way of thinking about optical rotation, however, is to consider linearly polarized light as a superposition of right-handed and left-handed circularly polarized light. Because circularly polarized light has a handedness like chiral molecules, it is not surprising that right- and left-handed circularly polarized light interact differently with chiral molecules. Specifically, the index of refraction of a chiral substance is different for left- and right-handed circularly polarized light. Thus, the right- and left-handed components of linearly polarized light travel through a chiral medium with different velocities, and one handedness of light is retarded with respect to the other. The net effect of this retardation is to rotate the direction of the polarization of the linearly polarized light.

No easy method can predict whether a particular chiral compound will rotate light clockwise or counterclockwise. Distinguishing between two enantiomers by the direction in which they rotate the polarization of light is often convenient. By convention, left-rotating enantiomers are labeled (-) and right-rotating ones (+). Some chiral compounds rotate light more than others, and chiral compounds can be assigned specific rotation values, which tell to what extent the compound rotates light. The specific rotation is defined as

$$[\alpha] = \frac{\alpha}{lc}$$

where $\alpha$ refers to the rotation (in degrees) the electric field vector of the light undergoes in traveling a distance $l$ (in dm) through a solution with a concentration $c$ (in g/mL).
Specific rotations are often labeled with a superscript that indicates the temperature (in °C) and a subscript that indicates the wavelength of light (in nm). The specific rotation of the solutions in this experiment might be reported as

\[ [\alpha]_{25}^{632.8} \]

if a He-Ne laser is used, because the wavelength of light produced by a red He-Ne laser is 632.8 nm.

**PROCEDURE:**

1. Take the solution of sucrose, note its concentration.
2. Switch on the supply of sodium polarimeter.
3. In steady flask (100mL) mix solutions of 1M H₂SO₄ and sucrose in proportion given by the assistant.
4. Fill the polarimeter tube to the mark with the solution and slide over the glass making sure to remove any air bubbles.
5. Place the polarimeter tube in the polarimeter.
6. Set up the sharpness using accessible handwheels.
7. Take your first polarimeter reading as soon as possible so you get the earliest starting point possible and note the time of your first measurement (remember in ocular you cannot see any striae).
8. Repeat readings every 15-20 minutes during 2.5h.
9. Compile your results in the table.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>( \alpha_t )</th>
<th>( \alpha_\infty - \alpha_t )</th>
<th>( \ln \left( \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \infty )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

10. After your first measurement place your steady flask in the 60ºC thermostat. After 2 hours cool the solution down to the room temperature and read out \( \alpha_\infty \) value. We assume that at 60ºC the reaction is fast enough to be finished within 2 hours.

**CALCULATIONS:**

1. For each time \( t \) calculate the value of \( \ln \left( \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty} \right) \)
2. Compile your results in the table.
3. Plot \( \ln \left( \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty} \right) \) against \( t \).
4. The slope of the plot is equal to \( k \).
EXAMPLE CALCULATIONS.

**Specific Rotation**

**Determining the Specific Rotation**

The observed rotation is dependent upon the path length of the light passing through the sample compartment and is also dependent upon the number of molecules of the isomer.

The observed rotation is converted to a specific rotation by using the following formula:

\[
\text{Specific Rotation} = \frac{\text{Observed Rotation}}{(\text{conc.g/ml}) \times (\text{length of sample tube, decimeters})}
\]

Let's take an example (1): Suppose that the observed rotation of an optically active isomer produced an observed rotation of +13.00 degrees. The sample had a concentration of 1000g/liter and the sample tube was 20 cm in length. What would be the reported specific rotation of this dextrorotatory isomer?

1. Convert the concentration to g/ml
   
   \[
   \frac{1000 \text{g}}{\text{liter}} \times \frac{1 \text{liter}}{1000 \text{ml}} = 1.0 \text{ g/ml}
   \]

2. Convert the length of the tube to decimeters knowing that 10 cm = 1 decimeter.
   
   \[
   20 \text{ cm} \times \frac{1 \text{ dm}}{10 \text{ cm}} = 2 \text{ dm}
   \]

3. Using the above formula plug in the observed rotation, the length and concentration.
   
   \[
   \text{Specific Rotation} = \frac{+13.00 \text{degrees}}{(1.0 \text{ g/ml}) \times (2 \text{ dm})} = +6.50 \text{ degrees}
   \]

(2) Let’s see if you can do one of these. Suppose that the observed rotation was -45.5 degrees of rotation. The concentration was 3.00 grams/ml and the length of the tube was 20 cm. Identify whether this is a dextrorotatory or levorotatory isomer and determine the specific rotation.

Answer:

The procedure is as follows:

1. Convert the length of the tube to dm
   
   \[
   20 \text{ cm} \times \frac{1 \text{ dm}}{10 \text{ cm}} = 2 \text{ dm}
   \]

2. Plug in the concentration in g/ml and the length of the tube into the formula.
   
   - Specific Rotation = -45.5 degrees / (3.0 g/ml) (2 dm) = -7.58 degrees rotation.
   - Since the specific rotation is negative it will be the levorotatory isomer.
**Experimental**

**Properties of the polarized light.**

1. Design and build optical scheme that provides the rotation of polarization by 90° using two mirrors.
2. Using polarizer and photodiode to measure the intensity of the laser beam you have to check the Malus law for determination of the light intensity passed through the polarizer.

**Questions for quiz.**

1. The unpolarized light with intensity $I_0$ propagates through two crossed polarizers. The intensity of the light after second polarizer is obviously equal to zero. The third polarizer is placed between first and second polarizer. The angle between its axis and the that of the first polarizer is equal to 30°. What is the intensity of the light after second polarizer now?

2. Which molecules can not be optically active: $\text{H}_2$, $\text{CH}_4$, $\text{CHClBr}_2$, $\text{CHClBrF}$, $\text{C}_3\text{H}_6\text{Br}_2$, $\text{CH}_3\text{CHCICH}_2\text{Cl}$.

3. 15 g sucrose were added to 100 ml of water. What is the rotational angle if the polarized light passes through 10 cm of such solution? Assume that solution density is 1.07 g/cm³ and specific rotation is equal to 66.4°?

4. Through what angle should an analyzer be rotated from the incoming plane of polarization to reduce the intensity to one-fourth?
IV.B. KINETICS INVESTIGATIONS OF THE RATE CONSTANT OF INTRAMOLECULAR REARRANGEMENT BY FLASH PHOTOLYSIS

INTRODUCTION

Photochemistry, a sub-discipline of chemistry, is the study of the interactions between atoms, small molecules, and light or electromagnetic radiation.

Photochemistry may also be introduced to laymen as a reaction that proceeds with the absorption of light. Normally a reaction (not just a photochemical reaction) occurs when a molecule gains the necessary activation energy to undergo change. A simple example can be the combustion of gasoline (a hydrocarbon) into carbon dioxide and water. This is a chemical reaction where one or more molecules/chemical species are converted into others. For this reaction to take place activation energy should be supplied. The activation energy is provided in the form of heat or a spark. In case of photochemical reactions light provides the activation energy. The absorption of a photon of light by a reactant molecule may also permit a reaction to occur not just by bringing the molecule to the necessary activation energy, but also by changing the symmetry of the molecule's electronic configuration, enabling an otherwise inaccessible reaction path.

Flash photolysis is a pump-probe technique, in which short light pulse are used. The technique was developed in 1949 by Manfred Eigen, Ronald George Wreyford Norrish and George Porter, who won the 1967 Nobel Prize in Chemistry for this invention.

Flash photolysis was developed shortly after World War II as a result of the military attempts to build cameras fast enough to photograph missiles in flight. Within the past 40 years the technique became more powerful and sophisticated due to the developments in optics and lasers. Also the interest in this method grew considerably as the practical applications expanded from chemistry to biology, materials science, environmental sciences, etc. Nowadays flash photolysis facilities are extensively used by researchers to study light induced processes in organic molecules, polymers, nanoparticles, semiconductors, photosynthesis in plants, signaling and light induced conformational changes in biological systems, etc.

Substituted benzopirene (TMINBS) excited by a short-pulse light from a flash lamp undergo an instantaneous rearrangement from colorless form A (leukoform) to the colored form B (blue).

Form B is unstable and undergoes the transformation to the form A in tens of seconds. This transformation proceeds according to the first order kinetics with the rate proportional to the concentration $c$ of created B form.
\[ \frac{dc}{dt} = kc \]
\[ \ln(c) = \ln(c_0) - kt \]

**PROCEDURE:**

1. Take the set containing the tray with the solution of dye.
2. Get acquainted with the lay-out.
4. After few minutes adjust the position of the pen on the tape of the recorder.
5. Switch on the shift of the recorder and release the flash of the lamp.
6. After measurement switch off the lamp and the recorder.
7. Note the shift’s speed of the recorder.

**CALCULATIONS:**

1. Plot S=f(t), where S is the deflection of the marker.
2. Find \( t_{1/2} \) characterizing this reaction of rearrangement.
3. Using \( t_{1/2} \) calculate \( k \) according to the formula \( k = \frac{0.693}{t_{1/2}} \).
4. Transfer S=f(t) plot into lnS=f(t) plot.
5. The slope of the latter is equal to \(-k\).
6. Compare values of \( k \) obtained with these two methods.
IV.C. KINETIC INVESTIGATIONS OF THE RATE CONSTANT OF REARRANGEMENT OF THE BROMOPHENYL BLUE

INTRODUCTION

The rearrangement of the mononion of the bromophenyl blue dye to the tri anion proceeds in the strong alkaline environment, where the concentration of OH⁻ is equal 0.5-2mol/L. The scheme introduced below illustrated changes in the structure of dye molecule taking place when the pH increases.

\[
\begin{align*}
\text{Br} & \text{Br} & \text{Br} & \text{Br} & \text{OH} \\
& & & & \downarrow \text{OH}^- \\
\text{Br} & \text{Br} & \text{Br} & \text{Br} & \text{SO}_3^- \\
& & & & \downarrow \text{H}^+ \\
\text{Br} & \text{Br} & \text{Br} & \text{Br} & \text{O}^- \\
& & & & \downarrow \text{OH}^- \\
\text{Br} & \text{Br} & \text{Br} & \text{Br} & \text{O}^- \\
& & & & \downarrow \text{OH}^- \\
\text{Br} & \text{Br} & \text{Br} & \text{Br} & \text{SO}_3^- \\
& & & & \downarrow \text{H}^+ \\
\end{align*}
\]

This reaction can be analyzed comfortably by colorimetric method, because the solution of monoanion is blue while the solution of tri anion is colorless. The rate of this reaction depends on the dye concentration and the concentration of OH⁻ ions according to the second-order rate law:

\[
-\frac{dc_{\text{monoanion}}}{dt} = k \cdot c_{\text{monoanion}} \cdot c_{OH^-}
\]

because the concentration of OH⁻ ions exceeds that of monoanion by several order of magnitudes we can consider it to be constant and the reaction can be described by the first-order rate law

\[
-\frac{dc_{\text{monoanion}}}{dt} = k_{\text{exp}} \cdot c_{\text{monoanion}}
\]

the real rate constant we can calculate as follows:
\[ k_{\text{exp}} = k'' \cdot c_{OH}^- \]

where:

\( k_{\text{exp}} \) - experimentally observed rate constant
\( k'' \) - "true" second order rate constant

and

\[ \ln c = \ln c_0 - k_{\text{exp}} t \]

**PROCEDURE:**

1. Take the cuvette, flasks and blue dye solution.
2. Get acquainted with the SPECOL manual.
3. Take 0.2 mL of the blue dye solution to 10mL flask and fill up the flask with NaOH solution of a given concentration.
4. Fill up the cuvette with the newly prepared solution.
5. Take your first reading as soon as possible so you get the earliest starting point possible.
6. Continue readings every 2min during two hours.
7. Compile your results in the table.
8. Reaped your measurements for the other concentrations of NaOH.
9. For each concentration plot \( \ln A = f(t) \)
10. The slope is equal to \(-k\).
11. Plot \( k_{\text{exp}} = f(c_{\text{NaOH}}) \).
12. The slope is equal to \( k'' \).

**EXAMPLES:**

1. The rate of the reaction \( A + 3B \rightarrow C + 2D \) was reported as \(1.0 \text{mol/L} \cdot \text{s} \). State the rates of formation and consumption of the participants.
2. At 518˚C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363Torr, was 1.07Torr s\(^{-1}\) when 0.5 per cent had reacted and 0.76Torr s\(^{-1}\) when 20 per cent had reacted. Determine the order of the reaction.
3. The rate constant for the decomposition of a certain substance is \(2.8 \times 10^{-3} \text{Lmol}^{-1} \text{s}^{-1}\) at 30˚C and \(1.38 \times 10^{-2} \text{Lmol}^{-1} \text{s}^{-1}\) at 50˚C. Evaluate the Arrhenius parameters of the reaction.