Exercise 8  KINETICS OF THE HYDROLYSIS OF ETHYL ACETATE

Theory
CHEMICAL KINETICS

Chemical reactions, reaction rate

Chemical kinetics is the part of physical chemistry that studies reaction rates. The reaction rate or rate of reaction for a reactant or product in a particular reaction is intuitively defined as how fast a reaction takes place. For example, the oxidation of iron under the atmosphere is a slow reaction which can take many years, but the combustion of butane in a fire is a reaction that takes place in fractions of a second.

Consider a typical chemical reaction:

\[ aA + bB \rightarrow pP + qQ \]

The lowercase letters (a, b, p and q) represent stoichiometric coefficients, while the capital letters represent the reactants (A and B) and the products (P and Q).

According to IUPAC’s Gold Book definition the reaction rate (v) for a chemical reaction occurring in a closed system under constant-volume conditions, without a build-up of reaction intermediates, is defined as:

\[
\frac{1}{p} \frac{dc_P}{dt} = \frac{1}{q} \frac{dc_Q}{dt}
\]

\[
\frac{1}{a} \frac{dc_A}{dt} = \frac{1}{b} \frac{dc_B}{dt}
\]

where: \(c_I\) (I= A, B, P. or Q) – is concentration of substance

The IUPAC recommends that the unit of time should be the second always. Reaction rate usually has the units of \(\text{mol dm}^{-3}\text{s}^{-1}\). It is important to on mind that the previous definition is only valid for a single reaction, in a closed system of constant volume.

The quantity:

\[
\xi = \frac{d\xi}{dt}
\]

defined by the equation:

\[
\xi = \frac{1}{a} \frac{dn_A}{dt} = \frac{1}{b} \frac{dn_B}{dt} = \frac{1}{p} \frac{dn_P}{dt} = \frac{1}{q} \frac{dn_Q}{dt}
\]

where: \(n_I\) - designates the amount of substance I (I=A, B, P, or Q) conventionally expressed in units of mole

\(\xi\) is called the 'rate of conversion' (extent of reaction) and is appropriate when the use of concentrations is inconvenient, e.g. under conditions of varying volume. In a system of constant volume, the rate of reaction is equal to the rate of conversion per unit volume throughout the reaction.

The rate law or rate equation for a chemical reaction is an equation which links the reaction rate with concentrations or pressures of reactants and constant parameters (normally rate coefficients and partial reaction orders). To determine the rate equation for a particular system
one combines the reaction rate with a mass balance for the system. For a generic reaction:

\[ \text{A + B} \rightarrow \text{C} \]

the simple rate equation is of the form:

\[ v = k c_A^a c_B^b \]  

(4)

the concentration is usually in mol dm\(^{-3}\) and \(k\) is the \textit{reaction rate coefficient} or \textit{rate constant}. Although it is not really a constant, because it includes everything that affects reaction rate outside concentration: mainly temperature, ionic strength, surface area of the adsorbent or light irradiation.

The exponents \(a\) and \(b\) are called \textit{reaction orders} and depend on the reaction mechanism. The stoichiometric coefficients and reaction orders are very often equal, but only in one step reactions, molecularity (number of molecules or atoms actually colliding), stoichiometry and reaction order must be the same.

The \textit{Arrhenius equation} is a simple, but remarkably accurate formula for the temperature dependence of the rate constant, and therefore rate of a chemical reaction. Actually, the Arrhenius equation gives:

"the dependence of the rate constant \((k)\) of chemical reactions on the temperature \((T)\) (in Kelvin) and \textit{activation energy} \((E_a)\) ", as shown below:

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

(5)

where: \(A\) – is the \textit{pre-exponential factor} or simply the \textit{prefactor}

\(R\) – is the molar gas constant.

The units of the pre-exponential factor are identical to those of the rate constant and will vary depending on the order of the reaction. It can be seen, that either increasing the temperature or decreasing the activation energy (for example through the use of catalysts) will result in an increase in rate of reaction.

The \textit{activation energy} can be interpreted as the minimal energy of the molecules to undergo reaction. This energy is needed, either, to rupture a chemical bond, eg. in free radical gas reactions, or to allow rearrangements when the molecules collide.

Taking the natural logarithm of the Arrhenius equation yields:

\[ \ln k = -\frac{E_a}{R T} + \ln A \]  

(6)

So, when a reaction has a rate constant which obeys the Arrhenius equation, a plot of

\[ \ln k = f\left(\frac{1}{T}\right) \]

gives a straight line, which slope and intercept can be used to determine thr \(E_a\) and \(A\).

This procedure has become common in experimental chemical kinetics. To determine the activation energy of a reaction, one must know a rate constant of the reaction at least at two different temperatures. Applying the \textbf{Equation 6}, one can easy express:
\[
\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

where: 
- \(k_1\) – is rate constant correspond to temperature \(T_1\)
- \(k_2\) – is rate constant correspond to temperature \(T_2\)

Since the rate of a given reaction depends on the concentration of the reactants, the speed of the process falls off as the reaction proceeds, for the reactants being continuously consumed. The reaction is becoming slower and slower but theoretically never ceases. It is, therefore, not possible to define the general rate of a reaction, and so in practice the rate is considered at a particular instant. The rate may be defined in any convenient way, usually, the rate of change of concentration (\(c\)) of one of the reactants or products is chosen. The experimental data then follow a change of concentration with time (\(t\)), and the rate at any instant is given by the tangent to a curve of the plot:

\[c = f(t)\]

**THE SECOND-ORDER REACTION**

depends on the concentrations of one second-order reactant (scheme C and Equation 8), or two first-order reactants (scheme D and Equation 9):

- \(2A \rightarrow \text{Products}\)
- \(A + B \rightarrow \text{Products}\)

For a second order reaction, its reaction rate is given by:

\[v = k c_A^2\]  
\[v = k c_A c_B\]

We will deal with the bimolecular reaction – D, supposing the *same initial concentration* of A and B reactants:

\[c_{0A} = c_{0B} = c_0\]

The differential rate law for the second-order reaction is then:

\[-\frac{dc}{dt} = k c^2\]

Solving the differential equation, one can obtain:

\[\frac{1}{c} - \frac{1}{c_0} = k t\]

where:
- \(c\) – is the concentration of reactant at time \(t \rightarrow (c_A = c_B = c)\)
- \(k\) – is the second-order constant, which has dimension \(\text{concentration}^{-1}\text{time}^{-1}\) (eg. \(\text{dm}^3\text{mol}^{-1}\text{s}^{-1}\))
In this case, a characteristic plot which will produce a linear function is \( \frac{1}{c} = f(t) \) with the slope \( k \) (Figure 1).

The **half-life of reaction** describes the time needed for half of the reactant to be depleted. The **half-life of a second-order reaction**, which depends on one second-order reactant, is:

\[
t_{1/2} = \frac{1}{k c_0} \quad \text{[time]}
\]

Figure 1 Plots \( c = f(t) \) and \( 1/c = f(t) \) for a second-order reaction

**Task**

Determine the rate constant and the activation energy of the alkaline hydrolysis of ethyl acetate using sodium hydroxide.

This experiment illustrates a bimolecular reaction (reacting species are ethyl acetate and sodium hydroxide):

\[
\text{CH}_3\text{–COO–CH}_2\text{–CH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{–COONa} + \text{CH}_3\text{–CH}_2\text{–OH} \quad (\text{E})
\]

The initial concentrations of the reacting species are the same:

\[
C_{0A} = C_{0B}
\]

where: \( c_{0A} \) - is the initial concentration of ethyl acetate

\[
c_{0B} \quad \text{- is the initial concentration of sodium hydroxide}
\]

**Equipments and chemicals**

thermostat

pipettes

burette

volumetric flasks,

titrimetric flasks

stop-clock

solution of ethyl acetate \( (c = 0.04 \text{ mol dm}^{-3}) \)

solution of sodium hydroxide \( (c = 0.04 \text{ mol dm}^{-3}) \)

solution of hydrochloric acid \( (c = 0.04 \text{ mol dm}^{-3}) \)
phenolphthalein

**Procedure**

1. Transfer **50 ml** of the solution of ethyl acetate ($c = 0.04 \text{ mol dm}^{-3}$) into a volumetric flask ($V = 50 \text{ ml}$) and **50 ml** of the solution of sodium hydroxide ($c = 0.04 \text{ mol dm}^{-3}$) into another volumetric flask ($V = 200 \text{ ml}$).

   Both flasks cork down and put them in the thermostated bath ($t = 20 ^\circ C$).

2. Fill the burette with the solution of sodium hydroxide ($c = 0.04 \text{ mol dm}^{-3}$).

3. Pipette $V_{\text{HCl}} = 5 \text{ ml}$ solution of hydrochloric acid ($c = 0.04 \text{ mol dm}^{-3}$) into a clean and dry titrimetric flask.

4. After 10 minutes, take out the flasks with the solutions from the thermostated bath and pour the solution of ethyl acetate to the solution of sodium hydroxide, put the mixture to the thermostated bath.

   Start the stop-clock.

5. 5 minutes after mixing, pipette **10 ml** of reaction mixture (leave the flask in the bath!) to the titrimetric flask (with 5 ml of HC - $V_{\text{HCl}}$).

   Remark: HCl stops the reaction given by the scheme D.

6. Titrate with the solution of sodium hydroxide adding 1 drop of phenolphthalein as indicator.

   When the endpoint of titration has been reached, read the used volume of NaOH from the burette ($V_{\text{NaOH}}$). Write it down to the Table 1.

7. Repeat the step 5 and 6 every 5 minutes six times more (in the 10th, 15th, 20th, 25th, 30th and 35th minutes from the moment of mixing).

8. Write down to the Table 1 the temperature of the bath.

9. Repeat the same experiment at 30 °C. Because the reaction is faster, the times for titrations will be in the 5th, 10th, 15th, 20th, and 25th min. from the mixing.

   Write down to the Table 1 the used volume of NaOH for each titration.

### Table 1 Measured and calculated values

<table>
<thead>
<tr>
<th>$t$ [min]</th>
<th>$t = 20 ^\circ C$</th>
<th>$t = 30 ^\circ C$</th>
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</thead>
<tbody>
<tr>
<td>$V_{\text{NaOH}}$ [ml]</td>
<td>$c$ [mol dm$^{-3}$]</td>
<td>$1/c$ [dm$^3$ mol$^{-1}$]</td>
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<td>5</td>
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<td>35</td>
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### Data treatment

1. Calculate the concentration ($c$) in the Table 1 according to:

   $$
c = \frac{V_{\text{HCl}}c_{\text{HCl}} - V_{\text{NaOH}}c_{\text{NaOH}}}{V}
   $$

   where: $c_{\text{HCl}}$ - is concentration of HCl ($c_{\text{HCl}} = 0.04 \text{ mol dm}^{-3}$)
$V_{\text{HCl}}$ - is the volume of HCl (5 ml)
$c_{\text{NaOH}}$ - is concentration of NaOH ($c_{\text{NaOH}} = 0.04 \text{ mol dm}^{-3}$)
$V_{\text{NaOH}}$ - is the volume of NaOH from Table 1 (ml)
$V$ - is the volume of the reaction mixture used in titration (10 ml)

2 Calculate the $1/c$ values.
3 Use MS Excell to create the dependence $1/c = f(t)$ at given temperature.
   Fit the experimental points with a linear function. The slope represents the value of the rate constant ($k$) at given temperature.
   If the time is in minutes, the unit of the rate constants is $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$.
4 Calculate the activation energy ($E_a$) according to Equation 7.

**Report**

The report must include:
- Theoretical principles
- Equipments and chemicals
- Experimental procedure and measurements
- Table of results, calculations, diagrams $1/c = f(t)$ at two temperatures, and the value of the activation energy.

**Literature**

- KOPECKÝ, F., et al.: Practical and numerical exercises from physical chemistry for students of pharmacy, Faculty of Pharmacy, Comenius University in Bratislava, (1989), in Slovak
- OREMUSOVÁ, J., GREKSÁKOVÁ, O.: Manual for laboratory practice in physical chemistry for students of pharmacy, Department of Physical Chemistry, Faculty of Pharmacy, Comenius University in Bratislava, (2007), in Slovak