

DETERMINATION OF REACTION RATE CONSTANT AND ACTIVATION ENERGY

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Task 41

DETERMINATION OF REACTION RATE CONSTANT AND ACTIVATION ENERGY

I. Aim of the task

The aim of the task is determination of reaction rate constant of the saponification of ethyl acetate at two different temperatures and calculating activation energy of the process.

II. Introduction

1. Definition of reaction rate.
2. Order and molecularity of reaction.
3. Influence of temperature on the reaction rate.
4. Arrhenius equation, active complex and collision theory.

References:

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2. H. Kuhn, H-D. Försterling, D.H. Waldeck, “Principles of Physical Chemistry”, 2nd edition, Wiley, 2009, Chapter 24.
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III. Theory

III. 1. Definition of reaction rate

Chemical reaction is a process of changing substrates into products in certain time. Concerning the form of the substrates and mechanism of the reaction along with system in which it occurs, one can make simple observation that each and every chemical reaction has its own speed. During chemical transformation, concentration of substrates gradually decreases and product concentrations rise. For the given reaction:



loss of substrates at any time t is given by instantaneous **rate of reaction** v and can be noted as:

$$v = - \frac{d[A]}{dt} = - \frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = \frac{d[D]}{dt} \quad (2)$$

The negative sign standing in front of substrates is conventional and maintains reaction rates calculated from substrate loss positive (negative value of the speed of the reaction would make no sense). Let us notice that the speed of the reaction at the beginning (just after the reagents are mixed) usually differs from the reaction rate after some time. Thus to describe it at any given moment it is necessary to use the time derivative of reactant concentration. Mathematically, in a more formal way the instantaneous rate of reaction for any reagent can be expressed:

$$v = \frac{1}{z_j} \frac{d[J]}{dt} \quad (3)$$

where z_j – the stoichiometric factor, negative for substrates, positive for products,
 $[J]$ – the concentration [mol dm^{-3}] of chemical species.

The reaction rate is expressed in [$\text{mol dm}^{-3} \text{s}^{-1}$]. The overall reaction rate is derived from experiment and it is usually proportional to the concentration of the reactants raised to certain powers. Reaction rate proportional to two reagent concentrations can be written as follows:

$$v = k[A]^\alpha[B]^\beta \quad (4)$$

The coefficient k is called the rate constant and it is independent of reactant concentrations but dependent on the temperature. Although it is called the rate constant, its dimension is restricted by order of reaction and is strictly bound to it. Actually equation (4) noted in this way is called **the rate law**. Basically the rate law is an equation that expresses reaction rate as a function of reactant concentrations at any time in the system. In a more formal way it can be noted:

$$v = f([A], [B], \dots) \quad (5)$$

This relationship between the reaction rate and the reactant concentrations is determined experimentally and should not be inferred from the chemical equation for the reaction.

Synthesis of hydrogen bromide is a good example of existing discrepancy between the rate law and the stoichiometry of the reaction. The overall equation of reaction is expressed by:



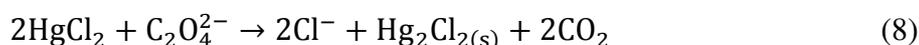
and the rate law is given by:

$$v = \frac{k[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + k'[\text{HBr}]} \quad (7)$$

The differences between powers and stoichiometric factors can be explained on the basis of complex mechanism of the reaction.

III. 2. Order and molecularity of reaction

If the rate law for the reaction can be written in the form of equation (4) then the reaction order is classified as α -order in A and β -order in B. Those orders noted with respect to certain reagents are also called ‘**partial reaction orders**’. Overall order of reaction is defined as a sum of all powers in the kinetic equation. When equation (4) is taken into consideration, overall order of reaction simply equals $\alpha + \beta$. The order of reaction can be expressed by positive and negative integers, by zero and also by fractions. In some cases the order of reaction can be unknown (e.g. the order of reaction (7) with respect to bromine is unknown despite the fact that the rate law is fully known). Based on the reaction:



and the rate law:

$$v = k[\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^2 \quad (9)$$

it can be concluded that order of the reaction with respect to HgCl_2 and $\text{C}_2\text{O}_4^{2-}$ is 1 and 2 respectively. The overall order for this reaction equals 3 (notice that this is the second time when discrepancy between the stoichiometric factors and the empirical rate law occurs.)

When writing about kinetics it is impossible to omit another important factor: **half-life** $t_{1/2}$. Half-life of reaction is defined as a time after which half of the substrate concentration is transferred into products. Its value depends on the reaction order (see Table 1).

Table 1. Rate laws. Index 0 stands for the initial concentration of reagent and k is the reaction rate constant.

Reaction order	Elementary step	Rate law	Straight line plot	Half-life
0	$A \rightarrow P$	$v = k$	$[A]$ vs t	$\frac{[A]_0}{2k}$
1	$A \rightarrow P$	$v = k[A]$	$\ln[A]$ vs t	$\frac{\ln 2}{k}$

2	$A \rightarrow P$	$v = k[A]^2,$	$\frac{1}{[A]}$ vs t	$\frac{1}{k[A]_0}$
	$A + B \rightarrow P$	$v = k[A][B]$	$\ln\left(\frac{[B]}{[A]}\right)$ vs t	

Molecularity of reaction is the number of reactant molecular entities that are involved in transforming into product. In other words it is a number of substrates that take part in the reaction. The reaction with a molecularity of one is called 'unimolecular', with a molecularity of two 'bimolecular' and three 'termolecular'. Unimolecular reactions usually refer to isomerization, radioactive decay and thermal decomposition of chemical compounds. When estimating molecularity one should base on each step of the mechanism of reaction and not on the summary chemical equation of the whole process. As a good example of this rule one can take a closer look at the explosive water synthesis (10):



At first glance it looks as if this is a termolecular reaction but in reality it is a multistage radical process where initiation (11), propagation (12) and termination (13) are unimolecular, bimolecular and termolecular respectively.



Of course, explosive synthesis of water is a far more complex process and cannot be restricted to those three equations above. They are only mentioned here to emphasize that molecularity should be estimated for each and every step of chemical reaction.

III. 3. Activation energy

Numerous experimental data has led to a conclusion that for most of chemical reactions the reaction rate increases along with the temperature. To make that general assumption more quantitative it has been concluded that for most of the reactions its speed doubles every 10 degrees Centigrade higher (**van't Hoff's rule**). To be more accurate one can use **the temperature coefficient of a reaction** n which is given by:

$$n = \frac{k_{T+10}}{k_T} \quad (14)$$

where k_T stands for the reaction rate constant at T temperature and k_{T+10} is the reaction rate constant at $T+10$ temperature. Basically the temperature coefficient provides information about multiplication of the reaction rate along with the temperature increase by 10 degrees Centigrade. Value n might be also expressed in a more convenient way (especially when the difference between both temperatures is not equal to 10):

$$n = \left(\frac{v_2}{v_1} \right)^{\frac{10}{T_2 - T_1}} \quad (15)$$

where v_2, v_1 are the reaction rates at given temperatures T_2 and T_1 . Sometimes the temperature coefficient of a reaction is noted with Q_{10} or γ symbol in the literature. The value of n has no dimension and usually it is within the range from 2 to 4, but sometimes (mostly for biochemical processes) it exceeds these limits. The reaction rate constants can be also connected with the temperature and thermodynamic functions by using the van't Hoff's isotherm (see Table 3).

The basis of understanding chemical kinetics and its dependence on the temperature was discovered in 1872 by Swedish scientist Svante **Arrhenius**. He was able to deduce a formula which combined speed of chemical reaction with the system in which it occurs at absolute temperature. When $\ln k$ is plotted against $1/T$, it gives a straight line. Value of the slope is characteristic of a reaction.

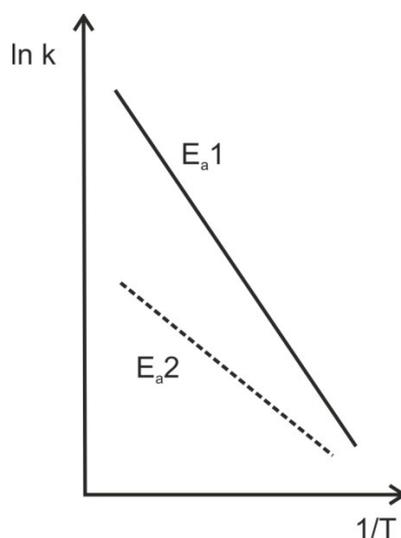


Fig. 1. Plot of $\ln k = f(1/T)$ for two reactions. Activation energy of the first reaction is higher than that of the second one.

Mathematically it can be described as:

$$\ln k = A + \frac{B}{T} \quad (16)$$

if $B = \frac{E_a}{R}$, then:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (17)$$

It can be also written in an exponential notation:

$$k = A e^{-\frac{E_a}{RT}} \quad (18)$$

where: k – the rate constant, A – the pre-exponential factor, R – the gas constant, T – the absolute temperature.

From the Arrhenius equation it can be concluded that the higher activation energy is the stronger impact temperature has on the rate constant. In other words for $E_a = 0$ the rate constant is independent of temperature.

III. 4. Interpretation of Arrhenius equation parameters

III.4.1. Collision Theory

Collision theory refers to the reactions that take place in the gaseous state. It is based on an assumption that molecules need to collide to yield a product. However, not every collision among substrates is effective. Successful impact requires kinetic energy of molecules equal or higher than activation energy of the process. Thus activation energy is the minimal amount of energy necessary for reaction to occur. Basically when two molecules are too far from each other nothing happens. When they approach towards themselves the energy rises. The closer they are the more intense interactions between them are. If they collide they are able to form new bonds. The product is on the lower energy level than substrates were.

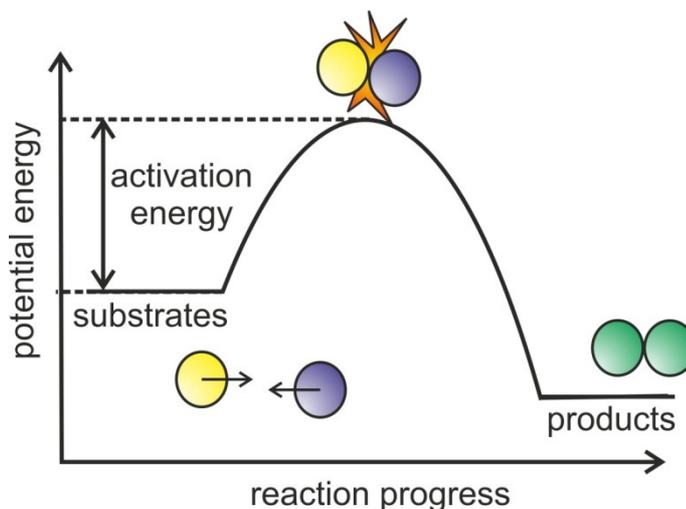


Fig. 2. Reaction profile based on the collision theory.

Table 2. Interpretation of the Arrhenius equation parameters in terms of collision theory [5].

Reaction occurs when substrate molecules collide.	
Reaction rate is proportional to the collision frequency Z .	$v \sim Z$
Frequency of collisions is proportional to the amount of molecules in the system. Thus Z is proportional to the concentration of substrates (i.e. A, B are substrates).	$Z \sim [A][B],$ $v \sim [A][B]$

Only collisions that have energy no smaller than activation energy lead to chemical reaction. Fraction of molecules f having that level of energy can be calculated from the Boltzmann distribution.	$f = e^{-\frac{E_a}{RT}}$
Taking all the above into consideration the reaction law can be obtained:	$V \sim f[A][B] \Rightarrow V \approx e^{-\frac{E_a}{RT}}[A][B],$ If $e^{-\frac{E_a}{RT}} = k$, then $V = k[A][B]$.

The parameter A can be estimated either from the kinetic gas state theory or experimentally. It was noticed that in many cases the experimental value of A is much higher than the theoretical one. This phenomenon can be explained by the fact that molecules not only need energy excess (above the activation energy) but also they have to be oriented in a certain way. Thus theoretical A needs to be multiplied by steric factor P . Usually the values of P vary from 0 (no orientation of molecules will yield a product) to 1 (100% of collisions with $E \geq E_a$ results in product formation). However, there are several cases where P is greater than 1 (mostly for the reaction where ionic bond is formed).

III.4.2. Activated Complex Theory

The second theory which can be used to describe the Arrhenius equation parameters is called **Activated Complex Theory**. It applies to the reactions occurring in both liquid and gaseous phases. Basically the profile of the reaction in this theory is quite similar to that in the collision theory. The difference is in the interpretation of the process mechanism. When the substrate molecules are close enough they form a complex. During this action potential energy increases to the point where it reaches its maximum and the activated complex K^A is formed. To yield a product, energy of the complex has to be equal or higher than the activation energy. If the energy is below that level, a complex will break down into substrates. Basically an activated complex is a kind of transition state of an assembly of atoms on an infinitesimally small area, which occurs while new bonds are formed. Thus it cannot be isolated from the system.

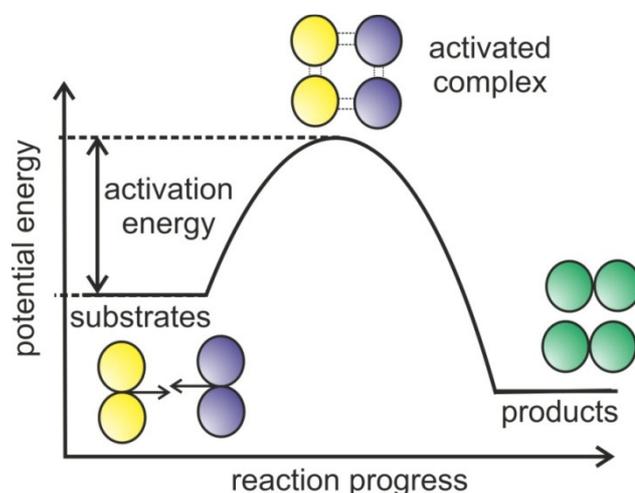


Fig. 3. Reaction profile based on an activated complex theory.

Table 3. Interpretation of Arrhenius equation parameters in terms of activated complex theory [5].

<p>Activated complex (K^A) is in equilibrium with substrates S.</p>	$S \leftrightarrow K^A$
<p>Equilibrium constant can be expressed:</p>	$K^* = \frac{K^A}{[S]}$
<p>Reaction rate is proportional to both concentration of substrates and activated complex.</p>	<p>$V \sim [K^A]$, $V \sim K^*[S]$, and if $V \sim k[A][B]$, then $k \sim K^*$</p>
<p>Value of equilibrium constant might be related to thermodynamic functions (by van't Hoff isotherm).</p>	$K = e^{-\frac{\Delta G}{RT}} \Rightarrow K^* = e^{-\frac{\Delta G^*}{RT}}$ <p>where ΔG^* is free energy of activation</p>
	<p>Because $\Delta G = \Delta H - T\Delta S$, in the case of the activated complex:</p> $\Delta G^* = \Delta H^* - T\Delta S^*$ <p>Where ΔH^*, ΔS^* is enthalpy and entropy of activation respectively.</p>
<p>Since: $k \approx K^*$,</p> $K^* \approx e^{-\frac{\Delta G^*}{RT}},$ $\Delta G^* \approx \Delta H^* - T\Delta S^*,$ $k \approx e^{-\frac{\Delta H^* - T\Delta S^*}{RT}},$	
<p>Value of activation entropy provides a piece of information on orientation of molecules. If substrates must be aligned in a certain way to yield product, formation of activated complex will lead to less chaotic distribution of particles in the system causing ΔS^* to be negative and in consequence, decreasing the value of A ($A = e^{\frac{\Delta S^*}{RT}}$).</p>	$k \approx e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}},$ $k = Ae^{-\frac{E_a}{RT}}.$

IV. Experimental

A. Devices and materials

1. **Devices:** thermostat and electrical conductivity meter.
2. **Equipment:**
 - thermostat cylinders (tc): 200 cm³ – 6 u,
 - graduate pipettes: 2 and 20 cm³,
 - volumetric flasks: 100 cm³ (2 u) and 200 cm³ (1 u),
 - graduated cylinder: 100 cm³ – 3 u.
3. **Materials:**
 - aqueous solution of NaOH (0.1 mol/dm³),
 - ethyl acetate (M = 88.1 g/mol, d = 0.902 g/cm³).

B. Preparation of the thermostat

1. Plug the thermostat into the white socket above the device.
2. Switch the red button into the position “on”. The value (303K) of set temperature should be displayed next to the red button, only if necessary alter the displayed value using ‘+’, ‘-’ buttons.
3. Turn on the internal thermostatic stirrer using the green button (next to the displayer).

C. Preparation of the electrical conductivity meter (EC-meter)

1. Plug the EC-meter into the white socket above the device.
2. Press ON/OFF button on the device panel.
3. Values of the temperature and electrical conductivity should be displayed on the front panel of the device.

D. Preparation of stock solutions

Using given stock solutions and distilled water make:

- 200 cm³ of 0.01 mol/dm³ NaOH aqueous solution,
- 100 cm³ of 0.02 mol/dm³ NaOH aqueous solution,
- 100 cm³ of 0.02 mol/dm³ ethyl acetate aqueous solution.

Dispense into three glass flasks immersed in the thermostatic bath:

- 80 cm³ of 0.01 mol/dm³ NaOH aqueous solution (I tc),
- 40 cm³ of 0.02 mol/dm³ NaOH aqueous solution (II tc),
- 40 cm³ of 0.02 mol/dm³ ethyl acetate aqueous solution (III tc).

Wait until the dispensed solutions reach the desired temperature (approx. 30 min.).

E. Measurements

Measurement at 303K.

1. Rinse using distilled water EC-meter electrodes and dry them with paper towel.
2. Immerse electrodes in I tc solution (0.01 M NaOH). The measured value is G_0 (write it down).
3. Take out the electrodes and see point 1.
4. Pour solution from the II tc (0.02 M NaOH) into III tc (0.02 M ethyl acetate). **Start the timer.** The moment of mixing both solutions is the $t = 0$ min for saponification of ethyl acetate.
5. Immerse clean electrodes into the III tc with mixed solutions. Write down electric conductivity G_t of investigated solution **every 2 minutes**. The experiment is over when G_t is constant in three consecutive measurements.

The minimum amount of noted values is 10.

6. Take out the electrodes and see point 1.

Repeat whole procedure at 318 K.

F. Results and conclusions

Saponification of ethyl acetate proceeds according to the reaction:



During the reaction, concentration of hydroxyl anion decreases and the amount of acetic anion increases. Since the ability to transport electrical charge of both anions in solution is very different, progress of this process can be monitored by conductivity measurements. Hydroxyl anions have much greater conductance than the acetic ones, thus it is anticipated that during the reaction the measured values of conductivity will drop.

At the start of the experiment ($t = 0$) the concentrations of substrates are equal to the stock concentrations and:

$$C_0 = C_{A^-} \sim G_0 - G_\infty \quad (20)$$

where: C - the concentration of hydroxyl anion in solution, G_0 - the conductivity at $t = 0$ (before the reaction starts), G_∞ - the conductivity of the solution in the equilibrium state.

After some time t amount of OH^- will be depleted and in consequence the conductivity will drop. The concentration of substrates after time t might be expressed:

$$C = C_0 - x \quad (21)$$

where x is the concentration of reacted substrate

$$x = C_0 - C \quad (22)$$

Because:

$$C_0 \sim G_0 - G_\infty \quad (23a)$$

$$C \sim G_t - G_\infty \quad (23b)$$

G_t - conductivity after time t .

$$x \sim G_0 - G_\infty \quad (24)$$

$$(C_0 - x) \sim (G_t - G_\infty) \quad (25)$$

Saponification of ethyl acetate is a second-order reaction and thus from second-order law can be noted:

$$v = \frac{dC_A}{dt} = \frac{dC_B}{dt} = kC_A C_B \quad (26)$$

where k – reaction constant, $C_A C_B$ - concentration of the substrates.

If assumed that $C_A = C_B$ than reaction constant can be calculated:

$$k = \frac{1}{C_0 t} \cdot \frac{x}{C_0 - x} \quad (27)$$

using equations 24 and 25:

$$k = \frac{1}{C_0 t} \cdot \frac{G_0 - G_t}{G_t - G_\infty} \quad (28)$$

which leads to expression for conductivity G_t :

$$G_t = \frac{1}{C_0 t} \cdot \frac{G_0 - G_t}{t} + G_\infty \quad (29)$$

Basically eq. 29 represents linear function $y = ax + b$, where $y = G_t$, $a = \frac{1}{C_0 k}$, $b = G_\infty$, $x = \frac{G_0 - G_t}{t}$. Plotting this function $G_t = f\left(\frac{G_0 - G_t}{t}\right)$ will provide information on slope (tga) and thus it can be used to obtain values of k at different temperatures.

Basic relation between k and T is given by Arrhenius equation in a logarithmic form (see equation 17) might be differentiated to obtain equation:

$$\frac{d \ln k}{dt} = \frac{E_a}{RT^2} \quad (30)$$

Calculating definite integral from T_1 to T_2 , one can conclude that:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \cdot \frac{T_2 - T_1}{T_1 T_2} \quad (31a)$$

or

$$\log \frac{k_2}{k_1} = \frac{E_a}{2,303R} \cdot \frac{T_2 - T_1}{T_1 T_2} \quad (31b)$$

Knowing k_1 , k_2 at both temperatures, it is possible to estimate activation energy $E_a \left[\frac{J}{mol} \right]$ of a process.

The results should be displayed in the table below for each temperature.

$t[s]$	$G_t [S]$	$\frac{G_0 - G_t}{t} \left[\frac{S}{s} \right]$	$tga = k_1$

Making your calculations keep in mind that:

1. During the experiment stock solutions are diluted,
2. EC-meter shows values in [mS] and calculations should be made in [S].

For calculating the slope of linear function described by eq. 29 use **the least squares method** (appendix to the tasks). Conclusions should provide information about activation energy of observed process. Compare the obtained value of activation energy with those available in the literature (table values). If the discrepancy between two values exists check your calculations for mistakes. If an error is found, correct it. If correction is not possible (i.e. the experiment was conducted without proper accuracy) make sure that you will explain the discrepancy on the scientific ground in the conclusions.