Determining the decomposition rate of methyl acetate in acidic solutions

Theoretical background: P.W. Atkins: *Physical Chemistry*.
Type of the practice: Pairwise.
Purpose of the practice: To determine the rate coefficient of the acidic decomposition of methyl acetate and to calculate the activation energy of the reaction according the Arrhenius equation.

1 Introduction

Methyl acetate (MeAc) and water reacts in an equilibrium reaction, resulting in acetic acid (HAc) and methanol (MeOH) formation:

$$CH_3COOCH_3 + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_3COOH + CH_3OH\,.$$

The equilibrium constant of the reaction is 5.24 at T=25°C. Accordingly, in non-concentrated solutions ($[MeAc]_0 < 2\,M$ and $[H_2O] \approx 55.5\,M$) nearly all the reactants are consumed at equilibrium. Under these conditions the reaction can be described by only the k_2 second order rate coefficient (up to ca. T= 80 °C, based on the temperature dependence of the equilibrium constant (not detailed here)).

In dilute aqueous solutions ($[MeAc]_0 < 1\,M$) the molarity of water doesn't change significantly during the reaction, hence it the reaction can be treated mathematically as a pseudo-first order reaction:

$$MeAc \xrightarrow[(+H_2O)]{k_{1n}} HAc + MeOH\,,$$

Accordingly, the methyl acetate concentration change in time follows a first order expression during the reaction:

$$[MeAc]_t = [MeAc]_0 \cdot e^{-k_{1n}\cdot t}\,,$$

where $k_{1n} = k_2 \cdot [H_2O]$. The value of k_{1n} is ca. 25 °C-on $1.5 \times 10^{-10}\,s^{-1}$, which translates to a 150 years reaction half-life. The reaction rate is significantly higher in both alkaline and acidic media (water is not shown in the following reactions for simplicity):

$$MeAc \xrightarrow[H^+]{k_{2s}} HAc + MeOH, \qquad \frac{d[MeAc]}{dt} = -k_{2s} \cdot [MeAc] \cdot [H^+]$$

$$MeAc \xrightarrow[OH^-]{k_{2b}} HAc + MeOH, \qquad \frac{d[MeAc]}{dt} = -k_{2b} \cdot [MeAc] \cdot [OH^-],$$

At T=25 °C $k_{2s} = 1.1 \times 10^{-4}\,M^{-1}s^{-1}$ and $k_{2b} = 0.11\,M^{-1}s^{-1}$. Accordingly, the half-life of the reaction is around 2 hours in 1 M strong acid or alkaline solutions, making it possible to study the process during a laboratory practice.

In what follows, only the acid catalyzed decomposition of methyl acetate will be detailed as this is studied during the laboratory practice. H^+ is catalyst in the reaction, hence its concentration is constant ($[H^+] \cong [H^+]_0$). The concentration of methyl acetate therefore changes according to the first order rate equation:

$$[MeAc]_t = [MeAc]_0 \cdot e^{-k_{1s}\cdot t}\,, \tag{1}$$

where $k_{1s} = k_{2s} \cdot [H^+]$. Following $[MeAc]_t$ in time k_{1s} can be determined according to equation (1).

$[MeAc]_t$ can be determined through acid-base titration, as from every decomposed MeAc molecule one HAc forms (in protonated form, due to the highly acidic conditions). Based on the stoichiometry of the reaction:

$$[MeAc]_0 = [MeAc]_t + [HAc]_t \tag{2}$$

Note, that during the acid-base titration the strong acid in the sample is also neutralized. However, as the concentration of the strong acid is constant, the titrant volume is directly proportional with $[HAc]_t$. $[HAc]_t$ can therefore be measured at any time, from which $[MeAc]_t$ can be calculated according to equation (2).

2 Equations and considerations for the evaluation of the measured data

Calculating the exact concentration of $[HAc]_t$ is not necessary for the evaluation of the data, as proved by the following considerations. Assume, that at a given time (t), a sample of V_s volume is titrated with a C_B concentration alkaline solution. The concentration of the strong acid in the sample is C_A and the endpoint of the titration is at V_t alkaline solution volume. The molar amount of the base equals the total molar amount of the acids (the strong acid and HAc together), hence

$$(C_A + [HAc]_t) \cdot V_s = C_B \cdot V_t$$

Including equation (2) into this leads to the following expression:

$$(C_A + [MeAc]_0 - [MeAc]_t) \cdot V_s = C_B \cdot V_t \tag{3}$$

At the end of the reaction ($t = \infty$), when all the methyl acetate decomposed, this translates to:

$$(C_A + [MeAc]_0) \cdot V_s = C_B \cdot V_\infty \tag{4}$$

while at the beginning of the reaction we get the following equation:

$$C_A \cdot V_s = C_B \cdot V_0 \tag{5}$$

$[MeAc]_0$ can be expressed as the difference of equation (4) and (5), while $[MeAc]_t$ is calculated as the difference of equation (4) and (3):

$$[MeAc]_0 = \frac{c_B \cdot (V_\infty - V_0)}{V_s} \quad \text{and} \quad [MeAc]_t = \frac{c_B \cdot (V_\infty - V_t)}{V_s}.$$

Including these in equation (1) gives:

$$V_\infty - V_t = (V_\infty - V_0) \cdot e^{-k_{1s} \cdot t}$$

Taking the natural logarithm of both sides:

$$\ln(V_\infty - V_t) = \ln(V_\infty - V_0) - k_{1s} \cdot t \tag{6}$$

This offers the simplest way to calculate k_{1s}., as its determination only necessitates taking samples at regular time intervals and titrating these with the strong alkaline solutions. Plotting $\ln(V_\infty - V_t)$ in function of reaction time, k_{1s} can be determined from the slope of the fitted linear. Subsequently, (k_{2s}) can be calculated from this, according to what is detailed above. Equation (6) simplifies the measurements (and data evaluation) as compared to equation (1), as:

- The measured data (i.e., volume of the base solution) is used directly, the calculation of the concentrations is not needed.
- Neither the concentration of the strong acid nor that of the base solution (titrant) is needed for the calculations.
- It is not necessary to measure the initial concentration, as in equation (6), V_0 only affects the intercept of the linear, but not its slope, which is used to calculate k_{1s}.

Knowing k_{1s} at the given temperature (T), the activation energy (E_a) of the reaction can be calculated according the Arrhenius equation:

$$k_{1s}(T) = A \cdot e^{-\frac{E_a}{R \cdot T}} \quad \text{and} \quad k_{1s}(298.15\,K) = A \cdot e^{-\frac{E_a}{R \cdot 298.15\,K}}, \tag{7}$$

The value of k_{1s} at 298.15 K: $k_{1s}(298.15\,\mathrm{K}) = C_A \cdot k_{2s}(298.15\,\mathrm{K}) = C_A \cdot 1.1 \times 10^{-4}\,\mathrm{M^{-1}s^{-1}}$. After experimentally determining the pseudo first order rate coefficient at a different temperature, the activation energy from equation (7) is calculated as:

$$E_a = \frac{R \cdot \ln \dfrac{k_{1s}(T)}{k_{1s}(298.15\,\mathrm{K})}}{\dfrac{1}{298.15\,\mathrm{K}} - \dfrac{1}{T}}. \tag{8}$$

3 Experimental

At the beginning of the practice, the instructor provides the following data:

- The temperature of the reaction (T), between 35 – 43 °C. If not instructed otherwise, the default value is 37 °C.
- Concentration of the hydrochloric acid stock solution between (C_{HCl}) 3.0 – 3.8 M. If not instructed otherwise, the default value is $C_{HCl} = 3.2\,\mathrm{M}$.
- The volume of methyl acetate to be measured in the reaction mixture in the range of (V_{MeAc}) 10 – 14 $\mathrm{cm^3}$. If not instructed otherwise, the default value is $V_{MeAc} = 11\,\mathrm{cm^3}$.
- The approximate reaction times, when samples should be taken from the reaction mixture. As the default schedule, take samples after 2, 4, 6, 9, 12, 15, 20, 25, 30, 35, 40, 50, 60, and 80 minutes reaction time. Importantly, always record the exact time of sampling!

As the first step, the thermostat should be turned on and set to the reaction temperature (T). Until it heats up, prepare the acid and alkaline stock solutions:

- 100 $\mathrm{cm^3}$ C_{HCl} hydrochloric acid solution (from the dilution of a concentrated acid solution)
- 1000 $\mathrm{cm^3}$ ($C_B = 0.2\,\mathrm{M}$) NaOH solution (using solid NaOH) for the titration.

Using graduated cylinders, measure 75 $\mathrm{cm^3}$ C_{HCl} stock solution and $(200 - 75 - V_{MeAc})$ $\mathrm{cm^3}$ ion-exchanged water in a pure, dry, 250 $\mathrm{cm^3}$ Erlenmeyer-flask and close it with a Taper stopper. Measure the given volume of methyl acetate in another closed Erlenmeyer-flask (or in a small graduated cylinder), and put both of these in the thermostat (using burette stands and clamps) for at least 30 minutes. Shake the liquids periodically to speed up the temperature equilibration.

The samples taken during the reaction should be immediately added to previously prepared freezing solutions (each sample is added to a new freezing solution!). The freezing solution contains precisely 25.00 $\mathrm{cm^3}$ NaOH titration solution, and roughly 25 $\mathrm{cm^3}$ water, dosed with a graduated cylinder, poured in a 250 $\mathrm{cm^3}$-es Erlenmeyer-flask. These freezing solutions are placed in a $\sim 0\,^\circ\mathrm{C}$ ice bath. [1]

Adding the samples to the freezing solution decreases the reaction rate in two different ways: *(1)* the temperature of the sample decreases by 30 – 40 °C, and *(2)* large portion of the strong acid (which is a catalyst of the reaction) is neutralized in the sample.

The reaction can be started when the freezing solutions have been prepared and the solutions in the thermostat have reached the desired temperature (ca. 30 minutes). The reaction is initiated by mixing the given volume of methyl acetate with the acid-water mixture in the 250 $\mathrm{cm^3}$ Erlenmeyer-flask, which must be closed and put back in the thermostat (keep it there until the reaction is studied!!). The stopper should be started at the exact moment of mixing the two liquids. *Don't forget to properly homogenize the reaction mixture!*

5 $\mathrm{cm^3}$ liquid aliquots should be taken at the marked reaction times using a medical syringe and needle (see Notes), added to a freezing solution (a new freezing solution should be used for each sample!), and

[1] This 25.00 $\mathrm{cm^3}$ should be very precise, as it directly affects the result of the titration. Note, that using a burette, some portion of the solution gets stuck on the inner wall for some time. This time might even be 2-3 minutes, which must be waited before reading/setting the exact volumes.

Table 1: Experimental results and values calculated thereof.

T= ..... K, C_{HCl}= ..... M, V_{MeAc}= .....cm^3, V_∞= .....cm^3

Exact sampling time	t/s	V_t/cm^3	$\frac{V_\infty - V_t}{cm^3}$	$\ln\left(\frac{V_\infty - V_t}{cm^3}\right)$

titrated with the NaOH solution using phenolphthalein indicator, as soon as possible. Importantly, the exact time of the sampling should be used for the data evaluation. It is not a problem if this differs from the planned sampling time (note the equations above!). As the sampling time, if possible, record the moment when half of the sample is added to the freezing solution.[2] When determining the titrant volume, also consider the 25.00 cm^3 NaOH solution in the freezing solution! When a sample was titrated, the Erlenmeyer-flask should be cleaned, and a new freezing solution should be prepared (if still needed).

For data evaluation according to equation (6) V_∞ must also be measured. For this, in the first 10 – 15 minutes of the reaction 35 – 40 cm^3 of the reaction mixture is taken and poured in a separate, closed 50 cm^3 Erlenmeyer-flask (Hint: this could be used to thermostate the methyl acetate prior the reaction. After mixing the methyl acetate in the reaction vessel to start the decomposition reaction, some portion of the reaction mixture could be poured back into this smaller Erlenmeyer flask. Repeating this 2-3 times, the total amount of methyl acetate is transferred to the reaction mixture, which is also properly mixed. At the end of this operation, 35 – 40 cm^3 of the reaction mixture could be left in the 50 cm^3 Erlenmeyer-flask for the determination of V_∞). This solution portion should be kept in 70 – 80 °C hot water bath during the the whole time of the reaction. The reaction rate is significantly increased at this temperature, hence all the methyl acetate decompose during this time. 10 minutes before the total reaction time (at ca. 2 hours), place this 50 cm^3 Erlenmeyer-flask in the thermostat to reach the original reaction temperature. Subsequently, take at least two samples from it, add them to separate freezing solutions and titrate them the same way as the other samples. The average of the titrant volumes determined for these samples is V_∞.

Remarks:

- Graduated cylinders are used to measure volumes during this laboratory practice. This would suggest that precision is not important, *but it is not the case!* The sampling and the titration should be performed with analytic precision to get an accurate result for k_{1s}. The reason for using graduated cylinders in some cases is that small variations in the initial concentrations don't affect the results significantly, as shown during the derivation of equation (6). V_t and V_∞ should however be determined precisely!
- The two students should work together in a quick and organized way, which is only possible if they clarify the schedule of the experiments and the responsibilities.

4 Data evaluation

1. Summarize the experimental conditions, the measured data and the calculated values in Table 1.
2. Plot the experimental data according to equation (6) and fit a linear on the data points. Determine k_{1s} and its standard deviation (see Appendix; Excel LINEST function, Origin, QtiPlot, etc.). Neglect the the data points which are clearly not following the trend (if any. Note: these should also be shown in the figure, and explanation on their exclusion should be given in the report). If the measured data systematically deviate from the linear relationship, the points measured at the end of the reaction should be omitted since the calculation of the logarithm of $(V_\infty - V_t)$ magnifies the effect of the experimental errors in this range.

[2] Practice the reproducible sampling with pure water before starting the reaction.

3. Calculate C_A from C_{HCl}. Calculate k_{2s} and its standard deviation at the temperature of the measurement using k_{1s} and C_A (see Appendix: Standard deviation propagation).
4. The activation energy of the reaction should be calculated from equation (8): E_a= ..... kJ/mol. Evaluate and discuss the results in light of the literature data.

Note:

Using a syringe for sampling is significantly faster compared to using a pipette. However, the volume of the sample is typically not exactly 5.00 cm^3 (the difference could be as high as 10 %). Important to note, however, that the sample volume can be very reproducible (within 1 %). The exact volume of the samples only affect the intercept of the fitted linear, but not its slope, which is used in the data evaluation.

Questions

1. What is the reaction between methyl acetate and water?
2. What is a pseudo first order reaction?
3. Under what experimental conditions could the decomposition of methyl acetate be considered a pseudo first order reaction?
4. What is the role of HCl in the reaction?
5. How can we calculate the methyl acetate concentration at a given time (t) from the measured acetic acid concentration?
6. What is the relation between the titrant volume, the sample volume and the concentrations?
7. How is the reaction frozen in the taken samples?
8. How can we calculate the pseudo first order rate coefficient from the results of the titrations?
9. How can we prepare a sample to determine the total methyl acetate concentration in the reaction mixture?
10. Give the integrated expression (with concentrations) for the calculation of a first order rate coefficient!
11. Give the Arrhenius equation! What parameters can be determined from it?
12. How would you prepare a $100\,\mathrm{cm}^3$ 3.5 M HCl solution from a concentrated stock solution? How large volume (in cm^3) should be measured from a 37 wt, $1.185\,\mathrm{g/cm}^3$ density solution? $\mathrm{A_r(H)} = 1.01$ and $\mathrm{A_r(Cl)} = 35.45$.
13. In a first order reaction, the rate coefficient at 25 °C is $0.12\,\mathrm{s}^{-1}$, while at 40 °C it is $0.39\,\mathrm{s}^{-1}$. Calculate the activation energy of the reaction!
14. In a first order reaction, the concentration of the reactant decays to its half in 10 minutes. Calculate the rate coefficient of the reaction!