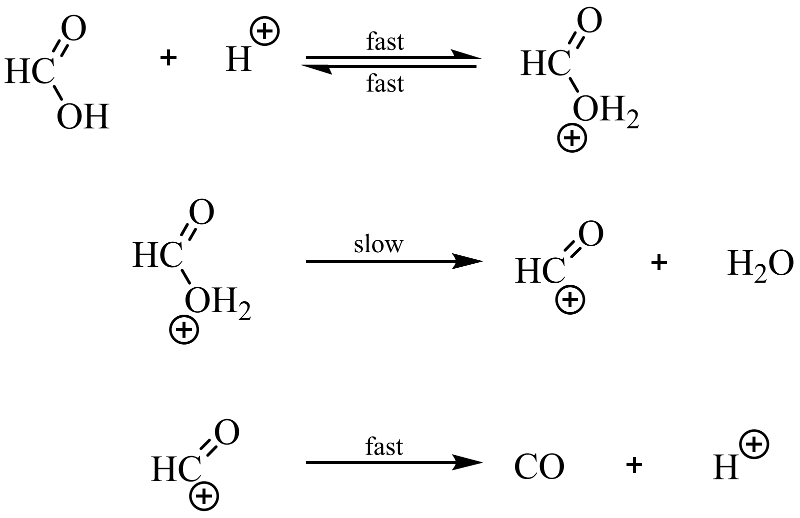
A 35 Decomposition of Formic Acid

Task:

Determine the rate coefficient of the decomposition of formic acid in concentrated sulphuric acid at 30 °C and 40 °C, as well as the pre-exponential factor and the activation energy of the Arrhenius equation.

Basics:

The decomposition of formic acid in sulphuric acid proceeds according to the following mechanism:



Under the experimental conditions, the decomposition proceeds completely and follows a rate law of the first order.

In a first order reaction

$$A \overset{k}{\rightarrow} B$$

the differential rate law for the progress of the concentration of A is:

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k[\mathrm{A}] \,. \tag{1}$$

Solving the differential equation with the initial conditions $[\mathrm{A}]_{t=0} = [\mathrm{A}]_0$ gives for [A]:

$$[\mathrm{A}] = [\mathrm{A}]_0 \cdot e^{-kt}. \tag{2}$$

In order to determine the rate coefficient *k* with graphic application, equation (2) is converted to:

$$\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]}\right) = kt. \tag{3}$$

Since, in the experiment, the reaction progress is observed by a gasometric measurement of the resulting CO, additional considerations are necessary.

Assuming ideal gas behavior at a constant temperature and pressure, the amount of generated CO at time *t* proportional to the volume increase in the gas burette is

$$n_{\mathrm{CO},t} \propto V_t - V_0 \tag{4}$$

where V_0 is the volume at the beginning of the reaction.

The concentration of the formic acid at the beginning of the reaction is proportional to the amount of CO after complete conversion:

$$[\mathrm{A}]_0 \propto n_{\mathrm{CO},\infty} \propto V_\infty - V_0 \, . \tag{5}$$

For the concentration of formic acid [A] at time *t*:

$$[\mathrm{A}] \propto n_{\mathrm{CO},\infty} - n_{\mathrm{CO},t} \propto V_\infty - V_t \, . \tag{6}$$

Consequently, the equation for the determination of the rate coefficient *k* is:

$$\ln\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right) = kt. \tag{7}$$

In most cases, for the temperature dependency of the rate coefficient in a not too large temperature range, the empirically determined Arrhenius equation is valid:

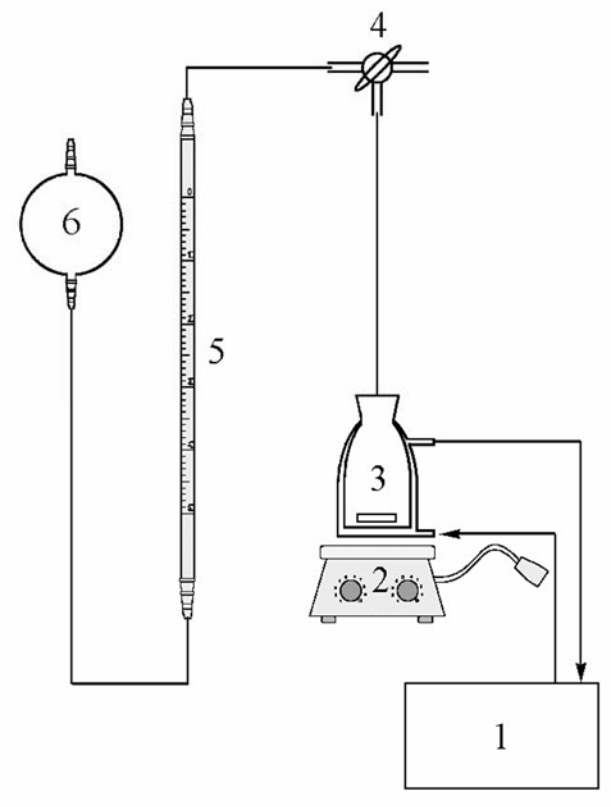
$$k = A \cdot \exp\left(-\frac{E_\mathrm{A}}{RT}\right). \tag{8}$$

where A is the pre-exponential factor, E_A is the activation energy, R is the universal gas constant, and T is the temperature in Kelvin. According to Arrhenius, E_A is defined by the relation

$$\frac{\partial \ln k}{\partial\left(\frac{1}{T}\right)} = -\frac{E_\mathrm{A}}{R}. \tag{9}$$

Experimental Procedure:

Attention! Caution is advised when handling concentrated acids! Wear gloves and protective goggles! Pay attention that the sealing liquid (water) of the burette is not pressed into the reaction container! (Why?)



1. Recirculation thermostat
2. Magnetic stirrer
3. Double-walled beaker
4. Three-way valve
5. Gas burette
6. Levelling vessel

Figure 1: Experimental Setup

At the beginning of the experiment, there are ca. 20 ml of concentrated sulphuric acid in the double-walled beaker. While stirring, the acid is heated to the desired reaction temperature.

Once the temperature in the recirculation thermostat is reached, stir for another 15 min. The three-way valve is open on all sides (position: ┬). Verify, with slow up and down movements of the levelling vessel, if the pressure equalisation in the gas burette is functioning, i.e. if the level of the liquid column in the gas burette equals that in the levelling vessel. This is done for the connection to the reaction container (position of the three-way valve: ┤) as well as to the environment (position of the three-way valve: ┴, the outflow must be removed from the reaction container). If necessary, remove the plug from the three-way valve and remove the sealing grease from the openings. Coat the plug with silicone grease before reinstalling, and then repeat the above procedure.

The liquid column in the burette should be a little over the zero point. The ground-glass joint between the reaction container and the outflow must be sealed with sulphuric acid. To do this, apply as much sulphuric acid to the joint of the outflow so that it turns clear when the reaction container is closed (**gloves, protective goggles!**). Two drops of concentrated formic acid are added to the sulphuric acid (**don't let the formic acid run down the side of the container**) and, as soon as the formation of air bubbles in the reaction solution is observed, the double-walled beaker is connected to the outflow. Close the three-way valve (┤) and start the timed measurement as soon as the zero point in the gas burette is reached ($V_0 = 0$ ml). To record a measurement, the levelling vessel must be held in such a way that the liquid level in the glass sphere stands at the same level as that in the burette (why?). At the beginning, take a measurement every 2 minutes. After approx. 15 minutes, take a measurement every 5 minutes. The value for V_∞ is achieved when there is no change in the liquid level in the burette over a 15-minute period.

At the end of the experiment, open the three-way valve (┬), clean the sulphuric acid from the ground-glass joints, and return the levelling vessel to its original position (water level just over the zero point of the burette).

Data Analysis:

1. Plot $\ln\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$ against *t* and determine the value of *k* in using linear regression. Account for the errors in V_∞, V_0, and V_t on $\ln\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$ in the form of error bars on the graph.
2. From the values of *k* at 303 K and 313 K, determine the pre-factor *A*, and the activation energy E_A (without graphic analysis!). Calculate the maximum error estimation for E_A and *A*. Account for all error quantities (estimate ΔT in each case reasonably).

Discuss the results.

What you should know:

- Reaction order and molecularity of a reaction
- Differential rate laws of the 0, first, and second order
- Parallel, consecutive, and reversible reactions
- Temperature and pressure dependency of rate coefficients
- Basic methods of calculating rate coefficients (Collision Theory, Transition State Theory)

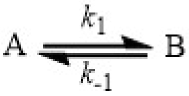
Extra Questions:

1. Show that, for a mechanism of the type:

$$\mathrm{X + Y} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Z} \xrightarrow{k_2} \mathrm{P}$$

a rate law of the second order for the formation of P can be derived when $k_{-1} >> k_2$. Why is there a rate law of the first order for the decomposition of formic acid (X) in concentrated sulphuric acid ($H^+ = Y$)?

2. Observe the homogenous reversible reaction of the first order



$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

with the initial conditions $[A]_0 = [A]_{t=0}$, $[B]_0 = 0$. Why can this reaction not completely, i.e to 100%, yield B? How high must $\Delta_R G^0$ be so that the end conversion of the reaction will be
   a. 50 %
   b. 99 %
   c. 99.999999 % ?

3. Estimate, if the MAC value (maximum allowable concentration) for carbon monoxide is exceeded while conducting the experiment (MAC(CO) = 30 ppm; ppm = parts per million. Therefore, the MAC value of CO is 30 molecules of CO to 10^6 molecules). Formic acid has a density of ρ=1.22 g/cm^3 at 293 K, the laboratory has a volume of 100 m^3.