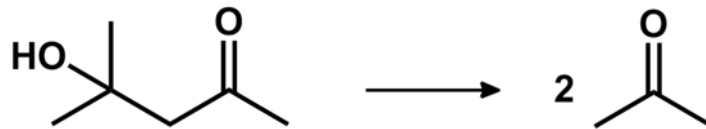# A 31 Decomposition of Diacetone Alcohol

Task:

Determine the reaction rate coefficient for the decomposition of diacetone alcohol at 293 and 303 K.

Basics:

Diacetone alcohol (ρ (20 °C) = 0,931 g/cm³) decomposes in an alkaline solution under volume expansion in Acetone (ρ (20 °C) = 0,786 g/cm³)

In a diluted solution, the decomposition can be determined as complete. At a constant OH^- concentration, the differential change of the concentration c_A of the precursor is

$$\frac{dc_A}{dt} = -k \cdot c_A \tag{1}$$

Integration gives:

$$c_A = c^O_A \cdot \exp(-k \cdot t) \tag{2}$$

Or:

$$\ln(c_A / c^O_A) = -k \cdot t. \tag{3}$$

c^O_A is the initial concentration of the diacetone alcohol

k is the rate coefficient of the reaction.

The temperature dependency of k in a not too large temperature range can be described with the Arrhenius equation

$$k = A \cdot \exp\left(-\frac{E_A}{RT}\right) \qquad (4)$$

where E_A is the activation energy, A the pre-factor and R the molar gas constant ($R = 8.314$ J K^{-1} mol^{-1}). From the Arrhenius equation, the definition of the activation energy is determined as:

$$E_A = -R\frac{\partial \ln k}{\partial \frac{1}{T}} \qquad (5)$$

By measuring k at various temperatures, E_A and A can be determined. Consider the practicable application of a graphic determination of E_A and A.

The following preliminary considerations of the experimental procedure are made:

The volume change in the dilatometer runs proportionally to $c_A(t)$. If the difference of the correspondent readings on the dilatometer (height change of the liquid column) is labelled h, then:

$$c^O_A \sim h_\infty - h_0 \qquad \text{and} \qquad c_A(t) \sim h_\infty - h.$$

Where:

$$h_\infty = h\,(t = \infty)$$

$$h_0 = h\,(t = 0)$$

$$h = h\,(t).$$

Applied to equation (3) gives:

$$\ln\frac{h_\infty - h}{h_\infty - h_0} = -kt \qquad (6)$$

$$\ln(h_\infty - h) = -kt + \ln(h_\infty - h_0) \tag{7}$$

To determine h_∞, the value at the end of the reaction, an interval of time larger than $1/k$ must be used. h_∞ can be eliminated from equation (7). For this, $2n$ measurements in the following pattern must be conducted:

$h_1, h_2, \ldots, h_n$ at the times $t_1, t_2, \ldots, t_n$

$h'_1, h'_2, \ldots, h'_n$ at the times $t_1 + \tau, t_2 + \tau, \ldots, t_n + \tau$

In the experiment, the constant time difference τ is approximately $2 \ln(2/k)$.

Considering equation (6). With

$$(h_\infty - h)/(h_\infty - h_0) = \exp(-kt) \tag{8}$$

we obtain:

$$h = h_\infty - (h_\infty - h_0) \cdot \exp(-kt). \tag{9}$$

For the values at the times t_i and $t_i + \tau$ we obtain:

$$h_i = h_\infty - (h_\infty - h_0) \cdot \exp(-kt_i) \tag{10a}$$

$$h'_i = h_\infty - (h_\infty - h_0) \cdot \exp(-kt_i) \cdot \exp(-k\tau). \tag{10b}$$
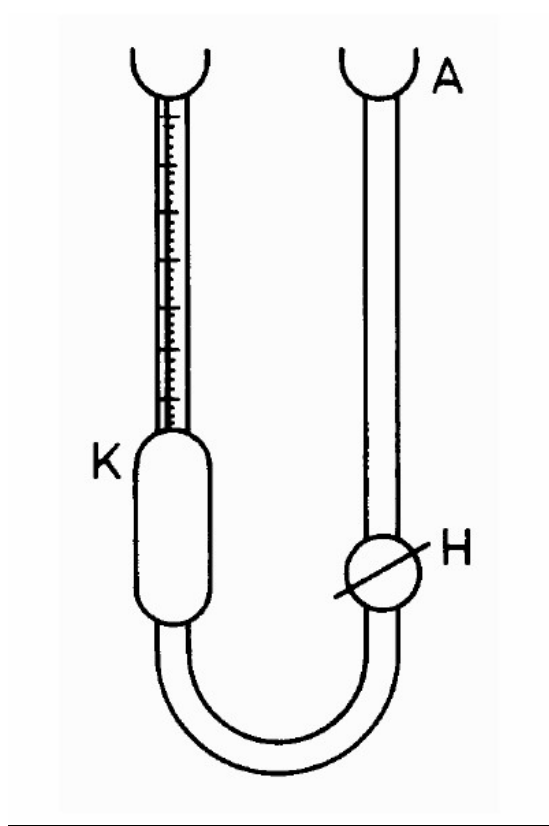
The difference of the equations (10a) – (10b) gives:

$$h'_i - h_i = (h_\infty - h_0) \cdot \exp(-kt_i) \cdot [1 - \exp(-k\tau)] \tag{11}$$

and finally:

$$\ln(h_i' - h_i) = -kt_i + \ln((h_\infty - h_0) \cdot [1 - \exp(-k\tau)]). \qquad (12)$$

To determine k, $\ln(h_i' - h_i)$ is plotted against t_i. The result is a straight line with a gradient of $-k$.

Experimental Procedure:

Before every experiment, the dilatometer (diameter of the capillaries ca. 2 mm, volume of the container ca. 52 cm^3) must be cleaned with distilled water and acetone and dried with the aspirator pump. The tap H is made of Teflon and must not be greased. Clean and dry two Erlenmeyer flasks. In Flask I pipette 10 cm^3 of diacetone alcohol and 40 cm^3 of distilled water, in Flask II pipette 10 cm^3 0,5 n NaOH and 40 cm^3 of distilled water. For thermostatic control, place the dilatometer and the Erlenmeyer flasks into the thermostats (frequently shake the Erlenmeyer flasks lightly). After ca. 15 minutes, mix the contents of Flasks I and II together (pour the contents of Flask II into Flask I then, to flush the mixture, pour the entire mixture back into Flask II). Remove the dilatometer from the thermostat and slowly pour the reaction mixture in through the opening A until the meniscus reaches the capillary at point K (a moistening of the capillary walls due to liquid which has risen too high will falsify results). In the process, the dilatometer is tilted and the tap H is open. Close the tap H, and submerge

the dilatometer in the thermostat up to the point K. There must be no bubbles under the tap. Start the stopwatch, then note the values h_i and h'_i for the following times respectively.

Work under the following conditions:

1st Experiment: $T = 293$ K, $\tau = 40$ min

  h at $t = 4, 8, 12......40$ min

  h' at $t + \tau = 44, 48, 52......80$ min

2nd Experiment: $T = 303$ K, $\tau = 20$ min

  h at $t = 2, 4, 6......20$ min

  h' at $t + \tau = 22, 24, 26......40$ min

Data Analysis:

1. Plot $\ln(h'-h)$ against t and determine the value of the reaction rate coefficient k in s^{-1}. Estimate the error in h_i and h_i' and determine the margin of error for $\ln(h_i'-h_i)$. From this, use graphical evaluation to determine the error in k.
2. From the values of the reaction rate coefficients at 293 K and 303 K, determine the activation energy E_A in kJ/mol and the pre-factor A in s^{-1}. Calculate the maximum error estimation for E_A and A.

What you should know:

- Rate laws of 0, 1st, and 2nd order reactions
- Half-life period
- Simple consecutive and parallel reactions
- The Arrhenius Model of the temperature dependence of reaction rate coefficients
- Basics of the Collision Theory and the Transition State Theory

Extra Questions:

1. Differentiate between the terms "Reaction Order" and "Molecularity"
2. Discuss the Chapman-mechanism (see textbooks). Why is it important?