BASICS OF REACTION KINETICS

Objective

To determine the order of the rate law and rate coefficient for an iodine clock reaction using the method of initial rates and to determine the energy of activation of a reaction

Theoretical background

The general form of a chemical reaction can be given as

$$\sum_{i=1}^{k} \nu_i A_i = 0 \quad , \tag{1}$$

where A_i is the i-th species of the reaction and ν_i is its stoichiometric coefficient. The latter is an integer and negative for reactants, while positive for products. The rate of the reaction (r) — defined as

$$r = \frac{1}{\nu_i} \frac{d[A_i]}{dt} \quad , \tag{2}$$

where $d[A_i]/dt$ is the change of the concentration of the i-th species with respect to time — is always positive.

It was found experimentally that the reaction rate is proportional to the certain power of the concentration of the species involved in the reaction. The empirical rate law in gneral given as

$$r = k \prod_{j=1}^{m} [A_j]^{\beta_j} \quad , \tag{3}$$

where $[A_j]$ is the concentration of the j-th species, β_j the order of the j-th species, and k is the rate coefficient. The sum of the order of the species ($\sum_{j=1}^{m} \beta_j$) is the order of the reaction. The rate coefficient is constant at given experimental conditions, i.e., same temperature, ionic strength etc, and its unit depends on the order of the reaction. If the reaction is first-order, the unit of k is s^{-1}; if the reaction is second order, then the unit of k is $dm^3 mol^{-1} s^{-1}$.

The temperature dependence of the rate coefficients is described by the so-called Arrhenius equation

$$k = A e^{-\frac{E_A}{RT}}, \tag{4}$$

where E_A is the activation energy, A is the preexponential factor, R is the gas constant, and T is the temperature.

Rate laws must be determined experimentally as one cannot predict them from the balanced overall equation in general, because the exponents of the concentrations are not necessarily equal to the stoichiometric coefficients.

OXIDATION OF POTASSIUM IODIDE WITH POTASSIUM PERSULFATE (10A)

Theoretical background

The orders of the iodide and persulfate will be determined in the reaction of

$$S_2O_8^{2-} + 2I^- = 2SO_4^{2-} + I_2 \tag{5}$$

The evolving iodine with iodide ions will form triiodide ions via a fast equilibrium as

$$I^- + I_2 \rightleftharpoons I_3^- \tag{6}$$

which yields, in the presence of starch, intensive blue color because of the formation of starch-triiodide complex.

The reaction proceeds in two steps: in the first step, a complex anion is formed from the peroxodisulfate- and the iodide ion, which, upon collision with another iodide ion, is rapidly converted to products.

$$S_2O_8^{2-} + I^- \rightarrow (S_2O_8I)^{3-} \tag{7}$$

$$(S_2O_8I)^{3-} + I^- \rightarrow 2SO_4^{2-} + I_2 \tag{8}$$

The iodide-peroxodisulphate reaction in itself is not a clock reaction, as iodine is continuously produced during the reaction, indicated by the gradual darkening of the solution. The system can become a clock reaction by adding a small amount of thiosulphate ion to the system, so that the iodine produced in the reaction of

$$I_2 + 2S_2O_3^{2-} = S_4O_6^{2-} + 2I^- \tag{9}$$

is instantaneously reacts with the thiosulphate ion, preventing the blue color from appearing. After the thiosulphate ion is consumed, the blue color appears immediately. If exactly the same experimental conditions are used, the color of the solution - within experimental error - appears at the same time, so even a clock could be calibrated to the process, which is why it is called a clock reaction.

The rate of the reaction is written in terms of the consumption of the peroxodisulfate ion as

$$r = \frac{1}{\nu_{S_2O_8^{2-}}} \frac{d[S_2O_8^{2-}]}{dt} \approx -\frac{\Delta[S_2O_8^{2-}]}{\Delta t} = k[S_2O_8^{2-}]^{\beta_{S_2O_8^{2-}}}[I^-]^{\beta_{I^-}} \quad . \tag{10}$$

If we measure the discoloration time (Δt), and we take into account that during that period the decrease of the persulfate concentration can be calculated from the initial thiosulphate concentration as

$$-\Delta[S_2O_8^{2-}] = [S_2O_3^{2-}]_0/2 \tag{11}$$

then the initial reaction rate can be calculated as

$$r_0 = \frac{[S_2O_3^{2-}]_0}{2\Delta t} \tag{12}$$

which is determined from the stoichiometry of the overall reaction.

We can take the natural logarithm of the empirical rate law given in Eqn. (10):

$$\ln r = \ln k + \beta_{S_2O_8^{2-}} \ln[S_2O_8^{2-}] + \beta_{I^-} \ln[I^-] \tag{13}$$

If we also consider that the thiosulphate concentration added to the reaction mixture is small compared to the reactants, then it means that the conversion is small when the thiosulphate is consumed and the solution turns blue. The measured reaction rate is thus a good approximation of the initial reaction rate, i.e.,

$$\ln r_0 = \lg k + \beta_{S_2O_8^{2-}} \ln[S_2O_8^{2-}]_0 + \beta_{I^-} \ln[I^-]_0 \tag{14}$$

2

where r_0 is the initial reaction rate, $[X]_0$ is the initial concentration of the reactant considered. If the iodide ion concentration is held constant and the persulfate ion concentration is varied systematically, then the order of peroxodisulphate can be determined from the following equation

$$\ln r_0 = \ln k' + \beta_{S_2O_8^{2-}} \ln[S_2O_8^{2-}]_0 \quad , \tag{15}$$

when $\ln r_0$ is plotted as a function of $\ln[S_2O_8^{2-}]_0$. The slope of the fitted straight line gives the order of persulfate, while the intercept is $\ln k'$, where

$$\ln k' = \ln k + \beta_{I^-} \ln[I^-]_0 \quad . \tag{16}$$

Using the same considerations, the order of iodide ion can be determined as

$$\ln r_0 = \ln k'' + \beta_{I^-} \ln[I^-]_0 \tag{17}$$

where the iodide concentration is varied while keeping the persulfate concentration constant and we plot $\ln r_0$ as a function of $\ln[I^-]_0$. The slope of the fitted straight line gives the order of the iodide ions and the intercept yields $\ln k''$m where

$$\ln k'' = \ln k + \beta_{S_2O_8^{2-}} \ln[S_2O_8^{2-}]_0 \quad . \tag{18}$$

Once the orders of the iodide and persulfate ions have been determined, and the initial concentrations are known, the rate coefficient ($\ln k$) itself can be easily calculated from the intercepts.

Materials

beaker of 100 cm³ volume (9 pieces)   *buret (5 pieces)*

beaker of 50 cm³ volume (14 pieces)   *pipet of 2 cm³ volume or automatic pipet*

stop watch   *wash bottle*

Experimental procedure

- You will work in pairs.
- You have to perform all measurements, therefore prepare all the 9 solutions from Table I unless instructed otherwise.
- Number or label two beakers for each measurements.
- One of you should measure out the volumes of KI, $Na_2S_2O_3$ and KNO_3 solutions with a buret or an automatic pipet into the larger labelled beaker. The other should measure out the volumes of starch, K_2SO_4 and $K_2S_2O_8$ solutions with a buret or an automatic pipet into the smaller labelled beaker.
- Test the stopwatch usage.
- Place white tiles next to the beakers.
- One of you pour the smaller beaker of sample V into the larger one as quick as possible while the other starts the stopwatch and records the start time as time of mixing in the record sheet. Pour the solution back and forth to mix thoroughly.
- Place the larger beaker with the solution on the white tile.
- Record the time of discoloration when the solution turns blue. Watch constantly as the blue color will appear suddenly.
- Start the reaction similarly for all the other samples but do not forget to record the time of mixing and the time of discoloration for each sample.
- Once finished all observations, wash all the material and return them to the lab technician.
- Continue with the calculation.

1. táblázat. Solution composition

No.	Volume of reagents (cm^3)					
	KI	$Na_2S_2O_3$	KNO_3	starch	K_2SO_4	$K_2S_2O_8$
	0.05 M	0.01 M	0.05 M	0.2 %	0.05 M	0.05 M
I	2	2	6	2	0	8
II	3	2	5	2	0	8
III	4	2	4	2	0	8
IV	6	2	2	2	0	8
V	8	2	0	2	0	8
VI	8	2	0	2	6	2
VII	8	2	0	2	5	3
VIII	8	2	0	2	4	4
IX	8	2	0	2	2	6

Calculations

- Calculate $[Na_2S_2O_3]_0$ and record it in the record sheet.

- Calculate the discoloration time (Δt) in seconds and record it in the record sheet. At least one calculation should be shown in detail in the record sheet.

- Calculate the initial rate and its natural logarithm and record them in the record sheet. At least one calculation should be shown in detail in the record sheet.

- Calculate the initial concentrations of KI and $K_2S_2O_8$ in the mixed solution and record them in the second table of the record sheet. At least one calculation should be shown in detail in the record sheet.

- To determine the order of KI, use the date corresponding to samples I–V as in those cases $[K_2S_2O_8]_0$ is constant. Plot $\ln r_0$ as a function of $\ln[KI]_0$. Fit a straight line on the points and determine its slope and intercept with their standard deviations. Determine from the slope the order of KI.

- To determine the order of $[K_2S_2O_8]_0$, use the date corresponding to samples V–IX as in those cases $[KI]_0$ is constant. Plot $\ln r_0$ as a function of $\ln[K_2S_2O_8]_0$. Fit a straight line on the points and determine its slope and intercept with their standard deviations. Determine from the slope the order of $K_2S_2O_8$.

- If both the order of KI and that of $K_2S_2O_8$ is determined, calculate the rate coefficient from the intercept.

TEMPERATURE-DEPENDENT DECOMPOSITION OF THIOSULFURIC ACID (10B)

Theoretical background

The activation energy of the decomposition of the thiosulfuric acid will be determined. The reaction can be described by the following equation:

$$H_2S_2O_3 \longrightarrow SO_2 + H_2O + S \tag{19}$$

Colloidal sulfur is produced in the reaction which even in small concentration will turn the initially transparent solution opalescent.

Combination of the empirical rate law in Eqn. (3) and the Arrhenius equation in Eqn. (4) leads to

$$r = A e^{-\frac{E_A}{RT}} \prod_{j=l}^{m} [A_j]^{\beta_j}. \tag{20}$$

The reaction rate in Eqn. (2) can be approximated as

$$r \approx \frac{1}{\nu_i} \frac{\Delta[A_i]}{\Delta t}, \tag{21}$$

the substitution of which into the reaction rate in Eqn. (20) and taking the natural logarithm leads to

$$\ln \frac{1}{\Delta t} = C - \frac{E_A}{RT} = C - \frac{E_A}{R} T^{-1}, \tag{22}$$

where

$$C = \ln A + \sum_{j=l}^{m} \beta_j \ln[A_j] - \ln \frac{\Delta[A_i]}{\nu_i} \tag{23}$$

Term C is constant if the concentration of the reactants is constant and at each temperature the reaction is monitored to the same conversion, i.e., to the same opalescence. Therefore, the activation energy (E_A) can be determined based on Eqn. (22) by plotting $\ln(1/\Delta t)$ as a function of the reciprocal of the thermodynamic temperature (T^{-1}) and fitting a straight line onto the points. The activation energy can be determined by multiplying the slope by $-R$, while the intercept gives term C.

Materials

beaker of 100 cm^3 volume (5 pieces)

beaker of 600 cm^3 volume

pipet of 10 cm^3 volume (2 pieces)

test tube (5 pieces)

test-tube rack

stop watch

thermometer

wash bottle

Experimental procedure

- You will work in pairs.

- One of you pipet out into 5 clean and dry test tubes 10–10 cm^3 volume of sodium thiosulfate with 0.02 mol/dm^3 concentration. The other will pipet out into 5 clean and dry test tubes 10–10 cm^3 volume of sulfuric acid with 0.10 mol/dm^3 concentration.

- Fill the small beaker with tap water of room temperature. It will serve as a waterbath.

- Take one test tube from both the sodium thiosulfate and sulfuric acid solution and place them in the waterbath. Make sure that the solutions in the test tube will be covered by the water in the waterbath. Wait for 5-10 minutes until the solutions will get thermostated.

- One of you quickly mixes the two test tubes, while the other starts the stopwatch. Once the solution starts to become opalescent, stop the stopwatch and record the time required for opalescence in the record sheet.

- Repeat the measurements at four more temperatures. The selected temperatures should be 10, 20, 30, 40 and 50 °C with ±2°C unless otherwise instructed. Always record the exact temperature in the record sheet. *Tips: Wash immediately the test tube after each measurements as the cleaning becomes difficult after the colloidal sulfur sticking on the wall of the test tube.*

Calculations

- Convert the reaction time to seconds and record it in the record sheet.

- From the measured temperature calculate the thermodynamic temperature along with its reciprocal and record them in the record sheet.

- Calculate the reciprocal of the reaction time and its natural logarithm and record them in the record sheet.

- Plot $\ln(1/\Delta t)$ as a function of T^{-1}. Fit a straight line on the points. Record the slope and the intercept with their standard deviations. Calculate from the slope the activation energy by multiplying it with $-R$.