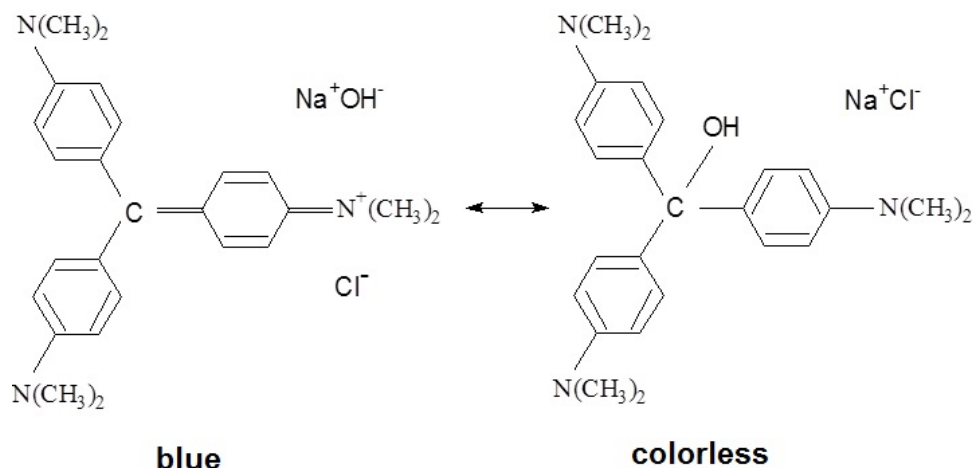# 1. Chemical kinetics

1.a. Photometric study of reaction kinetics

Crystal Violet (Gentian Violet) is an acid-base indicator (transition pH of 0.0 - 2.0), its blue-colored form is converted by hydroxyl anions in a colorless neutral form with a half-life of a few minutes.

blue   colorless

The rate equation is:

$$v = -\frac{d[VIOL]}{dt} = k[OH^-]^r \cdot [VIOL]^p \qquad (1.1.)$$

where k is the rate constant, $[VIOL]$ is the concentration of crystal violet in cationic form, and $[OH^-]$ is the concentration of the hydroxide anoints. p and r are the orders of the reaction with respect to the corresponding reacting ions. In an alkaline environment where $[OH^-]_0 >> [VIOL]_0$ (index 0 indicates the initial concentration), the concentration $[OH^-]$ is nearly unchanged during the reaction and it can be included in the rate constant k'. The rate equation has then the form:

$$-\frac{d[VIOL]}{dt} = k'[VIOL]^p \qquad (1.2.)$$

where

$$k' = k[OH^-]^r \qquad (1.3.)$$

thus the constant k' depends on the concentration $[OH^-]$. Assuming that the order of reaction is $p=1$ resp. $p=2$, we obtain the integral forms of equation (1.2.):

$$[VIOL]_t = [VIOL]_0 \cdot \exp(-k't) \qquad \text{resp.: } [VIOL]_t = \frac{[VIOL]_0}{1 + k' \cdot t \cdot [VIOL]_0} \qquad (1.4.)$$

These equations can be rearranged in linear formulas:

$$\ln[VIOL]_t = \ln[VIOL]_0 - k't \qquad \text{resp.: } 1/[VIOL]_t = 1/[VIOL]_0 + k' \cdot t \qquad (1.5.)$$

The decision whether the partial order p is equal to 1 or 2 can be made by comparing the values of the correlation coefficients of the lines fitted on experimental dependencies $ln[VOIL]_t$ resp. $1/[VOIL]_t$ vs. time t according eqns (1.5.).

The dependence of the velocity constant k on the ionic strenght I is given by the relationship:

$$\log k = lok\, k_0 + 1.02 \cdot z_a \cdot z_b \cdot \sqrt{I} \qquad\qquad (1.6.)$$

where z_a and z_b are the charges of the reacting particles (including their sign) and k_0 is the rate constant of the reaction at ionic strength equal to zero.

? **TASK:** Determine the orders of reaction with respect to crystal violet cation and hydroxide anion. Evaluate the rate constants (k' and k). Verify the charges of the reacting ions and determine the rate constant k_0 from the dependence of the rate constant k on the ionic strength I.

✂ **LABORATORY AIDS AND CHEMICALS:** $0.5 \cdot 10^{-4}$ M crystalline violet solution (CAS No 548-62-9), 0.1 M NaOH, 1 M KNO$_3$, 6 volumetric flasks ($25\ cm^3$), 3 beakers ($50\ cm^3$) 2 scale pipettes ($5\ cm^3$), volume pipette ($10\ cm^3$), spectrophotometer with accessories, stopwatch.

▤ **INSTRUCTIONS:** Work at laboratory temperature, which should not be noticeable changed during the experiment.

Calibration curve of spectrophotometer. Pipette successively *1, 2; 3, 4* and *5 cm^3* of the stock solution of the dye into 6 volumetric flasks (each of *25 cm^3* volume) and fill them with distilled water up to marking. Measure the absorbance of the dye solutions at the absorption maximum wavelength (574 nm). Note the pipette volume *y cm^3* of the dye stock solution, which was applies to prepare a solution exhibiting an absorbance in the range of 0.7-0.9.

1. Monitoring of reaction for different concentrations of hydroxide.

a) Pipette the volume *2y cm^3* of the stock solution of the dye into *25 cm^3* volumetric flask and fill with distilled water up to marking. Prepare volume *25 cm^3* of *8·10^{-3} M NaOH* from the stock solution of the *NaOH* in the second volumetric flask. Mix the contents of the volumetric flasks together in beaker and switch the stopwatches in this moment on.

b) Start absorbance measurement (i.e. decolourisation) of the reaction mixture at *574 nm* in *3 minute* intervals for *30 minutes*.

c) Repeat the measuring by the same way using *25 cm^3* of *1.6·10^2 M NaOH*.

2. Monitoring of reaction for different ionic strenght.

Take *25 cm^3* of the dye solution having the same concentration as for measurement **1a** and mix it with *25 cm^3* solution containing *NaOH* and *KNO$_3$* (to adjust the ionic strength) with following concentrations:

a) *1.6·10^{-2} M* NaOH and *4·10^{-2} M* KNO$_3$.

b) *1.6·10^{-2} M* NaOH and 1.2·10^{-1} M KNO$_3$.

c) *1.6·10^{-2} M* NaOH and *2·10^{-1} M* KNO$_3$.

Monitor the decrease in the absorbance of the reaction mixtures by same way as in the case **1a**.

🖥️ **DATA ANALYSIS:** Make linear regression of the calibration curve. Calculate the experimental sample concentrations using regression parameters.

1. EVALUATION OF REACTION ORDERS

a) Order with respect to dye (p**).** Use the results of the experiments **1a,b**. Create **Common graph 2**: i.e. plot $ln[VIOL]_t$ vs. time t for both concentration of $[OH^-]$. Create **Common graph 3**: i.e. plot $1/[VIOL]_t$ vs. time t for both concentration of $[OH^-]$. Make linear regressions of all plots and calculate the correlation coefficients. The order $p = 1$ is valid if correlation coefficients obtained from linear regression of the plot in Common graph 2 is closer to value 1.000 than the coefficients obtained from regression in Common graph 3. Otherwise $p = 2$ can be more suitable. Calculate the rate constants k' from slopes of regression lines (see linear forms (1.5.)) for both concentrations of hydroxide $[OH^-]$.

b) Order with respect to $[OH^-]$ **(r):** Use two calculated rate constants k' valid for two experimental hydroxide concentrations $[OH^-]$. They give together two equations of type (1.3.) with two unknowns r and k. Find the unknowns and round off the value r to the whole number. The rounded order r should be used for recalculus of rate constant k.

2. Evaluation of influence of ionic strenght

a) Use the results of the experiments **1a,b** and **2a,b,c**. Calculate ionic strength I for all reaction mixtures (use eqn ==6.5==). Create **Common graph 4**: i.e. plot $ln[VIOL]_t$ (or $1/[VIOL]_t$ if $p = 2$) vs. time t for all experiments. Make linear regressions of all experimental dependences and calculate the rate constants k` and k.

b) Create **Graph 5**: i.e. plot $log(k)$ vs. $\sqrt{I}$. Make linear regression of data in Graph 5 and find the parameters of the regression line. Apply eqn (1.6.) and calculate values k_0 and product $z_a \cdot z_b$. Compare the product with value $p \cdot r$.

✎ **REPORT: Calibration table 1:** for all standard solution s: dye concentration and absorbance A_s. **Calibration graf 1:** plot A_s vs. concentration. **Table 2:** for experiment **1a**,**b**: time t, values A_t , $[VIOL]_t$, $ln[VIOL]_t$, $1/[\mathrm{VIOL}]_t$. **Common graph 2 and 3:** see data analysis. **Tabulka 3:** for experiment **2a,b,c**: time t, values A_t , $[VIOL]_t$ and $ln[VIOL]_t$ (or $1/[\mathrm{VIOL}]_t$). **Common graph 4:** see data analysis. **Table 5:** for all experiment: concentrations *[OH]* and *[NO₃ ⁻], I,* $\sqrt{I}$, k', k, *log(k)*. **Graph 5:** dependence $\log k$ on $\sqrt{I}$. **Next:** orders of reaction *p, r*. Calculated value k_0 and product $z_A \cdot z_B$.