



## IONIC STRENGTH INFLUENCE ON THE CHEMICAL REACTION RATE CONSTANT

### INTRODUCTION

Considering the chemical reaction between ions A and B in the solution



When the reaction proceeds by the by-product C and the first stage is a reversible reaction described by equilibrium constant K, the system of the reaction can be described as follows:



(K – equilibrium constant of the first reaction, k' – rate constant of the second step of reaction)

In this type of consecutive reaction, the first step occurs quickly and therefore the slower second step determines the reaction rate.

$$v = \frac{dD}{dt} = k'[C] \quad (3)$$

Where:

v – rate equation

[D] – concentration of species D (usually expressed by moles · dm<sup>-3</sup>)

The equilibrium constant can be described by the equation:

$$K = \frac{a_C}{a_B \cdot a_A} = \frac{f_C}{f_B \cdot f_A} \cdot \frac{[C]}{[A] \cdot [B]} \quad (4)$$

where  $a_i$  - activity,  $f_i$  – activity coefficient

which leads to the equation:

$$v = \frac{dD}{dt} = k' \cdot K \frac{f_A \cdot f_B}{f_C} \cdot [A] \cdot [B] \quad (5)$$

Values of the activity coefficients  $f_i$  can be estimated by the *Debye-Hückel equation*:

$$\log f_i = -A' z_i^2 \sqrt{I} \quad (6)$$

where I is ionic strength:



$$I = \frac{1}{2} \sum c_i z_i^2 \quad (7)$$

$z_i$  - charge of the ion.

Taking into account that:

$$z_C = z_A + z_B \quad (8)$$

activity coefficients described by equations (4) and (5) can be expressed as an equation:

$$\log \frac{f_A \cdot f_B}{f_C} = -A' \sqrt{I} [z_A^2 + z_B^2 - (z_A - z_B)^2] = 2A' \sqrt{I} \cdot z_A \cdot z_B \quad (9)$$

Equation (5) can be rearranged:

$$v = \frac{d[D]}{dt} = k[B] \quad (10)$$

Where:

$$k = k' K \frac{f_A \cdot f_B}{f_C} \cdot [A] \quad (11)$$

Equations (10) and (11) are valid when concentration of species A is much higher than species B, which means that concentration of species A is assumed to be constant throughout the reaction. Moreover, from equation (1) we can consider:

$$v = \frac{d[D]}{dt} = -\frac{d[B]}{dt} \quad \text{and} \quad -\frac{d[B]}{dt} = k[B] \quad (12)$$

Comparison of equation (9) and (11) leads to equation:

$$\log \frac{k}{k' K [A]} = 2A' z_A z_B \sqrt{I} \quad (13)$$

Or simply:

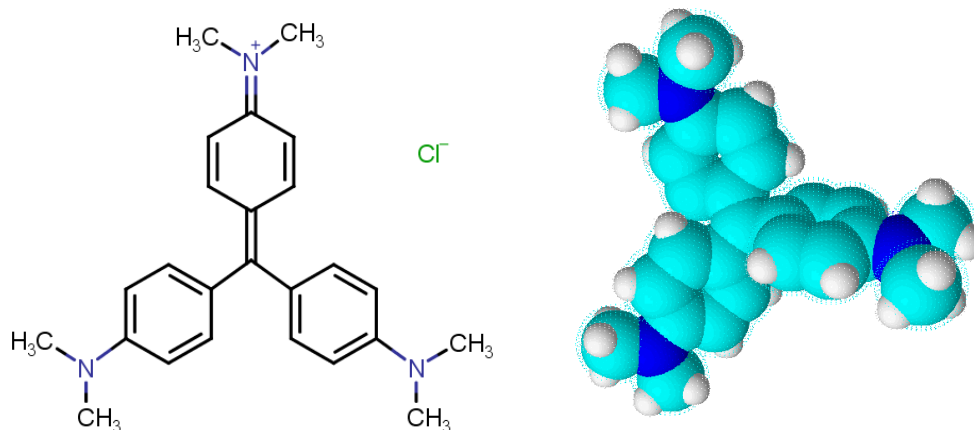
$$\log k = X - Y \sqrt{I} \quad (14)$$

Where:

$$X = \log k' K [A] \quad \text{and} \quad Y = 2A' z_A z_B \quad (15)$$

Equation (14) points at dependence of the rate constants on ionic strength solutions (concentration of the bulk electrolyte).

A reaction of  $OH^-$  ions (reagent A) with crystal violet (CV, or Gentian Violet, or Methyl Violet 10B) is an example of the above type of reaction.



**Figure 1.** One of the resonance structures of the crystal violet (Hexamethylpararosaniline chloride)  
CAS number 548-62-9

The reaction can be observed by the colorimetric method, crystal violet absorbs the light in the visible range. Moreover, the product of the chemical reaction is colorless.

Integrated equation (12):

$$\ln \frac{c}{c_0} = -kt \quad (16)$$

Where:

- $c$  - concentration of the crystal violet in time  $t$
- $c_0$  - starting concentration of the CV (for  $t = 0$ ),
- $t$  - reaction time (in seconds).

The absorbance value of  $A$  is proportional to the concentration  $c$  of CV so that equation (16) can be rearranged:

$$\ln \frac{A}{A_0} = -kt \quad (17)$$

Where

- $A$  - Absorbance of the solution in the time  $t$ ,
- $A_0$  - Absorbance of the solution at the starting moment  $t = 0$  (in this context  $A$  means **absorbance** and **does not mean concentration** of the  $A$  species).

### EXERCISE PURPOSE

The aim of this measurement is to determine the influence of ionic strength on the rate constant of the chemical reaction of the crystal violet with  $OH^-$  ions.

### APPARATUS



- Spectrophotometer SPECOL:
- Glass cuvette 4 pieces,  $l = 1$  cm

## LAB GLASS

- Beaker 100 ml - 2 pcs.
- Volumetric Flask 50 ml - 4 pcs.
- Volumetric pipette 5 ml and 10 ml.
- Wash bottle.

## CHEMICALS

- Potassium nitrate ( $\text{KNO}_3$ ) solution (or other salt, i.e. potassium chloride KCl) -  $1 \text{ mol}\cdot\text{dm}^{-3}$
- Potassium hydroxide KOH (or sodium hydroxide NaOH) -  $0.1 \text{ mol}\cdot\text{dm}^{-3}$
- Crystal violet solution -  $10^{-4} \text{ mol}\cdot\text{dm}^{-3}$

## EXPERIMENT PROCEDURES

1. Prepare the Crystal Violet solution of concentration  $2\cdot 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ . Measure the values of absorbance in the range 450 to 620 nm, every 10 nm, of the above-prepared solution. Plot the diagram (dependence of absorbance on wavenumber) and find out the wave number at maximal values of the absorbance.
2. Prepare the six solutions of concentration mentioned in the table below. Measure absorbance changes in time vs. water as reference.

Solution No.	1	2	3	4	5	6
	Concentration / $\text{mol}\cdot\text{dm}^{-3}$					
Crystal Violet	$2\cdot 10^{-5}$	$2\cdot 10^{-5}$	$2\cdot 10^{-5}$	$2\cdot 10^{-5}$	$2\cdot 10^{-5}$	$2\cdot 10^{-5}$
NaOH	0.01	0.01	0.01	0.01	0.01	0.01
$\text{KNO}_3$ (or KCl)	0	0.01	0.05	0.1	0.2	0.25

Remember that the reaction begins with the addition of the  $\text{OH}^-$  solution. The absorbance should be measured every 5 min period for the next 30 min.

## CALCULATION

1. Plot the diagrams of absorbance changes vs. time of reactions.
2. Calculate the rate constant for particular solutions using equation (17).
3. Draw the figure of the logarithm of the rate constant as a function of the square root of ionic strength.
4. Determine the value of the *Debye-Hückel* constant and compare it to the literature data.



## Template of the table and draft of the study

<p>..... <i>Faculty</i></p> <p>..... <i>Field of study</i> <i>Full-time/ part-time studies</i></p>	<p>..... <i>Name and surname</i></p>	<p>..... <i>Date:</i></p>
<p><i>Group no.:</i> .....</p> <p><i>Team no.:</i> .....</p>	<p>..... <i>Exercise no.:</i></p>	<p>..... <i>Instructor:</i></p>

<p>..... <i>Wydział</i></p> <p>..... <i>Kierunek</i> <i>Studia stacjonarne/niestacjonarne</i></p>	<p>..... <i>Imię i Nazwisko studenta</i></p>	<p>..... <i>Data wykonywania ćwiczenia:</i></p>
<p><i>Nr grupy:</i> .....</p> <p><i>Nr zespołu:</i> .....</p>	<p>..... <i>Nr ćwiczenia:</i></p>	<p>..... <i>Nazwisko Prowadzącego:</i></p>

1. Temat ćwiczenia
2. Cel ćwiczenia:
3. Wstęp teoretyczny:
4. Pomiary:
5. Obliczenia:
6. Wykresy:
7. Wnioski

1. Exercise title:
2. The aim of the exercise:
3. Theoretical introduction:
4. Results:
5. Calculations:
6. Graphs:
7. Conclusions: