

LABORATORY SESSION 3
Kinetic study of the decolorization of phenolphthalein in alkaline solution
Material

1 spectrometer
 2 spectrometer cuvettes
 1 volumetric pipette of 5 mL
 1 volumetric pipette of 10 mL
 1 graduated pipette of 10 mL
 1 volumetric pipette of 20 mL
 1 graduated pipette 20 mL
 2 micropipettes
 1 volumetric flask of 200 mL
 1 volumetric flask of 500 mL
 3 Erlenmeyer flask of 250 mL
 1 burette of 50 mL

3 beakers of 100 mL

1 beaker of 250 mL
 1 glass rod / 1 dropper / 1 weighing bottle
 1 wash-bottle / 1 funnel / 1 propipette

Chemicals

Sodium chloride
 Sodium hydroxide
 0.08% phenolphthalein alcoholic solution
 Potassium hydrogen phthalate

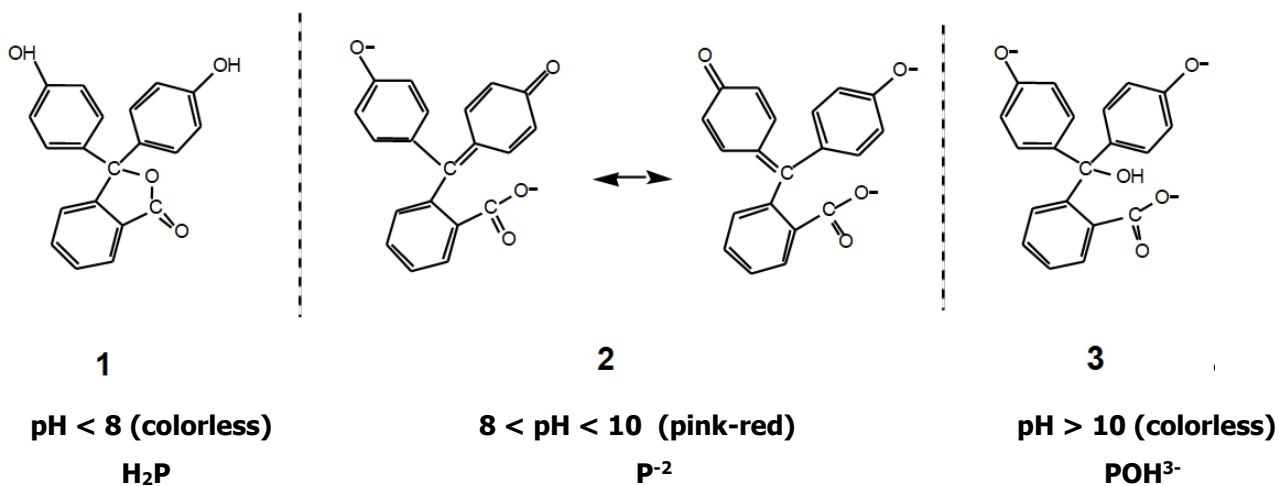
Objectives

1. Determine the rate equation of the phenolphthalein decolorization reaction in alkaline solution by absorption spectroscopy under irreversibility and reversibility conditions.
2. Determine kinetic parameters: partial orders, apparent constants, and absolute velocity constants.
3. Apply the Ostwald isolation method.
4. Analyze the effect of concentration on the reaction rate.
5. Use a spectrophotometer to measure absorbances and relate them to concentration.

Theory

Phenolphthalein is used as an acid-base indicator to determine the endpoint in a volumetric titration, changing from a colorless to a pinkish-red solution. However, if an excess base at the endpoint exists, the pink color of the phenolphthalein disappears over time. This fact is not due to the titration procedure, and it can be used as a good example of a pseudo-first order reaction.

Phenolphthalein is not a simple indicator with a conjugated acid-base pair HIn/In^- , it has complex structures. The structures of the most important forms of phenolphthalein are:



Phenolphthalein is colorless at pH below 8 and it has the structure 1 (H₂P). When the pH is between 8 and 10, the phenolic protons are removed and the lactone ring opens, giving rise to the familiar pink-red shape with the structure 2 (P²⁻). At higher pH, the pink color slowly fades and the structure 3 (POH³⁻) appears. All color changes are reversible; while the conversion of H₂P to P²⁻ is fast and complete, the conversion of P²⁻ to POH³⁻ at higher pH is quite slow, so the reaction rate can be easily measured.

The phenolphthalein decolorization reaction in alkali solution is:



and the rate law has the form:

$$v = k_1[P^{2-}]^n [OH^{-}]^m - k_{-1}[POH^{3-}]^p \quad (2)$$

where the reaction rate is first-order for the phenolphthalein, in the direct and reverse reaction (n=p=1):

$$v = k_1[P^{2-}] [OH^{-}]^m - k_{-1}[POH^{3-}] \quad (3)$$

If the initial mixture of the reaction is a strongly basic solution, the concentration of OH⁻ is much higher than that of phenolphthalein ([OH⁻]/[P²⁻][>]10⁴), and we can consider that the concentration of OH⁻ remains constant throughout the measurements ([OH⁻]₀ = [OH⁻] = cte). Thus, the rate law can be expressed as:

$$v = k_{ap}[P^{2-}] - k_{-1}[POH^{3-}] \quad (4)$$

where k_{ap} is an apparent reaction rate constant:

$$k_{ap} = k_1[OH^{-}]_0^m \quad (5)$$

Since the P²⁻ form has an intense color, the conversion from P²⁻ to POH³⁻ can be followed by absorbance changes of the solution. This magnitude is related to the concentration considering the **Lambert-Beer law**:

$$A = \varepsilon \ell [c] = cte [P^{2-}] \quad (6)$$

where ε is the molar absorption coefficient (it is an intrinsic property of the specie and constant at a given wavelength, λ); ℓ is the pathlength (o internal width of the cuvette) and [c] is the molar concentration of the solution.

The experiment can be performed under two different conditions:

- a) **Irreversible treatment**: in the first stages of the reaction.
- b) **Reversible treatment**: when the reaction reaches the equilibrium.

a) Irreversible treatment

While the concentrations of reagents and products are far from the equilibrium, we can consider the inverse reaction rate is negligible compared to the direct one, so equation (4) remains:

$$v = -\frac{d[P^{2-}]}{dt} = k_{ap}[P^{2-}] \quad (7)$$

which is first order with respect to phenolphthalein. By integrating eq (7) between $t=0$ and $t=t$, and rearranging, we have:

$$\ln[P^{2-}]_t = \ln[P^{2-}]_0 - k_{ap}t \quad (8)$$

and by introducing the Lambert-Beer law (eq (6)), finally, we have::

$$\ln A_t = \ln A_0 - k_{ap}t \quad (9)$$

where A_t is the phenolphthalein absorbance at the time t . Therefore, the graphical representation of $\ln(A_t)$ versus time must give a straight line (if the reaction is pseudo-first order) with a slope equal to $-k_{ap}$, which will allow us to determine the apparent reaction rate constant.

If we have k_{ap} values at different $[OH^-]_0$, we can obtain the partial order with respect to OH^- (m) and the absolute rate constant (k_1) by linearization of eq (5) by taking the logarithms on both sides:

$$\ln k_{ap} = \ln k_1 + m \ln [OH^-]_0 \quad (10)$$

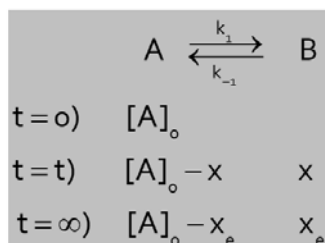
Another way to determine the constant k_1 is to obtain it for each experiment and average it, according to:

$$k_{1,i(\text{irrev})} = \frac{k_{ap,i}}{[OH^-]_0} \quad (11)$$

assuming $m=1$.

b) Reversible treatment:

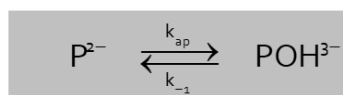
When the reaction is close to equilibrium, the reverse reaction cannot be underestimated. Thus, we will now propose a simple first-order reversible reaction, with a single reagent of the type:



where $[A]_0$ and x_e are known. Therefore, at any instant and at equilibrium, the reagent concentrations are, respectively: $[A]_t = [A]_0 - x$ and $[A]_e = [A]_0 - x_e$. The corresponding integrated equation is:

$$\ln \frac{x_e}{x_e - x} = \ln \frac{[A]_0 - [A]_e}{[A]_t - [A]_e} = (k_1 + k_{-1})t \quad (12)$$

In our case, the first-order reversible reaction with respect to phenolphthalein is:



The reaction rate will be given by eq (4), and the integrated rate equation (see eq (12)) will be:

$$\ln \frac{[P^{2-}]_o - [P^{2-}]_e}{[P^{2-}]_t - [P^{2-}]_e} = (k_{ap} + k_{-1})t \quad (13a)$$

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$$k_{-1} = k_{ap} \frac{[P^{2-}]_e}{[P^{2-}]_o - [P^{2-}]_e} \quad (13b)$$

and by using the Lambert-Beer law, eq (13a) is:

$$\ln(A_t - A_e) = \ln(A_o - A_e) - (k_{ap} + k_{-1})t \quad (14a)$$

Or by substitution of eq (13b) into eq (14a), we finally have:

$$\ln(A_t - A_e) = \ln(A_o - A_e) - k_{ap} \left(\frac{A_o}{A_o - A_e} \right) t \quad (14b)$$

on A_e is the absorbance at an infinite time where the reaction reaches the equilibrium. Since the value of A_e is known, $\ln(A_t - A_e)$ can be plotted against time to obtain k_{ap} and k_{-1} from the linear fitting, since, if we compare equations (14a) and (14b), we arrive at:

$$k_{-1} = k_{ap} \left(\frac{A_e}{A_o - A_e} \right) \quad (15)$$

Finally, the absolute constant of the direct reaction will be obtained from eq (5) applied to reversible conditions and assuming the order $m=1$:

$$k_{1(\text{rev})} = \frac{k_{ap(\text{rev})}}{[OH^-]_o} \quad (16)$$

Solutions

1. 500 mL of 0.3 M NaOH solution, from solid NaOH.
2. 200 mL of 0.3 M NaCl solution, from a NaCl solid (after the titration of NaOH solution).

Experimental procedure

The method used to study the kinetics of the reaction is to register the absorbance of phenolphthalein, in strongly alkali solutions, as a function of time. The reaction will be followed in four solutions with different NaOH concentrations to have 4 different series of absorbance.

We will work at a wavelength of 550 nm and a constant temperatura of 25 °C.

For a given NaOH concentration, the decolorization rate increases as the ionic strength does. To keep the ionic force constant, solutions of NaOH and NaCl with the same concentration, 0.30 M, are prepared. To prepare the most dilute NaOH solutions, solution 1 must be diluted with solution 2, i.e. the NaCl solution will be used as a solvent instead of water to try to keep the ionic strength constant.

1. Connect the spectrometer 15-20 minutes before the measurement, adjust the thermostatic temperature at 25°C and the wavelength to 550 nm.
2. Prepare the 0.3 M NaOH solution.
3. Titrate about 20 mL of 0.3 M NaOH solution with Potassium hydrogen phthalate using phenolphthalein as an indicator. Repeat at least 3 times.
4. Prepare the NaCl solution with the same concentration as the titrated NaOH solution.
5. Measure the absorbance of each series as a function of time at $\lambda=550$ nm.

Notes and Precautions: **(1)** the spectrophotometer cell should be clean; it should be washed with the appropriate blank; the walls should not be touched with the fingers; and it should not be filled to the brim but $\frac{3}{4}$ to about of its capacity. **(2)** The initial absorbance of the test solutions should be approximately 1.

Four sets of measurements will be made, and it is recommended to start with the highest NaOH concentration series.

The instructions accompanying the spectrophotometer should be read carefully.

SERIES 1: 0.3 M NaOH solution

- a) Prepare the blank: in this case, it is the same solution of 0.3 M NaOH.
- b) After cleaning it well with the blank, transfer to a cuvette 2700 μ L of the blank.
- c) Adjust the absorbance to 0 with the blank (ZERO).
- d) Remove the cuvette of the spectrometer and add 25 μ L of phenolphthalein. Invert the cuvette to homogenize the mixture, which will be the problem solution 1.
- e) Measure the absorbance every 30 seconds for 300 seconds.

SERIES 2: 0.2 M NaOH solution

- a) Prepare the blank in a beaker: 20 mL of 0.3 M NaOH and 10 ml of 0.3 M NaCl.
- b) After cleaning it well with the blank, transfer to a cuvette 2700 μ L of the blank.

- c) Adjust the absorbance to 0 with the blank (ZERO).
- d) Remove the cuvette of the spectrometer and add 25 μL of phenolphthalein. Invert the cuvette to homogenize the mixture, which will be the problem solution 2.
- e) Measure the absorbance every 30 seconds for 300 seconds.

SERIES 3: 0.1 M NaOH solution

- a) Prepare the blank in a beaker: 10 mL of 0.3 M NaOH and 20 ml of 0.3 M NaCl.
- b) After cleaning it well with the blank, transfer to a cuvette 2700 μL of the blank.
- c) Adjust the absorbance to 0 with the blank (ZERO).
- d) Remove the cuvette of the spectrometer and add 25 μL of phenolphthalein. Invert the cuvette to homogenize the mixture, which will be the problem solution 3.
- e) Measure the absorbance every 30 seconds for 600 seconds.

SERIES 4: 0.07 M NaOH solution

- a) Prepare the blank in a beaker: 7 mL of 0.3 M NaOH and 23 ml of 0.3 M NaCl.
- b) After cleaning it well with the blank, transfer to a cuvette 2700 μL of the blank.
- c) Adjust the absorbance to 0 with the blank (ZERO).
- d) Remove the cuvette of the spectrometer and add 25 μL of phenolphthalein. Invert the cuvette to homogenize the mixture, which will be the problem solution 4.
- e) Measure the absorbance every 30 seconds for 4800 seconds. (In this series, from 15 minutes onwards, the reverse reaction begins to be important, and to carry out the appropriate reversible treatment, it is necessary to reach equilibrium, approximately 1 hour after the start of the reaction).

Note: Remember that there are containers for waste disposal when you finish the experiment.

Experimental results: data presentation

1. Tabulate the data for the preparation of the solutions: calculated and real data.
2. Collect the results of the NaOH titration in a table.
3. Present in another table the absorbances measured in each series as a function of time.

Treatment and result discussion

1. Recalculate the real NaOH concentration from the titration with its random error, and with that of NaCl and solutions.

2. **Irreversible treatment:**

- 2.1 Draw in the same graph the values of $\ln(A_t)$ versus time for the four series (for series 4 only up to 600 seconds), and check that the reaction is of pseudo-first order with respect to phenolphthalein (eq 9).
- 2.2 Obtain, from the slope of the fittings, the apparent reaction rate constants of each series.
- 2.3 Represent eq (10) and obtain from the slope of the fitting, the order of reaction with respect to the OH^- (m).
- 2.4 Calculate the absolute rate constant ($k_{1(\text{irrev})}$) with its random error (eq 11).

3. **Reversible treatment (only for series 4):**

- 3.1 Determine the value of k_{ap} for series 4 representing eq (14b) and the value of k_{-1} (eq 15). Obtain $k_{1(\text{rev})}$ from eq (16) and the OH^- concentration of series 4. Compare it with that obtained by irreversible treatment (section 2.4).
- 3.2 Compare the values of $k_{\text{ap},4(\text{rev})}$ with the $k_{\text{ap},4(\text{irrev})}$, and comment.
- 3.3 Compare the values of k_1 and k_{-1} , and comment.

4. Calculate the ionic strength, I , of each series, check that it remains constant.

- 4.1 Recalculate the actual concentrations of NaOH, NaCl and initial phenolphthalein ($M_r = 318.33$) in each of the problem solutions.
- 4.2 Calculate the ionic strength of each series using the equation $I = \frac{1}{2} \sum_i m_i |z_i|^2$, where m_i and z_i are

the molality and charge of each ion present in the solution, respectively. The relationship between molality and molarity is $c_i = \rho_1 m_i$ and the density of water, $\rho_1 = 1\text{g/mL}$.