

1. Practice - Absorption Spectrum of a Conjugated Dye

1. Define chromophore.
2. Draw the structure of the chromophore of the dyes going to be examined.
3. Write down the equation for the possible energy levels of the free electrons moving in a one-dimensional box of length L . Define the symbols.
4. Write down the equation for the energy difference between the highest occupied energy level and the lowest unoccupied energy level (HOMO \rightarrow LUMO), for a chromophore with N π -electrons. Define the symbols.
5. Write down the energy difference between the highest occupied energy level and the second lowest unoccupied energy level for a chromophore with N π -electrons. Define the symbols.
6. Write down the wavelength of the lowest energy absorption peak for a chromophore with N π -electrons. Define the symbols.
7. Define the Beer–Lambert law.
8. How can the length of the C–C bond be estimated from the measured data?
9. Why do we consider the electrons to be conjugated from nitrogen atom to nitrogen atom in case of the examined dyes?

3. Practice - Determining the transport number

1. What is the transport number? Define it with charges and electrical mobility.
2. What is the relationship between the average migration rate of ions and the electric field strength. What is electric mobility?
3. What does the transport number of a given ion depend on?
4. Outline the structure of the Hittorf cell. What is the role of each part?
5. If the amount of dissolved copper (II) sulphate in a sample of 2.052 g is $2.11 \cdot 10^{-4}$ mol, what is the molality of copper (II) sulphate? $M_r(\text{CuSO}_4) = 159.62$
6. If the weight of the anode part solution is 87.90 g, the molality of copper (II) sulfate is $1.11 \cdot 10^{-4}$ mol/g, the molality of the initial solution was $1.02 \cdot 10^{-4}$ mol/g, what was the change in the amount of substance of copper (II) sulfate due to electrolysis? $M_r(\text{CuSO}_4) = 159.62$
7. How do you calculate the transport number if you have determined the total charge through the Hittorf cell and the change in the amount of substance of CuSO_4 in the anode part?
8. How do you calculate the transport number if you have determined the total charge through the Hittorf cell and the change in the amount of substance of CuSO_4 in the cathode part?
9. Why can the change in the amount of substance calculated from the total charge and from the amount actually measured differ from the anode of the Hittorf cell?

10. Why can the change in the amount of substance calculated from the total charge and the amount actually measured differ for the cathode of the Hittorf cell?
11. How much heat is generated in the cell if a charge of 300 C passes through the cell during electrolysis at 50 V? How much would this raise the temperature of 200 g of solution if there were no heat exchange with the environment? The specific heat capacity of the solution should be $4 \text{ J}/(\text{g K})$.
12. What are concentration cells? What kind of cell reaction takes place in them?
13. What is the diffusion potential and how does it affect the electromotive force of the concentration cells? When can we expect no diffusion potential?

4. Practice - Studying corrosion and corrosion inhibitors

1. What is the electrode potential and what is the standard electrode potential?
2. The electrode potential of the Standard Electrode Hydrogen Electrode (SHE) at 25 °C is defined as zero. How much will be its electrode potential at 0 °C and 50 °C?
3. What electrode can be a reference electrode? What reference electrodes do you know?
4. In what thermodynamic conditions can the corrosion of metals occur in simple aqueous electrolyte solutions?
5. Write the Nernst equation for the cell reaction potential for a $\text{Fe}|\text{Fe}^{2+} (a_{\text{Fe}}) :: \text{H}^+ (a_{\text{H}})|\text{H}_2 (p_{\text{H}})|\text{Pt}$ Galvanic (Voltaic) cell.
6. What sub-processes should be considered in the kinetic treatment of a charge transfer process?
7. Write the Butler-Volmer equation for a simple charge transfer process. How does the current depend on the electrode potential?
8. What does diffusion-limited current mean?
9. What is polarization resistance? How can it be determined?
10. What is the Tafel slope and how can it be determined?
11. What is the symmetry factor and how can it be determined?
12. What are adsorption inhibitors and how do they work?
13. How to determine the corrosion current with Tafel curves?

14. Calculate the rate of corrosion (mm/year) when $10 \mu\text{A}$ corrosion current occurs on an iron of 1 cm^2 surface area while Fe^{2+} ions are formed during corrosion. The iron has a density of 7.87 g/cm^3 , its relative atomic mass is 55.85, the Faraday constant is 96485 C/mol .

5. Practice - Determination of the dissociation constant of a weak acid from pH measurements

1. Define the ionic strength! What is the ionic strength in a solution containing $0.001 \text{ M CH}_3\text{COONa}$ and $0.02 \text{ M K}_2\text{SO}_4$?
2. Define activity and activity coefficient!
3. What is the Debye-Hückel theorem, and limit of its application?
4. What is the point of half-neutralization?
5. What is the calomel electrode? Why is it used widespread?
6. How can be the value of pK_d determined from the measured data?
7. Explain the Bronsted acid-base theorem in max. 5 sentences!
8. Give the formula to calculate the pH of a buffer solution!
9. Sketch a titration curve, if a weak acid is titrated with a strong base!
10. Calculate the pH of the following solutions ($\text{pK}_d=1.8 \times 10^{-5}$):
 - a. $0.01 \text{ M CH}_3\text{COOH} + 1.0 \text{ M CH}_3\text{COONa}$
 - b. $0.1 \text{ M CH}_3\text{COOH} + 0.001 \text{ M CH}_3\text{COONa}$
11. 5 cm^3 of 0.6 M NaOH solution is added to 15 cm^3 0.2 M acetic acid solution. What will be the equilibrium concentration of acetic acid and acetate ion? ($\text{pK}_d=1.8 \times 10^{-5}$)

6. Practice - Equilibrium constant determination of bromocresol green

1. Define the Beer–Lambert law. Define the symbols.
2. What circumstances allow the spectrophotometric determination of the dissociation constant?
3. What is the relationship between the dissociation constants, defined with activities and concentrations? Define pK_a and pK_c .
4. Deduce the formula which allows the determination of pK_a .
5. For a given compound, on which wavelength do you perform the absorbance measurements? How do you determine this wavelength?
6. Define ionic strength. Why was it introduced to physical chemistry?
7. Calculate the ionic strength of the following solutions:
 - a. 2.0 cm^3 0.1 M HAc, 2.5 cm^3 0.2 M NaAc and 5.0 cm^3 1.0 M KCl, diluted to 50 cm^3 .
 - b. 10^{-4} M indicator (HI), 0.025 M NaAc and 0.01 M KCl.
 - c. 5.0 cm^3 10^{-4} M indicator, 2.5 cm^3 0.2 M NaAc, 2.0 cm^3 0.1 M HAc, 5.0 cm^3 1.0 M KCl, diluted to 50 cm^3 .
8. How large volume of 1.0 M KCl should be given to 10 cm^3 0.1 M HCl, to achieve ionic strength of $I = 0.4 \text{ M}$ after dilution to 50 cm^3 ?
9. Deduce the formula, related to the concentration ratio of the protonated and deprotonated form of the indicator.

10. What considerations must be taken into account when planning the solutions, used for the determination of the pK_a value of an indicator?
11. What parameters are to be determined during the experiment? How is the value of pK_a determined from these?
12. Why is the absorbance of the fully protonated/deprotonated form of the indicator independent of the ionic strength?

7. Practice - Studying simultaneous solution equilibria

Week 1

1. What is the definition of stability constants and the cumulative stability constant? Write the three corresponding expressions for the following system:
$$M + 2 L \rightleftharpoons ML_2$$
2. What is the definition of ionic strength?
3. What is the ionic product of water?
4. Note down the possible complex formation equilibrium equations for the formation of copper(II) amine complexes from Cu(II) ions and NH_3 ligands! Consider the maximum coordination number to be 4.
5. What is the ionic strength in a 1 M NH_4NO_3 solution that contains 100 mM CuSO_4 ?

Week 2

1. What is the Beer-Lambert law? Define the symbols used in the formula!
2. Describe Job's method in 2-3 sentences!
3. Describe the molar ratio method in 2-3 sentences!
4. Describe Job's method in 2-3 sentences!
5. Describe the competition method!
6. What is the distribution diagram?

8. practice - Spectrophotometric determination of equilibrium constant.

Week 1

1. Describe the van't Hoff equation!
2. Define the followings: total concentration, equilibrium concentration, analytical concentration
3. How can you avoid the disproportion of I_2 during the reaction?
4. How do you use the ratio of triiodide and total iodine concentration when you planning the measurements?
5. Write down the basic equations of iodometry?! (thiosulfate-iodine and iodide-iodate reactions)
6. Define the ionic strength! What is the ionic strength of a 10^{-4} M concentration acetic acid solution ($K_d=1.8 \times 10^{-5}$)?
7. Define the ionic strength! What will be the ionic strength – assuming complete dissociation - after mixing the next solutions: 100.0 cm^3 $0.1 \text{ M Na}_2\text{SO}_4$, 300.0 cm^3 0.2 M FeCl_3 and 100.0 cm^3 1.0 M HCl ?
8. What will be the concentration of $[I_3^-]$, if we mix together $100,0-100,0 \text{ cm}^3$ $5 \times 10^{-4} \text{ M}$ of I_2 , and I^- solutions ($K_a=500$)?

Week 2

1. What kind of disturbing reactions may occur during the formation of triiodide?
2. What is the Beer-Lambert law? How can be expressed the absorbance in the $I_2/I^-/I_3^-$ equilibrium system?
3. Describe how to prepare the required I_2 solution?
4. How the total iodine concentration is determined?

5. What is the absorbance matrix?
6. How do you select the wavelength values for the evaluation process?

10. Practice: Kinetic study of iron (III) – thiocyanate reaction by stopped flow method

Week 1

- 1) What kind of complex formation processes can occur in the highly acidic solutions containing iron(III) and thiocyanate ions?
- 2) What kind of condition must be fulfilled to ensure that only complexes of a 1:1 composition are formed?
- 3) Write down the studied reaction and specify the color of the formed species!
- 4) How does the rate constant of the studied reaction change with the hydroxonium ion concentration?
- 5) Shortly describe the stopped-flow technique!
- 6) Why do you need to add a small (0.005 M) acid when you prepare the stock solution of the iron(III) salt?

Week 2

- 1) How would you determine the iron(III) content of a solution by complexometry?
- 2) Note the essence of the stopped flow method in several sentences!
- 3) Draw a schematic picture of the stopped-flow instrument!
- 4) What is the correlation between the apparent rate constant and the pH?
- 5) Calculate the weight of $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{ H}_2\text{O}$ needed to prepare $250,0 \text{ mL}$ of 0.04 M $\text{Fe}(\text{III})$ stock

solution! $A_r(\text{Fe}) = 55.85$, $A_r(\text{O}) = 16.00$, $A_r(\text{N}) = 14.01$, $A_r(\text{H}) = 1.01$

11. Practice - Characterization of the molecular mass distribution of polymers by fractional precipitation

1. Why is it important to know the molecular mass distribution of a polymer?
2. What parameters influence the molar mass distribution of polymer samples?
3. What is a differential distribution function?
4. What is an integral distribution function?
5. What does it mean if a polymer sample is (a) monodisperse, (b) polydisperse, and (c) paucidisperse?
6. Briefly (in 4 to 5 sentences) describe the method of fractional precipitation to determine the molecular mass distribution of the polymer.
7. What is turbidity and how can its measurement be used to determine the relative precipitated polymer mass?
8. What is epoxy resin, how can we produce it? Not the sub-steps, but the names of the characteristic reactants, the type of the reaction and 1 - 2 main features should be mentioned
9. If the expected relative molecular mass of a polymer fraction is 3750, what is the volume of precipitant (water) required for a 15 cm^3 polymer solution according to the Schulz equation if $B = 1.64 \cdot 10^5$ and $A = 7.3$?

12. Practice - Coagulation kinetic

1. According to DLVO theory, what interactions should be expected between dispersed colloidal particles?
2. What is slow coagulation, what is fast coagulation, and what is the stability factor?
3. What is the critical coagulation concentration?
3. What is the differential and integrated rate equation of $2A \rightarrow B$ kinetically second order processes.
4. What are absorbance, transmittance and turbidity? How does turbidity depend on the concentration and size of light scattering particles in the Rayleigh range?
5. How to determine the reduced turbidity from the registered voltage - time data?
6. Why is it necessary to calibrate the turbidimeter?
7. How do you determine the stability (deceleration) factor based on the time dependence of the reduced turbidities?

13. Practice – Viscosimetry of polymer solutions

1. What does the viscosity of the polymer solutions depend on?
2. What conformational parameters can be determined from viscosity measurements?
3. Note down and interpret the Kuhn's root law.
4. Note down and interpret the Kuhn's viscosity law.
5. Note down and interpret the Kuhn-Mark-Houwink law
6. Note down and interpret the Huggins law
7. How can you determine the α expansion factor from the measured viscosity data?
8. What parameters affect the size of a macromolecular coil?
9. How can you determine the statistical end-to-end distance from the measured viscosity data?

10. Why only the so-called $[\eta]$ intrinsic viscosity can be used to determine viscosimetric molecular weight?

14. Practice - Determination of thermodynamical and kinetical parameters of charge transfer processes. Chronoamperometry.

Week 1

1. What is the electrode potential, the standard electrode potential and the formal potential?
2. What are the ideally polarizable and ideally non-polarizable electrodes?
3. What sub-processes should be considered in the kinetics of a charge transfer process?
4. How is the reaction rate of heterogeneous reactions defined?
5. How can the rate of the electrochemical charge transfer processes be expressed with the measurable current?
6. How does the rate of charge transfer processes change with the electrode potential?
7. Write the Nernst equation for an elementary Red-Ox transformation.
8. What are the characteristic parameters of a linear voltammogram?
9. What are the characteristic parameters of a cyclic voltammogram?
10. What is the essence of potential step technique and what data can be derived from the measurements?
11. What does it mean: electrochemically reversible, quasi-reversible and irreversible system?

Week 2

1. What is the symmetry factor and what is the standard rate coefficient?
2. In an electrochemically reversible process how would you determine the formal potential, the symmetry factor, and the standard rate coefficient?
3. In an electrochemically quasi-reversible process how would you determine the formal potential, the symmetry factor, and the standard rate coefficient?
4. In an electrochemically irreversible process how would you determine the formal potential, the symmetry factor, and the standard rate coefficient?
5. How can you determine the diffusion coefficients of electroactive substances?
6. How does the formal potential change with the composition of the solution and why?
7. In an electrochemically reversible process, how does the peak current change with the sweep rate? What is the condition of reversibility?
8. In an electrochemically irreversible process, how does the peak current change with the sweep rate? What is the condition of irreversibility?
9. What is the electrode capacitance and how can you estimate its value?
10. Is the reaction rate of the charge transfer process dependent on the geometric or the actual surface area? What's the difference between the two?
11. Why is oxidation of L-ascorbic acid irreversible?