

CHEM-E4100 Laboratory projects in chemistry

Lauri Partanen

Kemian tekniikan korkeakoulu

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Laboratory work III: Spectroscopic determination of the equilibrium constant

Background information

Note! Laboratory work III does not include a separate lab instruction sheet. Instead, to enhance learning and train the students for independent laboratory work the students will prepare their own instructions based on this background information by answering the questions provided at the start of the laboratory session.

Introduction

The equilibrium constant is one of the most central concepts in chemistry. It can be experimentally determined through various methods such as conductometry. Because the species participating in the equilibrium absorb electromagnetic radiation in distinct ways, in some cases spectroscopic techniques can be used for the determination of the equilibrium constant. In this laboratory work, you will determine the equilibrium constant of the Bromothymol blue using UV-VIS spectroscopy.

Activity and the thermodynamic equilibrium constant

The thermodynamic equilibrium constant K is one of the most central concepts of chemical thermodynamics. For a general thermodynamic reaction



the equilibrium constant K is defined by the equation

$$K = \frac{a_C^{\nu_C} a_D^{\nu_D}}{a_A^{\nu_A} a_B^{\nu_B}}, \quad (2)$$

where a_i is the **activity** of species i . Both the activity and the equilibrium constant are unitless quantities. In very dilute solutions the activities can be replaced with concentrations $a_i \approx c_i/c_0$, where $c_0 = 1 \text{ mol/l}$ and the thermodynamic equilibrium constant transform to the familiar concentration equilibrium K_c .

$$K \approx K_c = \frac{\left(\frac{c_C}{c_0}\right)^{\nu_C} \left(\frac{c_D}{c_0}\right)^{\nu_D}}{\left(\frac{c_A}{c_0}\right)^{\nu_A} \left(\frac{c_B}{c_0}\right)^{\nu_B}} \quad (3)$$

As the solutions become less dilute the approximations in equation (3) no longer hold. In this case the activity can be presented as a product of the **activity coefficient** γ_i and concentration $a_i = \gamma_i c_i/c_0$. By combining equations (2) ja (3) we can write the equilibrium constant as

$$K = \frac{\gamma_C^{\nu_C} \gamma_D^{\nu_D}}{\gamma_A^{\nu_A} \gamma_B^{\nu_B}} K_c \quad (4)$$

Whereas the concentration only measures the amount of particles per volume of solution, the activity also accounts for the interactions between them through the activity coefficient. For example, when you add table salt to a glass of water, the formed Na^+ and Cl^- ions attract each other. Consequently, $\gamma_i < 1$ and the activity of the ions is smaller than would be predicted based purely on the concentration.

Lambert-Beer law

When monochromatic electromagnetic radiation of intensity I_0 passes through a substance, part of the radiation can be absorbed. According to the empirical Lambert-Beer law, the intensity I of the radiation decreases as

$$I = I_0 \cdot 10^{-\varepsilon[J]L}, \quad (5)$$

where $[J]$ is the concentration of the sample, and L is the length of the sample that the light must pass through. The quantity ε is called the **molar absorption coefficient**. It depends on both on the nature of the absorbing species J and the wavelength of the incident radiation. The Lambert-Beer law shows that upon hitting the sample J , the intensity of the radiation decreases exponentially with the concentration and the length of the sample the radiation has to pass through.

In spectroscopy, the amount of absorbed or emitted radiation is typically expressed in terms of the **transmittance, T** :

$$T = \frac{I}{I_0} \quad (5)$$

or the **absorbance, A** :

$$A = \log\left(\frac{I_0}{I}\right) \quad (5)$$

with the two related by $A = -\log T$. The Lambert-Beer law can be expressed in terms of the absorbance as

$$A = \varepsilon[J]L. \quad (5)$$