

A 24 pH-measurements with a glass electrode – Potentiometric Titration

Task:

Determine the titer of a given phosphoric acid solution, as well as the dissociation constants K_1 and K_2 of phosphoric acid, and the dissociation constant, K_B of an NH_4OH solution.

Basics:

When a weak acid $\text{RH} \rightleftharpoons \text{R}_{\text{aq}}^- + \text{H}_{\text{aq}}^+$ in an aqueous medium is continuously titrated with a base, the equilibrium increasingly shifts toward the products until the given amount of acid has been neutralised. This is the case at the inflection point of $\text{pH}(V_{\text{Base}})$ curve, whereby V is the volume of the given acid. The dissociation equilibrium is (disregarding the activity coefficients):

$$K_S = \frac{[\text{R}^-] \cdot [\text{H}^+]}{[\text{RH}]} \quad (1)$$

or

$$\log K_S = \log [\text{H}^+] + \log \frac{[\text{R}^-]}{[\text{RH}]} \quad (2)$$

$$\text{p}K_S = \text{pH} + \log \frac{[\text{RH}]}{[\text{R}^-]} \quad (3)$$

with $\text{p}K = -\log K_S$.

After half of the required neutralisation amount of acid has been added (buffer point) then,

$[\text{RH}] = [\text{R}^-]$ and thus, as per eq. (2) $\text{p}K_S = \text{pH}$.

Similar to the $\text{p}K_S$ -values of weak acids, the $\text{p}K_S$ -values of weak bases can be determined by potentiometric titration. In this case, it is recommended to calculate the equilibrium of the corresponding acid, as opposed to the base equilibrium. Then the K_S -value, in the case of the reaction $(\text{NH}_4^+)_{\text{aq}} \rightleftharpoons \text{NH}_3 + \text{H}_{\text{aq}}^+$, can be defined by:

$$K_S = \frac{[\text{NH}_3] \cdot [\text{H}^+]}{[\text{NH}_4^+]} \quad (4)$$

or respectively for the the corresponding base reaction $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ by:

$$K_B = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad (5)$$

Taking into account the ion product of water $K_W = [\text{H}^+][\text{OH}^-]$ and $[\text{NH}_3] = [\text{NH}_4\text{OH}]$, we get:

$$\frac{K_B}{K_W} = \frac{[\text{NH}_4^+]}{[\text{NH}_3][\text{H}^+]} = \frac{1}{K_S} \quad (6)$$

therefore:

$$K_S = K_W/K_B \text{ and } \text{p}K_S = -\log K_W + \log K_B, \text{ respectively.} \quad (7)$$

and thus, the $\text{p}K_B$ -value can be calculated from the $\text{p}K_S$ -value.

Experimental Procedure:

The determination of the pH-value takes place with a glass electrode, which is selectively responsive to H^+ -ions. The pH device displays the voltage value directly as a pH-value. An exact user manual for the pH device can be found in the work area instructions.

- To titrate the phosphoric acid, 10 ml of the phosphoric acid solution that is to be determined is diluted to 100 ml and then titrated (with ca. 1 cm³ of base, if the pH-value changes dramatically with the addition of the base, then with 0.1 cm³) with 0.1 n NaOH until an approximate pH-value of 11 is achieved.
- Potentiometrically titrate 0.01 n NH₃-solution with 0.1 n HCl and calculate the dissociation constant from the curve: $\text{pH} = f(\text{cm}^3 \text{ of added acid})$.

Data Analysis:

1. Determine the titer of the added phosphoric acid. Plot on a graph the measured pH-values against the added amount of base. The dissociation constants K_1 and K_2 should be determined from the titration curve $\text{pH} = f(V_{\text{Base}})$.
2. Specify, under which simplifications, the specified association for determination of the Dissociation Constant hold true.
3. Determine the Dissociation Constant K_B of a NH₄OH solution through potentiometric titration with HCl.
4. Compare the measured values with the known values from the literature.

What you should know:

Setup and operation of a glass electrode, electrochemical fundamentals of potentiometric titration (e.g. electrochemical potential, Nernst equation, electrodes of the second kind etc.)

Extra Question:

What is an ion-sensitive electrode?