1.a. Potentiometric determination of dissociation constant of weak acid

The dissociation constant of weak HA is

$$K_A = \frac{a_{H^+} \cdot a_{A^-}}{a_{HA}}$$

(1.1.)

where a_{HA}, a_{H^+} and a_{A^-} are activity of undissociated weak acid and activity of dissociation products respectively. By the mathematical rearrangement of the equation (1.1.), we obtain the Henderson-Hasselbalch equation:

$$-\log K_A = pK_A = pH + \log \frac{a_{HA}}{a_{A^-}}$$

(1.2.)

Activities can be replaced with molarities ($a_{HA} = [HA]$, $a_{A^-} = [A^-]$) in the case of dilute solutions below approx. $10^{-2}\ M$ in this case.

The dissociation constant pK_a can be determined by titration of weak acid using a strong base or acid. Measurement of pH changes during titration allows evaluating the molarity of the dissociated and undissociated form of weak acid. Titration may be done in two ways, depending on the pK_a value. The way depends whether pK_a of weak acid is below or above value 7.

TITRATION OF VERY WEAK ACID WITH STRONG HYDROXIDE.

Boric acid (HA) represents a very weak acid $pK_a > 7$. The first degree dissociation constant pK_a can be determined from the titration results of boric acid with strong potassium hydroxide (optionally sodium hydroxide).

Electroneutrality and mass conservation law of weak acid are respected at any addition of strong KOH hydroxide to to the weak HA solution:

$$[A^-] + [OH^-] = [K^+] + [H^+]$$

(1.3.)

$$c_{HA} = [HA] + [A^-]$$

(1.4.)

where c_{HA} means analytical concentration of HA. Potassium cation remains dissociated during titration and its concentration $[K^+]$ is equal to the total analytical concentration of strong hydroxide c_{KOH}. Then the eqn (1.3.) gives:

$$[A^-] = c_{KOH} + [H^+] - [OH^-]$$

(1.5.)

We obtain for the undissociated acid concentration $[HA]$ following if we insert the relation (1.5.) in the equation (1.4.) and then mathematically rearrange the result:

$$[HA] = c_{HA} - c_{KOH} - [H^+] + [OH^-]$$

(1.6.)

The obtained concentrations $[A^-]$ and $[HA]$ can be used in the Henderson-Hasselbalch equation (1.2.).

TITRATION OF SALT OF WEAK ACID WITH STRONG ACID.

Acetic acid (HA) represents a weak acid $pK_a < 7$. The dissociation constant pK_a can be determined from the titration results of salt KA (where K means sodium or potassium) of weak acid with strong acid HX (for example with hydrochloric acid HCl).

The mixed solution of KA and HX keep electroneutrality and the mass conservation law of salt of weak acid:

$$[A^-] + [OH^-] + [X^-] = [K^+] + [H^+] \tag{1.7.}$$

$$c_{KA} = [A^-] + [HA] \tag{1.8.}$$

The salt KA is completely dissociated, so the concentration $[K^+]$ during the titration is always equal to the total analytical salt concentration c_{KA}. For the same reason, the strong acid anion concentration $[X^-]$ is equal to the total analytical concentration c_{HX} of strong acid.

If we replace the concentrations $[K^+]$ a $[X^-]$ in eqn (1.7.) by analytical concentrations, we get:

$$[A^-] = c_{KA} + [H^+] - [OH^-] - c_{HX} \tag{1.9.}$$

We can insert this relation in eqn (1.8.), mathematically rearrange and to obtain:

$$[HA] = c_{HCl} + [OH^-] - [H^+] \tag{1.10.}$$

The concentrations $[A^-]$ and $[HA]$ we use in the Henderson-Hasselbalch eqn (1.2.).

? TASK: Determine pK_a of acetic acid and boric acid to the first stage. Compare the result with the values from literature.
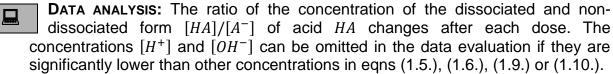
✄ LABORATORY AIDS AND CHEMICALS: automatic titrator equipped by pH detection, weighing boat, *2* volumetric flasks (*50ml*), *0,1M KOH* or *NaOH*, *0,1M HCl*, boric acid, sodium acetate, titration beaker (*100ml*).

▤ INSTRUCTIONS: Get study how to operate the automatic titrator and how to measure the pH, switch titrator on and prepare the device for measurement. Check pH measurements with calibration solutions (use buffers).

- Weigh 5.10^{-4} moles of boric acid (or sodium acetate) with maximum accuracy. Transfer the weight to a *50 ml* volumetric flask and dissolve in distilled water up to volume marking. Pour the solution into a dry titration beaker.
- Titrate with solution agent *0,1M* KOH (or *0,1M* HCl) by *0.5ml* dose to total dose *5ml*. Record the pH after stabilization.

🖳 DATA ANALYSIS: The ratio of the concentration of the dissociated and non-dissociated form $[HA]/[A^-]$ of acid HA changes after each dose. The concentrations $[H^+]$ and $[OH^-]$ can be omitted in the data evaluation if they are significantly lower than other concentrations in eqns (1.5.), (1.6.), (1.9.) or (1.10.).

✍ REPORT: For both very weak and weak acid: weight in *mg*, **TABULE 1:** for zero and each consequent titration dose: volume of added agent, total volume, analytical concentration of boric acid (or sodium acetate), experimental pH, $[H^+]$, $[OH^-]$, $[A^-]$, and $[HA]$ concentrations, expression $log[HA]/[A^-]$, pK_A calculated using eqn (1.2.). **NEXT:** mean value of pK_A and confidence interval using Student's t-distribution.