Determination of weak acids' dissociation constant via potentiometric titration

Introduction
The equation of titration curve

When titrating of a monobasic weak acid AH with NaOH standard solution, at any point in the titration the electro-neutrality principle is satisfied; that means the number of positive and negative charges are equal in the system

$$[Na^+] + [H^+] = [A^-] + [OH^-] \tag{1}$$

When the analytical concentration of the obtained acid is C_A, and its dissociation constant is K, then the concentration of $[A^-]$ anionic form (according to the definition of dissociation constant), is calculated the following way:

$$[A^-] = \frac{C_A K}{K + [H^+]}$$

The sodium ion concentration can be calculated in all of the points, from the concentration of the added base (C_B) considering the dilution:

$$[Na^+] = \frac{C_B V}{V + V_0}$$

where V_0 represents the initial volume of the sample, and V represents the volume of the added alkaline titrating reagent.

The latter two equations inserted into equation (1) - and using the water ion product (K_W), the concentration of hydroxyl ions are predictable in any point of the titration ($[OH^-]=K_W/[H^+]$) - we obtain the following relationship:

$$\frac{C_B V}{V_0 + V} + [H^+] = \frac{K}{K + [H^+]} C_A \frac{V_0}{V_0 + V} + \frac{K_W}{[H^+]} \tag{2}$$

The equation of the titration curve of acids of any number of functional group, can be rearranged using the electro neutrality principle under the considerations above.

The determination of dissociation constant

We can rearrange the describing equation of the titration curve (2) to the following form:

$$\frac{C_B V - \left(\frac{K_W}{[H^+]} - [H^+] \right)(V_0 + V)}{C_A V_0} = \frac{K}{K + [H^+]}$$

The left side of the equation marked as Y, and after the rearrangement, the following formula is obtained:

$$\frac{Y}{1-Y} = \frac{K}{[H^+]} \qquad (3)$$

In logarithmic form:

$$\log \frac{Y}{1-Y} = \log K - \log[H^+] \qquad (4)$$

The two equations above show that the determination of the dissociation constant in this simple case can be obtained from fitting a straight lines to measured data. According to equation (3) plotting, the left side of the equation in the function of $1/[H^+]$ we obtain a straight line, crossing through 0. Its slope gives the K value. Representing the left side of the equation (4) in function of the pH, we get a straight line whit unity slope which crosses the y-axis at the value of log (K).
All quantities of the left side of the expression are known with the exception of the water ion product (K_W), if we know the analytical concentration of titrated acid. Water ion product - as well as the dissociation constant - depends on the temperature and the ionic strength of the medium. Thus, if the valid values are not available for the present circumstances, we have to determine it performing another measurement.

The equivalence point of strong acid - strong base titrations can be given by evaluating the measuring data points. As the strong acid is considered to be completely dissociated, and the value of the $K/(K+[H^+])$ quotient in equation (2), containing the dissociation coefficient, equals with 1. Applying this after the rearrangement we get the following expression:

$$\frac{C_B V - C_A V_0}{V_0 + V} = \frac{K_W}{[H^+]} - [H^+] \qquad (5)$$

If $[H^+] << [OH^-]$ (above pH = 9), on the right we can count with $K_W/[H^+]$, so plotting the left side vs. $1/[H^+]$ we get a linear function, and its slope is equal with the water ion product we were looking for (1 Figure).

Carrying out the exercise
Calibrate the pH meter with calibration solutions of pH=4 and pH=10. (See at the end of this description!)
Determine the factor of the given 0.1M NaOH solution with a factorised 0.1 M HCl solution. This will be implemented as described in the definition of water ion product, however the factor of NaOH can be calculated from the volume of the titrant used until we reach the equivalent point. (It is possible to perform the two measurements in the same time as well!)
Pipette 20 cm^3 from the unknown weak acid solution of known concentration designated by the leading instructor. Place the combined glass electrode into the dish and turn on a magnetic stirrer. Add 0.5 cm^3 doses of 0.1 M NaOH standard solution from the burette, and after obtaining steady readings (about 30 sec) read the pH value. Finish the titration by adding 5-7 more doses after the equivalence point. Wash the titration vessels several times with double deionized water and dry them.
Then, in order to determine the water ion product pipette 20 cm^3 of the factorised 0.1M HCl solution into the titration beaker. Titrate the acid with NaOH solution, after the equivalence point - and from pH = 9 - take at least 8-12 measuring points in order to improve the accuracy of the calculation.
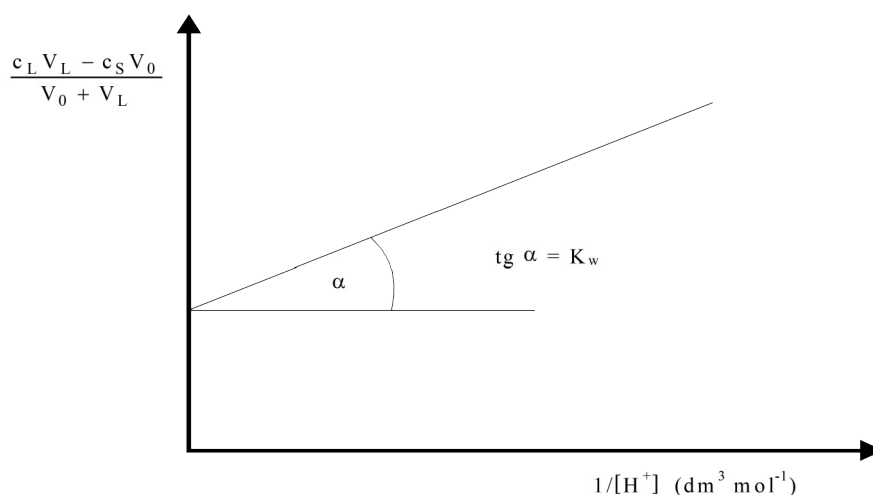
Fig. 1 Plot for determination of the water ion product by graphic method

The y-axis is labeled $\dfrac{c_L V_L - c_S V_0}{V_0 + V_L}$, the slope line has $\operatorname{tg}\alpha = K_w$, and the x-axis is labeled $1/[H^+]\ (dm^3\ mol^{-1})$.

The results of the measurement
Summarize results of the strong acid - strong base titration in a table:
Initial data and solutions:
      NaOH concentration:
      NaOH factor:
      Initial volume:
      HCl concentration:
      HCl factor:

Evaluation of measurement results in Table

V cm^3	V_0+V cm^3	pH	$[H^+]$ $mol\ dm^{-3}$	$1/[H^+]$ $dm^3\ mol^{-1}$	$(C_B V-C_A V_0)/(V_0+V)$ $mol\ dm^{-3}$
0					
0.5					
...					

Determine the value of the water ion product (K_W) graphically and plot the strong acid - strong base titration curve for low and high ionic strengths solutions as well!

Make a table based on the results of the measurement of the weak acid applying the water ion product, the containing following values:
      Initial data and solutions:
      Weak acid name:
      Concentration:
      Initial volume:
   Titrant Name:
      Concentration:

Evaluation table of measurement results

V cm^3	V$_0$+V cm^3	pH	[H$^+$] mol dm^{-3}	1/[H$^+$] dm^3 mol^{-1}	Y	Y/(1-Y)	lg(Y/(1-Y)).
0							
0.5							
...							

Determine the value of the dissociation constant applying both equation (3) and equation (4)!

Plot the titration curve of the weak acid. Take the solution volume used before the equivalent point as 100% and compare the calculated dissociation constants with the pH value, corresponding to the 50% titration degree!

Compare the results obtained for solutions of low and high ionic strengths!
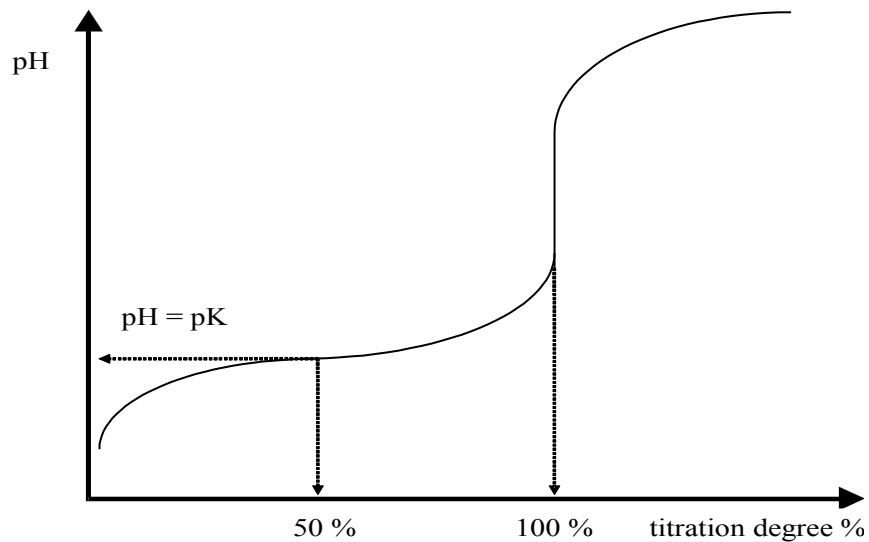
Fig. 2 Titration curve of weak acid, pH vs. titration degree

<u>**Appendix**</u>
WTW - computer-controlled pH meter
The WTW computer- controlled portable pH meter allows for laboratory and industrial pH measurement of samples and monitoring with 0.01 pH accuracy respectively. The built-in electronics allow 2 standard scale adjustment, this allows accurate pH measurements in a a wide range. In order to improve the accuracy of the measurement there are built-in thermometer, the measured pH value of the sample temperature corrected.
Structure of WTW pH meter with a combined electrode:
1 -electrical leads, 2 – electrode house, 3 - reference electrode, 4 -thermometer, 5 – glass electrode

Use of equipment
Turn on the ON/OFF switch on the device. After a short self-control of the instrument display shows the last measured pH value. After the switch, connect the plug of the electrode and the thermometer with the pods placed in the back. For the calibration of the instrument 2 standard solutions are used.

Calibration
1. When the CAL button is depressed "CT1" mark appears on the screen. (If this is not this subtitle read on the display, hold the CAL button until it does appear.)
2. Immerse the electrode (which was first rinsed with distilled water) into pH calibration solution (pH =10.00.) Push RUN / ENTER key to start the calibration, and then wait until the display shows "CT2". (During the calibration, the device may displays flashing "AR" indicating that the electrode potential changing.)
 3. Then rinse the electrode with distilled water and mop up the surface carefully with paper absorbent, then immerse into pH calibration solution 4.00. Press the ENTER button to continue the calibration. (If at the end of the calibration "E3" is displayed, you must repeat the calibration.)
4. If the calibration is successful (AR signal is not flashing,) the slope of the electrode respond curve is shown on the display in mV / pH units. Then press the ENTER button twice then the actual pH will be displayed.
5. If the calibration is finished, rinse the combined electrode with distilled water.

The measurement with the calibrated instrument is carried out as follows: immerse the electrode in the measuring solution, and then press the ENTER key. Then the display shows the actual pH and temperature values. Before inserting the electrode into new solution always flush with distilled water. After insertion into the new solution, wait until the electrode potential is stabilized and accept only after this the measured values as the pH of the sample. The optimal waiting time for the device can be automatically determined by the program: pressing AR button, AR flashes on the display as long as the electrode potential changes. When flashing on the screen ceases, the measured pH value can be read.