CONDUCTOMETRIC TITRATION

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Task 32

CONDUCTOMETRIC TITRATION

I. Aim of the task

The aim of the task is assignation of the conductometric titration curves for different systems and the quantitative analysis of the obtained samples.

II. Introduction

1. Specific and molar conductivity, concentration dependence.
2. Methods for conductivity determination.
3. Application of the conductivity measurements of the electrolyte solutions for the determination of different physicochemical quantities.
4. Conductometric titration:
   - strong acid – strong base,
   - strong acid – weak base,
   - weak acid – strong base,
   - weak acid – weak base,
   - mixture of a strong acid and a weak acid - strong base or a weak base,
   - displacement (or replacement) titrations,
   - precipitation titration and complex formation titration.

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3. H. Kuhn, H-D. Försterling, D.H. Waldeck, *Principles of Physical Chemistry*, 2nd edition, Wiley, 2009, Chapter 23.
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III. Theory

III. 1. Conductometry

The ability for electricity through a body is called its **conductance**. In metallic conductors it is caused by the movement of electrons, while in electrolytic solutions it is caused by ions of electrolyte. The electrolytic conductance, G, of a medium is equal to the reciprocal of its electrical resistance R in ohms:

$$G = \frac{1}{R} \tag{1}$$

Since a solution is a three-dimensional conductor, the exact resistance will depend on the spacing l and area A of the electrodes. The resistance of the solution in such situation is directly proportional to the distance between the electrodes and inversely proportional to the electrode surface area. If we consider the electrolytic shell with two electrodes having a cross-sectional area of A [m^2] and separated by l [m] then the resistance R of the electrolyte solution present between the electrodes is:

$$R = \rho \frac{l}{A} \tag{2}$$

where ρ is the proportionality constant called specific resistivity. It is a characteristic property of material and it is the resistance demonstrated by a conductor of unit length and unit area of cross section.
Substituting the value of R from Eq. (2) in Eq. (1), the expression for the conductance, G, is:

$$G = \frac{1}{\rho(A/l)} = \kappa \frac{A}{l} \tag{3}$$

where κ is the reciprocal of specific resistance called **specific conductance** or **conductivity**. It is measured in [Ω^{-1}m^{-1}]. However, in the SI system, the unit of conductance is "Siemens", S, hence the unit for conductivity will be [S m^{-1}] (1S = 1 Ω^{-1}). It should be remembered that S m^{-1} = 1/100 S cm^{-1}.

In order to compare quantitatively the conductivities of electrolytes, a quantity called molar conductivity is frequently used. The **molar conductivity**, Λ_m, is the conductivity per unit molar concentration of a dissolved electrolyte. It is connected with conductivity, κ, by the relation:

$$\Lambda_m = \frac{\kappa}{c} \tag{4}$$

where c is the concentration in [mol m^{-3}]. The molar conductivity is usually expressed in [S m^2 mol^{-1}] or [S cm^2 mol^{-1}].

The conductivity of an ionic solution increases with the increasing concentration. For strong electrolytes, the increase of conductivity with the increase of concentration is sharp. However, for weak electrolytes, the increase of conductivity is more gradual. In both cases the increase in conductivity with concentration is due to the increase in the number of ions per unit volume of solution. For strong electrolytes, which are completely ionised, the increase in conductivity is almost proportional to the square root of the concentration.

III. 2. Application of conductometry

The experimental determinations of the conducting properties of electrolytic solutions are very important as they can be used to study quantitative behaviour of ions in solution. They can be also used to determine many physical quantities such as degree of dissociation and dissociation constants of weak acids and bases, ionic product of water, solubility and solubility products of sparingly soluble salts and to form the basis for conductometric titration methods. It will be discussed in detail in the next section.

III. 2.1. Degree of dissociation of weak electrolyte and its dissociation constant

Ostwald derived a relationship between the molar conductivity (Λ_m) and the limiting molar conductivity (Λ^∞). The molar conductivity of weak electrolyte can be expressed as the product of degree of dissociation of the electrolyte (α) and its limiting molar conductivity:

$$\Lambda_m = \alpha\Lambda^\infty \tag{5}$$

This relationship is known as the Ostwald relation. Substituting Eq. (5) in the Ostwald's dilution law which has the form:

$$K = \frac{\alpha^2 c}{(1-\alpha)} \tag{6}$$

(K is a dissociation constant) gives:

$$K = \frac{(\Lambda_m / \Lambda^\infty)^2 c}{1-(\Lambda_m / \Lambda^\infty)} \tag{7}$$

Rearrangement of Eq. (7) gives:

$$\Lambda_m c = K\left[\frac{(\Lambda^\infty)^2}{\Lambda_m}\right] - K\Lambda^\infty \tag{8}$$

When we plot $\Lambda_m c$ against $1/\Lambda_m$, we will get a linear relation with the slope equal to $K(\Lambda^\infty)^2$. Therefore, K can be determined provided Λ^∞ is known. Thus, we can use this method for the determination of K of weak acids and bases.

III. 2.2. Ionic product of water

The ionic product of water (K_w) can be determined from conductivity measurements and the following equation:

$$K_w = a_{H_3O^+} a_{OH^-} \cong \left(\frac{\kappa_{H_2O}}{\Lambda^\infty_{H_3O^+} + \Lambda^\infty_{OH^-}} \right)^2 \qquad (9)$$

where $a_{H_3O^+}$ and a_{OH^-} are the activities of the hydronium ion and hydroxyl ion, respectively.

III. 2.3. Solubility and solubility product of sparingly soluble salt

The conductivity of a saturated solution of a sparingly soluble salt can be determined by subtracting the measured conductivity of the pure solvent from the measured conductivity of the saturated solution, i.e.

$$\kappa_{salt} = \kappa_{solution} - \kappa_{solvent} \qquad (10)$$

The molar conductivity of the salt in saturated solution is given by

$$\Lambda_{salt} = \kappa_{salt} / c \qquad (11)$$

Since the salt is sparingly soluble, its solution can be considered to be infinitely dilute and we can replace molar conductivity with limited molar conductivity of the salt. That is:

$$\Lambda_{salt} = \Lambda^\infty_{salt} = \Lambda^\infty_+ + \Lambda^\infty_- \qquad (12)$$

thus,

$$c = \frac{\kappa_{salt}}{\Lambda^\infty_+ + \Lambda^\infty_-} \qquad (13)$$

The limiting ionic conductivities can be obtained from the literature, the solubility *c* of a sparingly soluble salt can therefore be determined from conductivity values.

III. 2.4. Conductometric titration

The principle of **conductometric titration** is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point can be located graphically by plotting the changes of conductance as a function of the volume of the added titrant.

The most important advantages of this method are that it can be used for determination of:

- turbid and highly coloured solutions,
- very dilute solutions,
- reaction which is not complete and where there is no suitable indicator, e.g. reaction between weak acid and weak base.

Precaution to be considered in conductometric titrations:

1. Upon carrying on titration the titrant used should be at least 10 times concentrated as the solution to be determined, e.g. on determination of 0.01 M hydrochloric acid the titrant sodium hydroxide should be at least 0.1 M. By this way dilution that

takes place during titration is minimum and this is necessary because conductivity decreases with dilution.

2. Avoid the presence of ions which will not take part in the reaction, such as the presence of buffer or concentrated acids. These ions will increase the initial conductivity and its change during the titration will be comparatively small and can not be accurately observed.
3. The method is suitable for detection of end point in neutralization, complexation and precipitation reactions but not redox reaction, as there is no electron transfer at the electrode surface.

Some typical conductometric titration curves are:

1. Strong Acid with a Strong Base, e.g. HCl with NaOH

Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance decreases due to the replacement of hydrogen ions by the added cation as H^+ ions react with OH^- ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the high conductivity of OH^- ions (Fig. 1).

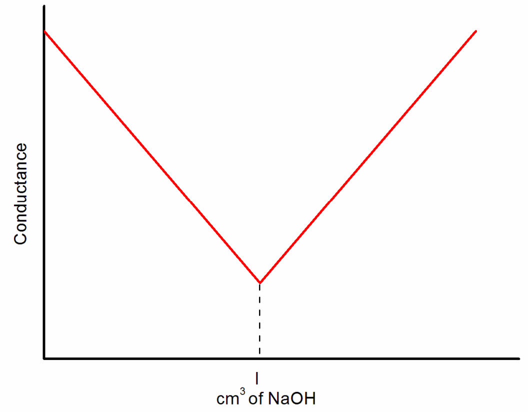

Fig. 1. Conductometric titration of strong acid (HCl) vs. strong base (NaOH).

2. Strong Acid with a Weak Base, e.g. HCl with dilute ammonia

Initially the conductance is high and then it decreases due to the replacement of H^+. But after the endpoint has been reached, the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium chloride (Fig. 2).

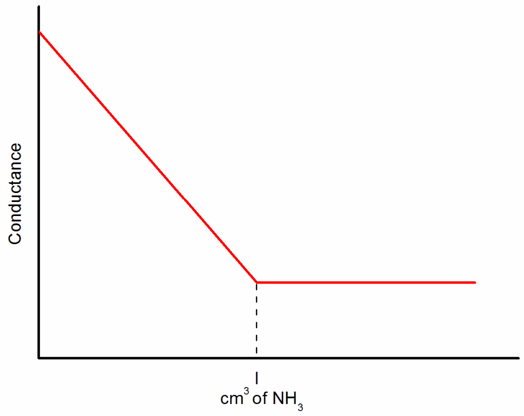

Fig. 2. Conductometric titration of strong acid (HCl) vs. weak base (NH_4OH).

3. Weak Acid with a Strong Base: e.g. CH_3COOH with NaOH

Initially a slight decrease in the conductance is caused by binding a small amount of hydrogen ions, originating from dissociation of acetic acid, into water molecules. Next, the gradual conductance increase is connected with the substitution of the weakly dissociated acetic acid by the well dissociated sodium acetate. After the equivalence point has been reached, the conductance increases significantly due to the increasing concentration of OH^- ions (Fig. 3).

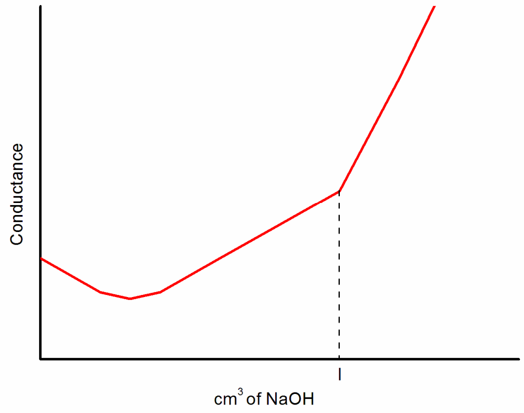

Fig. 3. Conductometric titration of weak acid (CH_3COOH) vs. strong base (NaOH).

4. Weak Acid with a Weak Base: e.g. CH_3COOH with dilute ammonia

Initially a slight decrease in the conductance is caused by binding a small amount of hydrogen ions originating from dissociation of acetic acid and next an increase is observed because of well dissociated salt - ammonium acetate formation. After the equivalence point the conductance increases but much less (Fig. 4).

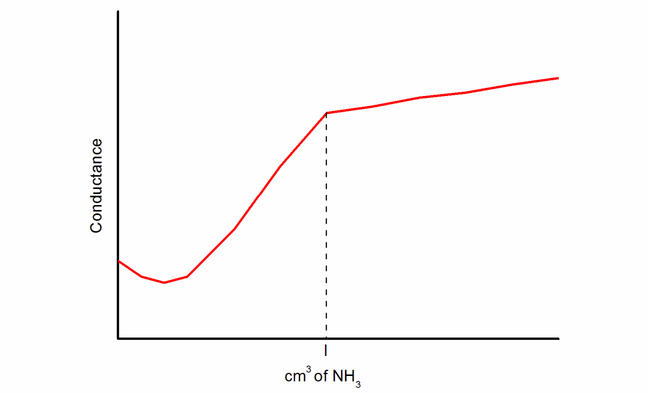

Fig. 4. Conductometric titration of weak acid (CH_3COOH) vs. weak base (NH_4OH).

5. Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base

In this curve there are two break points (Fig. 5). The first break point corresponds to the neutralization of strong acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing. The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of OH^- ions in the case of a strong base as the titrant. However, when the titrant is a weak base, it remains almost constant after the end point similar to that in Fig. 4.

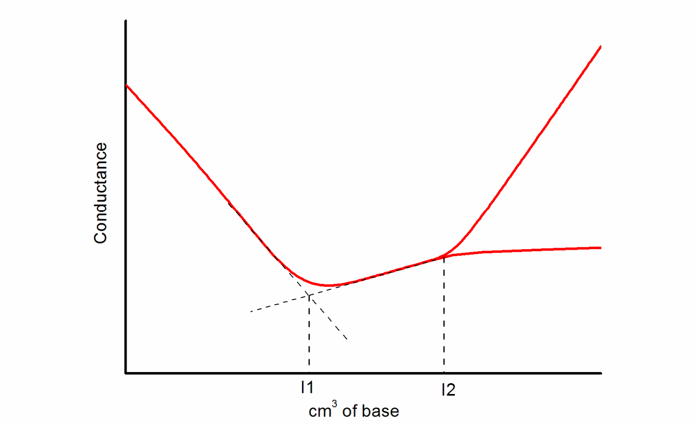

Fig. 5. Conductometric titration of a mixture of strong acid (HCl) and a weak acid CH_3COOH) vs. a strong base (NaOH) or a weak base (NH_4OH).

6. Displacement (or Replacement) Titrations

When a salt of a weak acid is titrated with a strong acid, the anion of the weak acid is replaced by that of the strong acid and weak acid itself is liberated in the undissociated form. Similarly, during the addition of a strong base to the salt of a weak base, the cation of the weak base is replaced by that of the stronger one and the weak base itself is generated in the undissociated form. If, for example, 1M HCl is added to 0.1M solution of sodium acetate, the curve shown in Fig. 6 is obtained, the acetate ion is replaced by the chloride ion after the end-point. The initial increase in conductivity is due to the fact that the conductivity of the chloride ion is slightly greater than that of acetate ion. Until the replacement is nearly complete, the solution contains enough amount of sodium acetate to suppress the ionization of the liberated acetic acid, thus resulting in a negligible increase in the conductivity of the solution. However, near the equivalent point, the acetic acid is sufficiently ionized to affect the conductivity and a rounded part of the curve is obtained. Beyond the equivalence point, when excess of HCl is present (ionization of acetic acid is very much suppressed), the conductivity arises rapidly. There must be taking some care when titrating a 0.1M salt of a weak acid, the dissociation constant should not be more than 5×10^{-4}, for a 0.01 M salt solution, $K < 5\times10^{-5}$ and for a 0.001M salt solution, $K < 5\times10^{-6}$, i.e., the ionization constant of the displaced acid or base divided by the original concentration of the salt must not exceed 5×10^{-3}. Fig. 5 also includes the titration of 0.01M ammonium chloride solution versus 0.1M sodium hydroxide solution. The decrease in conductivity during the displacement is caused by the displacement of ammonium ion of a grater conductivity by sodium ion of smaller conductivity.

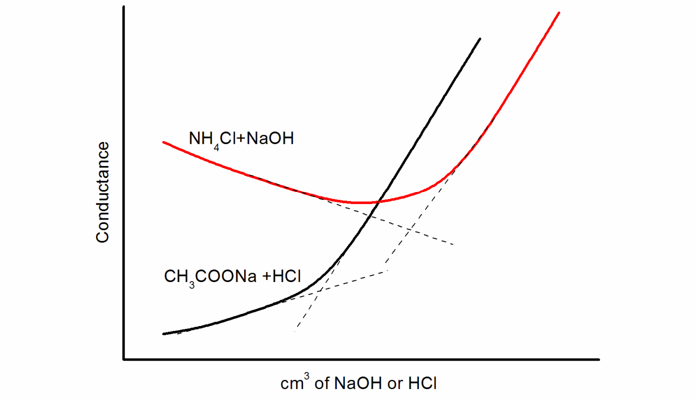

Fig. 6. Conductometric titration of a salt of weak acid (sodium acetate) vs. a strong acid (HCl); a salt of weak base (NH_4Cl) vs. a strong base (NaOH).

7. Precipitation Titration and Complex Formation Titration

A reaction can occur on the basis of a conductometric precipitation titration provided that the reaction product is sparingly soluble or is a stable complex. The solubility of the precipitate (or the dissociation of the complex) should be less than 5%. The addition of ethanol is sometimes recommended to reduce the solubility in the precipitations. An experimental curve is given in Fig. 7 (ammonium sulphate in the aqueous-ethanol solution with barium acetate). If the solubility of the precipitate were negligibly small, the conductance at the equivalence point should be given by *AB* and not the observed *AC*. The addition of excess of the reagent depresses the solubility of the precipitate and, if the solubility is not too large, the position of the point B can be determined by extrapolation of the linear sections of the two arms of the curve until they intersect (Fig. 7).

A slow rate of precipitation, particularly with micro-crystalline precipitate, prolongs the time of titration. Seeding or the addition of ethanol (concentration up to 30-40 %) can have a favourable effect. If the precipitate has pronounced adsorptive properties, the composition of the precipitate will not be constant, and appreciable errors may result. Occlusion may take place with micro crystalline precipitates.

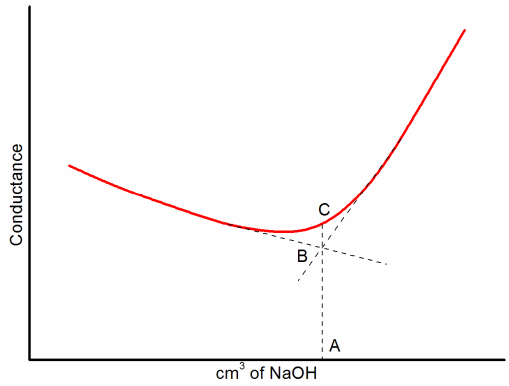

Fig. 7. Precipitation titration. Conductometric titration of $(NH_4)_2SO_4$ vs. barium acetate.

IV. Experimental

A. Devices and materials

1. **Device:** digital conductivity meter N5711.
2. **Equipment:**
   - probe,
   - magnetic stirrer,
   - burette – 10 cm^3,
   - graduated pipette: 10 and 25 cm^3,
   - beaker – 100 cm^3,
   - wash bottle
3. **Materials:**
   - 0.1M NaOH,
   - 0.1M HCl,
   - 0.1M CH_3COOH,
   - 0.1M NH_4OH,
   - 0.1M $C_2O_4H_2$.

B. Turning on the conductivity meter

Plug in the conductivity meter into the electric network and next turn it on by using a button on/off.

C. Conductometric titration of the studied systems

Perform the conductometric titration of the following systems:

- titration of HCl vs. NaOH,
- titration of CH_3COOH vs. NaOH,
- titration of CH_3COOH vs. NH_4OH,
- titration of $C_2O_4H_2$ vs. NH_4OH,
- titration of a mixture of HCl and CH_3COOH vs. NaOH.

Dilute the sample of the solution, given by the person commissioning the tasks, with the distilled water to the suitable volume, dependent on the capacity of the dish. Set the probe with the stir on the magnetic stirrer and turn on the stirrer with the suitable rotation.

Measure the conductivity with the temperature compensation - rinse and dry the probe and dip the temperature sensor in the solution in such a way that the distance of the electrode from the dish wall is larger than 2 cm. Prior to the measurements the sensor should be dipped in the solution for a few minutes. Next, turn on the button “cond”. Wait for the stabilization of the value on the left side of the conductivity meter and read the result. The obtained result is the conductivity of the solution at a given temperature.

Fill the burette with the titrant. Add the titrant to the studied solution in small portions (0.5 cm^3). After adding each portion of the titrant wait a while and next read the conductivity value. After the end point of the titration make the measurement up to significant changes in the conductivity. After the measurements the dish and the probe should be washed with distilled water.

D. Presentation of the obtained results

Place the obtain results in Table 1.

Table 1. Conductometric titration.

HCl/NaOH		CH_3COOH/NaOH		$C_2O_4H_2/NH_4OH$		$HCl+CH_3COOH$ /NaOH	
V [cm^3]	R^{-1} [mS]	V [cm^3]	R^{-1} [mS]	V [cm^3]	R^{-1} [mS]	V [cm^3]	R^{-1} [mS]
0							
0.5							
1.0							
1.5							
…							

1. Plot a relationship between the obtained conductivity vs. the volume of the added titrant, $R^{-1} = f(V)$.
2. Determine the amount of the titrated substance on the basis of the equivalence point of a given titration.