

## Practical Lesson No 4

### TITRATIONS

#### Reagents:

1. NaOH standard solution	0.1 mol/l
2. H <sub>2</sub> SO <sub>4</sub>	solution of unknown concentration
3. Phenolphthalein	
4. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> standard solution	0.1 mol/l
5. Starch solution	6 g/l
6. Solutio Lugoli	13 g I <sub>2</sub> in KI 25 g/l

#### ***Theory of titrations***

In general, chemistry often analyses unknown samples to answer two questions: *what substances* are present and *what is their amount*. There are therefore two parts of analytical chemistry: the qualitative and the quantitative analysis. As analytical methods for inorganic substances differ from those for the organic ones, there are two kinds of analytical chemistry: the inorganic and the organic analytical chemistry.

In this lesson we present some examples of the quantitative analysis of inorganic substances.

An important method for determination of the amount of a particular substance is based on measuring volumes of reactant solutions. The method is called a titration, and can be defined as a **procedure for determining the amount of substance A by adding a carefully measured volume of a solution with known concentration of substance B until the reaction of substance A with the substance B is just complete**. To make the course of the reaction visible, it is necessary to add another substance called an indicator. An indicator is a substance that undergoes a colour change when the reaction approaches completion, i.e. at the equivalence point.

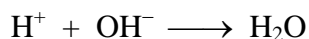
The titration analysis can be based on various sorts of chemical reactions, from which we give three examples here:

#### A. Neutralisation reaction

When an acid is mixed with an alkali (base), neutralisation reaction occurs, e.g.:



In ionic terms:



An acid-base titration is a special kind of titration, used for measuring the amount of acid (or base) in a solution by determining the volume of base (or acid) of known concentration (titrant, titration reagent, standard solution) that will completely neutralise it.

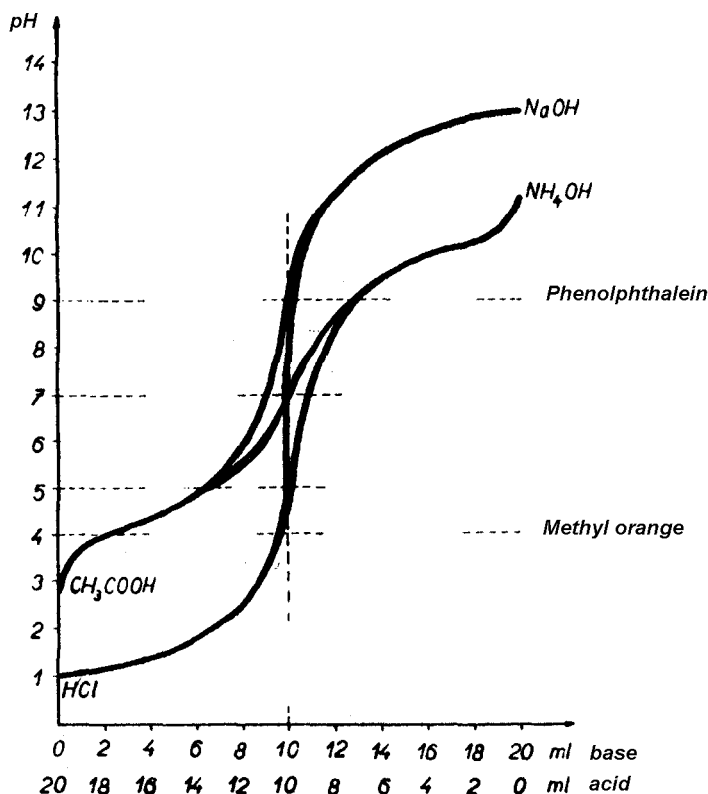


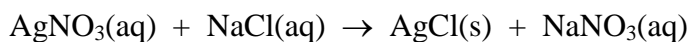
Fig 1. Acid-base titration curves: To a certain amount of weak ( $\text{CH}_3\text{COOH}$ ), or strong ( $\text{HCl}$ ) acid, small amounts of weak ( $\text{NH}_4\text{OH}$ ) or strong ( $\text{NaOH}$ ) alkali were added and pH was measured after each addition. Note the sharp increase in pH at the equivalence point, where all the acid has been just consumed for the neutralisation reaction with the added base. The differences in the curve shapes between weak and strong acids/bases, respectively, will be discussed later, in conjunction with principle of pH buffering.

pH can be measured during the course of an acid-base titration; the resulting plot of pH against the volume of alkali (or acid) added to the original sample of acid (or alkali) is called an acid-base titration curve (Fig 1). Such curves can be used to gain insight into the titration process. Usually, however, the equivalence point is more conveniently visualised using a suitable acid-base indicator. Acid-base indicators are organic dyes that change colour with pH (in other words, the spectral properties of the dye depend on its protonation). Two examples of these substances are:

Indicator	Colour at lower pH	pH range for colour change	Colour at higher pH
Methyl orange	red	3.0 – 4.4	yellow
Phenolphthalein	colourless	8.2 – 10.0	pink

## B. Precipitation reaction

Certain combinations of aqueous cations and anions produce insoluble products (precipitates), e.g.:



This reaction can be employed for quantification of chloride ions in unknown solution by means of titration with silver nitrate solution of known concentration. This technique, called argentometry, uses chromate  $\text{K}_2\text{CrO}_4$  as an indicator. Chromate forms also an insoluble salt with Ag. How, then, can it be used as an indicator? Simply stated,  $\text{AgCl}$  is less soluble than  $\text{Ag}_2\text{CrO}_4$ . Initially the  $\text{Ag}^+$  ions (the titrant) enter the solution where there is an excess of chloride ions, and all the silver ions are being consumed for formation of the white precipitate of  $\text{AgCl}$ . When the equivalence point is reached, the  $\text{Cl}^-$  ions are no longer available, and the  $\text{Ag}^+$  concentration is allowed to rise to the point where the red-brown insoluble  $\text{Ag}_2\text{CrO}_4$  appears.

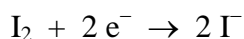
The argentometry can be used for determination of halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ), mercaptans (thioalcohols), fatty acids and several divalent anions.

Another similar approach is called mercurimetry. In this case the titrating reagent contains mercury(II) ions that react with chloride in the sample to produce soluble but non-dissociated mercury(II) chloride,  $\text{HgCl}_2$ . The indicator in this case is sodium nitroprusside  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ . The appearance of free  $\text{Hg}^{2+}$  ions at the point of equivalence results in formation of white precipitate of mercury(II) nitroprusside.

## C. Oxidation-reduction reaction

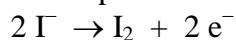
Oxidation means loss of electron(s) and reduction means gain of electron(s); reactions where a transfer of electrons is involved are thus called oxidation-reduction (redox) reactions. In addition to neutralisation (acid-base) and precipitation reactions, the redox processes can be utilised in quantitative titrimetric chemical analysis. Iodometry is one example; encompasses a wide range of methods for determination of substances that either reduce iodine to iodide anion (and are themselves oxidised by iodine) or oxidise iodide to iodine (and themselves are reduced). The reaction  $\text{I}_2 + 2 \text{e}^- \rightleftharpoons 2 \text{I}^-$  is fully reversible and its direction depends on the reducing or oxidising power of the other (estimated) substance, and also on the pH of the solution. Redox iodometric methods are divided into two groups:

1. Determination of substances with reducing power, able to be oxidised by iodine. Iodine is consumed in the reaction since it is reduced to iodide:



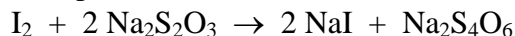
This can be used for estimation of thiosulphate, sulphite, formaldehyde etc. Although it is possible to titrate the sample directly with the solution of iodine (direct iodometry), more convenient is to add known excess of iodine and then titrate the remaining (non-consumed) iodine with thiosulphate (back-titration).

2. Determination of substances with oxidising power, which at pH below 7 and excess of iodide produce stoichiometric amount of iodine, and are themselves reduced:



The released iodine is titrated with thiosulphate (indirect iodometry). This approach is suitable for estimation of  $\text{Cl}_2$ ,  $\text{Br}_2$ , iodates, hydrogen peroxide, ethanol in blood etc.

The final step is the same in both cases: titration of iodine with sodium thiosulphate:



(At neutral or slightly acidic pH iodine  $\text{I}_2$ , or better  $\text{I}_3^-$ , oxidises thiosulphate to tetrathionate). Although iodine has red-brown colour and its presence in the solution could be followed directly, for greater accuracy an indicator is used. The indicator in iodometry is starch that forms a blue complex with iodine.

### **Titration calculations**

Regardless of the type of reaction used in the titration experiment, the subsequent calculation is based on the known stoichiometry with which the titrated substance (unknown) reacts with the titrant. Although it can be accomplished in several ways, usage of the following simple formula is recommended:

$$\mathbf{c_1 \cdot v_1 = c_2 \cdot v_2}$$

where  $c_1$  ... concentration of the substance to be titrated (the unknown)

$v_1$  ... volume of the unknown sample taken for the titration

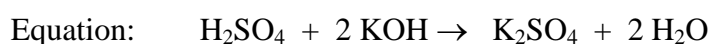
$c_2$  ... concentration of the titrant (known)

$v_2$  ... volume of the titrant solution consumed for titration until the equivalence point is reached (the actual experimental data from the titration analysis)

Obviously values of 'c' and 'v' on both sides of the equation must be in the same units. In cases where the stoichiometry of the titration reaction differs from simple 1:1 ratio, it must be taken into account in calculation as well.

#### Example of usage:

An unknown sample of sulfuric acid  $\text{H}_2\text{SO}_4$  was titrated with the known KOH solution. It was found that 12 ml of the KOH  $c = 0.1 \text{ mol/l}$  was necessary for just complete neutralisation of 10 ml of the unknown sample of  $\text{H}_2\text{SO}_4$ . What is concentration of sulfuric acid in the sample ?



Calculation:	$\text{H}_2\text{SO}_4$		$\text{KOH}$	
	$c_1 \cdot v_1$	=	$c_2 \cdot v_2$	
	$c_1$	=	$c_2 \cdot v_2 / v_1$	
		=	$0.1 \cdot 12 / 10 = 0.12$	

The concentration of  $\text{H}_2\text{SO}_4$  would be 0.12 mol/l. However, it goes from the reaction above that 2 moles of KOH are required for neutralisation of 1 mol of  $\text{H}_2\text{SO}_4$ . Therefore, the result, 0.12, must be divided by 2, giving the concentration of sulfuric acid in the unknown sample 0.06 mol/l.

## **EXPERIMENTAL**

The task is to perform two titrations:

- 1) determination of concentration of sulfuric acid by means of acid-base titration,
- 2) determination of iodine in Lugol solution by means of iodometry (redox titration)

**Do not confuse the samples, reagents and equipment (burettes) designated for each of these two experiments!**

In general, each titration is to be performed three times, first to get a rough reading, the other two for accurate determination of the equivalence point. For the calculation, the average (arithmetic mean) of the second and third readings is used.

### **1. Titrimetric estimation of molar and mass concentration of sulfuric acid**

#### **Procedure:**

- a.* Measure 10.0 ml of the unknown solution of sulfuric acid into 100 ml titration flask using a glass pipette and dilute with approximately 10 ml of distilled water. Add a few drops of phenolphthalein as the indicator.
- b.* Titrate with standard NaOH solution ( $c = 0.1 \text{ mol/l}$ ). The point of equivalence (the end of titration) occurs when the solution turns slight red-violet.
- c.* Perform the titration three times, for further calculation use arithmetic mean of the results from the second and the third runs.
- d.* Calculate the molar as well as the mass concentrations of sulfuric acid in the unknown sample.
- e.* Write a net ionic equation for the neutralisation reaction that occurs in the titration flask.

### **2. Direct iodometry: Determination of iodine in the Lugol solution**

#### **Procedure:**

- a.* Pipette 10 ml of Lugol solution into a titration flask, and add about 10 ml of distilled water.
- b.* Titrate with sodium thiosulphate standard solution ( $c = 0.1 \text{ mol/l}$ ) to faint yellow colour.
- c.* Add 2 ml of the indicator and titrate until the starch-iodine blue colour completely disappears.
- d.* Carry out three times and use the last two results for calculation.
- e.* Write an ionic equation of  $\text{I}_2$  reaction with sodium thiosulphate.
- f.* Calculate the molar as well as the mass concentration of iodine in Lugol solution.