

Titration

Introduction

General procedure used in manual titration

Before starting, make sure that all glassware, especially the burette, is clean and dry.

Accurately measure a volume of the reactant into a beaker or Erlenmeyer flask.

Add a suitable indicator to the flask.

Pour the titrant into the burette, read the start-point of the liquid on the burette.

Turn the tap of the burette to allow the titrant to slowly fall into the reactant. Swirl the flask with the other hand or with a magnetic stirrer.

The indicator should change colour as the titrant is added, but then quickly return to its original color.

As the end-point is approached, the indicator takes longer to turn back to its starting color. Add the titrant more slowly at this point (one drop at a time).

When the indicator remains at its end colour, the reaction has reached the end point.



Measure the amount of titrant liquid used, as shown on the scale of the burette.

Repeat as many trials as needed, and then average the volumes.

Once the number of moles of reactant that have been neutralised has been determined then calculate the concentration in moles per litre or other unit.

Titration is a quantitative measurement of an analyte in solution by its complete reaction without a reagent. Titration is used in analytical chemistry to determine the amount or concentration of a substance. In a titration, one reagent (the titrant) is slowly added to a solution containing the species being measured (the analyte). As it is added, a chemical reaction occurs between the titrant and analyte. The point where all analyte is consumed, and an equal quantity of titrant and analyte are present, it is called the equivalence-point. This is determined by one type of indicator that it is also present in the solution, or by a measurable physical change in the solution, like pH, electrode potential, conductivity, or light absorption (color). In practice, an abrupt change of this physical property signals the end of titration, called the endpoint.

The purpose of titration (also called volumetric analysis) is to determine the analyte quantity or concentration, the titrant concentration being known beforehand. Titrations are based on chemical reactions, and these reactions must fulfill four requirements:

- The reaction must be fast, so that after the titrant's addition, the reaction occurs within approximately one second
- The reaction must go to completion
- The reaction must have well-known stoichiometry (reaction ratios)
- A convenient method of endpoint detection must be available

In any titration, there must be a quick, quantitative reaction taking place as the titrant is added.

Manual titration is done with a burette and a long graduated tube that holds the titrant. The amount of titrant used in the titration is determined by reading the difference between the volume of titrant in the burette before the titration and when the endpoint is reached. The most important factor for making accurate titrations is to read the burette volumes repeatedly. Generally, chemists use the bottom of the meniscus (rounded liquid level) to read the reagent volume in the burette. Additional required instrumentation would be: a burette, a beaker, a pipette - to measure the sample volume, an indicator solution and the (standardized) titrant.



Automatic Titration

Automatic titration is done with automatic titrators. These titrators deliver the titrant, stop at the endpoint and calculate the concentration of the analyte automatically. They are the best for repetitive titrations. A certain type of electrochemical measurement usually detects the endpoint.

Some complex analysis performed by automatic titrators are...

- Acid-base, specific ion redox determination by pH/mV measurement with potentiometric detection.
- Determination of water with Karl Fischer reagent using coulometric detection.
- Determination of chlorine in aqueous solution with phenylarsene oxide using amperometric detection.

The required equipment would be the automatic titrator, the (standardized) titrant, a titrant reservoir, a pipette (to measure the sample volume), a beaker, and possibly a magnetic stir-bar for stirring.

The automatic titrator must have an accurate liquid dispensing system. In high accuracy systems, this is typically a stepper motor driven piston burette, a valve system to switch between titrant inlet and outlet, and a titration tip to dispense the titrant into the sample solution. These three main subsystems must be as accurate as possible, with very low gear backlash in the burette drive mechanism, low piston seal flexing, accurate burette glass cylinder diameter, low dead volume in the valve, evaporation/permeation and chemically resistant tubing and an anti-diffusion titrant dispensing tip.



In 1855, the German chemist, Friedrich Mohr, defined titration as the "weighing without scale" method, because this process allows determination of the concentration of a sample without using complex instrumentation.

A manual titration requires high accuracy and precision, both in the preparation of the material, and the use of precisely dosed reagents. The operation must be repeated at least 3 times to obtain a reliable measured value. This procedure makes the manual analytical technique very long and fastidious; however, the infinite applications that titration presents, can't be neglected for both organic and inorganic parameters. In some applications, for example, in the food industry, the determination of the content of sulphur dioxide in must and wine and the level of acidity in cheese are still determined manually using the Soxhlet method.

The growing need for faster results has lead HANNA to develop the HI 901 and HI 902C titrators, two instruments that permit the automation of the titration procedures, while providing quick and reliable data.

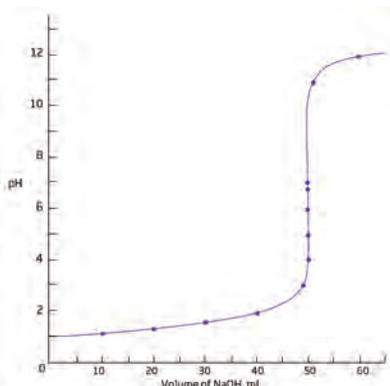
Standards and Standardization

One of the substances involved in a titration must be used as a standard for which the amount of substance is present is accurately known. The standard can be present either in the form of a pure substance or as a standard solution, a solution whose composition is accurately known. The titrant solution can be standardized in two ways; using a primary standard, or more commonly, titrating it against a previously standardized solution.

Type of Titrations

Acid-base titrations This is the most common type of titration - an acid-base reaction (simply exchange of protons). On the following table and graph you can see the variation of pH during the titration of a solution of 0.1 M HCl with one solution of NaOH 0.1 M

Volume of NaOH, mL	pH
0.00	1.00
10.00	1.18
20.00	1.37
30.00	1.60
40.00	1.95
49.00	3.00
49.90	4.00
49.99	5.00
50.00	7.00
50.01	9.00
50.10	10.00
51.00	11.00
60.00	11.96



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Potentiometric titrations are those where the potential from an electrode system is used as the analytical signal for the change occurring during the titration. Examples include pH electrodes used for acid-base titrations, ORP electrodes (platinum) used in a redox titration, ion selective electrodes used in a specific ion titration, and silver electrodes used to follow the silver ion concentration in argentometric titrations.

Precipitation titrations

Complexometric titrations In a complexometric titration metal ions are titrated using a titrant that binds strongly to the metal ions.

Amperometric titrations

Spectrophotometric titrations

Back-titrations In this type of titration, a large excess of a reagent is added to the sample solution, helping a slow reaction to go to completion; the unreacted excess reagent is then titrated.

Multiple endpoints titrations

Instrumental End-point Determination

Karl Fischer titrations (KFT) (HI 903) KFT use the Karl Fischer reaction between water, iodine and sulfur dioxide. There are 2 types of Karl Fischer titrations: coulometric and volumetric. In the volumetric KFT, methanol solvent is pretitrated to the dryness endpoint, sample is added, and the water in the sample solution that is titrated. The titrant contains iodine and SO₂. The CH₃OH solvent and SO₂ react to form (CH₃SO₃)⁻ that reacts in the Karl Fischer reaction with water:



Were RN = base

In the coulometric KFT, the sample is added to a special reagent solution that contains CH₃OH solvent, SO₂ and iodide. During the titration, iodine (the active titrant) is generated electrochemically

in-situ from iodide, by passing electricity across two platinum electrodes immersed in the reagents solution. A separate dual-platinum indicator electrode monitors the end-point, just as in the volumetric KFT. The quantity of passed electricity is measured and it is used to calculate the quantity of water that was present in sample.

The fundamental calculation for all titrations is based on:

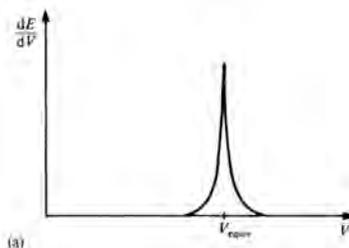
$$C_1V_1 = C_2V_2 \text{ or } N_1V_1 = N_2V_2 \text{ or } C_1V_1E_1 = C_2V_2E_2$$

Where C is the concentration in moles/liter, V is volume in liters or mL, N is the concentration in normality in equivalents. Liter, and E is the equivalents/mole factor for the analyte and titrant.

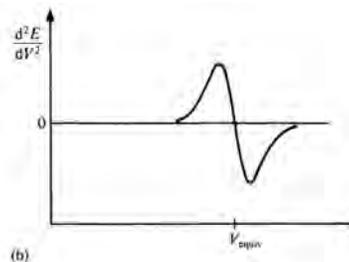
$$C_{\text{sample}} = C_{\text{titrant}} V_{\text{titrant}} / V_{\text{sample}}$$

This equation is the most basic form used for calculating the result of a titration. As will be shown in following illustrations, there are modifications to this basic equation necessary for obtaining results in other certain situations.

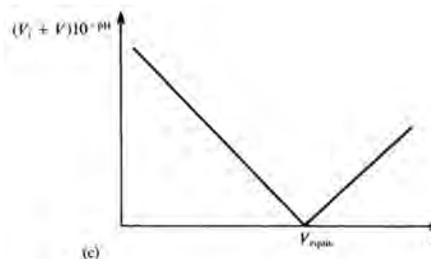
Methods for determining the equivalence point of a potentiometric titration curve (including acid-base titrations):



The first derivative (a); the equivalence point corresponds to the top of the peak.



The second derivative (b); the equivalence point is where the curve crosses the V-axis.



The Gran plot (c); this method consists of the mathematical transformation of the titration curve into straight lines via rearranged Nernst equations (titration of a strong acid with a strong base; V₁ is the initial volume of acid and V the volume of base added)

