

Chapter 13

Titration in Analytical Chemistry

Titrations in Analytical Chemistry

- Titration methods are based on determining the quantity of a reagent of known concentration that is required to react completely with the analyte.
- The reagent may be a standard solution of a chemical or an electric current of known magnitude.
- **Volumetric titrations** involve measuring the volume of a solution of known concentration that is needed to react completely with the analyte.
- In **Gravimetric titrations**, the mass of the reagent is measured instead of its volume.
- In **Coulometric titrations**, the “reagent” is a constant direct electrical current of known magnitude that consumes the analyte. For this titration, the time required (and thus the total charge) to complete the electrochemical reaction is measured (see Section 22D-5).
- This chapter provides introductory material that applies to all the different types of titrations

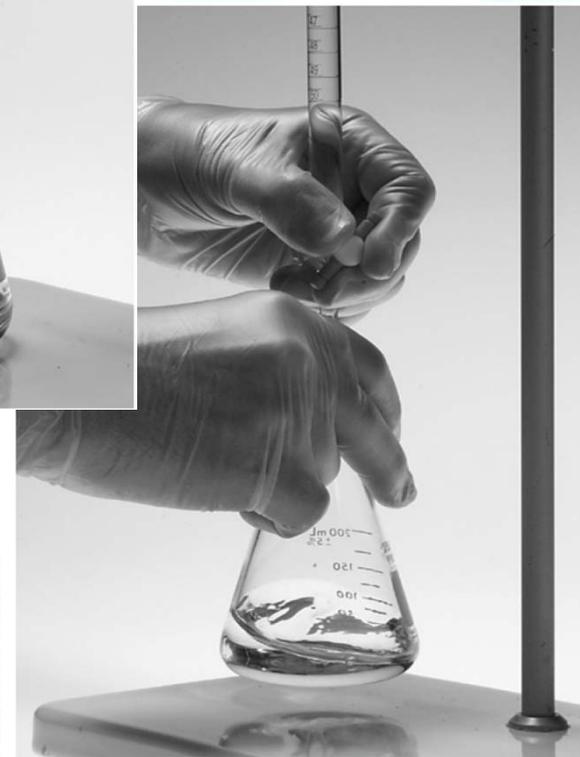


Typical setup for carrying out a titration

The reference point on the meniscus and the proper position of the eye for reading are depicted in Figure 2-21.



Before the titration begins indicator should be added.



The titrant is added to the flask with swirling until the color of the indicator persists

13A SOME TERMS USED IN VOLUMETRIC TITRATIONS

A **standard solution** (or a standard titrant) is a reagent of known concentration that is used to carry out a volumetric titration.

The **titration** is performed by slowly adding a standard solution from a buret or other liquid-dispensing device to a solution of the analyte until the reaction between the two is judged complete.

The volume or mass of reagent needed to complete the titration is determined from the difference between the initial and final readings.

It is sometimes necessary to add an excess of the standard titrant and then determine the excess amount by **back-titration** with a second standard titrant.

Back-titrations are often required when the rate of reaction between the analyte and reagent is slow or when the standard solution lacks stability.

13A-1 Equivalence Points and End Points

- The equivalence point is the point in a titration when the amount of added standard reagent is equivalent to the amount of analyte.
- The equivalence point of a titration cannot be determined experimentally.
- It can only be estimated by observing some physical change associated with the condition of chemical equivalence called the end point for the titration.
- Indicators are often added to the analyte solution to produce an observable physical change (signaling the end point) at or near the equivalence point.
- The difference in volume or mass between the equivalence point and the end point is the titration error.

The titration error is given as: $E_t = V_{ep} - V_{eq}$

Where

V_{ep} is the actual volume of reagent required to reach the End Point

V_{eq} is the theoretical volume necessary to reach the equivalence point.



Charles D. Winters

13A-2 Primary Standards

A primary standard is an ultrapure compound that serves as the reference material for a titration or for another type of quantitative analysis.

A primary standard must fulfill the following requirements:

1. High purity.
2. Atmospheric stability.
3. Modest cost.
4. Absence of hydrate water so that the composition of the solid does not change with variations in humidity.
5. Reasonable solubility in the titration medium.
6. Reasonably large molar mass so that the relative error associated with weighing the standard is minimized.

* Very few compounds meet or even approach these criteria, and only a limited number of primary-standard substances are available commercially. As a consequence, less pure compounds must sometimes be used in place of a primary standard. The purity of such a **secondary standard must be established by careful analysis.**

* A **secondary standard** is a compound whose purity has been determined by chemical analysis. The secondary standard serves as the working standard material for titrations and for many other analyses.

13 B STANDARD SOLUTIONS

The ideal standard solution for a titrimetric method will:

1. be sufficiently stable so that it is necessary to determine its concentration only once;
2. react rapidly with the analyte so that the time required between additions of reagent is minimized;
3. react more or less completely with the analyte so that satisfactory end points are realized;
4. undergo a selective reaction with the analyte that can be described by a balanced equation.

The accuracy of a titration depends on the accuracy of the concentration of the standard solution used. Two basic methods that are used to establish the concentration are:

1. Direct method
2. Standardization

The direct method is a method in which a carefully determined mass of a primary standard is dissolved in a suitable solvent and diluted to a known volume in a volumetric flask.

The second is by standardization in which the titrant to be standardized is used to titrate

- (1) a known mass of a primary standard,
- (2) a known mass of a secondary standard, or
- (3) a measured volume of another standard solution

13 C Volumetric calculations

- The concentration of solutions may be expressed in several ways. For standard solutions, either molar concentration, c , or normal concentration, c_N , is used.
- Molar concentration is the number of moles of reagent contained in one liter of solution, and normal concentration is the number of equivalents of reagent in the same volume.

13C-1 Some Useful Relationships

For the chemical species A, we can write

$$\text{amount A (mol)} = \text{mass A (g)} / \text{molar mass A (g/mol)}$$

$$\text{amount A (mmol)} = \text{mass A (g)} / \text{millimolar mass A (g/mmol)}$$

$$\text{Amount A (mol)} = V(\text{L}) \times c_A (\text{mol A/L})$$

$$\text{amount A (mmol)} = V (\text{mL}) \times c_A (\text{mmol A/L})$$

13C-2 Calculating the Molar Concentration of Standard Solutions

EXAMPLE 13-1

Describe the preparation of 2.000 L of 0.0500 M AgNO_3 (169.87 g/mol) from the primary-standard-grade solid.

Solution

$$\begin{aligned}\text{amount AgNO}_3 &= V_{\text{soln}}(\text{L}) \times c_{\text{AgNO}_3}(\text{mol/L}) \\ &= 2.00 \text{ L} \times \frac{0.0500 \text{ mol AgNO}_3}{\text{L}} = 0.100 \text{ mol AgNO}_3\end{aligned}$$

To obtain the mass of AgNO_3 , we rearrange Equation 13-2 to give

$$\begin{aligned}\text{mass AgNO}_3 &= 0.1000 \text{ mol AgNO}_3 \times \frac{169.87 \text{ g AgNO}_3}{\text{mol AgNO}_3} \\ &= 16.987 \text{ g AgNO}_3\end{aligned}$$

Therefore, the solution should be prepared by dissolving 16.987 g of AgNO_3 in water and diluting to the mark in a 2.000 L volumetric flask.

EXAMPLE 13-2

A standard 0.0100 M solution of Na^+ is required to calibrate an ion-selective electrode method to determine sodium. Describe how 500 mL of this solution can be prepared from primary standard Na_2CO_3 (105.99 g/mol).

Solution

We wish to compute the mass of reagent required to produce a species concentration of 0.0100 M. In this instance, we will use millimoles since the volume is in milliliters. Because Na_2CO_3 dissociates to give two Na^+ ions, we can write that the number of millimoles of Na_2CO_3 needed is

$$\begin{aligned}\text{amount Na}_2\text{CO}_3 &= 500 \text{ mL} \times \frac{0.0100 \text{ mmol Na}^+}{\text{mL}} \times \frac{1 \text{ mmol Na}_2\text{CO}_3}{2 \text{ mmol Na}^+} \\ &= 2.50 \text{ mmol}\end{aligned}$$

From the definition of millimole, we write

$$\begin{aligned}\text{mass Na}_2\text{CO}_3 &= 2.50 \text{ mmol Na}_2\text{CO}_3 \times 105.99 \frac{\text{mg Na}_2\text{CO}_3}{\text{mmol Na}_2\text{CO}_3} \\ &= 264.975 \text{ mg Na}_2\text{CO}_3\end{aligned}$$

Since there are 1000 mg/g, or 0.001 g/mg, the solution should be prepared by dissolving 0.265 g of Na_2CO_3 in water and diluting to 500 mL.

EXAMPLE 13-3

How would you prepare 50.0-mL portions of standard solutions that are 0.00500 M, 0.00200 M, and 0.00100 M in Na^+ from the solution in Example 13-2?

Solution

The number of millimoles of Na^+ taken from the concentrated solution must equal the number in the dilute solutions. Thus,

$$\text{amount Na}^+ \text{ from concd soln} = \text{amount Na}^+ \text{ in dil soln}$$

Recall that the number of millimoles is equal to the number of millimoles per milliliter times the number of milliliters, that is,

$$V_{\text{concd}} \times c_{\text{concd}} = V_{\text{dil}} \times c_{\text{dil}}$$

where V_{concd} and V_{dil} are the volumes in milliliters of the concentrated and diluted solutions, respectively, and c_{concd} and c_{dil} are their molar Na^+ concentrations. For the 0.00500-M solution, this equation can be rearranged to

$$V_{\text{concd}} = \frac{V_{\text{dil}} \times c_{\text{dil}}}{c_{\text{concd}}} = \frac{50.0 \text{ mL} \times 0.005 \text{ mmol Na}^+/\text{mL}}{0.0100 \text{ mmol Na}^+/\text{mL}} = 25.0 \text{ mL}$$

Therefore, to produce 50.0 mL of 0.00500 M Na^+ , 25.0 mL of the concentrated solution should be diluted to exactly 50.0 mL.

Repeat the calculation for the other two molarities to confirm that diluting 10.0 and 5.00 mL of the concentrated solution to 50.0 mL produces the desired

13C-3 Working with Titration Data

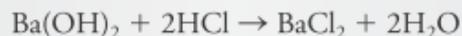
1. Concentrations of solutions that have been standardized against either a primary standard or another standard solution.
2. In the second, we calculate the amount of analyte in a sample from titration data.

Calculating Molar Concentrations from Standardization Data

A 50.00-mL portion of an HCl solution required 29.71 mL of 0.01963 M Ba(OH)₂ to reach an end point with bromocresol green indicator. Calculate the molar concentration of the HCl.

Solution

In the titration, 1 mmol of Ba(OH)₂ reacts with 2 mmol of HCl:



Thus, the stoichiometric ratio is

$$\text{stoichiometric ratio} = \frac{2 \text{ mmol HCl}}{1 \text{ mmol Ba(OH)}_2}$$

The number of millimoles of the standard is calculated by substituting into Equation 13-4:

$$\text{amount Ba(OH)}_2 = 29.71 \text{ mL Ba(OH)}_2 \times 0.01963 \frac{\text{mmol Ba(OH)}_2}{\text{mL Ba(OH)}_2}$$

To find the number of millimoles of HCl, we multiply this result by the stoichiometric ratio determined from the titration reaction:

$$\text{amount HCl} = (29.71 \times 0.01963) \text{ mmol Ba(OH)}_2 \times \frac{2 \text{ mmol HCl}}{1 \text{ mmol Ba(OH)}_2}$$

To obtain the number of millimoles of HCl per mL, we divide by the volume of the acid. Therefore,

$$(29.71 \times 0.01963 \times 2) \text{ mmol HCl}$$

EXAMPLE 13-5

Titration of 0.2121 g of pure $\text{Na}_2\text{C}_2\text{O}_4$ (134.00 g/mol) required 43.31 mL of KMnO_4 . What is the molar concentration of the KMnO_4 solution? The chemical reaction is



Solution

From this equation we see that

$$\text{stoichiometric ratio} = \frac{2 \text{ mmol KMnO}_4}{5 \text{ mmol Na}_2\text{C}_2\text{O}_4}$$

The amount of primary-standard $\text{Na}_2\text{C}_2\text{O}_4$ is given by Equation 13-2

$$\text{amount Na}_2\text{C}_2\text{O}_4 = 0.2121 \text{ g Na}_2\text{C}_2\text{O}_4 \times \frac{1 \text{ mmol Na}_2\text{C}_2\text{O}_4}{0.13400 \text{ g Na}_2\text{C}_2\text{O}_4}$$

To obtain the number of millimoles of KMnO_4 , we multiply this result by the stoichiometric ratio:

$$\text{amount KMnO}_4 = \frac{0.2121}{0.1340} \text{ mmol Na}_2\text{C}_2\text{O}_4 \times \frac{2 \text{ mmol KMnO}_4}{5 \text{ mmol Na}_2\text{C}_2\text{O}_4}$$

The concentration of KMnO_4 is then obtained by dividing by the volume consumed. Thus,

$$c_{\text{KMnO}_4} = \frac{\left(\frac{0.2121}{0.13400} \times \frac{2}{5} \right) \text{ mmol KMnO}_4}{0.04331 \text{ L}} = 0.01462 \text{ M}$$

Calculating the Quantity of Analyte from Titration Data

EXAMPLE 13-6

A 0.8040-g sample of an iron ore is dissolved in acid. The iron is then reduced to Fe^{2+} and titrated with 47.22 mL of 0.02242 M KMnO_4 solution. Calculate the results of this analysis in terms of (a) % Fe (55.847 g/mol) and (b) % Fe_3O_4 (231.54 g/mol).

Solution

The reaction of the analyte with the reagent is described by the equation



$$(a) \quad \text{stoichiometric ratio} = \frac{5 \text{ mmol Fe}^{2+}}{1 \text{ mmol KMnO}_4}$$

$$\text{amount KMnO}_4 = 47.22 \text{ mL KMnO}_4 \times \frac{0.02242 \text{ mmol KMnO}_4}{\text{mL KMnO}_4}$$

$$\text{amount Fe}^{2+} = (47.22 \times 0.02242) \text{ mmol KMnO}_4 \times \frac{5 \text{ mmol Fe}^{2+}}{1 \text{ mmol KMnO}_4}$$

The mass of Fe^{2+} is then given by

$$\text{mass Fe}^{2+} = (47.22 \times 0.02242 \times 5) \text{ mmol Fe}^{2+} \times 0.055847 \frac{\text{g Fe}^{2+}}{\text{mmol Fe}^{2+}}$$

The percent Fe^{2+} is

$$\% \text{Fe}^{2+} = \frac{(47.22 \times 0.02242 \times 5 \times 0.055847) \text{ g Fe}^{2+}}{0.8040 \text{ g sample}} \times 100\% = 36.77\%$$

(b) To determine the correct stoichiometric ratio, we note that



Therefore,



and

$$\text{stoichiometric ratio} = \frac{5 \text{ mmol Fe}_3\text{O}_4}{3 \text{ mmol KMnO}_4}$$

As in part (a),

$$\text{amount KMnO}_4 = \frac{47.22 \text{ mL KMnO}_4 \times 0.02242 \text{ mmol KMnO}_4}{\text{mL KMnO}_4}$$

$$\text{amount Fe}_3\text{O}_4 = (47.22 \times 0.02242) \text{ mmol KMnO}_4 \times \frac{5 \text{ mmol Fe}_3\text{O}_4}{3 \text{ mmol KMnO}_4}$$

$$\text{mass Fe}_3\text{O}_4 = \left(47.22 \times 0.02242 \times \frac{5}{3} \right) \text{ mmol Fe}_3\text{O}_4 \times 0.23154 \frac{\text{g Fe}_3\text{O}_4}{\text{mmol Fe}_3\text{O}_4}$$

$$\% \text{Fe}_3\text{O}_4 = \frac{\left(47.22 \times 0.02242 \times \frac{5}{3} \right) \times 0.23154 \text{ g Fe}_3\text{O}_4}{0.8040 \text{ g sample}} \times 100\% = 50.81\%$$

EXAMPLE 13-7

A 100.0-mL sample of brackish water was made ammoniacal, and the sulfide it contained was titrated with 16.47 mL of 0.02310 M AgNO_3 . The analytical reaction is



Calculate the concentration of H_2S in the water in parts per million, c_{ppm} .

Solution

At the end point,

$$\text{stoichiometric ratio} = \frac{1 \text{ mmol H}_2\text{S}}{2 \text{ mmol AgNO}_3}$$

$$\text{amount AgNO}_3 = 16.47 \text{ mL AgNO}_3 \times 0.02310 \frac{\text{mmol AgNO}_3}{\text{mL AgNO}_3}$$

$$\text{amount H}_2\text{S} = (16.47 \times 0.02310) \text{ mmol AgNO}_3 \times \frac{1 \text{ mmol H}_2\text{S}}{2 \text{ mmol AgNO}_3}$$

$$\begin{aligned} \text{mass H}_2\text{S} &= \left(16.47 \times 0.02310 \times \frac{1}{2} \right) \text{ mmol H}_2\text{S} \times 0.034081 \frac{\text{g H}_2\text{S}}{\text{mmol H}_2\text{S}} \\ &= 6.483 \times 10^{-3} \text{ g H}_2\text{S} \end{aligned}$$

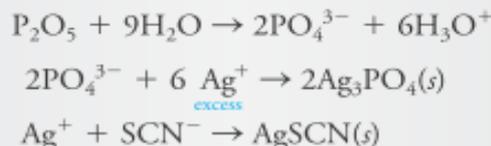
$$\begin{aligned} c_{\text{ppm}} &= \frac{6.483 \times 10^{-3} \text{ g H}_2\text{S}}{100.0 \text{ mL sample} \times 1.00 \text{ g sample/mL sample}} \times 10^6 \text{ ppm} \\ &= 64.8 \text{ ppm} \end{aligned}$$

EXAMPLE 13-8

The phosphorus in a 4.258-g sample of a plant food was converted to PO_4^{3-} and precipitated as Ag_3PO_4 by adding 50.00 mL of 0.0820 M AgNO_3 . The excess AgNO_3 was back-titrated with 4.06 mL of 0.0625 M KSCN . Express the results of this analysis in terms of % P_2O_5 .

Solution

The chemical reactions are



The stoichiometric ratios are

$$\frac{1 \text{ mmol P}_2\text{O}_5}{6 \text{ mmol AgNO}_3} \quad \text{and} \quad \frac{1 \text{ mmol KSCN}}{1 \text{ mmol AgNO}_3}$$

$$\text{total amount AgNO}_3 = 50.00 \text{ mL} \times 0.0820 \frac{\text{mmol AgNO}_3}{\text{mL}} = 4.100 \text{ mmol}$$

$$\begin{aligned}\text{amount AgNO}_3 \text{ consumed by KSCN} &= 4.06 \text{ mL} \times 0.0625 \frac{\text{mmol KSCN}}{\text{mL}} \\ &\quad \times \frac{1 \text{ mmol AgNO}_3}{\text{mmol KSCN}} \\ &= 0.2538 \text{ mmol}\end{aligned}$$

$$\begin{aligned}\text{amount P}_2\text{O}_5 &= (4.100 - 0.254) \frac{\text{mmol AgNO}_3}{6 \text{ mmol AgNO}_3} \times \frac{1 \text{ mmol P}_2\text{O}_5}{6 \text{ mmol AgNO}_3} \\ &= 0.6410 \text{ mmol P}_2\text{O}_5\end{aligned}$$

$$\% \text{P}_2\text{O}_5 = \frac{0.6410 \text{ mmol} \times \frac{0.1419 \text{ g P}_2\text{O}_5}{\text{mmol}}}{4.258 \text{ g sample}} \times 100\% = 2.14\%$$

EXAMPLE 13-9

The CO in a 20.3-L sample of gas was converted to CO₂ by passing the sample over iodine pentoxide heated to 150°C:



The iodine was distilled at this temperature and was collected in an absorber containing 8.25 mL of 0.01101 M Na₂S₂O₃.



The excess Na₂S₂O₃ was back-titrated with 2.16 mL of 0.00947 M I₂ solution. Calculate the concentration of CO (28.01 g/mol) in mg per liter of sample.

Solution

Based on the two reactions, the stoichiometric ratios are

$$\frac{5 \text{ mmol CO}}{1 \text{ mmol I}_2} \quad \text{and} \quad \frac{2 \text{ mmol Na}_2\text{S}_2\text{O}_3}{1 \text{ mmol I}_2}$$

We divide the first ratio by the second to get a third useful ratio

$$\frac{5 \text{ mmol CO}}{2 \text{ mmol Na}_2\text{S}_2\text{O}_3}$$

This relationship reveals that 5 mmol of CO are responsible for the consumption of 2 mmol of Na₂S₂O₃. The total amount of Na₂S₂O₃ is

$$\text{amount Na}_2\text{S}_2\text{O}_3 = 8.25 \text{ mL Na}_2\text{S}_2\text{O}_3 \times 0.01101 \frac{\text{mmol Na}_2\text{S}_2\text{O}_3}{\text{mL Na}_2\text{S}_2\text{O}_3}$$

The amount of $\text{Na}_2\text{S}_2\text{O}_3$ consumed in the back-titration is

$$\begin{aligned}\text{amount Na}_2\text{S}_2\text{O}_3 &= 2.16 \text{ mL I}_2 \times 0.00947 \frac{\text{mmol I}_2}{\text{mL I}_2} \times \frac{2 \text{ mmol Na}_2\text{S}_2\text{O}_3}{\text{mmol I}_2} \\ &= 0.04091 \text{ mmol Na}_2\text{S}_2\text{O}_3\end{aligned}$$

The number of millimoles of CO can then be calculated by using the third stoichiometric ratio:

$$\begin{aligned}\text{amount CO} &= (0.09083 - 0.04091) \text{ mmol Na}_2\text{S}_2\text{O}_3 \times \frac{5 \text{ mmol CO}}{2 \text{ mmol Na}_2\text{S}_2\text{O}_3} \\ &= 0.1248 \text{ mmol CO}\end{aligned}$$

$$\text{mass CO} = 0.1248 \text{ mmol CO} \times \frac{28.01 \text{ mg CO}}{\text{mmol CO}} = 3.4956 \text{ mg}$$

$$\frac{\text{mass CO}}{\text{vol sample}} = \frac{3.4956 \text{ mg CO}}{20.3 \text{ L sample}} = 0.172 \frac{\text{mg CO}}{\text{L sample}}$$

13D GRAVIMETRIC TITRATIONS

- Mass (weight) or gravimetric titrations differ from their volumetric counterparts in that the mass of titrant is measured rather than the volume.
- Therefore, in a mass titration, a balance and a weighable solution dispenser are substituted for a buret and its markings.

13D-1 Calculations Associated with Mass Titrations

Concentration for mass titrations is expressed as the weight concentration, c_w , in weight molar concentration units, M_w , which is the number of moles of a reagent in one kilogram of solution or the number of millimoles in one gram of solution.

$$C_w = \frac{\text{no. mol A}}{\text{no. kg soln}} = \frac{\text{no. mmol A}}{\text{no. g soln}} \quad C_w (A) = \frac{n_A}{m_{\text{soln}}}$$

Where:

n_A is the number of moles of species A and
 m_{soln} is the mass of the solution.

13D-2 Advantages of Gravimetric Titrations

In addition to greater speed and convenience, mass titrations offer certain other advantages over their volumetric counterparts:

1. Calibration of glassware and tedious cleaning to ensure proper drainage are completely eliminated.
2. Temperature corrections are unnecessary because the mass (weight) molar concentration does not change with temperature, in contrast to the volume molar concentration. This advantage is particularly important in non-aqueous titrations because of the high coefficients of expansion of most organic liquids (about 10 times that of water).
3. Mass measurements can be made with considerably greater precision and accuracy than can volume measurements.
4. Gravimetric titrations are more easily automated than are volumetric titrations.

13 E TITRATION CURVES

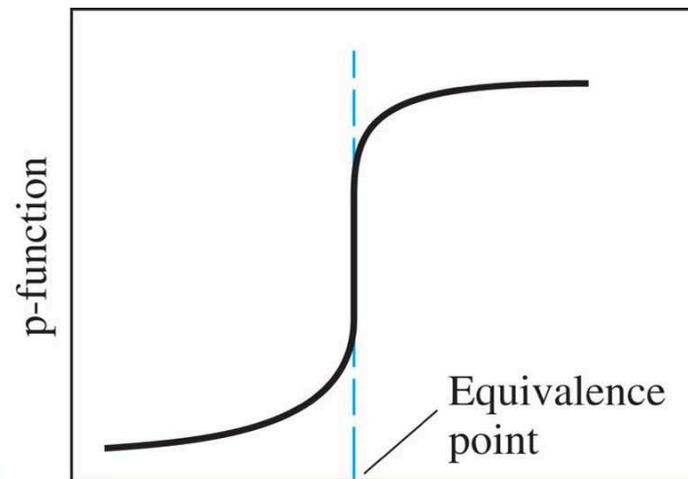
➤ A titration curve is a plot of some function of the analyte or titrant concentration on the y axis versus titrant volume on the x axis.

13E-1 Types of Titration Curves

There are two types of titration curves:

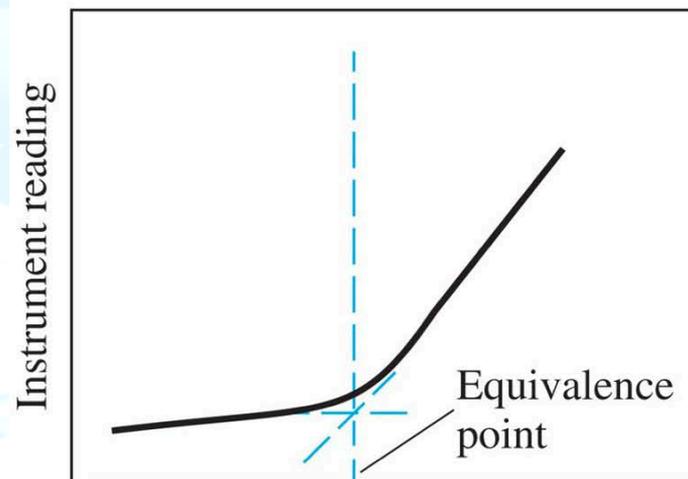
* **A sigmoidal curve** in which the p-function of analyte (or sometimes the titrant) is plotted as a function of titrant volume. Important observations are confined to a small region (typically ± 0.1 to ± 0.5 mL) surrounding the equivalence point.

* **A linear segment curve** in which measurements are made on both sides of, but well away from, the equivalence point. The vertical axis represents an instrument reading that is directly proportional to the concentration of the analyte or the titrant.



Reagent volume

(a) Sigmoidal curve



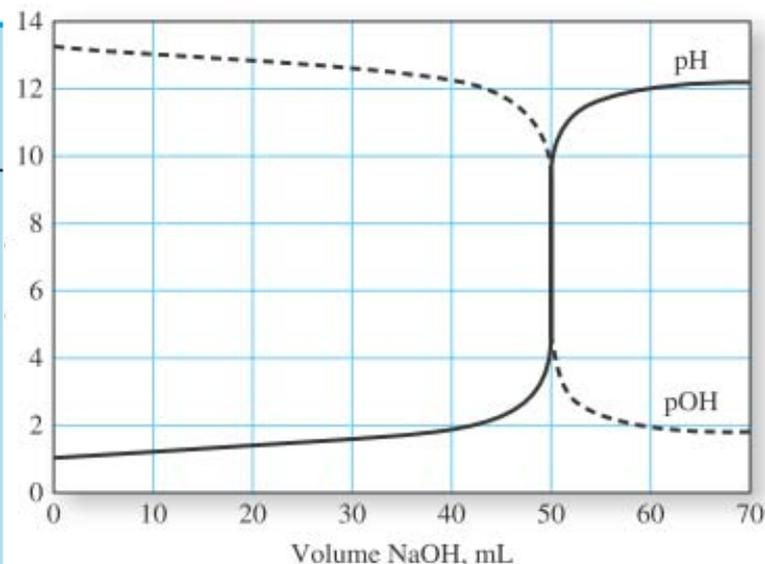
Reagent volume

(b) Linear segment curve

13E-2 Concentration Changes During Titrations

Concentration Changes During a Titration of 50.00 mL of 0.1000 M HCl

Volume of 0.1000 M NaOH, mL	$[\text{H}_3\text{O}^+]$, mol/L	pH	pOH
0.00	0.1000	1.00	13.00
40.91	0.0100	2.00	12.00
8.11	1.000×10^{-3}	3.00	11.00
0.89	1.000×10^{-4}	4.00	10.00
0.09	1.000×10^{-5}	5.00	9.00
0.009	1.000×10^{-6}	6.00	8.00
0.001	1.000×10^{-7}	7.00	7.00
0.001	1.000×10^{-8}	8.00	6.00
0.009	1.000×10^{-9}	9.00	5.00
0.09	1.000×10^{-10}	10.00	4.00
0.91	1.000×10^{-11}	11.00	3.00
10.10	1.000×10^{-12}	12.00	2.00



The concentration of HCl is equal to the original number of millimoles of HCl (50.00 mL x 0.1000 M) **minus** the number of millimoles of NaOH added ($V_{\text{NaOH}} \times 0.1000 \text{ M}$) divided by the total volume of the solution:

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Figure 13-3 Titration curves of pH and pOH versus volume of base for the titration of 0.1000 M HCl with 0.1000 M NaOH.

The equivalence point in a titration is characterized by major changes in the relative concentrations of reagent and analyte.

Homework (Due 13/03/2018)

Chapter 13, Questions and Problems

13-1, 13-3, 13-6, 13-8, 13-10, 13-11, 13-12, 13-13, 13-14,
13-16, 13-18, 13-20, 13-22, 13-24, 13-26, 13-28, 13-30.

End of Chapter 13