# Electrochemical Titrations

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*One of the most widely used applications of electrochemistry is for determining the endpoint of titrations. Advantages of electrochemical methods over other methods (e.g., visual methods) include greater sensitivity, as well as increased accuracy and precision. These methods are based on simple electrochemical techniques, which are all available on epsilon™ instruments. Inexpensive motorized pipettes as well as stepper motor-controlled miniature syringe pumps (e.g., BAS Bee infusion pumps) can facilitate titrations in small volumes, both for research and teaching purposes.*

A number of different titrations are commonly used. These are reviewed in instrumental analysis and quantitative analysis textbooks (1-3).

- **Acid-Base Titrations** - These titrations are based on the neutralization reaction between acids and bases. The precise shape of the titration curve depends upon the number of ionizable groups present, and the degree of ioniziation.
- **Redox Titrations** - These titrations involve electron transfer reactions between two redox species; for example, cerium(IV) + iron(II) = cerium(III) + iron(III). The shape of the titration curve can depend upon the reversibility of the redox couple.
- **Precipitation Titrations** - This method can be used if the analyte ion forms a low solubility salt (e.g., silver chloride).
- **Complexation Titrations** - This method is used for titration of transition metal ions and requires that the metal ion form a soluble complex with the titrating ligand (e.g., EDTA).

## *Potentiometric Endpoint Methods*

The basis of potentiometry is the Nernst equation, which relates the concentration of electroactive species at the surface of an electrode ($C^S$) to the potential of that electrode (E); that is, for the reaction $O + e^- = R$

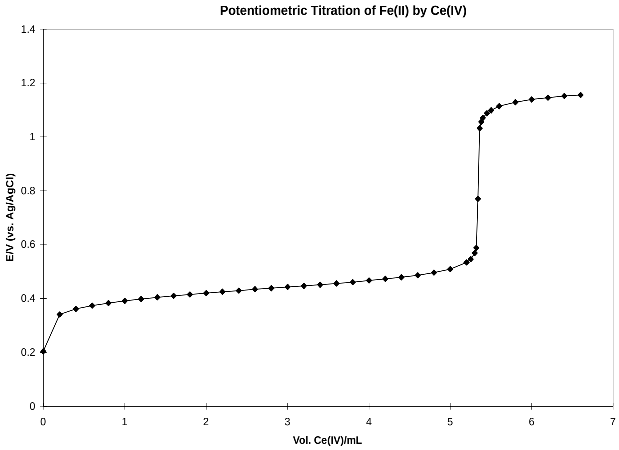
$$E = E^{o'} + \frac{0.059}{n} \log \frac{C^S_O}{C^S_R}$$

where $E^{o'}$ is the formal redox potential of the electron transfer reaction. In a potentiometry experiment, the open-circuit potential (i.e., there is no measurable current through the cell) is measured between two electrodes: the *indicator* electrode and the *reference* electrode. The potential of the indicator electrode is sensitive to the concentration of the analyte in solution, and the reference electrode (typically the saturated calomel or the silver/silver chloride electrode) provides a stable reference potential for measurement of the potential of the indicator electrode. Therefore, the potential of this electrochemical cell depends upon the analyte concentration.

There are a number of different indicator electrodes. The simplest one is an inert metal such as platinum, which can be used to measure the ratio of the concentrations of the oxidized and reduced species. These are therefore suitable for redox titrations (the curve for the titration of iron(II) by cerium(IV) recorded by an epsilon™ prototype using a platinum indicator electrode is shown in ***F1***). Alternatively, if the $M^{n+} + ne^- = M$ half-reaction is reversible, then an M electrode can be used for the determination of $M^{n+}$ ions.

***F1***

*Curve for the potentiometric titration of iron(II) by cerium(IV).*



Another metallic indicator electrode is the mercury/mercury(II)EDTA electrode, which is used for the complexometric titration of metal ions that form EDTA complexes that are less stable than mercury(II)EDTA.

The other major class of indicator electrodes is based on the potential difference across a membrane brought about by the difference in analyte concentration on the two sides of the membrane. The most commonly used membrane electrode is the glass membrane electrode that is used to measure proton concentration (i.e., pH). This is made by sealing a thin glass bulb to the end of a heavy-walled glass tube (***F2***). This bulb contains a solution of known chloride and hydrogen ion concentration ($c_2$). A silver wire coated with silver chloride is immersed in the solution to form a silver/silver chloride reference electrode. The potential of the glass electrode is measured relative to a second reference electrode (e.g., a saturated calomel electrode), and is determined by the concentration of protons in the external solution ($c_1$). At 25 °C, the following relationship applies:

$$E = E_{Ag,AgCl} - E_{SCE} + 0.059\log\frac{c_1}{c_2} + j$$

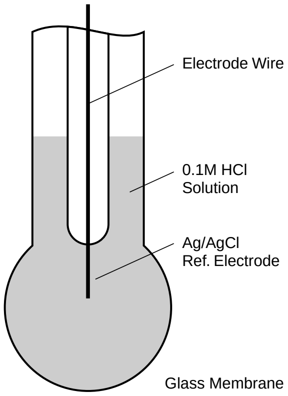
The only variable on the right side of the equation is $c_1$ (j is the asymmetry factor, which is due to non-ideal behavior of the electrode), and hence the equation can be rewritten as follows:

$$E = A - 0.059\text{pH}$$

That is, measurement of pH is a measurement of potential difference. A curve for the titration of acetic acid by sodium hydroxide run using an epsilon prototype is shown in ***F3***.

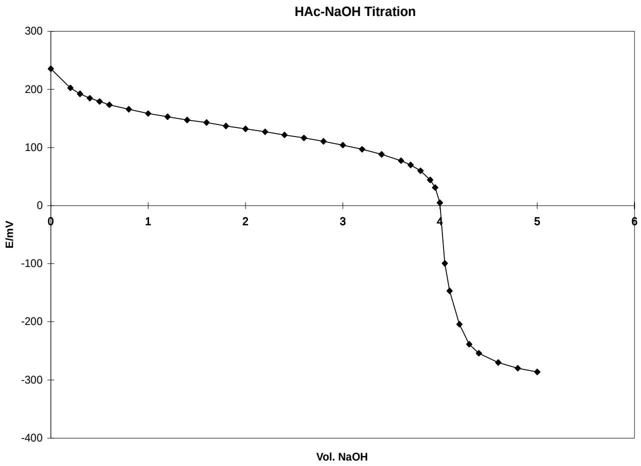
***F2***

*The glass electrode.*



***F3***

*Curve for the potentiometric titration of acetic acid by sodium hydroxide.*



Liquid-polymer membrane electrodes form another class of indicator electrodes. The membrane in these electrodes contains an ionophore or ion-exchange agent that can selectively extract ionic species from the external solution (and hence are referred to as ion-selective electrodes (ISEs)). ISEs are widely used for precipitation and complexometric titrations. Examples of ionophores include valinomycin, which is a highly selective ionophore for potassium ions (based on size exclusion), and di(*n*-decyl)phosphate, which is used as an ion-exchange agent for calcium ions. The selectivity of ISEs (i.e., their ability to discriminate against competing ions) varies considerably. Liquid-polymer ISEs have also been developed for the following ions: ammonium, lithium, sodium, magnesium, copper, lead, nitrate, perchlorate, tetrafluoroborate, and chloride.

ISEs can also be made using single crystals or salts of the ion of interest. For example, fluoride is detected using a lanthanum fluoride crystal as a membrane, and pressed-pellet membranes of silver sulfide and another silver or sulfide salt have been used for chloride, bromide, iodide, cyanide, thiocyanide, ($AgX/Ag_2S$), sulfide, silver, copper, lead, and cadmium ($MS/Ag_2S$).

ISEs can be modified to act as gas-sensing electrodes by separating the ISE from the analyte solution via a gas-permeable membrane. Gases pass through this membrane and dissolve in the thin layer of electrolyte between the ISE and the membrane. Perturbations in equilibria caused by the dissolved gas are detected by the ISE. For example, dissolution of carbon dioxide, ammonia, and sulfur dioxide alter the pH of the solution, which is detected using a glass pH electrode. Hydrogen cyanide, hydrogen fluoride, and hydrogen sulfide can be detected using an ISE appropriate for the anion.

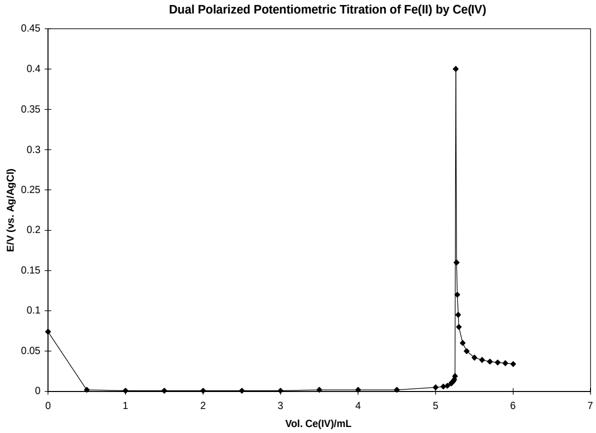
The detection capabilities of an ISE can be further enhanced by adding a biocatalytic membrane, which contains an enzyme that converts the analyte to a product that is detectable by the ISE. Analytes include urea (urease) and glucose (glucose oxidase).

One variation of potentiometric endpoint detection that can be used for redox titrations is dual-polarized electrode potentiometry. In this method, a constant current (typically about 2 - 10 µA) is applied between two identical platinum electrodes. Equal and opposite redox reactions must occur at the electrode surfaces (an oxidation at one electrode, a reduction at the other) in order to support the applied current. The potential difference between the two electrodes therefore depends upon composition of the solution and the reversibility of the redox couples of the species present in the solution.

Let us first consider titration of iron(II) by cerium(IV). Before the addition of any cerium(IV), the electrode reactions are the oxidation of iron(II) and electrolyte reduction; hence, the potential difference is large. However, once cerium(IV) is added, iron(III) is generated in solution by chemical oxidation, and the electrode reactions are now oxidation of iron(II) and reduction of iron(III) (since the oxidation of iron(II) is reversible); the potential difference is therefore now close to zero, and will remain close to zero while both iron(II) and iron(III) are present in solution. However, at the endpoint, the solution contains iron(III) and cerium(III), so the electrode reactions are the oxidation of cerium(III) and the reduction of iron(III), and the potential difference is now significantly greater than zero. Since the cerium(III)/cerium(IV) couple is also reversible, an excess of cerium(IV) will cause the potential difference to drop back to close to zero. Therefore, the endpoint for the titration of a reversible redox species with another reversible species is shown by a spike in the potential vs. volume curve, as shown in ***F4***. If either the analyte or the titrant undergoes an irreversible electron transfer reaction, then the endpoint is again characterized by a dramatic change in the potential from a large *constant* value (in the region where the irreversible species is present in excess) to a *constant* value close to zero (in the region where the reversible species is present in excess). This is the basis of the determination of water by the Karl-Fischer method, where the titrant is iodine (which is either added volumetrically (volumetric titration) or generated *in situ* by controlled current coulometry (coulometric titration)) (4).

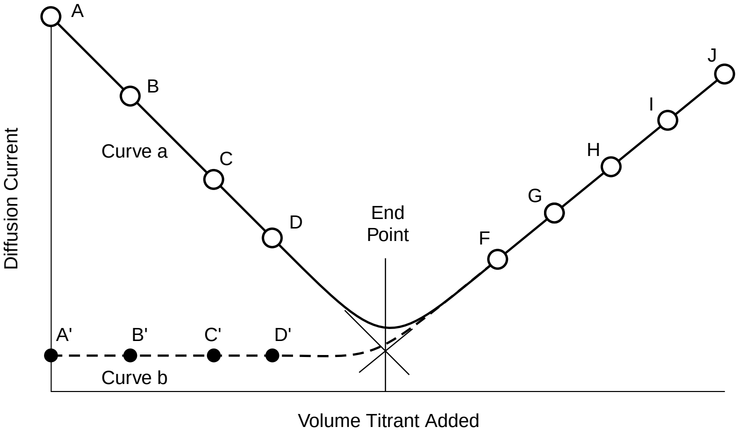
***F4***

*Curve for the dual-polarized titration of iron(II) by cerium(IV).*



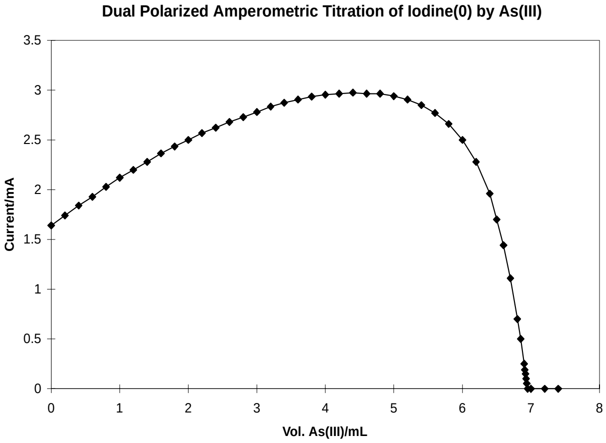
***F5***

*Curves for the amperometric titration of lead(II) ions by dichromate at -0.8V (a) and OV (b).*



***F6***

*Curve for the dual-polarized amperometric titration of iodine by arsenic(III).*



### Amperometric Endpoint Methods

Amperometric endpoint methods are based on the current response to an applied potential and are suitable for redox titrations. The potential is chosen such that either the analyte or the titrant is electrolyzed at a mass transport controlled rate. ***F5*** shows the typical curves for the precipitation titration of lead(II) ions by dichromate at two different potentials. The solid line shows the data from a titration at a potential of -0.8 V (vs. the saturated calomel electrode), and the current response in the first part of the curve represents the reduction of lead(II) ions. If a potential of 0 V is used, then the first part of the curve is a flat line (dashed line), since lead(II) ions cannot be reduced at this potential. Once all the lead(II) ions in solution have been titrated (precipitated), the current response is due to the reduction of dichromate, and the current increases. The end point is characterized by change in the slope of the current response and can be determined by extrapolation of the linear portions of the current response before and after the endpoint.

There is an alternative amperometric method based on dual polarized electrodes. In this method, a small potential difference is applied across two identical platinum electrodes. A non-zero current response requires equal and opposite electron transfer reactions at the two electrodes (i.e., oxidation at one electrode and reduction at the other electrode). Furthermore, the potentials required for these reactions must lie within the potential difference applied between the electrodes. Therefore, in order for there to be a current, *both* species of a *reversible* redox couple must be present in solution. For example, in the titration of iodine by arsenite, the initial current is non-zero (***F6***) since the iodine solution is actually represented by the equilibrium $I^- + I_2 = I_3^-$; that is, both the zero and the -1 oxidation states of this reversible couple are present in solution. The addition of arsenite as the titrant changes the relative proportions of the two iodine oxidation states, and hence the magnitude of the current varies as a function of the volume of arsenite added. At the endpoint, none of the zero oxidation state remains, and hence the current is zero. Further addition of arsenite will not increase the current from zero, since the oxidation of arsenite is irreversible. In contrast, titration of a reversible couple by another reversible couple will show a non-zero current at all points other than the starting point and the endpoint.

The aim of this article has been to illustrate the various electrochemical methods available for the determination of titration endpoints. These methods can be potentiometric, amperometric, or galvanostatic, and all lie within the capabilities of epsilon instruments.

## *References:*

1. *D.C. Harris, "Quantitative Chemical Analysis," Fourth Edition, W. H. Freeman and Co., New York, 1995, Chapters 7, 10, 12-13, 16, 18.*
2. *D.A. Skoog, D.M. West and F.J. Holler, "Fundamentals of Analytical Chemistry," Seventh Edition, Saunders College Publishing, Philadelphia, 1996, Chapters 6, 10-14, 16-17, 19-20.*
3. *H.A. Strobel and W.R. Heineman, "Chemical Instrumentation: A Systematic Approach," Third Edition, Wiley-Interscience, New York, 1989, Chapters 11, 28, 31.*
4. *The Karl-Fischer titration is based on the reaction*

$$I_2+2H_2O+SO_2= 2HI+H_2SO_4$$

*performed in methanol in the presence of a base such as imidazole.*