

6.2 General principles and terms of titration processes

A *titration* is the process of determining the quantity of a substance *A* by adding measured increments of substance *B*, with which it reacts (almost always as a *standardized solution* called the *titrant*, but also by electrolytic generation, as in *coulometric titration*) with provision for some means of recognizing (indicating) the point, the *end point* at which essentially all of *A* has reacted. If the end point coincides with the addition of the exact chemical equivalence, it is called the *equivalence point* or *stoichiometric* or *theoretical end point*, thus allowing the amount of *A* to be found from known amount of *B* added up to this point, the reacting weight ratio of *A* to *B* being known from stoichiometry or otherwise.

Terms for varieties of titration can reflect the nature of the reaction between *A* and *B*. Thus, there are *acid-base*, *complexometric*, *chelatometric*, *oxidation-reduction*, and *precipitation titrations*.

Additionally, the term can reflect the nature of the titrant, such as *acidimetric*, *alkalimetric*, *iodimetric titrations* as well as *coulometric titrations*, in which the titrant is generated electrolytically rather than being added as a standard solution.

A parallel series of terms involves substituting the word *titrimetry* for titration, or, more economically, eliminating either word and using -metry endings denoting either the chemistry involved, as in *acidimetry*, *alkalimetry*, *iodimetry*, and *complexometry*, or the means of end point detection, as in *amperometric*, *chronopotentiometric*, *conductometric*, *fluorometric*, *high frequency*, *nephelometric*, *potentiometric*, *radiometric*, *spectrophotometric*, *thermometric*, and *turbidimetric titrations*.

The *titrant* solution, containing the active agent with which a titration is made, is *standardized*, i.e., the concentration of the active agent is determined, usually by titration with a *standard solution* of accurately known concentration.

Standard solutions are prepared using *standard substances* in one of several ways. A *primary standard* is a substance of known high purity which may be dissolved in a known volume of solvent to give a *primary standard solution*. If stoichiometry is used to establish the strength of a titrant, it is called a *secondary standard solution*. The term *secondary standard* can also be applied to a substance whose active agent contents have been found by comparison against a primary standard. Concentration units of standard solutions may be expressed in kmol/m^3 , mol/dm^3 , or in terms closely related to those used in specific titrations (as titers). Concerning the terms of this paragraph see also section 18.7, reference materials.

The *titer* describes the reacting strength of a standard solution, usually as the weight (mass) of the titrated substance equivalent to cm^3 of the solution.

In order to recognize the end point (v.s.) of the titrations, *indicators* can be used. These may be visual or instrumental. In the former, the indicator is a substance which participates in the

titration reaction so as to give a visual change (colour, fluorescence, precipitate, or turbidity) at or near the equivalence point of a titration. Thus, an *acid-base indicator* is itself an acid or base which exhibits a visual change on neutralization by the basic or acidic titrant at or near the equivalence point. Similar terms apply to complexometry (metallochromic indicator), oxidation-reduction, and precipitation titrimetry. In the last cases, substances which are adsorbed or desorbed, with concomitant colour changes at or near the equivalence point, are termed *adsorption indicators*. Generally, visual indicators undergo a relatively gradual change over a range of concentration of the relevant species (H^+ ion, metal ion, etc.) involved in the titration, but are perceived to undergo "sharp changes" because of the very large concentration changes occurring at or near the equivalence point. This range of concentration over which the eye is able to perceive change in hue, colour intensity, fluorescence or other property of a visual indicator arising from the varying ratio of the two relevant forms of the indicator is called its *transition interval*. It is usually expressed in terms of the negative decadic logarithm of the concentration (e.g., pH, pM) or, for oxidation-reduction titrations, in terms of a potential difference. Colour indicators are classified as *one-* or *two-colour* indicators, depending on whether they are colourless on one side of the transition interval or possess a different colour on each side of this range. A *mixed indicator* is one containing a supplementary dye selected to heighten the overall colour change. When the course of the titration reaction is monitored by some instrumental method for determining the concentrations (or activities) of a reactant or product species, this method is usually included in the description of the titration.

Titration error is the difference in the amount of titrant, or the corresponding difference in the amount of substance being titrated, represented by the expression:

$$(\text{End-point value}) - (\text{Equivalent-point value})$$

Titration curve is a plot of a variable related to a relevant concentration (activity) as the ordinate vs. some measure of the amount of titrant, usually titration volume (titre), as the abscissa. If the variable is linearly related to concentrations, such as the electrical conductance or the photometric absorbance, the term *linear titration curve* is used. When a logarithmic expression of the concentration or activity is used, such as the pH, pM, or the electrical potential in mV, the curve is referred to as a *logarithmic titration curve*.