6.3 The use of the equivalence concept

The concept of equivalence between the amounts of reacting substances has played a fundamental part in the history of quantitative chemistry and its development as an exact science. Its role in titrimetric analysis is equally fundamental. Consider for example the basic type of reaction

$$n_{\mathrm{A}} + n_{\mathrm{B}} \rightarrow products \qquad (1)$$

between a species *A* (the analyte) in one solution (the sample solution) and a species *B* which reacts with it stoichiometrically and is contained in a second solution (the titrating solution or titrant) the molar masses of the two species which are equivalent are $n_A M_A$ and $n_B M_B$ where M_A and M_B are the masses of the two species (formerly called the gram molecular weights), and n_A and n_B are the respective number of reacting entities (now termed the stoichiometric number of the components).

A development of profound importance in practical analysis was the realisation that titrimetric procedures could be carried out with greater speed and convenience if the concentrations of the two reacting solutions were such that the reaction with the analyte was complete when comparable *volumes* of sample and titrant solutions had been brought together. More specifically, if volumes V_A and V_B of these solutions were mixed the reaction would be stoichiometric when $N_A V_A = N_B V_B$ where 'N_X' the 'normality' of the solution designated the number of 'gram equivalents' per litre.

The concept of *equivalence* and the use of the term *equivalent* is well established in studies of ion-exchange phenomena and in electroanalytical chemistry (notably in electrogravimetry and coulometric procedures). Thus any proposals made for standardisation of terminology in titrimetric analysis must be equally applicable to these and relevant fields.

Equivalence factor $f_{eq}(X)$

The equivalence factor for a reacting component of a specified titrimetric reaction is a pure number derived from consideration of the overall stoichiometry of the reaction.

For a reaction

$$n_A A + n_B B \rightarrow products \qquad (2)$$

where $n_A > n_B$, the equivalence factor of reagent A, $f_{eq}(A)$, is taken as unity and for B, $f_{eq}(B)$, it is n_B/n_A. A consequence of this definition is that $f_{eq}(X)$ is always unity or less than unity.

N.B. Modifications to this general rule exist for acid-base and oxidation-reduction titrations.

In the case of a reaction that can be clearly identified as acid-base, the equivalence factor for each reacting component must be related to one entity of titratable hydrogen ions.
Thus for a reaction

$$\begin{gathered} H_2X + B(OH)_2 = BX + 2H_2O \\ f_{eq}(H_2X) = 1/2 = f_{eq}(B(OH)_2) \end{gathered} \qquad (3)$$

In the case of a reaction that can be clearly identified as oxidation-reduction, the equivalence factor for each reacting component must be related to one entity of transferable electrons.
Thus for a reaction

$$\begin{gathered} M^{n+} + 2e^- = M^{(n-2)+} \\ f_{eq}(M^{n+}) = 1/2 \end{gathered} \qquad (4)$$

The equivalent

The equivalent of a species *X* is that entity which in a specified reaction would combine with or be in any other appropriate way equivalent in

(a) an acid-base reaction to one entity of titratable hydrogen ions, H^+

or (b) a redox reaction to one entity of electrons, e^-.

In both instances the equivalent can be established from a knowledge of the equivalence factor and the chemical formula of the species and is

$$f_{eq}(X)\,X \qquad (5)$$

Normal solution

A solution in which the amount-of-substance concentration of the equivalent of the reagent is 1 mol dm^{-3} (i.e. 1 mol l^{-1}) was termed a Normal solution, symbol *N*.

Decimalised fractions of *N* was used, e.g. 0.326 N H_2SO_4, that is a solution with c(1/2 H_2SO_4) = 0.326 mol l^{-1}.

Note: Because confusion may exist when a reagent has different equivalence factors according to circumstances, the statements of normality must be accompanied by the equivalence factor, e.g.

0.1 N KIO_3 ; $f_{eq}(KIO_3) = 1/6$
0.05 N KIO_3 ; $f_{eq}(KIO_3) = 1/4$

The use of the terms "*Normal solution*, *Normality*" are not recommended.