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RECOMMENDATIONS ON THE USAGE OF THE TERMS 'EQUIVALENT' AND 'NORMAL'

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INTRODUCTION

Following the introduction of the SI and the IUPAC Manual of Symbols and Terminology for Physicochemical Quantities and Units it has become necessary to clarify the conditions under which the traditional and technologically convenient 'Equivalence' and 'Normal' concepts and terms should now be used for quantitative analytical work in aqueous solutions. The argument is restricted to the consideration of acid-base and redox reactions in aqueous solutions since this is the only area in which these terms are widely used.

In this document [prepared by Professor H.M.N.H. Irving and members of Commission V.3 of the International Union of Pure and Applied Chemistry] these concepts are examined and defined against the new system of using the mole as the fundamental unit of amount of substance. The original document circulated as Information Bulletin No. 3 from Pure and Applied Chemistry 1969 *18* 427-436, received widespread comments and has been revised in the light of these and many discussions of subsequent drafts by the Commission and representatives of the Interdivisional Committee on Nomenclature and Symbols.

The present report does not imply any recommendation that the terms 'Equivalent' and 'Normal' should continue to be used. It does, however, provide the necessary guidelines for those who are required to or may still wish to use such terms.

THE CONCEPT OF EQUIVALENCE AND NORMAL SOLUTIONS

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[1]. Its role in titrimetric analysis is equally fundamental and scarcely needs stressing. If, for example, we consider a basic type of reaction

$$\nu_A \mathrm{A} + \nu_B \mathrm{B} \longrightarrow \text{products} \qquad (1)$$

between a species A (the analyte) in one solution (the sample solution) and a species B which reacts with it stoicheiometrically and is contained in a second solution* (the titrating solution or titrant) the molar masses of the two species which are equivalent are $\nu_A M_A$ and $\nu_B M_B$ where M_A and M_B are the molar masses of the two species (formerly called the gram molecular weights), and ν_A and ν_B are the respective number of reacting

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* In many early procedures the titrant was added as a solid to a solution of the analyte though the reverse of this procedure was also common.

entities (now termed the stoicheiometric number of the components)[2].

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 stoicheiometric 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.

Since it has become clear[3] that there is still a general desire among those who use titrimetric procedures extensively to continue to use much of this convenient terminology it becomes essential to re-examine the nomenclature to make sure that terms such as 'normal' and 'equivalent' should be clearly defined and that any units employed must be those approved by *Le Systême International d'Unités* (SI); furthermore, there should be no inconsistencies with established IUPAC recommendations already approved and published[3,4].

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 conductimetric procedures) and any proposals made for standardisation of terminology in titrimetric analysis must, of course, be equally applicable to these and other relevant fields.

THE SI SYSTEM AND ITS IMPLICATION

The international adoption of SI, especially the new base unit for *amount of substance* (the mole), has meant that a number of terms widely used in analytical chemistry are no longer really necessary. Some are undoubtedly being used in senses which are not in accordance with and even conflict with the precise use of SI.

The vast majority of chemists who received their education before the early 1970s have regarded and may still regard the expression 'one mole of NaOH' to be defined as a definite mass (weight) of this compound, *i.e.* 'one gram molecular weight', 40 g of sodium hydroxide.

The term 'mole' is now used in a more precise sense, and before further progress can be made it seems essential to restate some basic ideas to establish unambiguously the relationship between the current and older terminologies. Only then will it be possible to formulate proposals covering the use of such concepts as 'equivalence' and 'normality'.

THE AMOUNT OF SUBSTANCE

The SI base unit for 'amount of substance' is the *mole* defined as follows. "The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12. When the mole is used the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles or specified groups of such particles".

The symbol for amount of substance is n ; the amount of substance of species X is symbolised $n(\mathrm{X})$.

Examples $n(Mg^{2+}) = 5\ \text{mmol}$
$n(KMnO_4) = 0.1\ \text{mol}$
$n(F) = 6\ \text{mmol}$
$n(C_2H_5OH) = 1\ \text{kmol}$
$n(H^+) = 10^{-6}\ \text{mol}$

Knowing values for A_r, the *relative atomic mass* (formerly the 'atomic weight') from appropriate Tables for each constituent element, we can calculate the corresponding mass.

Examples 5 mmol of Mg^{2+} has a mass of 0.012116 g
0.1 mol of $KMnO_4$ has a mass of 15.804 g
6 mmol of F has a mass of 0.114 g
1 kmol of C_2H_5OH has a mass of 46.070 kg

It must be emphasized that the mole concept refers to any specified particle or group of particles and we can speak of electrons

$$n(e^-) = 1\ \text{mol (with a mass of } 0.548\,6 \times 10^{-3}\ \text{g)}$$

or of a doped crystal of specified composition, *e.g.*

$$n(Na_{0.93}Tl_{0.07}) = 0.2\ \text{mol (with a mass of 7.138 g)}$$

Although the SI base unit of mass is the kilogram, decimal multiples and submultiples are, of course, acceptable.

MOLAR MASS The molar mass (symbol M) is defined as mass divided by amount of substance. The SI base unit is kg mol^{-1} and the practical unit is usually g mol^{-1}.

Examples $M(Cu) = 63.54\ \text{g mol}^{-1}$
$M(H^+) = 1.0074\ \text{g mol}^{-1}$
$M(Cl_2) = 70.916\ \text{g mol}^{-1}$

RELATIVE ATOMIC MASS

The *relative atomic mass*, A_r (formerly called the 'atomic weight'), is the average mass per atom of the element A with its natural isotopic composition to 1/12 of the mass of an atom of carbon-12.

For example, $A_r(Br) = 79.916$; $A_r(Zr) = 91.22$

RELATIVE MOLECULAR MASS

The *relative molecular mass*, M_r (formerly called the 'molecular weight'), is the average mass 'per formula' of the compound with its constituent atoms in their natural isotopic composition to 1/12 of the mass of an atom of carbon-12. For example,

$M_r(KCl) = 74.56$; $M_r(Na_2H_2Y.2H_2O) = 372.23$ (for the hydrated sodium salt of EDTA (H_4Y).

For 'ferric alum' we have

$M_r((NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O) = 964.42$, whereas if the halved formula is adopted,

$M_r((NH_4)Fe(SO_4)_2.12H_2O) = 482.21$

Note Every *physical quantity* is the product of a *numerical value* (a pure number) and a *unit*. It will be appreciated that when the *molar mass*, $M(X)$, is correctly expressed in its proper units (g mol^{-1}) the pure number is identical with that for the *relative atomic mass*, A_r (formerly atomic weight), or *relative molecular mass*, M_r (formerly molecular weight).

Examples $M(Ca^{2+}) = 40.08\ \text{g mol}^{-1}$; $A_r(Ca^{2+}) = 40.08$
$M(Et_2O) = 74.124\ \text{g mol}^{-1}$; $M_r(Et_2O) = 74.124$

The analytical chemist will, therefore, find no numerical changes when replacing the older concept of 'molecular weight' by the modern term 'molar mass', but he must never forget that the latter term must be associated with the appropriate unit (g mol^{-1}).

CONCENTRATION

The amount-of-substance concentration (symbol c) is the amount of substance divided by the volume of solution*. The SI base unit is mol m^{-3}, but the practical units are mol dm^{-3} or or mol l^{-1}. These two are in fact identical since the litre has been redefined as being 1 dm^3

Examples

$c(\mathrm{HCl}) = 0.1\ \mathrm{mol\ l}^{-1}$

$c(\mathrm{H_3PO_4}) = 0.5\ \mathrm{mol\ dm}^{-3}$

$c(\mathrm{S_2O_3}^{2-}) = 3\ \mathrm{mmol\ l}^{-1}$

Note (i) There is seldom in practice any confusion caused by abbreviating the description 'amount-of-substance concentration' to the more familiar 'concentration'.

(ii) A solution with an amount-of-substance concentration of 0.1 mol dm^{-3} is often called a 0.1 molar solution and written as a 0.1 M solution. See ref. (2), page 6 , footnote (5).

(iii) The term molality (amount of substance of X divided by the mass of solvent; unit mol kg^{-1}) will be preferred when quantitative measurements are carried out under non-isothermal conditions, because the molality, but not the concentration, is independent of temperature.

(iv) For linguistic reasons the approved term *molality* could easily be confused with 'molarity', a term formerly used - and still very widely used - to denote concentration (generally in terms of 'gram-molecules per litre'). Since 'molarity' is fully covered by the term *amount-of-substance concentration* it is clearly redundant and it has been recommended that its use should be abandoned. Use of the adjective *molar* is, however, still permitted (cf. Note (ii) above).

To summarise so far: the practising chemist need only realise that many of the physical quantities which he has been accustomed to use have not changed their numerical values, provided they are now associated with particular SI units, and that these changes are concomitant with certain changes in terminology and in the symbols to be used.

Before proceeding further, two other general terms, already defined, should be restated here.

STANDARD SOLUTION A standard solution is one having an accurately known concentration of the active substance, or an accurately known titre[4].

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* Since volume, V, is a function of temperature, the concentration, c, must also be a function of temperature. Strictly speaking, this should always be specified and (ideally) the operating temperature for a titrimetric analysis should be that for which glassware has been calibrated and at which solutions have been made up. The practising analyst will, of course, be aware of the effect of temperature variations on his results and can make the appropriate corrections if these are justified by the level of accuracy sought for. When a high degree of accuracy and precision is essential, weight burettes may be preferred.

EQUIVALENCE-POINT The point in a titration at which the amount of titrant added is chemically equivalent to the amount of substance titrated[4]. The terms stoicheiometric point and theoretical end-point are synonymous with equivalence-point[4].

EQUIVALENCE

The amount of substance reacting according to equation (1) should clearly be measured in terms of the appropriate unit, the mole, and all concentrations should preferably be expressed in mol dm^{-3} or mol l^{-1}.

Taking a specific case of the general equation (1)

$$HCl + NaOH = NaCl + H_2O \qquad (2)$$

the equivalence point will be reached when each elementary entity of HCl has reacted with just one of NaOH; this will correspond to equal volumes of solutions of HCl and NaOH if they are of equal concentrations, *i.e.*

$$c(HCl) = c(NaOH)$$

For the reaction

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O \qquad (3)$$

it is clear that each reacting entity of sulphuric acid will be equivalent to two of sodium hydroxide at the equivalence point. If this reaction is rewritten in the form

$$NaOH + \tfrac{1}{2}H_2SO_4 = \tfrac{1}{2}Na_2SO_4 + H_2O \qquad (3a)$$

we see that the amount of the two reactants would be equivalent when $n(NaOH) = n(\tfrac{1}{2}H_2SO_4)$, for the definition of the mole permits us to refer to *any* specified entity, *e.g.* $(\tfrac{1}{2}H_2SO_4)$. Clearly if $n(NaOH) = 1$ mol this amount has a mass of 40 g, and if $n(\tfrac{1}{2}H_2SO_4) = 1$ mol it has a mass of 49 g; these symbols clearly express the quantitative relationship in the form to which we are already accustomed.

The appropriate standard solutions which would neutralise each other when mixed in equal volumes will have $c(NaOH) = c(\tfrac{1}{2}H_2SO_4) =$ (say) 0.1 mol l^{-1} and can be specified as having concentrations of 4.0 g l^{-1} and 4.9 g l^{-1} respectively.

It would appear possible to generalize this approach by writing equation (1) in the form

$$A + (\nu_B/\nu_A)B \longrightarrow \text{products} \qquad (1a)$$

$$\text{where } \nu_A \geqslant \nu_B$$

which signifies that one entity of species A will be equivalent to (ν_B/ν_A) entity of B (in this particular reaction). Let us denote the ratio (ν_B/ν_A) by the symbol $f_{eq}(B)$, and term it the *equivalence factor* of B. The equivalence factor (which will take the form of an integral fraction equal to or less than unity) is a pure number which can be calculated from a knowledge of the stoicheiometry of the given reaction (but see below* and Appendix A). In the above example $f_{eq}(A) = 1$.

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* Some analytical reactions that proceed reproducibly under carefully controlled conditions cannot be represented by equations in which ν_A and ν_B are small integers and an empirical 'factor' must be used.

According to equation (1a) one entity of A will have reacted with $f_{eq}(B)$ entity of B at the equivalence point. However, since the whole concept allows us to refer to any designated species we can equally well refer to one entity of A as reacting with one entity of $f_{eq}(B)$ B.

It is convenient to relate the amount of substance and the amount of substance concentration of an analytical reagent X to the entity $f_{eq}(X)X$ rather than the entity X itself when $f_{eq} \neq 1$. This may be called the equivalent entity of X or the equivalent of X. It is not a physical quantity like $n(f_{eq}(X)X)$ *e.g.* $n(\frac{1}{2}H_2SO_4)$ but is in the nature of a chemical formula which is a common way of designating an entity. With this choice, if $c(f_{eq}(A)A) = c(f_{eq}(B)B)$ then the equivalence point is reached when equal volumes of the solutions have been mixed. Where $f_{eq}(X)$ varies with the nature of the reaction, this reaction must be specified.

Thus for reaction (3) we have

$$n(NaOH) = n(\tfrac{1}{2}H_2SO_4)$$

at the equivalence point and similarly for the reactions

$$H_3PO_4 + 2KOH = K_2HPO_4 + 2H_2O \tag{4}$$

$$n(KOH) = n(\tfrac{1}{2}H_3PO_4)$$

whereas for

$$H_3PO_4 + KOH = KH_2PO_4 + H_2O \tag{5}$$

$$n(KOH) = n(H_3PO_4)$$

and for

$$H_3PO_4 + 3AgOH = Ag_3PO_4(s) + 3H_2O \tag{6}$$

$$n(AgOH) = n(\tfrac{1}{3}H_3PO_4)$$

As is well known, the equivalent of a substance is not invariable and may change according to the reaction in which it is involved. The reaction must, therefore, always be specified unless there is no possibility of ambiguity in the context.

EQUIVALENCE FOR ACID-BASE REACTIONS

If for any reason the reaction

$$H_2SO_4 + Ca(OH)_2 = CaSO_4 + 2H_2O \tag{7}$$

were to be conducted titrimetrically to an acid-base end-point we would have $n(H_2SO_4) = n(Ca(OH)_2)$. If one were to use the general definition of equation (1), then $f_{eq}(H_2SO_4)$ would be 1 in contrast to equation (3a) which gives $f_{eq}(H_2SO_4) = \frac{1}{2}$. To avoid such inconsistency it is recommended that one refer all neutralization reactions to a common basis which is covered by the following definition.

The *equivalent* of an acid (or a base) is that entity which, in a specified reaction, would release (or combine with), or be in any other appropriate way equivalent to, 1 entity of titratable hydrogen ions.

On this basis solutions with amounts of substance denoted by $n(HCl)$, $n(NaOH)$, $n(\frac{1}{2}H_2SO_4)$, $n(\frac{1}{2}H_2C_2O_4)$, $n(H_3PO_4)$ for reaction (5), $n(\frac{1}{2}H_3PO_4)$ for reaction (4) and $n(\frac{1}{3}H_3PO_4)$ for reaction (6) and where $n(X) = 1$ mol will each contain one mole of equivalent acid or base.

EQUIVALENCE FOR REDOX REACTIONS

Again, since the mole can refer to any specified entity it will be convenient in redox reactions to correlate the amount of reactant with the number of electrons per mole which it combines with or releases.

The *equivalent* of an oxidising (or a reducing) agent is that entity which in a single specified reaction can accept, release, or be in any other way equivalent to one entity of electrons. On this basis solutions with amounts of substance denoted by $n(\mathrm{Fe^{2+}})$, $n((\mathrm{NH_4})_2\mathrm{SO_4.FeSO_4.6H_2O})$, $n(\frac{1}{5}\mathrm{KMnO_4})$, $n(\frac{1}{2}\mathrm{H_2C_2O_4})$, $n(\frac{1}{2}\mathrm{Na_2C_2O_4})$, $n(\frac{1}{4}\mathrm{KH_3(C_2O_4)_2.2H_2O})$, $n(\frac{1}{6}\mathrm{K_2Cr_2O_7})$, $n(\frac{1}{2}\mathrm{I_2})$, $n(\mathrm{I^-})$, $n(\mathrm{S_2O_3{}^{2-}})$ etc., where $n(\mathrm{X}) = 1$ mol in each example will each contain one mole of equivalent oxidizing or reducing agent.

If one mole of the equivalent of X is dissolved in one litre of solution this particular standard solution can be termed a normal solution which can be defined as follows.
A *normal solution* of the species X has an amount-of-substance concentration $c(f_{\mathrm{eq}}(\mathrm{X})\mathrm{X}) = 1\ \mathrm{mol\ dm^{-3}}$ (or $1\ \mathrm{mol\ l^{-1}}$), where $f_{\mathrm{eq}}(\mathrm{X})$ is the equivalence factor for X in the reaction under consideration, which must be specified unless there is no ambiguity in the context.

Such a solution can be referred to as 1 normal X (and written N X).

Examples

$c(\mathrm{NaOH}) = 1\ \mathrm{mol\ l^{-1}}$ is the concentration of a normal solution of sodium hydroxide (N NaOH) containing 40 g $\mathrm{l^{-1}}$;

$c(\frac{1}{2}\mathrm{H_2SO_4}) = 1\ \mathrm{mol\ l^{-1}}$ is the concentration of a normal solution of sulphuric acid (N $\mathrm{H_2SO_4}$) containing 49 g $\mathrm{l^{-1}}$;

$c(\frac{1}{5}\mathrm{KMnO_4})$ is the concentration of a normal solution of potassium permanganate (for reactions in acid solution) (N $\mathrm{KMnO_4}$) containing 31.606 g $\mathrm{l^{-1}}$)

$c(\frac{1}{2}\mathrm{I_2}) = 1\ \mathrm{mol\ l^{-1}}$ is the concentration of a normal solution of iodine (N $\mathrm{I_2}$) containing 126.92 g $\mathrm{l^{-1}}$.

Note that while all these normal solutions have the same amount-of-substance concentration ($1\ \mathrm{mol\ l^{-1}}$) of the equivalent of the named substance they may differ in content from the corresponding molar solutions because different entities are specified (*e.g.* $\frac{1}{2}\mathrm{H_2SO_4}$ rather than $\mathrm{H_2SO_4}$).

Similarly it is possible to designate the content of other standard solutions as, for example, 0.1268 N $\mathrm{H_2SO_4}$, *i.e.* 0.0634 M $\mathrm{H_2SO_4}$, etc.

In principle then, there can be no difficulty in specifying the equivalent amount of a substance taking part in a specified reaction and deriving the corresponding amount-of-substance concentration of a normal solution, provided the equivalence factor can be determined. This can present some small difficulties which are discussed in Appendix A, to which is appended a Table giving values of $f_{\mathrm{eq}}(\mathrm{X})$ for a number of common analytical reactions of interest in titrimetry.

In complexometric titrations the essential reaction is most commonly the formation of a 1:1 complex between a cation $\mathrm{M^{n+}}$ and a ligand $\mathrm{Y^{4-}}$ and there is no change in the oxidation

state of either reactant, nor are there relevant changes due to the release of protons from the conjugate acid of the ligand which may be used as the titrant. As for example:
$M^{n+} + H_jY^{(4-j)-} = MY^{(4-n)-} + jH^+$ (taken up in a buffer solution).

In this case, normal solutions of the reactants have the same concentrations as molar solutions of the same reacting species. There is clearly no advantage here in using the concept of a normal solution.

In other cases, however, it is quite possible to give a rigorous definition for a normal solution of the same substance acting as a titrant in two different reactions because two different values for $f_{eq}(X)$ may be involved. For example (see Appendix), a normal solution of potassium iodate is based on $f_{eq}(KIO_3) = \frac{1}{6}$ for reaction with potassium iodide in dilute acid solution (equation (11)), but $f_{eq}(KIO_3) = \frac{1}{4}$ for the reaction in 2N HCl (Andrews titration); equation (10). If the same standard solution of potassium iodate were to be used for both of these reactions, mistakes could occur if solutions were labelled merely in terms of their normality, unless the value of $f_{eq}(KIO_3)$ is also specified.

APPENDIX A

METHODS OF COMPUTING THE EQUIVALENCE FACTOR, $f_{eq}(X)$

Textbooks of analytical chemistry (written before the widespread adoption of SI) devote a considerable amount of space to discussions of how to arrive at the composition of a normal solution of a titrant for a given reaction. In acid-base titrations the number of replaceable hydrogen atoms has invariably formed the basis for calculating equivalents. In redox reactions the earliest approach was tied to this by way of oxidisable hydrogen or 'available oxygen'. For example, the once familiar $2\ KMnO_4 = K_2O.2MnO.5O$ when $2\ KMnO_4 = 5\ O = 10\ H$ leading to $f_{eq}(KMnO_4) = \frac{1}{5}$. The same result is obtained by the overall stoicheiometry of equation (9). A more recent approach is to base the equivalence factor on the change in oxidation number $|\Delta Z|$ (6). Reference to the following five reactions shows that these two approaches are not always adequate and that they can lead to inconsistent values for $f_{eq}(X)$.

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O \qquad (3)$$

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O \qquad (9)$$

$$M^{n+} + H_jY^{(4-j)-} = MY^{(4-n)-} + jH^+ \qquad (8)$$

$$KIO_3 + 2KI + 6HCl = 3ICl + 3KCl + 3H_2O \qquad (10)$$

$$KIO_3 + 5KI + 6HCl = 3I_2 + 6KCl + 3H_2O \qquad (11)$$

Using the relationship $f_{eq}(B) = \nu_B/\nu_A$ consideration of stoicheiometry leads correctly to $f_{eq}(H_2SO_4) = 1/2$, $f_{eq}(KMnO_4) = 2/10$ and $f_{eq}(H_jY) = 1/1$ for equations (3), (9) and (8), but gives the wrong values for the two reactions involving potassium iodate.

Considerations based on changes in oxidation number are of course inapplicable to equations (3) and (8) but give the correct value for (9) when written in the form

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O \qquad (9a)$$

since the change in oxidation number^5 is from +7 to +2 whence $|\Delta Z| = 5$ and the equivalence factor is 1/5. For equation (10) (Andrew's titration) we have

$$IO_3^- + 6H^+ + 4e^- = I^+ + 3H_2O \qquad (10a)$$

leading (correctly) to $|\Delta Z| = 5 - (+1) = 4$, and $f_{eq}(KIO_3) = 1/4$. However, for equation (11) we can write

$$IO_3^- + 6H^+ + 5e^- = \frac{1}{2}I_2 + 3H_2O \text{ with } |\Delta Z| = |5 - 0| = 5, \text{ and}$$

$f_{eq}(KIO_3) = 1/5$ which is incorrect. (It would be appropriate only if the reaction were followed potentiometrically by noting changes in I_2). The complication arises here from the fact that the element iodine is involved in both titrant and analyte and in different oxidation states. Furthermore the actual titrimetric reaction involves further titration of the liberated elementary iodine to iodide with thiosulphate, thus:

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6 \qquad (12)$$

The overall stoicheiometry is thus $KIO_3 = 3I_2 = 6NaI$ (or $6e^-$) leading to $f_{eq}(KIO_3) = 1/6$.

In reactions of copper (II) we have

$$Cu^{2+} + 2e^- = Cu \qquad (13)$$

in electrogravimetry leading to $f_{eq}(Cu^{2+}) = 1/2$ for the cupric ion. In contrast $f_{eq}(Cu^{2+}) = 1$ will be appropriate for the reaction.

$$2Cu^{2+} + 4I^- = 2CuI + I_2 \qquad (14)$$

since $2Cu^{2+} = I_2 = 2I^-$ (or $2e^-$), with $f_{eq}(Cu^{2+}) = 2/2 = 1$.

Similarly we note different titrimetric reactions involving Ag^+ which can lead to different values for the equivalent depending upon the actual reaction under consideration. For example:

$$Ag^+ + Cl^- = AgCl \qquad (15)$$
$$Ag^+ + 2CN^- = Ag(CN)_2^- \qquad (16)$$
$$2Ag^+ + Ni(CN)_4^{2-} = 2Ag(CN)_2^- + Ni^{2+} \qquad (17)$$

(Ni^{2+} determined complexometrically with EDTA)

Provided the stoicheiometry of an effective *overall* analytical reaction is considered, the analyst will have no difficulty in computing the appropriate value for the equivalence factor $f_{eq}(X)$. It then becomes readily possible to compute the amount of substance of the equivalent of X, *i.e.* $n(f_{eq}(X)\ X)$ and the corresponding amount-of-substance concentration $c(f_{eq}(X)\ X)$ the favoured units being mol and mol dm^{-3} (or mol l^{-1}) respectively.

Where $f_{eq}(X) = 1$ there is clearly no point in preferring the use of normal to molar solutions. Where $f_{eq}(X)$ is less than one the practical advantage of specifying normal solutions derives entirely from the ability to work with comparable volumes in achieving the equivalence-point: against this must be set the disadvantages and possibilities for error when using a reagent (*e.g.* KIO_3 which has different equivalence in different reactions) for which the same standard solution could well be applied.

Where the use of normal solutions is preferred it is recommended that the designation of the standard solution should be explicit on the lines of the following examples.

(a) 0.1257 N sulphuric acid; $f_{eq}(H_2SO_4) = 1/2$; 6.114 g l^{-1} H_2SO_4
(b) 0.1030 N potassium dichromate; $f_{eq}(K_2Cr_2O_7) = 1/6$; 5.0504 g l^{-1} $K_2Cr_2O_7$
(c) 0.1 N potassium iodate; $f_{eq}(KIO_3) = 1/4$; 5.351 g l^{-1} KIO_3;
reaction $KIO_3 + 2KI + 6HCl \longrightarrow 3ICl + 3KCl + 3H_2O$

Table I gives a selection of titrimetric reactions and the appropriate values for $f_{eq}(X)$.

TABLE I

REACTANTS	EQUATION	EQUIVALENTS, $f_{eq}(X)$ X
HCl , $NaOH$	$HCl + NaOH = NaCl + H_2O$	$1\ HCl$, $1\ NaOH$
H_2SO_4 , KOH	$H_2SO_4 + 2\ KOH = K_2SO_4 + 2\ H_2O$	$\frac{1}{2}\ H_2SO_4$, $1\ KOH$
H_3PO_4 , KOH	$H_3PO_4 + KOH = KH_2PO_4 + H_2O$	$1\ H_3PO_4$, $1\ KOH$
H_3PO_4 , KOH	$H_3PO_4 + 2\ KOH = K_2HPO_4 + 2\ H_2O$	$\frac{1}{2}\ H_3PO_4$, $1\ KOH$
H_3PO_4 , KOH	$H_3PO_4 + 3\ KOH = K_3PO_4 + 3\ H_2O$	$\frac{1}{3}\ H_3PO_4$, $1\ KOH$
$H_2C_2O_4$, $NaOH$	$H_2C_2O_4 + 2\ NaOH = Na_2C_2O_4 + 2\ H_2O$	$\frac{1}{2}\ H_2C_2O_4$, $1\ NaOH$
HCl , $Ba(OH)_2$	$2\ HCl + Ba(OH)_2 = BaCl_2 + 2\ H_2O$	$1\ HCl$, $\frac{1}{2}\ Ba(OH)_2$
$R.COOH$, $Ba(OH)_2$	$2\ R.COOH + Ba(OH)_2 = Ba(R.COO)_2 + 2\ H_2O$	$1\ R.COOH$, $\frac{1}{2}\ Ba(OH)_2$
HNO_3 , Na_2CO_3	$2\ HNO_3 + Na_2CO_3 = 2\ NaNO_3 + H_2O + CO_2$	$1\ HNO_3$, $\frac{1}{2}\ Na_2CO_3$
HNO_3 , Na_2CO_3	$HNO_3 + Na_2CO_3 = NaHCO_3 + NaNO_3$	$1\ HNO_3$, $1\ Na_2CO_3$
$AgNO_3$, KCN	$2\ KCN + AgNO_3 = KAg(CN)_2 + KNO_3$	$\frac{1}{2}\ AgNO_3$, $1\ KCN$
$AgNO_3$, KCN	$KCN + AgNO_3 = AgCN + KNO_3$	$1\ KCN$, $1\ AgNO_3$
$CuSO_4$, KI	$CuSO_4 + 2\ KI = CuI + \frac{1}{2}\ I_2 + K_2SO_4$	$\frac{1}{2}\ CuSO_4$, $1\ KI$
$KMnO_4$, $FeSO_4$	$2\ KMnO_4 + 10\ FeSO_4 + 8\ H_2SO_4 = K_2SO_4 + 2\ MnSO_4 + 5\ Fe_2(SO_4)_3 + 8\ H_2O$	$\frac{1}{5}\ KMnO_4$, $1\ FeSO_4$
$KMnO_4$, H_2O_2	$2\ KMnO_4 + 5\ H_2O_2 + 3\ H_2SO_4 = K_2SO_4 + 2\ MnSO_4 + 8\ H_2O + SO_2$	$\frac{1}{5}\ KMnO_4$, $\frac{1}{2}\ H_2O_2$
$KMnO_4$, $H_2C_2O_4$	$2\ KMnO_4 + 5\ H_2C_2O_4 + 3\ H_2SO_4 = K_2SO_4 + 2\ MnSO_4 + 10\ CO_2 + 8\ H_2O$	$\frac{1}{5}\ KMnO_4$, $\frac{1}{2}\ H_2C_2O_4$
$KMnO_4$, As_2O_3	$4\ KMnO_4 + 5\ As_2O_3 + 12\ HCl = 4\ KCl + 4\ MnCl_2 + 5\ As_2O_5 + 6\ H_2O$	$\frac{1}{5}\ KMnO_4$, $\frac{1}{4}\ As_2O_3$
$K_2Cr_2O_7$, $FeCl_2$	$K_2Cr_2O_7 + 6\ FeCl_2 + 14\ HCl = 2\ KCl + 2\ CrCl_3 + 6\ FeCl_3 + 7\ H_2O$	$\frac{1}{6}\ K_2Cr_2O_7$, $1\ FeCl_2$
$Ce(SO_4)_2$, $FeSO_4$	$2\ Ce(SO_4)_2 + 2\ FeSO_4 = Ce_2(SO_4)_3 + Fe_2(SO_4)_3$	$1\ Ce(SO_4)_2$, $1\ FeSO_4$
$TiCl_3$, $FeCl_3$	$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4$	$1\ FeCl_3$, $1\ TiCl_3$
$SnCl_2$, $Fe_2(SO_4)_3$	$SnCl_2 + Fe_2(SO_4)_3 + 2\ HCl = SnCl_4 + 2\ FeSO_4 + H_2SO_4$	$\frac{1}{2}\ SnCl_2$, $\frac{1}{2}\ Fe_2(SO_4)_3$

SUMMARY

1. 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 stocheiometry of the reaction.

For a reaction

$$\nu_A A + \nu_B B \longrightarrow \text{Products}$$

where $\nu_A > \nu_B$ the equivalence factor of reagent A, $f_{eq}(A)$, is taken as unity and for B, $f_{eq}(B)$, it is ν_B/ν_A. A consequence of this definition is that $f_{eq}(X)$ is always unity or less than unity. See p. 331.

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

$$H_2X + B(OH)_2 = BX + 2H_2O$$

$$f_{eq}(H_2X) = 1/2 = f_{eq}(B(OH)_2)$$

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 transferrable electrons.

Thus for a reaction

$$M^{n+} + 2e^- = M^{(n-2)+}$$

$$f_{eq}(M^{n+}) = 1/2$$

2. 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

$$f_{eq}(X)\ X$$

3. 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}) may be termed a Normal solution, symbol N.

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

Bottles containing standard solutions labelled in terms of normality must be labelled clearly and unequivocally to indicate the species and the normality. 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.*

$$0.1\ \mathrm{N}\ \mathrm{KIO_3}\ ;\ (f_{\mathrm{eq}}(\mathrm{KIO_3}) = \tfrac{1}{6})$$

$$0.05\ \mathrm{N}\ \mathrm{KIO_3}\ ;\ (f_{\mathrm{eq}}(\mathrm{KIO_3}) = \tfrac{1}{4})$$

REFERENCES

1. F. Szabadvary, *History of Analytical Chemistry*, 1966; cf. H.M.N.H. Irving, *The Techniques of Analytical Chemistry*, H.M. Stationery Office, London, 1974.
2. *Manual of Symbols and Terminology for Physicochemical Quantities and Units*, IUPAC, 1973 Edition, Butterworths, London, 1975.
3. *IUPAC Information Bulletin No. 36*, August 1974; cf. also *Proceedings of ISO/TC 47 Conference*, Moscow, April 1975.
4. *Pure and Applied Chem.* 1969, 18 (No. 3), 427-436.
5. *Nomenclature of Inorganic Chemistry*, IUPAC 2nd Ed., Butterworths, London, 1971, p.5.
6. *DIN* 32625 (1977).