VOGEL'S TEXTBOOK OF MACRO AND SEMIMICRO QUALITATIVE INORGANIC ANALYSIS

Fifth Edition
Revised by

G. Svehla, Ph.D., D.Sc., F.R.I.C.

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A textbook of macro and semimicro qualitative inorganic analysis

FROM PREFACE TO THE FIRST EDITION

Experience of teaching qualitative analysis over a number of years to large numbers of students has provided the nucleus around which this book has been written. The ultimate object was to provide a text-book at moderate cost which can be employed by the student continuously throughout his study of the subject.

It is the author's opinion that the theoretical basis of qualitative analysis, often neglected or very sparsely dealt with in the smaller texts, merits equally detailed treatment with the purely practical side; only in this way can the true spirit of qualitative analysis be acquired. The book accordingly opens with a long Chapter entitled 'The Theoretical Basis of Qualitative Analysis', in which most of the theoretical principles which find application in the science are discussed.

The writer would be glad to hear from teachers and others of any errors which may have escaped his notice: any suggestions whereby the book can be improved will be welcomed.

A. I. Vogel
Woolwich Polytechnic London S.E.18

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CHAPTER I THE THEORETICAL BASIS OF QUALITATIVE ANALYSIS

A. CHEMICAL FORMULAE AND EQUATIONS

I.1 SYMBOLS OF THE ELEMENTS To express the composition of substances and to describe the qualitative and quantitative changes, which occur during chemical reactions in a precise, short, and straightforward way we use **chemical symbols** and **formulae**. Following the recommendations of Berzelius (1811), the symbols of chemical elements are constructed by the first letter of their international (Latin) names with, in most cases, a second letter which occurs in the same name. The first letter is a capital one. Such symbols are: O (oxygen, oxygenium) H (hydrogen, hydrogenium), C (carbon, carbonium), Ca (calcium), Cd (cadmium), Cl (chlorine, chlorinum), Cr (chromium), Cu (copper, cuprum), N (nitrogen, nitrogenium), Na (sodium, natrium), K (potassium, kalium), etc. As well as being a qualitative reference to the element, the symbol is most useful in a quantitative context. It is generally accepted that the symbol of the element represents 1 atom of the element, or, in some more specific cases, 1 grammatom. Thus C represents 1 atom of the element carbon or may represent 1 grammatom (12·011 g) of carbon. In a similar way, O represents one atom of oxygen or one grammatom (15·9994 g) of oxygen, H represents one atom of hydrogen or 1 grammatom (1·0080 g) of hydrogen etc. Names, symbols, and relative atomic masses of the elements are given in Section **IX.1**.

I.2 EMPIRICAL FORMULAE To express the composition of materials whose molecules are made up of more atoms, empirical formulae are used. These are made up of the symbols of the elements of which the substance is formed. The number of atoms of a particular element in the molecule is written as a subscript after the symbol of the element (but 1 is never written as a subscript as the symbol of the element on its own represents one atom).

Thus, the molecules of **carbon dioxide** is formed by one carbon atom and two oxygen atoms, therefore its empirical formula is CO_2. In the molecule of **water** two hydrogen atoms and one oxygen atom are present, therefore the empirical formula of water is H_2O. In the molecule of **hydrogen peroxide** on the other hand there are two hydrogen and two oxygen atoms present, its empirical formula is therefore H_2O_2.

Although there are no strict rules as to the order of symbols appearing in a formula, in the case of **inorganic** substances the symbol of the metal or that of hydrogen is generally written first followed by non-metals and finishing with oxygen. In the formulae of **organic** substances the generally accepted order is C, H, O, N, S, P.

The **determination** of the empirical formula of a compound can be made experimentally, by determining the percentage amounts of elements present in the substance using the methods of quantitative chemical analysis. At the same time the relative molecular mass of the compound has to be measured as well. From these data the empirical formula can be determined by a simple calculation. If, for some reason, it is impossible to determine the relative molecular mass the simplest (assumed) formula only can be calculated from the results of chemical analysis; the true formula might contain multiples of the atoms given in the assumed formula.

If the empirical formula of a compound is known, we can draw several conclusions about the physical and chemical characteristics of the substance. These are as follows:

(*a*) From the empirical formula of a compound we can see which elements the compound contains, and how many atoms of each element form the molecule of the compound. Thus, hydrochloric acid (HCl) contains hydrogen and chlorine; in its molecule one hydrogen and one chlorine atom are present. Sulphuric acid (H_2SO_4) consists of hydrogen, sulphur, and oxygen; in its molecule two hydrogen, one sulphur, and four oxygen atoms are present etc.

(*b*) From the empirical formula the **relative molecular mass** (molecular weight) can be determined simply by adding up the **relative atomic masses** (atomic weights) of the elements which constitute the compound. In this summation care must be taken that the relative atomic mass of a particular element is multiplied by the figure which shows the number of its atoms in the molecule. Thus, the relative molecular mass of hydrochloric acid (HCl) is calculated as follows:

$$M_r = 1{\cdot}0080 + 35{\cdot}453 = 36{\cdot}4610$$

and that of sulphuric acid (H_2SO_4) is

$$M_r = 2 \times 1{\cdot}0080 + 32{\cdot}06 + 4 \times 15{\cdot}9994 = 98{\cdot}0736$$

and so on.

(*c*) **Based on the empirical formula one can easily calculate the relative amounts of the elements present** in the compound or the **percentage composition** of the substance. For such calculations the relative atomic masses of the elements in question must be used. Thus, in hydrochloric acid (HCl) the relative amounts of the hydrogen and chlorine are

$$\mathrm{H:Cl} = 1{\cdot}0080 : 35{\cdot}453 = 1{\cdot}0000 : 35{\cdot}172$$

and (as the relative molecular mass of hydrochloric acid is 36·461) it contains

$$100 \times \frac{1{\cdot}008}{36{\cdot}461} = 2{\cdot}76 \text{ per cent H}$$

and

$$100 \times \frac{35{\cdot}453}{36{\cdot}461} = 97{\cdot}24 \text{ per cent Cl}$$

Similarly, the relative amounts of the elements in sulphuric acid (H_2SO_4) are

$$\begin{aligned}\mathrm{H:S:O} &= 2 \times 1{\cdot}0080 : 32{\cdot}06 : 4 \times 15{\cdot}9994 \\ &= 2{\cdot}016 : 32{\cdot}06 : 63{\cdot}9976 \\ &\quad 1 : 15{\cdot}903 : 31{\cdot}745\end{aligned}$$

and knowing that the relative molecular mass of sulphuric acid is 98·0763, we can calculate its percentage composition which is

$$100 \times \frac{2{\cdot}0160}{98{\cdot}0736} = 2{\cdot}06 \text{ per cent H}$$

$$100 \times \frac{32{\cdot}06}{98{\cdot}0736} = 32{\cdot}69 \text{ per cent S}$$

and

$$100 \times \frac{63{\cdot}9976}{98{\cdot}0736} = 65{\cdot}25 \text{ per cent O}$$

and so on.

(*d*) Finally, if the formula is known – which of course means that the relative molecular mass is available – we can calculate the volume of a known amount of a gaseous substance at a given temperature and pressure. If p is the pressure in atmospheres, T is the absolute temperature in degrees kelvins, M_r is the relative molecular mass of the substance in g mol^{-1} units and m is the weight of the gas in grams, the volume of the gas (v) is

$$v = \frac{mRT}{pM_r}\ \ell$$

where R is the gas constant, 0·0823 ℓ atm K^{-1} mol^{-1}. (The gas here is considered to be a perfect gas.)

I.3 VALENCY AND OXIDATION NUMBER In the understanding of the composition of compounds and the structure of their molecules the concept of valency plays an important role. When looking at the empirical formulae of various substances the question arises: are there any rules as to the number of atoms which can form stable molecules? To understand this let us examine some simple compounds containing hydrogen. Such compounds are, for example, hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen iodide (HI), water (H_2O), hydrogen sulphide (H_2S), ammonia (H_3N), phosphine (H_3P), methane (H_4C), and silane (H_4Si). By comparing these formulae one can see that one atom of some of the elements (like Cl, Br, and I) will bind one atom of hydrogen to form a stable compound, while others combine with two (O, S), three (N, P) or even four (C, Si). This number, which represents one of the most important chemical characteristics of the element, is called the **valency**. Thus, we can say that chlorine, bromine, and iodide are monovalent, oxygen and sulphur bivalent, nitrogen and phosphorus tervalent, carbon and silicon tetravalent elements and so on. Hydrogen itself is a monovalent element.

From this it seems obvious that the valency of an element can be ascertained from the composition of its compound with hydrogen. Some of the elements, for example some of the metals, do not combine with hydrogen at all. The valency of such elements can therefore be determined only in an indirect way, by examining the composition of their compounds formed with chlorine or oxygen and finding out the number of hydrogen atoms these elements replace. Thus, from the formulae of magnesium oxide (MgO) and magnesium chloride ($MgCl_2$) we can conclude that magnesium is a bivalent metal, similarly from the composition of aluminium chloride ($AlCl_3$) or aluminium oxide (Al_2O_3) it is obvious that aluminium is a tervalent metal etc.

In conclusion we can say that the valency of an element is a number which expresses how many atoms of hydrogen or other atoms equivalent to hydrogen can unite with one atom of the element in question.* If necessary the valency of the element is denoted by a roman numeral following the symbol like Cl(I), Br(I), N(III) or as a superscript, like Cl^{I}, Br^{I}, N^{III}, etc.

Some elements, like hydrogen, oxygen, or the alkali metals, seem always to have the same valency in all of their compounds. Other elements however show different valencies; thus, for example, chlorine can be mono-, tri-, penta- or heptavalent in its compounds. It is true that compounds of the same element with different valencies show different physical and chemical characteristics.

A deeper study of the composition of compounds and of the course of chemical reactions reveals that the classical concept of valency, as defined above, is not quite adequate to explain certain phenomena. Thus, for example, chlorine is monovalent both in hydrochloric acid (HCl) and in hypochlorous acid (HClO), but the marked differences in the chemical behaviour of these two acids indicate that the status of chlorine in these substances is completely different. From the theory of chemical bonding† we know that when forming hydrochloric acid, a chlorine atom takes up an electron, thus acquiring one negative charge. On the other hand, if hypochlorous acid is formed, the chlorine atom releases an electron, becoming thus a species with one positive charge. As we know, the uptake or release of electrons corresponds to reduction or oxidation (cf. Section **I.35**), we can therefore say that though chlorine is monovalent in these acids, its oxidation status is different. It is useful to define the concept of **oxidation number** and to use it instead of valency. The oxidation number is a number identical with the valency but with a sign, expressing the nature of the charge of the species in question when formed from the neutral atom. Thus, the oxidation number of chlorine in hydrochloric acid is -1, while it is $+1$ in hypochlorous acid. Similarly we can say that the oxidation number of chlorine in chlorous acid ($HClO_2$) is $+3$, in chloric acid ($HClO_3$) is $+5$, and in perchloric acid ($HClO_4$) $+7$. The concept of oxidation number will be used extensively in the present text.

I.4 STRUCTURAL FORMULAE Using the concept of valency the composition of compounds can be expressed with structural formulae. Each valency of an element can be regarded as an arm or hook, through which chemical bonds are formed. Each valency can be represented by a single line drawn outwards from the symbol of the element, like

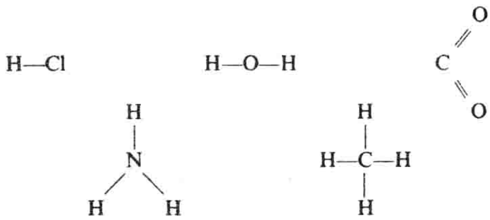
H— Cl— O= N≡ C≡

The structural formulae of compounds can be expressed with lines drawn between the atoms ‡ like

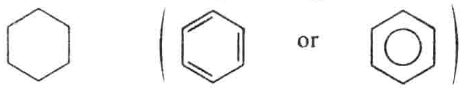
* Cf. Mellor's *Modern Inorganic Chemistry*, newly revised and edited by G. D. Parkes, Longman 1967, p. 99 et f.

† Cf. Mellor op. cit., p. 155 et f.

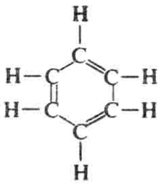
‡ There are no restrictions about the direction of these lines (unless differentiation has to be made between stereochemical isomers). Nor is there any restriction on the distances of atoms. Structural formulae must therefore be regarded only as a step in the approximation of the true structure. A three dimensional representation with true directions and proportional distances can most adequately be made with molecular model kits.



Structural formulae will be used in this text only when necessary, mainly when dealing with organic reagents. A more detailed discussion of structural formulae will not be given here; beginners should study appropriate textbooks.* Readers should be reminded that the simple hexagon



represents the benzene ring. Benzene (C_6H_6) can namely be described with the (simplified) ring formula in which double and single bonds are alternating (so-called conjugate bonds):



All the aromatic compounds contain the benzene ring.

I.5 CHEMICAL EQUATIONS Qualitative and quantitative relationships involved in a chemical reaction can most precisely be expressed in the form of chemical equations. These equations contain the formulae of the reacting substances on the left-hand side and the formulae of the products on the right-hand side. When writing chemical equations the following considerations must be kept in mind:

(*a*) Because of the fact that the formulae of the reacting species are on the left-hand side and those of the products are on the right, the sides generally cannot be interchanged (in this sense chemical equations are not equivalent to mathematical equations). In the cases of equilibrium reactions† when the reaction may proceed in both directions, the double arrow ($\rightleftarrows$) sign should be used instead of the equal ($=$) or single arrow ($\rightarrow$) sign.

(*b*) The individual formulae, used in the chemical reactions, must be written correctly.

(*c*) If more molecules (atoms or ions) of the same substance are involved in the reaction, an appropriate stoichiometric number has to be written in front of the formula. This number is a multiplication factor, which applies to all atoms in the formula. (Thus, for example $2Ca_3(PO_4)_2$ means that we have 6 calcium, 4 phosphorus, and 16 oxygen atoms in the equation.)

* Cf. Mellor's *Modern Inorganic Chemistry*, newly revised and edited by G. D. Parkes, Longman 1967, p. 155.

† Theoretically speaking, all reactions lead to an equilibrium. This equilibrium however may be shifted completely towards the formation of the products.

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