Law of Stoichiometry – The Law of Nature

Radhakrishnamurty Padyala
#282, DMLO, Yelahanka, Bangalore- 560064, India
Email: padyala1941@yahoo.com

ABSTRACT

The fundamental law of chemistry – the law of stoichiometry[♥] - is not properly understood even after two centuries of existence. The significance of the pivotal concept of 'equivalent of a reaction' is not recognized. This led to several misconceptions that include 'what a chemical reaction is'. The origin of the problems lies with lack of understanding of the distinction between a mixture of chemical reactions represented by the equation: $\sum\alpha_i X_i = 0$, and a chemical reaction represented by the equation: $\sum\nu_i X_i = 0$. $\nu_i \neq \alpha_{i;}$ (ν_i is the stoichiometric coefficient of species X_i and α_i is a rational number),. These problems are easily identified in the decomposition and combination of chemical reactions (that includes half cell reactions), specifically in case of disproportionation reactions. In these cases we find multiple values of z_{cell} (equivalents per mol of reaction) and properties such as E^0 (standard potential) for a given reaction. This is a paradox. It is impossible a for reaction under given conditions to have multiple values of a property (a thermodynamic state function). We critically analyze these issues and highlight in this paper the crucial aspects of a chemical reaction: That it must have a unique number of equivalents per mol, must be decomposable uniquely into two partial or half cell reactions, must be obtainable from combination of two partial or half cell reactions in a unique way; and, the distinction between a chemical reaction and a mixture of chemical reactions. Our analysis leads to: a new definition of chemical reaction; a new definition of linearly independent reactions, a new relation between the number of equivalents per mol of the partial or half cell reactions and the resultant chemical reaction; specify the two necessary and sufficient conditions to be satisfied in combining reactions to get resultant reactions. We apply the criteria to a few examples to show their applicability. We also comment on Avogadro number and the terminology - 'kJ per mol of reaction as written'. Chemistry must play an active role to bring back the preeminent role of chemistry in furtherance of natural sciences.

KEYWORDS: Chemical reaction definition, Mixture of chemical reactions, Law of stoichiometry, Combination of reactions, Linear independence of reactions, Chemical equivalent. Reaction cycle, Reaction as written.

Introduction

The significance of the fundamental law of chemistry – the law of stoichiometry – though known for more than two centuries is not clearly understood. Many publications[1-6] discussed the topic of stoichiometry from time to time. But the problems continue to persist. Unfortunately, the issues

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[♥] The law of stoichiometry is a universal law and has much broader scope. It is a concise statement of symmetry.

are discussed many times under the head 'Balancing chemical reactions'[7-12] which represents only one aspect of the general problem. Time plays no role in stoichiometry. Therefore, the terms 'before' and 'after' reaction in the context of discussing stoichiometry could give rise to misunderstanding. There exist no approximate or time dependent stoichiometric equations and the book of standards - IUPAC Gold book[17] itself falters on such issues. Similarly, mechanism of reaction plays no role in the stoichiometry of a reaction. The origin of the problems lies with lack of proper definition of a chemical reaction, lack of understanding of the distinction between a mixture of chemical reactions represented by the equation: $\sum\alpha_i X_i = 0$, and a chemical reaction represented by the equation: $\sum\nu_i X_i = 0$. $\nu_i \neq \alpha_i$; (ν_i is the stoichiometric coefficient of species X_i and α_i is a rational number). These problems are easily identified in the decomposition and combination of chemical reactions (that includes half cell reactions), especially in case of disproportionation reactions. In these cases we find multiple values of z_{cell} (equivalents per mol of reaction) and properties such as E^0 (standard potential) for a given reaction. This is a paradox. It is impossible a for reaction under given conditions to have multiple values of a property (a thermodynamic state function). The existence of these problems is clearly seen from the vague descriptions of: chemical reaction and other terms in IUPAC Gold Book (see Appendix).

We critically analyze these issues in this paper keeping in mind, that the conditions: a chemical reaction must have a unique equation, $\sum\nu_iX_i = 0$, representing it, it must have a unique value of 'number of equivalents per mol' or 'Faraday per mol', z_{cell}, and it must have a unique value of E^0, in order to satisfy the laws of conservation of mass, charge and energy. The requirement of uniqueness of z_{cell} demands a unique set of partial or component or half cell reactions that can be combined to yield a resultant reaction.

Our analysis leads to: a new definition of chemical reaction, a new definition of linearly independent reactions, a new relation between the number of equivalents per mol of the partial or half cell reactions and the resultant chemical reaction, the concept of a quantum of reaction or equivalent of a reaction, specification of the two necessary and sufficient conditions to be satisfied in combining reactions to get resultant reaction, and a better understanding of Avogadro number and the terminology - 'kJ per mol of reaction as written'.

Analysis

The lack of clear understanding of stoichiometry may be highlighted by way the following simple questions.

(i) What is a chemical reaction? Which of the following equations represent a chemical reaction?

$$2ClO_3^- + 2Cl^- + 4H^+ = 2ClO_2 + Cl_2 + 2H_2O \quad (1)$$

$$4ClO_3^- + 12Cl^- + 16H^+ = 2ClO_2 + 7Cl_2 + 8H_2O \quad (2)$$

$$8ClO_3^- + 16Cl^- + 24H^+ = 6ClO_2 + 9Cl_2 + 12H_2O \qquad (3)$$

$$ClO_3^- + 5Cl^- + 6H^+ = 3Cl_2 + 3H_2O \qquad (4)$$

(ii) Can there be more than one chemical reaction equation with a given set of reactants and of products as in Eqs. (1), (2) and (3)? Do equations (1) to (4) satisfy the law of stoichiometry?

(iii) Does a given reaction have a unique value for the number of equivalents per mole of a reaction? If yes, what is its value for the following reactions?

$$2Cu^+ = Cu^{2+} + Cu \qquad (2\ or\ 1?) \qquad (5)$$

$$5Mn^{4+} = 3Mn^{4+} + 3Mn^{4+} \qquad (6\ or\ 10\ or\ 15?) \qquad (6)$$

$$2CO = CO_2 + C \qquad (2\ or\ 4?) \qquad (7)$$

(iv) What are linearly independent reactions? Are the following reactions linearly independent?

$$Cu^{2+} + 2e = Cu \qquad (8)$$

$$Cu^{2+} + e = Cu^+ \qquad (9)$$

Problems (i) and (ii) arise due to the lack of understanding of what a chemical reaction is or the lack of appreciation of what the law of stoichiometry says. Problems (iii) and (iv) arise due to lack of understanding of rules governing combination of chemical reactions to get other reactions.

We start our analysis of the above issues by defining a ‘chemical reaction’. This will be followed by prescribing the necessary and sufficient conditions required to combine chemical reactions to form new chemical reactions.

Definition of a chemical reaction

A chemical reaction is a cyclic process that transforms chemical energy into other forms of energy and vice versa. It is represented by a mathematical equation of the form:

$$\sum_i v_i X_i = 0 \qquad (10)$$

Where, X_i is the ith species (it may even be a component reaction) in the reaction, v_i its stoichiometric coefficient. By convention v_i is positive for products and negative for reactants. v_i ‘s are integers.

The fundamental law that governs chemical reactions is called the '*Law of Stiochiometry'. It is defined by the following equation.*

$$\frac{dn_i}{\nu_i} = constant = d\xi \qquad (11)$$

Where, *dn$_i$* is the change in the number of moles of species *i* and ξ, is usually called the extent of reaction. It is the number of cycles of the reaction, when we perceive reaction as a cyclic process. In the case of electrochemical reactions, which are electron-transfer (or redox) reactions, equation (11) may be written as shown below to convey further information. It implicitly states that one equivalent of any species (or reaction) combines with one equivalent of any other species (or reaction) to give one equivalent of a (resultant) reaction.

$$\left\{\begin{aligned} \frac{dn_i}{\nu_i} = d\xi = \frac{dn_{ox}z_{ox}}{\nu_{ox}z_{ox}} = \frac{dn_{red}z_{red}}{\nu_{red}z_{red}} = \frac{d\xi\; z_{cell} \times e}{z_{cell} \times e} = \frac{1}{z_{cell}}\left(\frac{dq}{e}\right) \\ = \frac{No.of\ equivalents}{No.of\ equivalents\ per\ cycle} = \frac{1}{z_{cell}}\left(\frac{dqN_A}{e\,N_A}\right) = \frac{1}{z_{cell}}\left(\frac{dQ}{F}\right) = \frac{dn_i\; z_i \times u_i}{\nu_i z_i \times u_i} \\ = \frac{\Delta m_i\ in\ atomic\ mass\ units}{\Delta m_i\ in\ atomic\ mass\ units\ per\ cycle} = \frac{dn_i\; z_i \times u_i \times N_A}{\nu_i z_i \times u_i \times N_A} \\ = \frac{\Delta m_i\ in\ kg}{\Delta m_i\ in\ kg\ per\ cycle} = No.\ of\ cycles = \frac{\left(\frac{dq}{dt}\right)dt}{z_{cell}F} \\ = \frac{Idt}{z_{cell}F} \end{aligned}\right\} \qquad (12)$$

where, z$_{cell}$ is the number of equivalents per cycle (mole) of reaction, *F* is the Faraday constant and dq (*dQ)* is a small amount of charge in coulombs that passes through the cell or the change in number of equivalents of reaction. e, the electronic charge, N_A is the Avogadro number, u_i is the equivalent mass of ith species in the unified atomic mass (*u*) units. The last equation in the set of Eqs.(12) is given because it is used routinely and is easily recognized. *I* is the current flowing through the electrochemical cell (a measure of the time rate of the reaction in equivalents per unit time), *dt* is a small interval of time for which the current passes,

We see from Eq. (12) that:

$$e : F = u : kg = 1 : N_A \qquad (13)$$

Here, we have incidentally, an opportunity to learn something about Avogadro number.

Eq. (13) shows that N_A has the numerical value it does, because of the mass of the IPK being 1kg. If we had had a standard rod of different mass we would have got a different value of N_A. Again, since N_A is associated with number of entities, it was constrained to be an integer. But our result shows that N_A could as well be a rational number. Faraday's law does not require N_A to be an integer. From Eq. (11) we get,

$$\frac{dq \times E_{cell}}{z_{cell}e \times E_{cell}} = \frac{electrical\ energy}{chemical\ energy\ per\ cycle} = No.of\ cycles \qquad (14)$$

Eqs. (13) and (14) give the basis of considering chemical reactions as cyclic processes. In this sense chemical reactions can be treated similar to meshes or loops in an electrical network. Reaction with $z_{cell} = 1$ is an equivalent of reaction. It represents the quantum of a reaction. It is the unit of reaction. Chemical reactions occur in units of equivalents or quanta. With this understanding of chemical reactions, we proceed to consider methods of combining chemical reactions.

Combination of chemical reactions

It is important to note that chemical reactions can be combined in two different ways or by two different methods.

One method is to simply sum up two or more reaction equations in arbitrary proportions to get a *chemical equation* that resembles a chemical reaction equation but does not represent a chemical reaction (the second method is dealt with, in section on redox reactions). We may represent this combination as:

$$\sum_i \alpha_i X_i = 0 \qquad \propto_i \neq \nu_i \qquad (15)$$

Where α is a rational number. Note the similarity between Eq. (10) and Eq. (15). Eq. (15) represents a *mixture* of chemical reactions but not a chemical reaction, in particular, it violates the fundamental law of stoichiometry; it merely expresses the statements of laws of conservation of mass and of charge. Eq. (10) on the other hand represents a chemical reaction; it satisfies the law of stoichiometry. The relation between (10) and (15) is as that of a chemical compound, say, NaCl to a mixture of substances say, salt, sand and sugar.

The similarity between Eqs. (10) and (15) led to confusion and gave rise to issues raised under questions (i) and (ii) in the introduction. Eq. (15) does not represent a chemical reaction, Eqs. (2) and (3) do not represent reactions; they represent mixtures of reactions. Equations (1) and (4) represent reactions. We can decompose reaction (1) into two half cell reactions which when combined, give reaction (1). Similarly, we can do with reaction (4). The decompositions and combinations are unique. They are shown below.

$$2[ClO_3^- + 2\,H^+ + e = ClO_2 + H_2O] \qquad (16)$$
$$Cl_2 + 2e = 2Cl^- \qquad (17)$$

$$2\,ClO_3^- + 4H^+ + 2Cl^- = \ 2ClO_2 + 2H_2O + Cl_2 \qquad (1)$$

$$ClO_3^- \ + 6H^+ + 5e = \tfrac{1}{2}Cl_2 + 3H_2O \qquad (18)$$

$$5\left[\frac{1}{2}Cl_2 + e = Cl^-\right] \qquad (17)$$

$$ClO_3^- + 5Cl^- + 6H^+ = 3Cl_2 + \ 3H_2O \qquad (4)$$

Eqs. (1) and (4) are combined in different proportions to give equations (2) and (3). Therefore, Eqs (2) and (3) represent mixtures of reactions – they do not represent chemical reactions. This method of combining reactions is used in thermodynamics to obtain values of extensive properties such as ΔU, ΔH, ΔG, ΔS etc. ΔG^0 (standard free energy change) and E^0 (emf or standard potential) of a reaction are related through the equation: $\Delta G^0 = -zFE^0$. Eq. (13) applies equally well to both half cell reactions as well as to cell reactions.

For a mixture of reactions (or half cell reactions), obeying Eq. (15) we get,

$$\Delta G^0 = \sum_{i} \alpha_i \Delta G_i^0 = -\sum_{i} \alpha_i\, z_i F E_i^0 = -zFE^0 \qquad and\ \ z = \sum_{i} \alpha_i\, z_i \qquad (19)$$

A mixture of reactions does not have a unique value of either z_{cell} or E^0.

For a cell reaction, that is, for a chemical reaction, obeying Eq. (10) we get,

$$\Delta G^0 = \left(\Delta G_{ox}^0 \pm \Delta G_{red}^0\right) = \ -z_{cell}FE^0 \qquad (20)$$

$$E^0 = \ (E_{ox}^0 \pm E_{red}^0) \qquad (21)$$

Eq. (10) can be uniquely decomposed into two half cell reactions.

Here, we have, incidentally, an opportunity to comment on the terminology, ‘*per mol of reaction as written*’ used along with values of the intensive thermodynamic properties of reactions. We point out that, it is this method of combining reactions to give a mixture of reactions, that gave rise to the terminology, ‘*per mol of reaction as written*’ used along with values of the intensive thermodynamic properties of reactions. This has become an accepted practice and is taught as such to students in schools. This must change. Just as students are taught to distinguish mixtures of substances and compounds, they must also be taught to distinguish mixtures of reactions and pure reactions.

We now proceed to address the remaining issues (iii) and (iv). In order to discuss them, we take up redox reactions and disproportionation reactions. It is in these cases, issues (iii) and (iv) crop up prominently.

Redox reactions

Redox reactions bring into focus very important aspects of chemical reactions such as the concept of linear independence of chemical reactions, the number of equivalents per mole of reaction etc.

In principle, every chemical reaction can be considered to be (stoichiometric) combination of two ‘partial’ reactions. In electrochemistry, where we deal with electron-transfer reactions, such division is most prevalent. The partial reactions here are usually called half cell reactions. The half cell reactions occur at the spatially separated electrodes in an electrochemical cell and therefore, give a real feel for the partial reactions.

The second and more important method of combination of chemical reactions (component reactions) is to obtain a resultant chemical reaction. When applied to half cell reactions, it requires the electrons to get cancelled in the process of combination of the two half cells. However, it is only one of the conditions to be satisfied in the combination of reactions to get the resultant reaction. To show this, we take Eqs (8), (9) and equation (22) below.

$$Cu^{+} + e = Cu \qquad E^0 = 521V \qquad (22)$$

Taking two of the reactions (8), (9), (22) at a time, let us show the different combinations.

$$Cu^{2+} + 2e = Cu \qquad E^0 = 0.337V \qquad (8)$$

$$2[Cu^{2+} + e = Cu^{+}] \qquad E^0 = 0.153V \qquad (9)$$

$$2Cu^{+} = Cu^{2+} + Cu \qquad E^0 = 0.184V \quad z_{cell} = 2 \qquad (5)$$

$$2[Cu^{+} + e = Cu] \qquad E^0 = 0.521V \qquad (22)$$

$$Cu^{2+} + 2e = Cu \qquad E^0 = 0.337V \qquad (8)$$

$$2Cu^{+} = Cu^{2+} + Cu \qquad E^0 = 0.184V \quad z_{cell} = 2 \qquad (5)$$

$$Cu^{+} + e = Cu \qquad E^0 = 0.521V \qquad (22)$$

$$Cu^{2+} + e = Cu^{+} \qquad E^0 = 0.153V \qquad (9)$$

$$2Cu^{+} = Cu^{2+} + Cu \qquad E^0 = 0.368V \quad z_{cell} = 1 \qquad (5)$$

It can be seen that the three combinations lead to more than one value of emf, E^0, and the number of equivalents per mole of reaction, z_{cell} for reaction (5). This is paradoxical. Since E^0 is a thermodynamic state function, it must have a unique value for a given reaction. This paradox exposes the lack of proper definition of linearly independent reactions on the one hand and the lack of correct relation between z_{ox}, z_{red} and z_{cell} – representing respectively, the number of electrons involved in the oxidation, reduction half cell reactions and the cell reaction, on the other (more details below). Before proceeding further, it is would be useful to mention what disproportionation reactions are.

Disproportionation reactions

Disproportionation reactions are a group of reactions in which an element in a given oxidation state changes to two other oxidation states – one higher and the other lower, than the initial oxidation state. Reaction (5) is an example of disproportionation reaction in which Cu^+ changes to higher oxidation state Cu^{2+} and lower oxidation state Cu. In the combination of these half cell reactions paradoxes arise as we saw above. The origin of these paradoxes is tied up with the concept of linear independence of chemical reactions or the equations representing them.

Necessary and sufficient conditions to obtain a chemical reaction by combination of two chemical reactions

There are two conditions to be satisfied, that are necessary and sufficient to obtain a chemical reaction by the combination of two (component) chemical reactions. They are:

1. The component reactions must be linearly independent.
2. The component reactions must be combined stoichiometrically, i.e., in a fixed ratio dictated by the law of stoichiometry. This criterion decides the relation between z_{ox}, z_{red} and z_{cell}.

Linearly independent reactions

A number of publications[5-11] discussed different methods (ion-electron/half cell reaction method and matrix methods) of combination of reactions including half cell reactions, to get balanced reactions. Risteski[5] gives very useful information on the literature available. Among these methods, matrix methods seem to have over taken the others. The matrix methods deal with the issue of linear independency of equations[2,3,5,7-12]. These methods use conservation of mass and charge as the criteria to arrive at the set of independent equations from a given set of species. However, these methods do not lead to correct results. For example, using the matrix method, Colman and White[8] obtain the incorrect set of reactions (8) and (9) as linearly independent set for the aqueous copper sulfate system containing the species Cu^{2+}, Cu^+ and Cu. This set does not correspond to the correct set of linearly independent component reactions; it leads to incorrect values of the properties of the cell reaction as shown above. Even Weltin's matrix based approach[12], which is different from others, does not rule out the possibility of the incorrect set: C + O_2 = CO_2 and 2C + O_2 = 2CO for the system of species C, O_2, CO, CO_2. In fact, while the matrix method correctly identifies the number of independent equations for a given set of species, there is no unique choice of the set of linearly independent equations. This is because the equations of the set themselves are not unique[9,12]. Any equation of the set could be replaced by a linear combination of the members of the set. Thus the matrix method fails to distinguish between a reaction and a mixture of reactions. In other words it fails to distinguish between Eqs. (10) and (15). Therefore, the question arises: What are linearly independent reactions?

Following the definition given by Scott[13] for linearly independent equations that applies to mesh current equations in electric network analysis, we define *linearly independent reactions as the set of reactions each of which contains some information not contained in any other reaction*. Our concept of reaction as a cyclic process also supports this. This criterion helps us to reject the conventional matrix methods because they could lead to incorrect set of equations. Eq. (8) is the mixture (sum) of reactions (9) and (22); as such, Eq. (8) contains in it all the information contained in reaction (9). Consequently, reaction (9) contains no information not contained in reaction (8). Therefore reactions (8) and (9) do not form a pair of linearly independent set of reactions. Similarly, reaction (8) contains reaction (22) in it; so they too, cannot form the correct set either.

Therefore, to obtain reaction (4), the correct set of linearly independent reactions is the set of reactions (9) and (22). Their combination leads to the correct values of the properties of reaction (4) as shown above.

We may reiterate before ending this section that adding the same half cell reaction to the anodic and cathodic reactions occurring at the two electrodes in a cell, destroys their linear independency and thereby stoichiometry.

Stoichiometric combination of reactions and the relation between z_{ox}, z_{red}, z_{cell}.

The second criterion deals with stoichiometry i.e. fixed ratio of combination of reactions. This ratio decides the relation between z_{ox}, z_{red} and z_{cell}. Even when a set of linearly independent half cell reactions are given, incorrect values of properties of reactions (for eg., E^0, z_{cell}) would be obtained in the absence of the correct proportions in the combination. In common parlance z_{cell} is the number of equivalents per mol of reaction. The ratio of combination of the half cell reactions is governed by the relation below.

$$\nu_{ox}.z_{ox} = \nu_{red}.z_{red} = z_{cell} = LCM\ of\ z_{ox}\ and z_{red} \qquad (23)$$

Eq (23) gives a new definition of z_{cell}. This definition works in all cases and leads to the correct and unique values of the properties of reactions. For example, for reaction (1), we get LCM of 1 and 1 as 1 which is the correct value; in case of reaction (2) we get LCM of 3 and 2 which is 6 is the correct value that leads to correct and unique values of other properties of the reaction. Applying it to Daniel cell reaction (see below) we get $z_{cell} = 2$, the correct value.

In the literature[14-16] z_{cell} has been defined variedly. Laitinen[14] uses the definition of z_{cell} as the number of electrons cancelled in arriving at the cell reaction. Based on this criterion he found disproportionation reactions give more than one value of z_{cell} and consequently multiple values of E^0 for the same cell reaction. Gray[15] discussed this problem at length for disproportionation reactions. He concluded that there exists no general relation connecting z_{ox}, z_{red} and z_{cell}. According to Parsons[16] z_{cell} is the product of z_{ox} and z_{red}. Each of these definitions give different values for z_{cell} of a given reaction and consequently for E^0 and therefore, are mutually inconsistent. For example, let us take the well known Daniel cell reaction, to show the inconsistency between Laitinen's and Parson's definitions. The following two half cell reactions, (8) and (24) can be combined to get Daniel cell reaction (25);

$$Cu^{2+} + 2e = Cu \qquad (8)$$

$$Zn^{2+} + 2e = Zn \qquad (24)$$

$$Cu^{2+} + Zn = Cu + Zn^{2+} \qquad (25)$$

In arriving at reaction (25) from reactions (8) and (24) the number of electrons that got cancelled is 2. Therefore according to Laitinen, $z_{cell} = 2$. However, according to Parsons, $z_{cell} = 2 \times 2 = 4$. The correct value is 2. Again in cases where the component half cell reactions are linearly dependent, as in the case of combination of reactions (8), (9) and (8), (24), Laitinen's definition leads to wrong result $z_{cell} = 2$, since the correct value of $z_{cell} = 1$.

What we considered till now concerns combination of only two half cell reactions (or reactions). It is possible in some cases that a reduction reaction at one electrode is associated with more than one oxidation reaction at the other electrode in a cell, or vice versa. For example, the very complex redox reaction[8] below:

$$10\{[Cr(N_2H_4CO)_6]_4[Cr(CN)_6]_3\} + 1176KMnO_4 + 1399H_2SO_4 = 35K_2Cr_2O_7 +$$

$$1176MnSO_4 + 420CO_2 + 660KNO_3 + 223K_2SO_4 + 1879H_2O \qquad (26)$$

involves one reduction half cell reaction of Mn^{7+} to Mn^{2+} and four parallel oxidation half cell reactions: a) Cr^{2+} to Cr^{6+}, b) Cr^{3+} to Cr^{6+}, c) N^{-3} to N^{+5}, and d) $N^{-}5$ to N^{+5} with $\nu_{ox} = 10$, $z_{ox} = \sum z_{i,ox} = (12 + 12 + 384 + 180) = 588$, and $\nu_{red} = 1176$, $z_{red} = 5$, to give, 10x588 = 1176x5 = LCM of 5880 and 5880 = 5880 = z_{cell}.

Conclusion

Problems associated with lack of clear understanding of the fundamental law of chemistry – the law of stoichiometry - led to several misconcepts with regard to the definition of chemical reaction, combination of chemical reactions to form new chemical reactions, linear independence of reactions, the number of equivalents per mole of reaction etc. This is rectified by giving new definitions of the terms and applying them to a few typical reactions. The results are in accordance with the law of stoichiometry.

Appendix[17]

A few terms in IUPAC Gold book[17] are picked up to show the vague descriptions but no clear definitions. Our comments are added for each of the terms to high light the lack of clarity in IUPAC Gold book.

IUPAC Gold Book gives this under the head, *'stoichiometric*: Involving chemical combination in simple integral ratios, characterized by having no excess of reactants or products over that required to satisfy the balanced chemical equation representing the given chemical reaction.

Equation (15) satisfies this condition but it is not a stoichiometric equation representing any chemical reaction. IUPAC way of looking at stoichiometry lacks the spirit of stoichiometry. It fails to recognize chemical reaction as a cyclic process.

Under the head, *'Chemical reaction'* this definition is given: A process that results in interconversion of chemical species. Chemical reactions may be elementary reactions or stepwise reactions (It should be noted that this definition includes experimentally observable interconversions of conformers.) Detectable chemical reactions normally involve sets of molecular entities as indicated by this definition, but it is often conceptually convenient to use the term also for changes involving single molecular entities (i.e. 'microscopic chemical events').

This is a vague description of a chemical reaction at best.

Under the head, *'Chemical reaction equation'*, we find: Symbolic representation of a chemical reaction where the reactant entities are given on the left hand side and the product entities on the right hand side. The coefficients next to the symbols are formulae of entities are the absolute values of the stoichiometric numbers. Different symbols are used to connect the reactants and products with the following meanings: = for a stoichiometric relation; → for a net forward reaction; ⇆ for a reaction in both directions'; ⇋ for equilibrium."

We can see clearly the different perceptions. The reactants and products together make the cyclic process; from this view point the arrow symbols for net reaction, for a reaction in both directions don't make sense, because it is impossible for a reaction to occur in both directions (clockwise and anticlockwise) at any instant. This is also the reason why addition (or subtraction) of the forward and backward reactions to give the net reaction is meaningless.

Under the head, *'equivalent entity'*, is given, this: "Entity corresponding to the transfer of a H^+ ion in a neutralization reaction, of an electron in a redox reaction, or to a magnitude of charge number equal to 1 in ions. Examples: ½ H_2SO_4, 1/5 $KMnO_4$, 1/3 Fe^{3+}.

Given a species, it is not possible to find an equivalent entity, since equivalent is defined by a reaction, not by a species! Therefore, these examples are misleading.

Under the head, *'charge number n, ν_e, z of a cell reaction'*, is given, this: Number of electrons transferred according to the cell reaction equation. We discussed this point at length in our paper.

Charge number: Ratio of charge of a particle to the elementary chage.
Then what about the charge number of a reaction?

Acknowledgement

I thank Mr. Arunmozhi Selvan Rajaram, Davis Langdon KPK India Pvt Ltd, Chennai, India, for his constant support and encouragement of my research pursuits in every possible way.

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