

# The Basis of the Limiting Reagent Concept, Its Identification and Applications

Diego J. R. da Silva \*

Departamento de Química Fundamental Universidade Federal de Pernambuco, Recife, Brazil

\*Corresponding author: [diegoraposo@hotmail.com](mailto:diegoraposo@hotmail.com)

**Abstract** A general formalism for defining and identifying limiting reagent in closed systems is proposed and it is correlated to usual definitions and identification methods. An alternative definition of limiting reagent is proposed, based on real situations after the reaction is complete. Useful equations relating the limiting reagent to products and excess reagents (if the limiting reagent is completely consumed or not) and to reaction yields are given and briefly applied.

**Keywords:** limiting reagent, stoichiometry, percent yield, excess reagent

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## 1. Introduction

Stoichiometry is one of the fundamental and universal subjects in General Chemistry courses, and its connection to higher-level concepts such as limiting reagent (or limiting reactant) and reaction yields are unavoidable. Much work has been performed to address the difficulties in teaching those themes [1], and how to aid this teaching through analogies [2,3], graphics [4,5] and other techniques such as laboratory experiments [6,7]. However, the reverse situation has not been explored. Namely, once the student understands the conceptual basis of limiting reagent and percentage reaction yield, and acquires practical experience with problems concerning those concepts, it seems logical to go further and understand why and how those methods (for identifying limiting reagents, for instance) actually work. It is worthwhile to go beyond practical and common sense, usually evoked to explain them, to show the deeper physical-chemistry and mathematical structure behind them. Indeed, these issues have not been treated at this level of deepness in text-books, so here it is developed an introduction based on mathematical arguments as simplified as possible, but keeping certain rigor and clarity.

From this analysis, it was possible to derive some equations that can be used for limiting reagent identification and to calculate reaction yield and excess reagent quantities. Those equations can be an alternative to ordinary methods and are equally valid, with some pedagogical and didactical insights. Differently, though, they can be derived through physical-chemistry arguments and mathematical reasoning, which are presented in the "Demonstrations" section. This section can be skipped by the reader aiming solely at applications more than demonstrations, and some examples are given in the "Equations for practical proposes and applications" section.

It is noteworthy that the present approach has direct association with concepts from Chemical Kinetics, because the reaction extent is implicitly defined.

## 2. Common Definitions and Methods

There are at least two usual definitions of limiting reagent presented in text-books:

- The reagent that limits the amount of product to be generated [8,9,10,11];
  - The one that is completely consumed first [5,12,13,14];
- And, in a not necessarily correlated manner, some methods for limiting reagent identification such as:
- Comparing how much of one arbitrary reagent have to react completely (stoichiometrically) with another with the available quantity [8,15]. **Ex.:** For the reaction  $aA + bB \rightarrow cC$ , a reagent (A, for instance) is chosen and it is calculated how much of the other (B, in this case) is necessary in order to react completely with the first. Despite the real amount of B at the beginning of the reaction being  $n_{B,0}$ , it is defined and calculated the substance amount  $n'_{B,0}$  as,

$$n'_{B,0} = n_{A,0} \times \frac{b \text{ mol of B}}{a \text{ mol of A}} \quad (1)$$

If  $n_{B,0} > n'_{B,0}$ , B will be in excess at the end of the reaction, and therefore, A is considered a limiting reagent. If  $n_{B,0} < n'_{B,0}$ , however, A will be in excess and B is the limiting reagent.

- Comparing the amount of substance ratio of a couple of reagents with the respective stoichiometric coefficient ratio [8,9,15]. **Ex.:** Considering reaction  $aA + bB \rightarrow cC$ , a pair of reagents A and B (the only one in this case) is chosen and the ratio  $n_{A,0} / n_{B,0}$  (for instance) is

compared with  $a/b$  ("actual mole ratio" vs. "stoichiometric mole ratio", according to [1]). If  $n_{A,0}/n_{B,0} > a/b$ , part of A will not react (excess) and the limiting reagent is B, for this single pair case. If  $n_{A,0}/n_{B,0} < a/b$ , A is the limiting one. In general, for each  $N$  reagents,  $N-1$  reagent pairs must be compared according this method. It is intrinsically connected to method **a**), because using eq 1:

$$\frac{n_{A,0}}{n_{B,0}} > \frac{a}{b}$$

$$\frac{n_{A,0}}{n_{B,0}} = \frac{n'_{B,0} \times (a \text{ mol of A})}{n_{B,0} \times (b \text{ mol of B})} > \frac{a}{b}$$

$$\frac{n'_{B,0}}{n_{B,0}} > 1 \Rightarrow n'_{B,0} > n_{B,0}$$

That shows B as the limiting reagent by the relation  $n'_{B,0} > n_{B,0}$  used in method **a**).

- c) *Identifying which reagent gives the least amount of an arbitrary product* [11-14,16]. **Ex.:** Using the same reaction  $aA + bB \rightarrow cC$  as example, the amount of product if each reagent is completely consumed (assuming them to be limiting reagents, l. r.) is calculated:

$$n_C(\text{"A" as l. r.}) = \left(\frac{c}{a}\right) \times n_{A,0} \quad (2)$$

$$n_C(\text{"B" as l. r.}) = \left(\frac{c}{b}\right) \times n_{B,0} \quad (3)$$

The real limiting reagent is the one that gives the least amount of product, thus, if  $n_C(\text{"A" as l. r.}) < n_C(\text{"B" as l. r.})$  A is the limiting reagent, or  $n_C(\text{"A" as l. r.}) > n_C(\text{"B" as l. r.})$  implies B is the one. Its connection with method **b**) can be proved, assuming the following inequality as an example:

$$n_C(\text{"A" as l. r.}) > n_C(\text{"B" as l. r.})$$

Using eqs 2 and 3:

$$\left(\frac{c}{a}\right) \times n_{A,0} > \left(\frac{c}{b}\right) \times n_{B,0} \Rightarrow \frac{n_{A,0}}{n_{B,0}} > \frac{a}{b}$$

Indicating B as the limiting reagent according to method **b**).

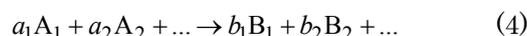
- d) *Verifying the reagent that has the smallest amount of the ratio between its amount of substance and its respective stoichiometric coefficient* [12,17]. **Ex.:** If the reaction is  $aA + bB \rightarrow cC$ , the relation  $n_{A,0}/a < n_{B,0}/b$  implies that A is the limiting reagent, whereas for  $n_{A,0}/a > n_{B,0}/b$ , the limiting reagent is B. This method can be simply correlated to method **b**) (and then to the others from it):  $n_{A,0}/a > n_{B,0}/b \Rightarrow n_{A,0}/n_{B,0} > a/b$  when B is the limiting reagent. This method will be generalized in the next section.

Definitions **i**) and **ii**) are equivalent, because the limiting reagent limits product formation (definition **i**) by

being completely consumed first (definition **ii**). Although these definitions are perfectly valid, especially for educational purposes, both refer to a situation to which at least one of the reagents is completely exhausted at the end of the reaction, condition that, for several reasons, cannot be attained in practice [11,15]. This prevents the construction of a general mathematical formalism that explains real cases and yielding of practical equations. In addition, *it lacks a clear relation between definition and method*. Namely, the definitions refer to the reaction completion, whereas the methods for limiting reagent identification are based on initial amounts of substance, with no given relation between them. Therefore, it is offered the following alternative definition for limiting reagent as **iii**) the reagent(s) with the least value of *stoichiometric amount of substance at the end of the reaction* [18], where the ratio between the amount of substance and its stoichiometric coefficient is its stoichiometric amount. This definition do not refer to any hypothetical situation, but leads to definitions **i**) and **ii**) as special cases, namely when the amount of the limiting reagent turns out to be zero when reaction is over. Also, it is directly related to method **d**) and through it, to other methods in any situation, real or hypothetical, thus showing its generality, rigorousness and usefulness. The proof of those assertions and their consequences will be provided in the next section.

### 3. Demonstrations

Consider the following general chemical reaction:



where  $a_i$  is the stoichiometric coefficient of reagent  $A_i$  and  $b_k$  is the stoichiometric coefficient of product  $B_k$ . Stoichiometric number of species  $X$ ,  $v_X$ , can be defined as [20],

$$v_X := \begin{cases} -a_i, & \text{if } X \text{ is a reagent } A_i \\ b_k, & \text{if } X \text{ is a product } B_k \end{cases} \quad (5)$$

In words, the stoichiometric number of a given reagent is the negative of its stoichiometric coefficient, and its own stoichiometric coefficient if it is a product. The distinction between stoichiometric number and stoichiometric coefficient is that the former can be positive (product) or negative (reagent), while the latter will always be positive. This definition is quite useful because it relates directly the variation of the amount of substance with reaction extent [22].

The amount of substance, often called "number of moles", is usually denoted by  $n$ . Although its unit is mol, it is recommended not to use "number of moles" to designate "amount of substance", by the same reason that "number of meters" should not be used to designate "length" [21]. To indicate a species  $i$ , the terms such as  $n_i$  or  $n(i)$  can be used.

There is a relationship between the amount of substance variation relative to another substance in the same reaction and their respective stoichiometric numbers. For a pair of substances  $i$  and  $j$  this relationship takes the form [24]:

$$\frac{dn_i}{dn_j} = \frac{v_i}{v_j} \quad (6)$$

According to eq 6, for a product B and a reagent A, an infinitesimal change in amount of B is related to an infinitesimal change in amount of A by the following equation:

$$\frac{dn_B}{dn_A} = \frac{v_B}{v_A} = -\frac{b_B}{a_A}$$

Because the derivative of  $n_B$  with respect to  $n_A$  is negative, the increase in the amount of reagent A implies a decrease in the amount of product B, and vice-versa. This has to be true for the conservation of the number of atoms (and mass) to be valid in closed systems (those with no exchange of mass with the surroundings), thus an increase in the number of certain species have to be balanced by a decrease in the number of others in order to keep the numbers of each given atom constant through the chemical reaction.

Equation 6 is valid for infinitesimal changes in the amount of substance as well as for finite variations. Namely, if  $n_{i,0}$  and  $n_{j,0}$  are the initial amounts of  $i$  and  $j$ , whereas  $n_{i,t}$  and  $n_{j,t}$  refer to the amount of substance at time  $t$ , the integration of eq 6 leads to:

$$\begin{aligned} \frac{dn_i}{v_i} &= \frac{dn_j}{v_j} \\ \int_{n_{i,0}}^{n_{i,t}} \frac{dn_i}{v_i} &= \int_{n_{j,0}}^{n_{j,t}} \frac{dn_j}{v_j} \\ \frac{n_{i,t} - n_{i,0}}{v_i} &= \frac{n_{j,t} - n_{j,0}}{v_j} \quad \{\forall(i, j)\} \end{aligned} \quad (7)$$

The symbol represents “for all”, therefore  $\forall(i, j)$  means “for all  $i$  and”, or for any pair of substances involved in the given reaction. If  $n_i$  and  $n_j$  represents the amount of  $i$  and  $j$  at the end of the reaction (instead of integration variables):

$$\frac{n_i - n_{i,0}}{v_i} = \frac{n_j - n_{j,0}}{v_j} \quad \{\forall(i, j)\} \quad (8)$$

In the reaction represented by the chemical eq 4, for instance:

$$\frac{n_{A1} - n_{A1,0}}{v_{A1}} = \dots = \frac{n_{B1} - n_{B1,0}}{v_{B1}} = \dots \quad (9)$$

Equation 8 is the most general form to be used in stoichiometric problems, and it is used implicitly in textbooks when dealing with excess reagents and chemical equilibrium, but sometimes explicitly when defining reaction rate according to different chemical species through the reaction extent definition [25].

### 3.1. Limiting Reagent

Definition **iii)** takes a simpler form when the definition of “stoichiometric amount of substance”, as the ratio

between amount of substance and its stoichiometric coefficient (therefore, it is a “reaction specific” quantity) is employed. In fact, it needs to be used only for reagents, so if  $n_i$  is the amount of a reagent  $i$  at the end of reaction,  $s_i := n_i / a_i$ ;  $s_i$  is the final stoichiometric amount of  $i$ . The initial stoichiometric amount of  $i$  is similarly defined as  $s_{i,0} := n_{i,0} / a_i$  [26].

For a given reaction, the stoichiometric amount of each reagent can be arranged or ordered according to its numerical value. For final stoichiometric amounts of a set of  $r$  reagents the following series of (in)equalities express the increasing values of  $s_i$ :

$$s_1 \leq s_2 \leq \dots \leq s_r \quad (10)$$

This always can be done, because the mathematical relation between  $n_i / a_i$  and  $n_j / a_j$  should be  $n_i / a_i > n_j / a_j$ ,  $n_i / a_i = n_j / a_j$  or  $n_i / a_i < n_j / a_j$ . Choosing an increasing order, from reagent 1 to reagent  $r$ , the (in)equations in 10 can be written accordingly. In this arrangement, reagent 1 is the (or one of the) reagent(s) that has the smallest value of  $s$ . That is the simpler form of the definition of limiting reagent according to **iii)**: *the reagent with the least value of final stoichiometric amount of substance*. Therefore, if L is a limiting reagent, its final stoichiometric amount is such that:

$$s_L \leq s_i \quad (\forall i) \text{ (definition iii)}. \quad (11)$$

That is the mathematical statement of definition **iii)**. If there is only one limiting reagent, the value  $n_L / a_L$  is the smallest when compared to all remaining values of  $s$ , for any reagent  $i$ . The equality  $s_L = s_i$  (if  $i \neq L$ ) refers to more than one limiting reagent, with same minimum value of  $s_L$ . In this case, if there is  $h$  limiting reagents  $L^{(1)}$ ,  $L^{(2)}$ , ...,  $L^{(h)}$ , eq 11 lead to the following arrangement:

$$s_{L^{(1)}} = s_{L^{(2)}} = \dots = s_{L^{(h)}} < s_{h+1} \leq s_{h+2} \leq \dots \leq s_r \quad (12)$$

Reagents that are not limiting reagents are defined as *excess reagents* (in eq 12 the substances  $h+1$ ,  $h+2$ , ...,  $r$ ). Their mathematical definition is “E is an excess reagent if there is at least one reagent  $i$  such that  $s_E > s_i$ ”, or  $(\exists i)(s_E > s_i)$ . In those cases, the equality between excess reagents  $i$  and in  $s_i \leq s_{i+1}$  can only be attained if the initial stoichiometric amounts of substance are the same:  $s_{i,0} = s_{i+1,0}$  ( $n_{i,0} / a_i = n_{i+1,0} / a_{i+1}$ ). The reason for this will be clear soon.

Definitions **i)** and **ii)** are limiting cases of definition **iii)** because they refer to the hypothetical case where  $s_L = 0$  (because  $n_L = 0$ ) in eq 11, when the limiting reagent is completely consumed. However, methods for limiting reagent identification are based on amounts of substance at the beginning of the reaction, because there is no practical means to obtain such information after the reaction is performed (even if it is referred to conceptually define limiting reagent). From methods **a)** through **d)**, values of  $n_{i,0}$  (not  $n_i$ ) for every reagent  $i$  are compared, considering their respective stoichiometric coefficients  $a_i$ .

To show the relationship between definition **iii**) and methods **a**) through **d**), but especially for method **d**), it is necessary (and sufficient) to prove that the increasing ordering of (in)equalities in eq 10 is maintained at the beginning of the reaction, that is, for values of  $s_{i,0}$ . In other words, if those (in)equalities are written in a shorter representation:

$$s_i \leq s_j \quad \{\forall(j > i)\}. \quad (13)$$

The following implication can be proved true [28]:

$$(s_i \leq s_j) \Rightarrow (s_{i,0} \leq s_{j,0}) \quad \{\forall(j > i)\}. \quad (14)$$

That means  $s_1 \leq s_2 \leq \dots \leq s_r$  implies  $s_{1,0} \leq s_{2,0} \leq \dots \leq s_{r,0}$ , and the limiting reagents identified by the minimum value of  $s$  can instead be identified by the least value of  $s_0$  (method **d** application). To demonstrate the implication in eq 14, the first step is to use eq 8 for a pair of reagents  $i$  and  $j$ , namely

$$\frac{n_i - n_{i,0}}{a_i} = \frac{n_j - n_{j,0}}{a_j} \quad \{\forall(i, j)\}. \quad (15)$$

If we consider an arbitrary reagent  $g$  from those  $r$  involved we have:

$$\begin{aligned} \frac{n_g - n_{g,0}}{a_g} &= \frac{n_j - n_{j,0}}{a_j} \quad \{\forall j\} \\ \frac{n_j}{a_j} - \frac{n_g}{a_g} &= \frac{n_{j,0}}{a_j} - \frac{n_{g,0}}{a_g} \quad \{\forall j\}. \end{aligned} \quad (16)$$

The hypothesis  $s_i \leq s_j \quad \{\forall(j > i)\}$  can be expressed in terms of the amounts of substance when reaction is finished as,

$$\frac{n_i}{a_i} \leq \frac{n_j}{a_j} \quad \{\forall(j > i)\}. \quad (17)$$

By subtracting  $s_g := n_g / a_g$  at both sides of eq 17, we can transform the (in)equalities from  $s_1 \leq s_2 \leq \dots \leq s_r$  into  $s_1 - s_g \leq s_2 - s_g \leq \dots \leq s_r - s_g$ :

$$\frac{n_i}{a_i} - \frac{n_g}{a_g} \leq \frac{n_j}{a_j} - \frac{n_g}{a_g} \quad \{\forall(j > i)\}. \quad (18)$$

Using eqs 18 and 16 for both  $j$  and  $i$ :

$$\frac{n_{i,0}}{a_i} - \frac{n_{g,0}}{a_g} \leq \frac{n_{j,0}}{a_j} - \frac{n_{g,0}}{a_g} \quad \{\forall(j > i)\}. \quad (19)$$

Adding  $s_{g,0} := n_{g,0} / a_g$  in both sides of eq 19 gives

$$\begin{aligned} \frac{n_{i,0}}{a_i} &\leq \frac{n_{j,0}}{a_j} \quad \{\forall(j > i)\} \\ s_{i,0} &\leq s_{j,0} \quad \{\forall(j > i)\}. \end{aligned} \quad (20)$$

Therefore the implication  $(s_i \leq s_j) \Rightarrow (s_{i,0} \leq s_{j,0}) \quad \{\forall(j > i)\}$  is proved. Actually, because all mathematical

operations involved in the demonstration admits inverse operation (subtraction/summation) it is straightforward to show, in a very similar way, the implication  $(s_{i,0} \leq s_{j,0}) \Rightarrow (s_i \leq s_j) \quad \{\forall(j > i)\}$ . That means  $(s_i \leq s_j) \quad \{\forall(j > i)\}$  if and only if  $(s_{i,0} \leq s_{j,0}) \quad \{\forall(j > i)\}$ , or [29]:

$$(s_i \leq s_j) \Leftrightarrow (s_{i,0} \leq s_{j,0}) \quad \{\forall(j > i)\}. \quad (21)$$

This important relation allows us to connect definition **iii**), which is a general case of definitions **i**) and **ii**), with method **d**). Namely, if eq 12 holds, so it does eq 22:

$$s_{L(1),0} = \dots = s_{L(h),0} < s_{h+1,0} \leq s_{h+2,0} \leq \dots \leq s_{r,0}. \quad (22)$$

And the limiting reagent(s) can be identified by its(their) minimum value of the initial stoichiometric amount of substance, which describes method **d**):

$$(s_{L,0} \leq s_{i,0}) \quad (\forall i) \text{ (method d)}. \quad (23)$$

Therefore, definition **iii**) (eq 11, from which eq 12 is derived) of limiting reagent is intrinsically related to the identification method **d**) (eq 23):  $(s_L \leq s_i) \Leftrightarrow (s_{L,0} \leq s_{i,0}) (\forall i)$  (according to eq 21).

Methods **a**) through **c**) should also be connected to definition **iii**), through their relationship with method **d**). From eq 23:

$$\frac{n_{L,0}}{a_L} \leq \frac{n_{i,0}}{a_i} \quad (\forall i)$$

$$\frac{n_{L,0}}{n_{i,0}} \leq \frac{a_L}{a_i} \quad (\forall i) \text{ (method b)}. \quad (24)$$

Equation 24 describes method **b**).

For a given reagent  $i$  and product  $k$ , eq 8 implies:

$$\frac{n_{i,0} - n_i}{a_i} = \frac{n_k - n_{k,0}}{b_k} \quad \{\forall(i, k)\}. \quad (25)$$

Assuming that the amount of limiting reagent at the end of the reaction is zero ( $n_L = 0$ ) and the amount of any product is zero at the beginning of the reaction ( $n_{k,0} = 0$ ), eq 25 gives:

$$\frac{n_{L,0}}{a_L} = \frac{n_k}{b_k} \quad (\forall k). \quad (26)$$

The amount of product according to eq 26 should be:

$$n_k (\text{"L" as l. r.}) = \frac{n_{L,0} b_k}{a_L} \quad (\forall k). \quad (27)$$

If  $i$  is a limiting reagent, and is completely consumed at the end of the reaction as well, the amount of product is:

$$n_k (\text{"i" as l. r.}) = \frac{n_{i,0} b_k}{a_i} \quad \{\forall(i, k)\}. \quad (28)$$

Substitution of eqs 27 and 28 into eq 23 gives the mathematical statement of method **c**):

$$\frac{n_{L,0}}{a_L} \leq \frac{n_{i,0}}{a_i} \quad (\forall i)$$

$$\frac{n_k(\text{"L" as l. r.})}{b_k} \leq \frac{n_k(\text{"i" as l. r.})}{b_k} \quad \{\forall(i, k)\}$$

$$n_k(\text{"L" as l. r.}) \leq n_k(\text{"i" as l. r.}) \quad \{\forall(i, k)\} \text{ (method c). (29)}$$

The connection between methods **a**) and **d**) can be established by defining the amount of limiting reagent L,  $n'_{L,0}(i)$ , that should react completely with reagent  $i$ , despite its true quantity is  $n_{L,0}$ :

$$n'_{L,0}(i) = \frac{a_L n_{i,0}}{a_i}. \quad (30)$$

From eq 23 (method **d** statement):

$$\frac{n_{L,0}}{a_L} \leq \frac{n_{i,0}}{a_i} \quad (\forall i)$$

$$\frac{n_{L,0}}{a_L} \leq \frac{n'_{L,0}(i)}{a_L} \quad (\forall i)$$

$$n_{L,0} \leq n'_{L,0}(i) \quad (\forall i) \text{ (method a). (31)}$$

And the limiting reagent is identified by the largest value of  $n'_{L,0}(i) - n_{L,0}$  for any reagent  $i$  (because eq 31 means  $n'_{L,0}(i) - n_{L,0} \geq 0$  ( $\forall i$ )), so it is the reagent that has the largest quantity needed to react with any other, considering every pair of reagents.

### 3.2. Reaction Percent Yield and Excess Reagent

The most important application of limiting reagent (definition/identification method) is to provide a mean to estimate the amount of product in a hypothetical situation, in which the limiting reagent(s) is(are) exhausted in order to give that amount. That gives an upper limit to the amount of a given product that should be obtained, quite relevant information. This estimation can only be done by means of limiting reagent because it is the only one with a well defined residual minimum at the end of the reaction, namely zero. It will be shown that the amounts of excess reagents can be used to calculate the amount of product, but only by means of limiting reagent identification and proper amounts (at the beginning and ending of a reaction).

Consider that for any reaction, such as exemplified in eq 4, the following equations are valid [30]:

$$\frac{n_{A_i,0} - n_{A_i}}{a_i} = \frac{n_{A_j,0} - n_{A_j}}{a_j} \quad \{\forall(i, j)\} \quad (32)$$

$$\frac{n_{A_i,0} - n_{A_i}}{a_i} = \frac{n_{B_k} - n_{B_k,0}}{b_k} \quad \{\forall(i, k)\}. \quad (33)$$

As consequences of eq 8, let us assume, for the sake of simplicity, that the amounts of any product at the beginning is zero, so eq 33 becomes

$$\frac{n_{A_i,0} - n_{A_i}}{a_i} = \frac{n_{B_k}}{b_k} \quad \{\forall(i, k)\} \quad (34)$$

In a hypothetical situation where the minimum amount of any reagent will remain after the reaction is complete, yielding a maximum product amount, eq 32 becomes:

$$\frac{n_{A_i,0} - n_{A_i}^{\min}}{a_i} = \frac{n_{A_j,0} - n_{A_j}^{\min}}{a_j} \quad \{\forall(i, j)\}. \quad (35)$$

Where  $n_{A_i}^{\min}$  is the minimum amount of reagent  $A_i$  that yields the maximum amount of product  $B_k$ ,  $n_{B_k}^{\max}$ .

Therefore, eq 34 in this hypothetical situation is:

$$\frac{n_{A_i,0} - n_{A_i}^{\min}}{a_i} = \frac{n_{B_k}^{\max}}{b_k} \quad \{\forall(i, k)\}. \quad (36)$$

However, we now know that

$$\frac{n_{L,0}}{a_L} \leq \frac{n_{A_i}}{a_i} \quad (\forall i) \quad (37)$$

for a limiting reagent L when compared to any other reagent. The same applies to the hypothetical situation in which every reagent has the least possible amount once the reaction is finished:

$$\frac{n_{L,0}^{\min}}{a_L} \leq \frac{n_{A_i}^{\min}}{a_i} \quad (\forall i). \quad (38)$$

The only reagent whose minimum amount at this situation is well defined is the limiting reagent, which is totally consumed, so  $n_{L,0}^{\min} = 0$  and cannot be less than that. Therefore, by eq 38, any excess reagent shows some positive amount in this hypothetical case:

$$0 \leq \frac{n_{A_i}^{\min}}{a_i} \quad (\forall i). \quad (39)$$

Thus, every reagent can be used to obtain  $n_{B_k}^{\max}$  (through eq 36), but for limiting reagent(s) this can be performed without any reference to its residual amounts at the end of the reaction, because there is none. For a given limiting reagent L, eq 36 can then be rearranged as

$$\frac{n_{L,0}}{a_L} = \frac{n_{B_k}^{\max}}{b_k} \quad (\forall k)$$

$$n_{B_k}^{\max} = \frac{b_k n_{L,0}}{a_L} \quad (\forall k). \quad (40)$$

It can be defined as the *largest amount of product* yielded by the complete consumption of the limiting reagent (because no other reagent can be completely consumed without violating mass conservation) as in eq 40, which can be compared to the actual amount of product, for any real reaction, to provide the reaction percent yield. Then the reaction percent yield,  $R(\%)$ , is defined as:

$$R(\%) := \frac{n_{B_k}}{n_{B_k}^{\max}} \times 100\% \quad (\forall k). \quad (41)$$

The reaction percent yield can also be determined by knowing only the initial and final amounts of the limiting reagent. For any reagent, dividing eq 34 by 36 gives

$$\frac{n_{B_k}}{n_{B_k}^{\max}} = \frac{n_{A_i,0} - n_{A_i}}{n_{A_i,0} - n_{A_i}^{\min}} \quad \{\forall(i,k)\}. \quad (42)$$

Notice, then, that can only be determined by means of eq 43:

$$\frac{n_{L,0}}{a_L} = \frac{n_{A_i,0} - n_{A_i}^{\min}}{a_i} \quad (\forall i). \quad (43)$$

Therefore, the maximum amount of product and the reaction percent yield, by one way or another, can only be estimated by the limiting reagent amounts, as stated before. In this case, properly using  $n_L^{\min} = 0$  in eq 42 for the limiting reagent L, we obtain

$$\frac{n_{B_k}}{n_{B_k}^{\max}} = 1 - \frac{n_L}{n_{L,0}} \quad (\forall k). \quad (44)$$

Which can be used to provide the reaction percent yield only from the limiting reagent amounts (substituting eq 44 in definition of eq 41) as,

$$R(\%) = \left(1 - \frac{n_L}{n_{L,0}}\right) \times 100\% \quad (\forall k). \quad (45)$$

The limiting reagent amounts can also be used to estimate amounts of excess reagents, because from eq 32:

$$\frac{n_{L,0} - n_L}{a_L} = \frac{n_{A_i,0} - n_{A_i}}{a_i} \quad (\forall i). \quad (46)$$

Thus, the knowledge of  $n_{L,0}$  and  $n_L$ , referring to limiting reagent L, provides the excess amount of  $A_i$ , namely,  $n_{A_i}$  as,

$$n_{A_i} = n_{A_i,0} + \frac{a_i(n_L - n_{L,0})}{a_L} \quad (\forall i). \quad (47)$$

The minimum possible amount of  $A_i$  that remain unreacted at the hypothetical case where the limiting reagent is completely consumed,  $n_{A_i}^{\min}$ , is (rearranging eq 43 or using  $n_L = 0$  in eq 47, case where  $n_{A_i} = n_{A_i}^{\min}$ ):

$$n_{A_i}^{\min} = n_{A_i,0} - \frac{a_i n_{L,0}}{a_L} \quad (\forall i). \quad (48)$$

It can be estimated from the product amounts as well, by rearranging eq 33,

$$n_{A_i} = n_{A_i,0} + \frac{a_i(n_{B_k,0} - n_{B_k})}{b_k} \quad \{\forall(i,k)\}. \quad (49)$$

If the initial amount of any product is zero ( $n_{B_k,0} = 0$ ), then,

$$n_{A_i} = n_{A_i,0} - \frac{a_i n_{B_k}}{b_k} \quad \{\forall(i,k)\}. \quad (50)$$

The hypothetical situation where a given product  $B_k$  has its maximum amount, so  $n_{B_k} = n_{B_k}^{\max}$ , leads to a minimum of excess reagent  $A_i$ :

$$n_{A_i}^{\min} = n_{A_i,0} - \frac{a_i n_{B_k}^{\max}}{b_k} \quad \{\forall(i,k)\}. \quad (51)$$

Equation 51 can easily be converted into eq 48 by using eq 40. However, once again it can be noted that the limiting reagent permeates the estimation of excess reagent, because  $n_{B_k}^{\max}$  can only be determined by knowing the value of  $n_{L,0}$ .

## 4. Equations for Practical Purposes and Applications

Some selected equations, in a simpler notation, are used, where "L" denotes any limiting reagent, "A" is for any excess reagents and "B" for products in general. Accordingly,

$$\frac{n_{L,0} - n_L}{a_L} = \frac{n_{A,0} - n_A}{a_A} = \frac{n_B - n_{B,0}}{b_B} \quad (52)$$

$$\frac{n_{L,0}}{a_L} < \frac{n_{A,0}}{a_A} \quad (53)$$

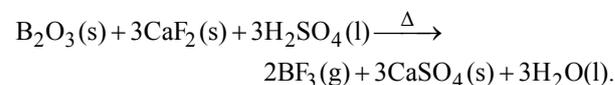
$$n_B^{\max} = \frac{b_B n_{L,0}}{a_L} \quad (54)$$

$$R(\%) = \frac{n_B}{n_B^{\max}} \times 100\% = \left(1 - \frac{n_L}{n_{L,0}}\right) \times 100\% \quad (55)$$

$$n_A^{\min} = n_{A,0} - \frac{a_A n_{L,0}}{a_L} \quad (56)$$

Equation 52 is the most general one, and relates the initial and final amounts of any substance of the reaction. Equation 53 represents method **d**) for limiting reagent identification. Equation 54 gives the maximum amount of product of a chemical reaction, assuming that the initial amount of product is zero and that the limiting reagent is completely consumed. Equation 55 gives the reaction percent yield and assumes that the initial amounts of products are zero; however, it obviously does not need the limiting reagent final amount to be zero, unless reaction percent yield is 100%. Equation 56 provides the minimum amount of excess reagent from the limiting reagent initial amounts, assuming that the limiting reagent final amount is zero.

To exemplify the application of these equations, consider the following heat promoted reaction [31]:



If, at the beginning of the reaction the amounts of  $\text{B}_2\text{O}_3$ ,  $\text{CaF}_2$  and  $\text{H}_2\text{SO}_4$  are 2.0 mol, 5.0 mol and 1.0 mol,

respectively, using eq 53 the limiting reagent can be identified:

$$\frac{n_{\text{B}_2\text{O}_3,0}}{a_{\text{B}_2\text{O}_3}} = \frac{2.0 \text{ mol}}{1} = 2.0 \text{ mol}$$

$$\frac{n_{\text{CaF}_2,0}}{a_{\text{CaF}_2}} = \frac{5.0 \text{ mol}}{3} = 1.7 \text{ mol}$$

$$\frac{n_{\text{H}_2\text{SO}_4,0}}{a_{\text{H}_2\text{SO}_4}} = \frac{1.0 \text{ mol}}{3} = 0.33 \text{ mol}$$

$$(0.33 \text{ mol} < 1.7 \text{ mol} < 2.0 \text{ mol}) \Rightarrow$$

$$\frac{n_{\text{H}_2\text{SO}_4,0}}{a_{\text{H}_2\text{SO}_4}} < \frac{n_{\text{CaF}_2,0}}{a_{\text{CaF}_2}} < \frac{n_{\text{B}_2\text{O}_3,0}}{a_{\text{B}_2\text{O}_3}}$$

Therefore  $\text{H}_2\text{SO}_4$  is the limiting reagent. From eq 54 the maximum amount of  $\text{CaSO}_4$ , for instance, can be estimated:

$$n_{\text{CaSO}_4}^{\text{max}} = \frac{b_{\text{CaSO}_4} n_{\text{H}_2\text{SO}_4,0}}{a_{\text{H}_2\text{SO}_4}} = \frac{3 \times 1.0 \text{ mol}}{3} = 1.0 \text{ mol}.$$

The reaction percent yield if the final amount of  $\text{CaSO}_4$  is 0.50 mol can be estimated by using eq 55:

$$R(\%) = \frac{n_{\text{CaSO}_4}}{n_{\text{CaSO}_4}^{\text{max}}} \times 100\% = \frac{0.50 \text{ mol}}{1.0 \text{ mol}} \times 100\% = 50\%.$$

If the limiting reagent were completely consumed, the excess of  $\text{B}_2\text{O}_3$ , for instance, should be, according to eq 56:

$$n_{\text{B}_2\text{O}_3}^{\text{min}} = n_{\text{B}_2\text{O}_3,0} - \frac{a_{\text{B}_2\text{O}_3} n_{\text{H}_2\text{SO}_4,0}}{a_{\text{H}_2\text{SO}_4}}$$

$$= 2.0 \text{ mol} - \frac{1 \times 1.0 \text{ mol}}{3} = 1.7 \text{ mol}.$$

If the reaction is such that  $n_{\text{CaSO}_4} = 0.50 \text{ mol}$ , as stated before (50% percent yield), the amount of  $\text{B}_2\text{O}_3$  that remains when the reaction is over is, through eq 52:

$$\frac{n_{\text{B}_2\text{O}_3,0} - n_{\text{B}_2\text{O}_3}}{a_{\text{B}_2\text{O}_3}} = \frac{n_{\text{CaSO}_4} - n_{\text{CaSO}_4,0}}{b_{\text{CaSO}_4}}$$

$$n_{\text{B}_2\text{O}_3} = n_{\text{B}_2\text{O}_3,0} - \frac{a_{\text{B}_2\text{O}_3} (n_{\text{CaSO}_4} - n_{\text{CaSO}_4,0})}{b_{\text{CaSO}_4}}$$

$$n_{\text{B}_2\text{O}_3} = 2.0 \text{ mol} - \frac{1 \times (0.50 - 0.00) \text{ mol}}{3} = 1.8 \text{ mol}.$$

Obviously  $n_{\text{B}_2\text{O}_3}^{\text{min}} < n_{\text{B}_2\text{O}_3}$ , because the reaction percent yield was not 100%, so the amount of excess reagent left cannot be the minimum.

## 5. Conclusion

Some of the relevant topics discussed are summarized as,

- 1) A new definition of limiting reagent is proposed, that can be applied to any real situation, rather than

hypothetical cases where no limiting reagent remains in the end of the reaction;

- 2) This definition is connected to usual ones and to methods for limiting reagent identification (especially method **d**) by means of mathematical proofs;
- 3) Equations for different situations were derived, and although some of them have been used previously such as eqs 53, 54 and 55, other equations that apparently have not been used in Stoichiometry where presented, such as eqs 52 and 56. The scope of applications of these equations were clearly specified and their alternative uses and rearrangement of them where proposed to increase their usefulness.

In addition, it has been provided through simple mathematical and logical operations an introduction to rigorous derivations of chemically relevant equations as a possible prelude to more elaborated derivations found in several subareas of Chemistry.

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- [22] Reaction extent at time  $t$  is defined as  $\xi_t := (n_{i,t} - n_{i,0}) / \nu_i (\forall t)$ , and it is always positive, since for reagents  $(n_{i,t} - n_{i,0}) < 0$  and  $\nu_i < 0$ , and for products  $(n_{i,t} - n_{i,0}) > 0$  and  $\nu_i > 0$ . It is frequently used in "equilibrium tables" in the form of  $x_t := \xi_t / V$  (without "t", mostly), if  $V$  is volume. For an advisable reading about its importance and scope, consult [23].
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- [25] See observation in [22].
- [26] Here it is assumed the stoichiometric coefficients do not change through the reaction, or that the reaction has a time-independent stoichiometry. For a brief comment on this matter, consult [27].
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- [28] The symbol " $\Rightarrow$ " stands for "conditional" or "implication" arrow, and means "if... then ...". Given two propositions  $p$  and  $q$ ,  $p \Rightarrow q$  means "if  $p$ , then  $q$ ".
- [29] The symbol " $\Leftrightarrow$ " stands for "biconditional" or "equivalence" arrow. The expression " $p \Leftrightarrow q$ " means " $p$  if and only if  $q$ ", that is to say the following implications hold:  $p \Rightarrow q$  and  $q \Rightarrow p$ .
- [30] Notice that eqs 32 and 33 have the following notation according to "stoichiometric amount of substance" definition:  
 $s_{A_i,0} - s_{A_i} = s_{A_j,0} - s_{A_j} \{\forall(i, j)\}$  (eq 32) and  
 $s_{A_i,0} - s_{A_i} = s_{B_k,0} - s_{B_k} \{\forall(i, k)\}$  (eq 33).
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