

Extent of Reaction Balances: A Convenient Tool to Study Chemical Equilibria

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Received November 13, 2014; Revised December 10, 2014; Accepted December 14, 2014

Abstract The extent of a chemical reaction has received little attention in the early stages of Chemistry teaching, despite allowing a general way to work with chemical reactions and equilibria. In this article, the concepts of extent of reaction and extent of reaction balances are revised and several applications to study the change in the concentrations of the species involved in chemical reactions are described for both single and multiple systems. Extent of reaction balances allow a general treatment that can be applied to problems of diverse complexity involving different types of equilibria, either in the gas phase or in solution (acid-base, complexation, precipitation and redox reactions). This treatment depends exclusively on the reactions stoichiometry and can be taught at several levels, for single or coupled equilibria. Several examples are given, from basic problems adequate for High School Chemistry to problems for College Chemistry.

Keywords: high school chemistry, first- and second-year undergraduate, chemical education research / applications of chemistry, problem solving, aqueous solution chemistry / equilibrium

Cite This Article: Juan José Baeza-Baeza, and María Celia García-Alvarez-Coque, "Extent of Reaction Balances: A Convenient Tool to Study Chemical Equilibria." *World Journal of Chemical Education*, vol. 2, no. 4 (2014): 54-58. doi: 10.12691/wjce-2-4-2.

1. Introduction

The study of chemical reactions and equilibria is an important part of General Chemistry and its knowledge is fundamental for the chemical curriculum in both Chemistry [1], and non-Chemistry majors [2], such as Biology, Environmental Sciences, Food Sciences or Geology. General Chemistry is also taught to Science students in High School [3,4] where the concepts of stoichiometry of chemical reactions, limiting reagent and chemical equilibrium, are introduced. The examples provided, in this context, correspond mainly to gas phase, acid-base, precipitation and redox reactions.

The general treatment of chemical equilibria considers a set of simultaneous equations, consisting in the equilibrium expressions, mass balances, and eventually, the charge balance and electron balance. The particularities of each type of equilibrium (e.g., acid-base, complexation, precipitation and redox) usually need different approaches [5,6,7,8]. Also, solving simultaneous chemical equilibria of different type is not so simple [9-13], unless some restrictions are assumed, such as a fixed pH, or the presence of an excess of reagent.

The interest in developing different approaches to treat the chemical equilibrium has been remarkable [12,14-19]. In this field, the extent of reaction has received less attention. This concept has been mainly applied to study the thermodynamics of chemical reactions [20], their stoichiometry [21,22] and treatment [23,24,25], or to

describe their progress [26,27]. In this work, a global approach is shown based on the extent of reaction balances, which allows a unifying treatment of the chemical equilibrium. The explicit teaching of the extent of reaction from the beginning of the equilibrium treatment permits the unification of the use of ICE (Initial, Change, Equilibrium) tables for single reactions and the more complex treatment based on the mass and charge balances for multiple equilibria. Examples of diverse complexity are presented for High School, and first- and second-undergraduate degrees in College, which can be used also in advanced courses.

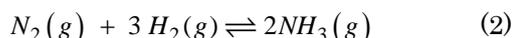
2. Extent of Reaction

According to the IUPAC [28], the extent of reaction is an extensive quantity describing "the progress of a chemical reaction". In molar units, it is expressed as:

$$\xi = \frac{n_A - n_A^0}{\nu_A} \quad (1)$$

where A is any chemical species involved in the reaction, ν_A its stoichiometric coefficient, and n_A^0 and n_A the moles of species A at the beginning of the reaction and when the extent of reaction ξ is reached, respectively. The sign of ν_A in eq 1 is positive for the products and negative for the reactants, so that the extent of reaction will be positive when the reaction proceeds from reactants to products (i.e., the amount of products increases and the

amount of reactants decreases). The extent of reaction is unique for a given reaction progress, regardless of the species used for its calculation. Thus, for the reaction between nitrogen and hydrogen:



the extent of reaction can be expressed in three ways, offering the same value:

$$\xi = \frac{n_{N_2} - n_{N_2}^0}{-1} = \frac{n_{H_2} - n_{H_2}^0}{-3} = \frac{n_{NH_3} - n_{NH_3}^0}{2} \quad (3)$$

For gas phase reactions inside sealed containers, or for reactions in solution, the volume V can be taken as constant. In such case, the extent of reaction is usually expressed as molar concentration, C :

$$x = \frac{\xi}{V} = \frac{n_A / V - n_A^0 / V}{\nu_A} = \frac{C_A - C_A^0}{\nu_A} \quad (4)$$

where x is the extent of reaction expressed as mol/L. Finally, it should be noted that in the study of reaction kinetics, the extent of reaction changes with time, and allows defining the reaction rate (r), independently of the compound chosen to measure it [29]:

$$r = \frac{1}{V} \frac{d\xi}{dt} = \frac{1}{V} \frac{1}{\nu_A} \frac{dn_A}{dt} \quad (5)$$

3. Reaction Balances

The extent of reaction facilitates the study of chemical reactions. It allows expressing the change in the concentration of the different chemical species involved in a reaction, as it proceeds [21,23,24,25,30]. From eq 4, a sort of mass balance is obtained:

$$C_A = C_A^0 + \nu_A x \quad (6)$$

There will be as many of such balances as chemical species are involved in the reaction. For multiple reactions, the extent of reaction balance for a chemical species is constructed by adding the (positive or negative) contributions of each reaction to the concentration of the chemical species:

$$C_A = C_A^0 + \sum_{j=1}^R \nu_{A,j} x_j \quad (7)$$

where R is the number of reactions taking place, x_j the extent of reaction j , and $\nu_{A,j}$ the stoichiometric coefficient of species A in that reaction. These balances have sometimes been called "Jouguet-de Donder equations" or "extent of reaction balances" (and also, "reaction balances" for simplicity). Thus, to study equilibria, an equation associated to each chemical species can be obtained, which together with the equilibrium expressions will form an algebraic non-linear system of equations, with as many equations as unknowns (the concentration of each chemical species and the extent of reaction). This system makes a realistic picture of the chemical problem being studied, and will allow to solve it independently of its complexity. However, this may require complex mathematical tools [25]. In that case, the application of the

systematic method proposed in Ref. 12, which offers more stable results, is advisable. On the other hand, eqs 6 and 7 are general and also used in kinetics studies, where the extent of reaction depends on time [31].

4. Case of Single Reactions

High School and College Chemistry textbooks use the concept of the extent of reaction to calculate the final concentrations of the chemical species for simple reactions, but in an implicit form. For this purpose, ICE tables are applied [1,27]. This approach makes use of the extent of reaction without a complete explanation of its meaning, which is an obstacle to fully understanding of equilibrium and to make a global study of multiple equilibria. We will first show the use of the reaction balances in the treatment of single reactions. Further, the approach will be extended to multiple equilibria.

4.1. Calculation of Equilibrium Concentrations

According to eq 6, the reaction balances at equilibrium for eq 2 are:

$$[N_2] = C_{N_2}^0 - x \quad (8)$$

$$[H_2] = C_{H_2}^0 - 3x \quad (9)$$

$$[NH_3] = 2x \quad (10)$$

By substituting eqs 8 to 10 in the equilibrium expression:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2x)^2}{(C_{N_2}^0 - x)(C_{H_2}^0 - 3x)^3} \quad (11)$$

which yields an equation with only one unknown (the extent of reaction), x . From this value, and eqs 8 to 10, the concentrations at equilibrium can be calculated. Only in simple cases, as in this example when the initial concentrations are mixed in their exact stoichiometric ratio ($C_{H_2}^0 = 3C_{N_2}^0$), the final equation can be solved directly. In other cases, the solution should be obtained by application of numerical methods.

4.2. Presence of a Limiting Reagent

As indicated, obtaining the equilibrium concentrations following the simple method described above usually leads to non-linear equations, whose solution is not easy. However, situations where the equilibrium constant is high enough to consider a full displacement of the equilibrium are usual. In this case, the extent of reaction is defined by the limiting reagent (i.e., the reactant which is totally consumed yielding the smallest extent of reaction) [22]. For example, for the formation of ammonia in eq 2 at 298°C, $K_c = 4.2 \times 10^8$ [1], which means that, based only on equilibrium considerations, the reaction is shifted almost completely to form the product. The maximal extent of reaction that each species may offer is obtained by equating to zero the balances for the reactants (eqs 8 and

9). For instance, taking as initial concentrations $C_{N_2}^0 = C_{H_2}^0 = 0.12 \text{ M}$:

$$[N_2] = C_{N_2}^0 - x_{N_2} = 0 \rightarrow x_{N_2} = \frac{C_{N_2}^0}{1} = 0.12 \text{ M} \quad (12)$$

$$[H_2] = C_{H_2}^0 - 3x_{H_2} = 0 \rightarrow x_{H_2} = \frac{C_{H_2}^0}{3} = 0.04 \text{ M} \quad (13)$$

Therefore, H_2 is the limiting reagent (i.e., it will be exhausted when the extent of reaction is $x = 0.04 \text{ M}$, while the amount of nitrogen is enough to reach a value $x = 0.12 \text{ M}$). Therefore, when the reaction is completed, $x = 0.04 \text{ M}$, and from eqs 8 to 10, $[H_2] = 0$, $[N_2] = 0.08 \text{ M}$ and $[NH_3] = 0.08 \text{ M}$. The remaining H_2 can be obtained from the equilibrium expression (eq 11):

$$[H_2] = \sqrt[3]{\frac{[NH_3]^2}{K_c[N_2]}} = \sqrt[3]{\frac{0.08^2}{4.2 \times 10^8 \times 0.08}} \quad (14)$$

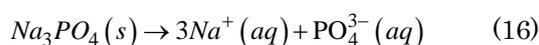
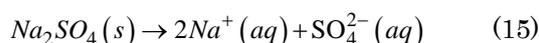
$$= 5.8 \times 10^{-4} \text{ M}$$

The exact solution obtained by solving eq 11 for x yield $x = 0.0398 \text{ M}$ and $[H_2] = 5.73 \times 10^{-4} \text{ M}$.

It should be noted that the extent of reaction is expressed in concentration units in systems where the volume remains constant. For gas reactions at constant pressure where the volume may change, the extent of reaction should be expressed in moles, instead of concentrations, by applying equations similar to eqs 6 and 7, and considering the volume as a new variable using the ideal gas law to relate volume with the total moles.

5. Quantitative Reactions

The reaction balances can also be used to explain the stoichiometric ratios in quantitative reactions. Let's take as example the dissociation of strong electrolytes such as Na_2SO_4 , and Na_3PO_4 . Considering the full dissociation of both salts:



The reaction balances will be:

$$[Na_2SO_4] = C_{Na_2SO_4} - x_1 = 0 \rightarrow x_1 = C_{Na_2SO_4} \quad (17)$$

$$[Na_3PO_4] = C_{Na_3PO_4} - x_2 = 0 \rightarrow x_2 = C_{Na_3PO_4} \quad (18)$$

$$[Na^+] = 2x_1 + 3x_2 = 2C_{Na_2SO_4} + 3C_{Na_3PO_4} \quad (19)$$

$$[SO_4^{2-}] = x_1 = C_{Na_2SO_4} \quad (20)$$

$$[PO_4^{3-}] = x_2 = C_{Na_3PO_4} \quad (21)$$

The ion concentrations will be the sum of the concentrations obtained from each salt, multiplied by the corresponding stoichiometric coefficients. This expression coincides with the ion mass balance.

The reaction balances can also be used to calculate the amount of reactants needed in quantitative parallel

chemical processes. Let's take as example the oxidation of kerosene in aviation fuel, which is a mixture of aliphatic and aromatic hydrocarbons. For simplicity, we will assume a mixture of 80% undecane and 20% naphthalene, mixed with an excess of oxygen, ξ_1 and ξ_2 being the extent of reaction for the combustion of each hydrocarbon, respectively. The reactions taking place and the corresponding reaction balances are the following:



$$n_{C_{11}H_{24}} = n_{C_{11}H_{24}}^0 - \xi_1 = 0 \rightarrow \xi_1 = n_{C_{11}H_{24}}^0 \quad (24)$$

$$n_{C_{10}H_8} = n_{C_{10}H_8}^0 - \xi_2 = 0 \rightarrow \xi_2 = n_{C_{10}H_8}^0 \quad (25)$$

$$n_{O_2} = n_{O_2}^0 - 17\xi_1 - 12\xi_2 \quad (26)$$

$$= n_{O_2}^0 - 17n_{C_{11}H_{24}}^0 - 12n_{C_{10}H_8}^0$$

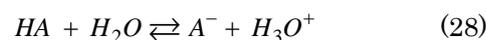
The moles of oxygen required for the combustion of a certain amount of kerosene is obtained by equating eq 26 to zero. Thus:

$$n_{O_2}^0 = 17n_{C_{11}H_{24}}^0 + 12n_{C_{10}H_8}^0 \quad (27)$$

For instance, the combustion of a mixture of 4 moles of undecane and 1 mole of naphthalene requires $n_{O_2}^0 = 17 \times 4 + 12 \times 1 = 80$ moles of molecular oxygen. Therefore, by means of the extent of reaction concept and the reaction balances, the most common stoichiometric problems can be solved, in a consistent and general way.

6. Multiple Equilibria

When a weak acid, such as acetic acid, is dissolved in water with an initial concentration C_{HA}^0 , it dissociates affecting the water autoprotolysis equilibrium (which is shifted to the left):



with extents of reaction x_1 and x_2 , respectively, and the following equilibrium expressions:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \quad (30)$$

$$K_w = [H_3O^+][OH^-] \quad (31)$$

The reaction balances will be:

$$[HA] = C_{HA}^0 - x_1 \quad (32)$$

$$[A^-] = x_1 \quad (33)$$

$$[H_3O^+] = x_1 + x_2 \quad (34)$$

$$[OH^-] = x_2 \quad (35)$$

As observed, the extents of reaction for eqs 28 and 29 agree with the concentrations of A^- and OH^- at equilibrium. Eqs 32 to 35 show the effect of the coupled equilibria and the contribution of each reaction to the final concentrations, where it is evident that some simplifications are possible, according to the equilibrium constants. Thus, since the equilibrium constant for eq 29 is very small and the reaction is controlled by the protons produced in the dissociation of the weak acid, it may be assumed that $x_2 \ll x_1$, and therefore, $[H_3O^+] \approx x_1$. Moreover, if the concentration of weak acid (C_{HA}^0) is sufficiently high, considering its small dissociation, $x_1 \ll C_{HA}^0$ and $[HA] \approx C_{HA}^0$. By substituting all these assumptions in eq 30, the well-known simplified equation used in the equilibrium treatment of weak acids is obtained:

$$K_a = \frac{x_1^2}{C_{HA}^0} \rightarrow x_1 = \sqrt{K_a C_{HA}^0} \quad (36)$$

The reaction balance approach allows us to be aware of all approximations that may be carried out to get the solution and checking its correct application. Thus, for an extremely weak acid, the contribution of water autoprotolysis cannot be ignored, but the dissociation of the acid can be neglected against its initial concentration if this is high enough. From eqs 30 to 35, considering $[HA] \approx C_{HA}^0$:

$$K_a C_{HA}^0 = x_1(x_1 + x_2) \rightarrow x_2 = \frac{K_a C_{HA}^0}{x_1} - x_1 \quad (37)$$

$$K_w = (x_1 + x_2)x_2 = \frac{K_a C_{HA}^0}{x_1} \left(\frac{K_a C_{HA}^0}{x_1} - x_1 \right) \quad (38)$$

$$\rightarrow x_1 = [A^-] = \frac{K_a C_{HA}^0}{\sqrt{K_a C_{HA}^0 + K_w}}$$

$$[H_3O^+] = x_1 + x_2 = \frac{K_a C_{HA}^0}{x_1} \quad (39)$$

$$\rightarrow [H_3O^+] = \sqrt{K_a C_{HA}^0 + K_w}$$

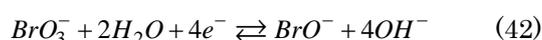
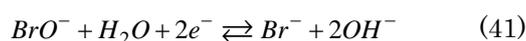
Other examples of multiple equilibria calculations using reaction balances to obtain simplified equations could be easily developed.

7. Obtaining Other Types of Balances from the Reaction Balances

In this section, the extent of reaction approach is related to the usual method based in conservation law balances [7,8]. The reaction balances for a system constitute a complete and independent set of equations that allow the calculation of the equilibrium concentrations. However, for systems with many reactions, the treatment is rather difficult due to the increase of the number of variables. Consequently, when the number of reactions is high or the ionic strength is considered, the use of conservation laws balances may be more convenient [13]. Sometimes the construction of conservation laws balances is cumbersome, but since these balances are just linear combinations of

extent of reaction balances, the students can find in the extent of reaction balances a safe way to construct them.

Let's consider a system that involves several redox and acid-base reactions. In this case obtaining the correct balances could be a challenge. Also, the use of half-reactions introduces the potential (E) as a new variable, increasing the number of balances needed to solve the equilibrium problem. Commonly, the electron balance equation is used for solving redox equilibria [32], however obtaining the electron balance is not straightforward. Extent of reaction balances can be a useful tool to deal with electron balances as it is shown in the next example dealing with the bromine disproportionation in water:



The number of needed conservation balances is obtained from the difference between the number of chemical species (N) and the number of reactions (R). In the present case, the number of reactions is $R = 4$ and the number of species is $N = 7$, then the number of needed balances is $B = N - R = 7 - 4 = 3$. It should be noted that for redox reactions using half-reactions, the electron is formally considered as a species related with the solution potential. Thus, the variables whose value must be obtained at equilibrium are the concentrations of Br_2 , Br^- , BrO^- , BrO_3^- , OH^- , H_3O^+ , and the potential E .

The electron balance can be obtained taking into account that the net balance of the electrons exchanged in a redox reaction must be zero. Then, the electron balance is the extent of reaction balance with respect to the electron equated to zero. In this case:

$$[e] = 0 = -2x_1 - 2x_2 - 4x_3 \quad (44)$$

The other reaction balances will be:

$$[Br_2] = C_{Br_2}^0 - x_1 \quad (45)$$

$$[Br^-] = 2x_1 + x_2 \quad (46)$$

$$[BrO^-] = x_3 - x_2 \quad (47)$$

$$[BrO_3^-] = -x_3 \quad (48)$$

$$[OH^-] = 2x_2 + 4x_3 + x_4 \quad (49)$$

$$[H_3O^+] = x_4 \quad (50)$$

From eqs 44, 46, 47, and 48, the electron balance is obtained:

$$[Br^-] = [BrO^-] + 5[BrO_3^-] \quad (51)$$

and the proton balance from the combination of eqs 47 to 50:

$$[OH^-] + 2[BrO^-] + 6[BrO_3^-] = [H_3O^+] \quad (52)$$

Finally, the mass balance from eqs 45 to 48:

$$2C_{Br_2}^0 = 2[Br_2] + [Br^-] + [BrO^-] + [BrO_3^-] \quad (53)$$

Consequently, it is also possible to use the reaction balances (which can be derived easily in a systematic way from the reaction stoichiometry), to obtain other types of balances, which may be especially useful for complex problems whose resolution requires the use of computer assisted tools [12,15,17,19].

8. Conclusions

A general approach is explained to study the chemical equilibrium, based on the extents of reaction. The reaction balances, which express the concentrations at equilibrium as a function of the extents of reaction, give a complete and clear description of the changes in chemical equilibria. From a pedagogical point of view, the use of extents of reaction to solve chemical equilibrium problems can be highly convenient, since it forces the students to examine conscientiously the reaction stoichiometry. It should be, therefore, addressed in the introductory General Chemistry courses. Moreover, the concepts of extent of reaction and reaction balances allow a systematic approach, which may be applied to any type of equilibrium or combination of simultaneous equilibria, independently of their complexity. Besides the establishment of the required set of equations, the students must decide the way to perform simplifications, or obtain other balances from the extent of reaction balances. The reaction balances provide a common perspective and a global tool to study chemical reactions that can give more confidence to students when addressing the equilibrium problem.

The extent of reaction is non-explicitly used in textbooks of General Chemistry to solve simple cases involving single reactions, or cases where there is a limiting reagent. Meanwhile, in more advanced courses, the treatment of multiple equilibria is performed using mass and charge balances. Both approaches can be connected by means of the extent of reaction balances.

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