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Dedicated to the memory of Professor Nicholas Alexandrou

Organic redox reactions are classified either as atom transfers (balanced by inspection) or as more complex transformations (balanced by change in oxidation number, ON, by change in DOX value, by electrochemical half-reaction, or by simultaneous linear algebraic equations). Examples presented include not only involvement of hydrogen or oxygen but also extensions to halogens, nitrogen, phosphorus, and sulfur. Complex reactions are subdivided into ones which proceed (a) without change in the number of carbon atoms per molecule, (b) with fragmentation of the carbon assemblage in the starting material, or (c) with condensation of two or more molecules of organic starting materials.

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Writing balanced equations is particularly important in experimental organic chemistry where emphasis is placed on (a) determining the relative amounts of starting materials to use in order to effect a proposed reaction and (b) calculating theoretical and percentage yields of products in syntheses. Balancing non-redox equations is generally a trivial exercise which can be completed by inspection. The same situation occurs in some types of redox reactions, but not in others. The goal of this communication is to categorize the major types of organic redox reactions and to illustrate methods for balancing their equations by means of chemically rational concepts. Particular attention is given to reactions which involve heteroatoms and heterocyclic compounds.

In a previous publication Klemm elaborated on the use of the degree of unsaturation (DU) of an organic compound in solving structural problems [1]. Subsequently, he defined the degree of oxidation (DOX) of an organic compound $C_nH_mE_p$, where E is any one or more of eleven elements more electronegative than hydrogen, *i.e.* the four halogens (F, Cl, Br, I), the four chalcogens (O, S, Se, Te), and three elements of Group VA (N, P, As) [2]. DOX, defined by the relationship $DOX = DU + p$, can be easily calculated either from a molecular formula or a structural formula. The numerical value of DOX indicates the extent to which the molecule has been oxidized from its parent alkane C_nH_{2n+2} (DOX = 0). Two molecules with the same value of n are considered to have equal extents of oxidation when they have the same values of DOX. The present communication extends the DOX concept to the classification and balancing of organic redox reactions.

Types of Redox Reactions.

A survey of organic redox reactions indicates that they can be categorized into the following five types, as based on the chemical process involved, or into various other types as based on the mechanism of balancing.

A. Atom transfer reactions (balanced by inspection)

1. One-way atom transfers
2. Two-way atom transfers

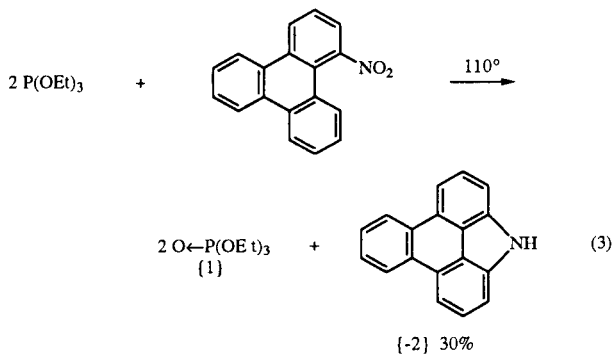
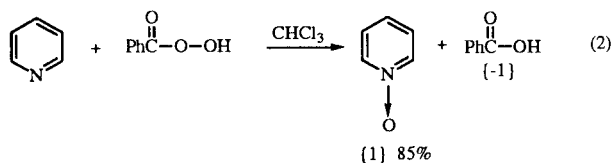
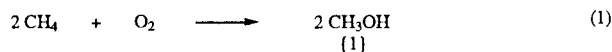
B. More complex reactions (balanced by change in oxidation number, ON, by change in DOX value, by electrochemical half-reaction, or by simultaneous linear algebraic equations)

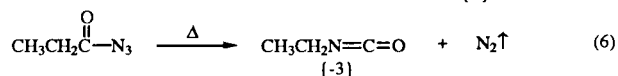
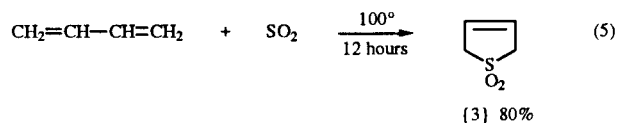
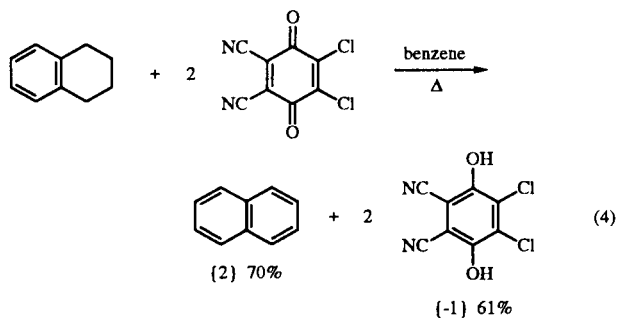
1. Reactions at constant n , the number of C atoms per molecule
2. Fragmentation reactions (n is subdivided)
3. Condensation reactions (n is increased)

Many reactions may be classified under more than one category.

One-way Atom-transfer Reactions.

Some examples of these reactions follow.

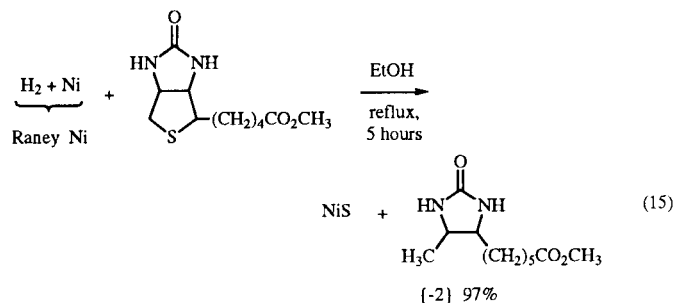
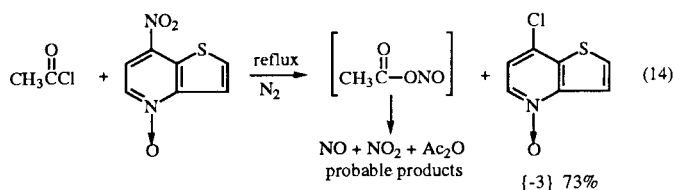
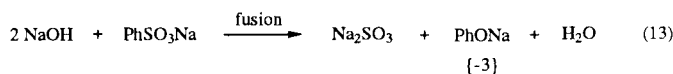
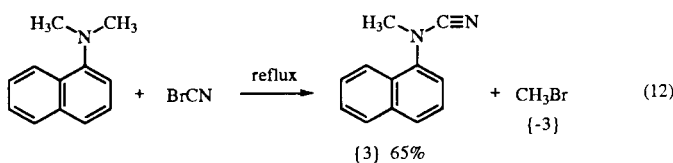
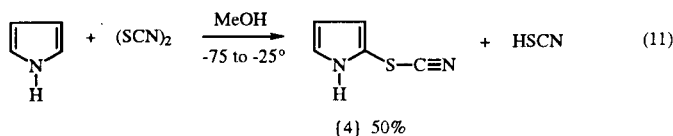
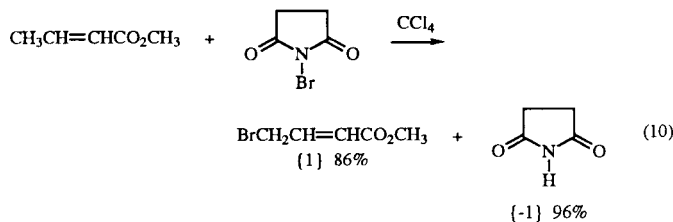
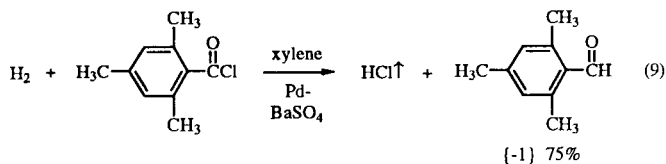
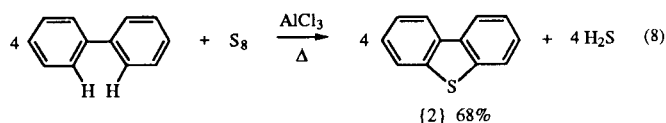
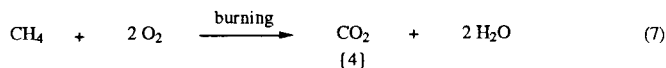




In equations 1-5 the reducing agent is given first and the oxidizing agent is shown next, although one need not establish these functional roles in order to balance the equations. In equation 6 (Curtius reaction) the acyl azide undergoes thermally activated dissociation with attendant oxidation-reduction [3]. Numbers in braces shown under products indicate the net change in degree of oxidation (ΔDOX) which the molecule undergoes during the reaction [2]. As expected, in a balanced equation ΔDOX for the compound oxidized equals $-\Delta\text{DOX}$ for the compound reduced, e.g., for equation 3, $2(1) = -1(-2)$. For most products shown the numerical value of ΔDOX is readily apparent. However, three more complex cases are discussed below. Reactions 1-3 involve oxygen transfer [4,5]. Transformation 3, an example of the Cadogan reaction, is believed to proceed *via* a nitrene [6]. For the conversion of nitrotriphenylene into naphthocarbazole there is no change in DU because the loss of a double bond in the nitro group is counterbalanced by formation of a pyrrole ring. ΔDOX of -2 results from loss of two oxygen atoms. Equation 4 involves intermolecular hydrogen transfer [7]. Reaction 5 shows oxidation of 1,3-butadiene with a molecule of sulfur dioxide (simultaneous transfer of 3 atoms, but no change in DU) to produce 3-sulfolene [8]. In reaction 6 it is clear that two nitrogen atoms are lost from the azide. Additionally, there is a decrease of one unit in DU since the equivalent hydrocarbon for the isocyanate product is C_3H_4 , while that of the azide is C_3H_2 [1].

Two-way Atom-transfer Reactions

These reactions involve metathesis or double decomposition wherein H and E atoms or different electronegative elements or groups (E and E') are transferred in opposite directions during the reaction process. Some examples are shown here.



Equations 7-9 illustrate reactions of free elements with organic compounds. Reactions 8 (a commercial method for synthesizing dibenzothiophene) and 9 (Rosenmund reduction) are effected by catalysts [9,10]. Equation 10

shows the use of *N*-bromosuccinimide to give allyl bromination [11], while 11 presents thiocyanation of the pyrrole ring [12,13]. Both of these transformations involve replacement of hydrogen by an oxidizing atom or group. Reactions 12-14 differ from 7-11 in that the groups which are exchanged do not involve atomic hydrogen [14-16]. Note that the presence of sodium in the organic compounds in reaction 13 does not complicate the calculation of ΔDOX . Equation 15 shows desulfurization of biotin methyl ester by means of Raney nickel [17]. The nickel not only catalyzes the reaction by hydrogen, but also undergoes reaction itself to form nickel sulfide [18].

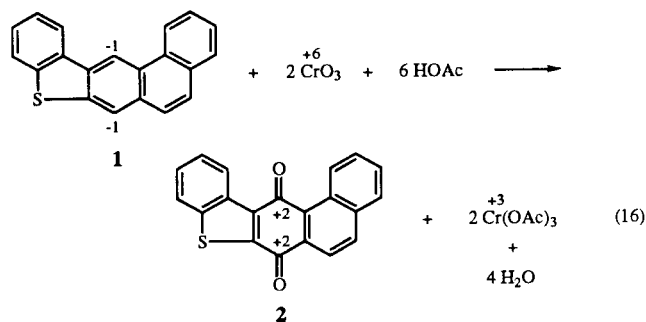
More Complex Reactions.

Examination of a number of organic chemistry textbooks, including laboratory ones, reveals that many authors do not address the question of balancing redox equations. Rather they either give the balanced equation directly or simply indicate a flow diagram to show the starting material(s), reagent(s), product(s), and sometimes reaction conditions. Authors who do introduce a method for balancing these equations normally extend the ion-electron method to organic reactions [19-21]. However, the chemical inconsistency of writing ion-electron half-reactions for organic oxidation-reductions, particularly ones conducted under non-aqueous conditions, has been pointed out lucidly by Sisler and Vanderwerf [22]. They recommend that the ion-electron method be used only for balancing known half-cell processes in electrochemical transformations, as exemplified in this paper. In other cases the chemically non-committal use of oxidation numbers (ON) and/or DOX values is preferred by the author. When these two methods fail or cause too much difficulty, balancing can be accomplished by using simultaneous linear algebraic equations.

I. Balancing by Means of ON and/or DOX Values.

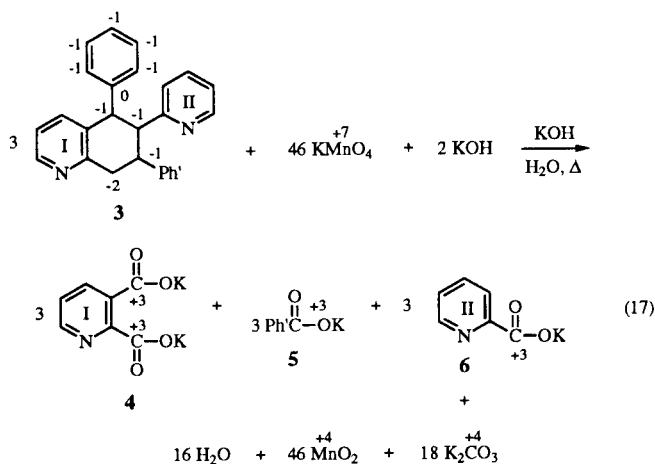
As regularly used an oxidation number (ON) refers to an individual atom in a molecule. It measures the capacity which the atom is showing in that molecule toward bonding with atoms more electronegative than itself [2]. Rules for calculating the ON of a particular carbon atom, A, in a molecule are as follow: (a) Ignore every substituent on A which is bonded by means of carbon (irrespective of whether this occurs by a single, a double, or a triple bond) [23]. (b) Assign regular ON values for other bonded elements and groups consistent with practice in general chemistry, normally +1 for H, -2 for O, -1 for Cl, -1 for OH, *etc.* [24]. (c) Set the sum of the ON values of A and those of its covalently bonded substituents (using zero for those bonded by carbon) equal to zero [25]. From this procedure the range of ON values for A will assume any integral value from -4 for methane to +4 for carbon dioxide, including 0 in some cases, *e.g.*, the central carbon of 2-propanol [26].

Case B-1 (the C_n unit remains unchanged):



For changes in ON one sees that two carbon atoms in 1 increase by 6 units in going to 2, while Cr in chromic anhydride decreases by 3 units. Thus, one takes a ratio of 1:2 for moles of 1:moles of chromic anhydride. Alternatively, one can avoid assigning ON values to carbon by noting that the change 1 \rightarrow 2 involves loss of two hydrogen atoms and gain of two oxygen atoms, *i.e.*, a ΔDOX of +3 (for the molecule) = 2 ΔON of +6 (for the atoms in the molecule) [27]. Thus, one can use either ΔDOX or ΔON values (or a combination of them) in balancing organic redox reactions.

Case B-2 (fragmentation of C_n unit on reaction):

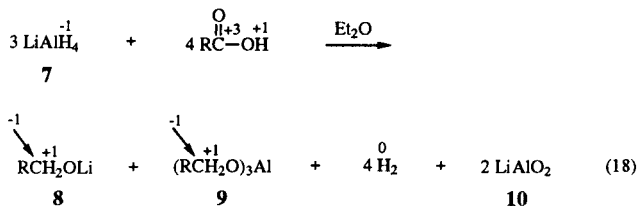


Equation 17 is typical of the use of alkaline permanganate to oxidize an alkyl or substituted alkyl group on a stable arene to a carboxylate group [28]. To balance this equation one first makes an assumption about the fate of each arene portion of the starting material 3. Here it is assumed that one mole of 3 will yield one mole of 4, one of 5, and one of 6. The Ph group is presumed to be oxidized completely, *i.e.*, to yield six moles of potassium carbonate. Equation 17 is readily balanced by either ON or DOX methods. In the ON procedure one calculates the overall change in ON's for carbons in going from 3 to the various products. ΣON 's in 3 = 0 + 8(-1) - 2 = -10; ΣON 's in carbon-bearing products =

$4(+3) + 6(+4) = +36$; ΔON for carbons = +46. ΔON for Mn = -3. Thus, one needs 46 moles of permanganate to oxidize 3 moles of **3**. To use the DOX method for the carbons replace potassium ions in the products with protons. Then note that a $\text{C}_{10}\text{H}_{10}$ portion of **3** is converted into $4 \text{CO}_2\text{H} + 6 \text{H}_2\text{CO}_3$, *i.e.*, to $\text{C}_{10}\text{H}_{16}\text{O}_{26}$; $\Delta\text{DOX} = -3 + 26 = +23 = +46$ in ΔON . Use of DOX values avoids the need to assign ON values in organic starting materials or products.

A Modified Case B-1:

Equations 16 and 17 are easily balanced once one has selected the oxidizing and reducing agents and assigned reasonable ON values [24,25] to the atoms undergoing change. A more complicated case, where a starting carboxylic acid is diverted into two distinct products, is given below, *e.g.*, for R = 3-methyl-2-furyl the yield of RCH_2OH is 90% [29]; for R = 5,6-methylenedioxybenzo[*b*]thienyl the yield is 72% [30].

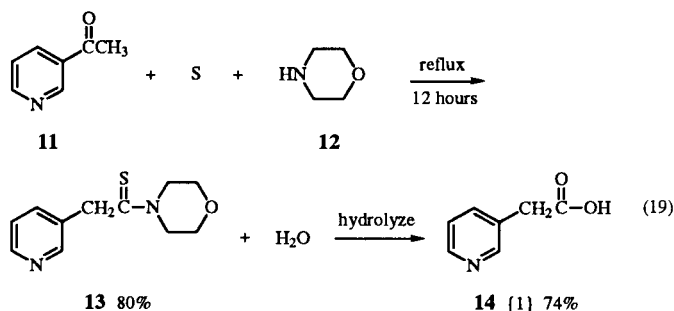


Two problems arise in an effort to balance equation 18 by the ON method. First, hydrogen occurs in three different oxidation states (-1, 0, +1) and, second, both hydrogen and carbon (which also changes in ON) occur in some of the same formulas [31]. However, one can balance the equation either directly by inspection or by logical combination of ON changes. By inspection one notes that in **7** and in **10** the ratio of Li:Al is 1:1. Then, likewise the ratio of coefficients of **8** and **9** must be 1:1. If one selects trial values of one for the coefficients of **8** and **9** one can then proceed to complete the balancing without use of ON values

Alternatively, one notes that the carboxylic acid unit is converted into $-\text{CH}_2\text{O}-$, where one hydrogen atom must come from **7**, *i.e.*, from H of ON -1, while the other hydrogen atom does not change in ON. So for the unit $-\text{CH}_2\text{O}-$ the combined change in ON is -2. All of the hydrogen atoms in the hydrogen gas formed must come from **7**, or correspond to an increase of two units per hydrogen gas molecule. Since one must take four carboxylic acid molecules to balance the carbon atoms in the RCH_2O groups, the coefficient of hydrogen gas must also be four.

A third procedure, specifically balancing equation 18 by means of simultaneous linear algebraic equations, will be presented later.

Case B-3 (condensation of carbon units upon reaction):

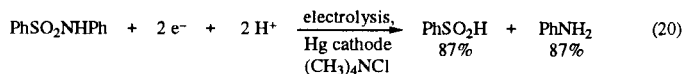


Reaction 19 is the Kindler modification of the Willgerodt reaction [32]. Since the thiomorpholide product **13** contains carbon atoms from starting material **11** plus reagent **12** it is necessary to remove the morpholinyl group by hydrolysis in order to obtain the ΔDOX value for the reaction. Balancing the equation is by inspection.

II. Balancing Electrochemical Half-Reactions.

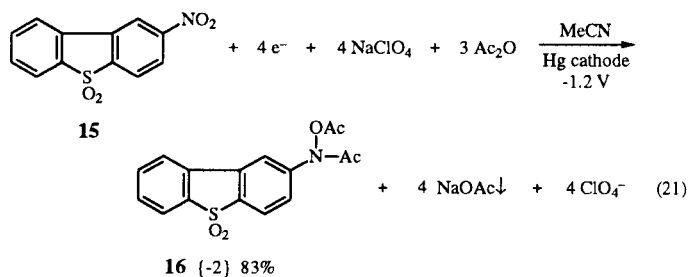
Sisler and Vanderwerf [22] noted that when one writes an ion-electron half-reaction it should be supported by electrochemical data. The three examples presented here conform to that situation and require only inspection for balancing.

Case B-2 (fragmentation reaction):



Equation 20 shows an electrochemical reduction for which $\Delta\text{DOX} = -1$ as evidenced by the uptake of 2 electrons (or effectively 2H). The reaction was described in the original literature as a reduction by free tetramethylammonium formed on the cathode [33]. Later, however, it was presented as the cathode reaction shown in equation 20 [34].

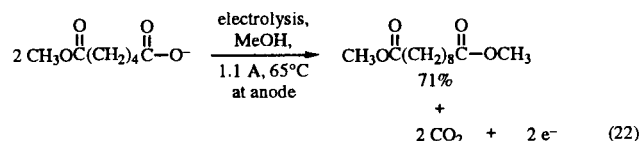
Case B-3 (condensation reaction):



Equation 21 illustrates an electrochemical reaction conducted in acetonitrile-acetic anhydride as solvent and at a controlled cathode potential—designed to effect reduction of the nitro group of **15** but not its sulfone group [35]. In the absence of a suitable hydrogen donor the reduction stops at the hydroxylamine stage of **16**. The stoichiometry

was established by coulometry, by weighing the insoluble sodium acetate formed, and by the yield of compound **16**. The value $\{-2\}$ is obtained either from the uptake of four electrons or by considering that hydrolysis of **16** would give an NHOH substituent on the ring, resulting from a loss of one oxygen atom and a gain of two hydrogen atoms from the nitro group in **15**.

A Mixed Case, B-2 and B-3:

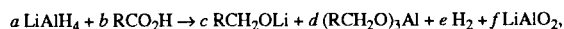


The Kolbe electrolytic oxidation involves both fragmentation and condensation [36]. The production of two electrons at the anode corresponds to $\{1\}$.

III. Balancing by Algebraic Equations.

Based on the conservation laws for atoms and groups, one can set up a system of simultaneous linear algebraic equations for solving for the coefficients in any unbalanced redox reaction. This would seem to be a convenient, general procedure for balancing. However, as the following two cases will illustrate, the method also has its shortcomings. Thus, procedure III might best be reserved for cases where use of ON or DOX presents problems and electrochemical data are not available.

First case, balancing equation 18, written in the general form

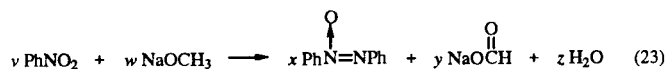


where letters a - f are coefficients to be determined:

Element or group	Relationship for mass balance
Li	$a = c + f$
Al	$a = d + f$
H	$4a + b = 2c + 6d + 2e$
R	$b = c + 3d$
C	$b = c + 3d$
O	$2b = c + 3d + 2f$

So one apparently has six linear equations in six unknowns. However, equations for R and C are identical. So there is no unique solution. By substitutions and simplification one can arrive at these correlations: $a = 3d$; $b = 4d$; $c = d$; $d = ?$; $e = 4d$; and $f = 2d$. One is allowed an integral choice for d . First there is a trivial choice of $d = 0$, but this is of no chemical significance. A choice of $d = 1$ gives suitable integral values for all of the other coefficients.

Second case, the reduction of nitrobenzene to azoxybenzene [37]:



Element or group	Relationship for mass balance
Ph	$v = 2x$
N	$v = 2x$
O	$2v + w = x + 2y + z$
Na	$w = y$
C	$w = y$
H	$3w = y + 2z$

Here one has only four independent equations in six unknowns. Simplifying to one equation gives $3x = 2y$. The simplest integral solution to this equation is $x = 2$, $y = 3$. Then, $v = 4$; $w = 3$; and $z = 3$. The answer arises surprisingly easily, and without one's having to ponder over the ON values for nitrogen.

However, it is noteworthy that one can also easily balance equation 23 by use of DOX values. Thus, for the N-bearing compounds one has 2 nitrobenzene \rightarrow 1 azoxybenzene + 3 oxygen atoms ($\Delta\text{DOX} = -3$), while for the oxidation process one has 1 sodium methoxide + 1 oxygen atom $-$ 2 hydrogen atoms \rightarrow 1 sodium formate ($\Delta\text{DOX} = +2$). Hence, one needs 4 moles of nitrobenzene for 3 moles of sodium methoxide.

Conclusion.

In organic chemistry it is important to be able to balance redox equations systematically, but the method of balancing chosen should be consistent with chemical intuition. Four general procedures make this possible. (a) First, many equations involving non-ionic molecules can be balanced by inspection as based on the concepts of atom transfers. (b) Second, electrochemical transformations can be balanced by the commonly used ion-electron method. (c) For most other cases the method of change in oxidation numbers (ON) or in degrees of oxidation (DOX) is recommended because it is simple and avoids the need for proposing chemically unrealistic half-reactions. (d) In cases where method (c) proves difficult to apply, one can use simultaneous linear algebraic equations; but one must be wary of the fact that an exact solution may not arise directly. It is noteworthy that $\Delta\text{DOX} = +1$ for a molecule is equivalent to $\Delta\text{ON} = +2$ for atoms in the molecule and also to the loss of two electrons.

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