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Research Article

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H-atom and O-atom methods: from balancing redox reactions to determining the number of transferred electrons

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Abstract: Defining and balancing redox reaction requires both chemical knowledge and mathematical skills. The prevalent approach is to use the concept of oxidation number to determine the number of transferred electrons. However, the task of calculating oxidation numbers is often challenging. In this article, the H-atom method and O-atom method are developed for balancing redox equations. These two methods are based on the definition of redox reaction, which is the gain and loss of hydrogen or oxygen atoms. They complement current practices and provide an alternate path to balance redox equations. The advantage of these methods is that calculation of oxidation number is not required. Atoms are balanced instead. By following standard operating procedures, H-atom, O-atom, and H_2O molecule act as artificial devices to balance both inorganic and organic equations in molecular forms. By using the H-atom and O-atom methods, the number of transferred electrons can be determined by the number of transferred H-atoms or O-atoms, which are demonstrated as electron-counting concepts for balancing redox reactions. In addition, the relationships among the number of transferred H-atom, the number of transferred O-atom, the number of transferred electrons, and the change of oxidation numbers are established.

Keywords: balancing redox reaction; change of oxidation numbers; number of transferred electrons; number of transferred hydrogen atoms; number of transferred oxygen atoms.

Introduction

Chemical equation is the language of chemistry. It is important for students to acquire competence in balancing chemical equations (Herndon, 1997; Porter, 1985; Kolb, 1981, 1979) because by doing so their chemistry knowledge, mathematical skills, and logical thinking can be consolidated. There are different approaches to balancing chemical equations. Arithmetic methods and inspection methods are applied for balancing simple reactions. Algebraic methods, such as linear simultaneous equations method (Dukov, 2017; Olson, 1997) and matrix method (Blakley, 1982) are used for balancing all types of chemical reactions.

In chemistry curriculum, the redox concept is taught "as an organizing structure for chemical knowledge, as a guide to the prediction of reactions, and as a mathematical device to enable the balancing of certain complex reactions" (Goodstein, 1970). According to IUPAC definitions, the terms of redox reactions can be understood in four different models: electron transfer, oxidation number, H-atom transfer, and O-atom transfer, shown in Table 1. Silverstein (2011) comments that a redox reaction has "too many definitions". Sisler & VanderWerf (1980) argue that a redox reaction is "an example of chemical sophistry". Paik, Kim & Kim (2017) discuss limitations of the four redox models and suggest a process-based model to define redox reactions.

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Table 1: Terms of redox reactions.

Redox terms	Oxidation number	Electron transfer	H-atom transfer	O-atom transfer
Oxidation	Increase	Loss e^-	Loss H	Gain O
Reduction	Decrease	Gain e^-	Gain H	Loss O
Reducing agent	Increase	Loss e^-	Loss H	Gain O
Oxidizing agent	Decrease	Gain e^-	Gain H	Loss O

The notion of redox reaction is commonly understood as the gain and loss of electrons in a reaction. Oxidation number (or oxidation state) acts as an electron-counting concept (Karen, 2015). To balance redox reactions, the commonly used methods are the oxidation number method (Kolb, 1979; Generalic & Vladislavic, 2018) and the inspection method (Guo, 1997). The oxidation number method includes the overall reaction method (Dukov, 2017; Kolb, 1979) and the half reactions ion-electron method (Fishtik & Berka, 2005; Generalic & Vladislavic, 2018). General chemistry textbooks tend to use the ion-electron method as a primary procedure for balancing redox equations (Chang & Goldsby, 2013; Tro, 2014). This method must assign all oxidation numbers of atoms; determine the transferred electrons; and use H^+, OH^-, and H_2O as balancing tools. The task of calculating oxidation numbers (ON), however, is challenging (Jurowski, Krzeczkowska & Jurowska, 2015). The oxidation number method is restricted in cases where oxidation numbers are uncertain (see Example 1), and where there are multiple sets of redox couples in the complex redox reaction (see Examples 2 and 3).

$$Fe_3C + HNO_3 \rightarrow Fe(NO_3)_3 + CO_2 + NO_2 \qquad \text{(Example 1)}$$
$$P_2I_4 + P_4 + H_2O \rightarrow PH_4I + H_3PO_4 \qquad \text{(Example 2)}$$
$$Pb(N_3)_2 + Cr(MnO_4)_2 \rightarrow Pb_3O_4 + NO + Cr_2O_3 + MnO_2 \qquad \text{(Example 3)}$$

H-atom and O-atom are present in the cosmos (Williams, 1999). The H-atom transfer reaction (Capaldo & Ravelli, 2017; Chuang, Fedoseev, Ioppolo, van Dishoeck & Linnartz, 2016; Rosado-Reyes, Manion & Tsang, 2011) and O-atom transfer reaction (Holm, 1987; Kovacs, Lee, Olson & Jackson, 1996; Moriarty, Gupta, Hu, Berenschot & White, 1981) are widely used in synthetic chemistry. The H-atom and O-atom function as intermediates in chemical processes (Cole-Filipiak, Shapero, Negru & Neumark, 2014; Dougherty & Rabitz, 1980; Gerasimov & Shatalov, 2013; Lucci et al., 2016; Simmie, 2003). They can act as reactants and/or products in chemical conversions (Bergner, Öberg & Rajappan, 2019; Casavecchia, Leonori & Balucani, 2015; Paulson, Mutunga, Shelby & Anderson, 2014; Ran, Yang, Lee, Lu, She, Wang & Yang, 2005; Sun, Lucas, Song, Zhang, Brazier, Houston & Bowman, 2019; Walker & Light, 1980; Wang, Masunov, Allison, Chang, Lim, Jin & Vasu, 2019; Xu, Jirasek & Petr, 2020). Although redox reaction can also be defined as the gain and loss of H-atoms or O-atoms (IUPAC, 2019) the H-atom and O-atom have rarely been introduced as redox balancing devices (Yuen & Lau, 2021). Based on these concepts, the new H-atom method and O-atom method for balancing redox reaction are explored. Consequently, the relationships among the number of transferred H-atom, the number of transferred O-atom, the number of transferred electrons, and the change of oxidation numbers are studied.

Dividing an overall redox reaction into two half reactions

"Any redox reaction may be decomposed into a sum of two half-reactions" (Fishtik & Berka, 2005). The critical step of the H-atom and O-atom methods is the division of the overall molecular redox reaction into two half reactions. An inspection method, termed "ping-pong method", is employed here. The ping-pong procedures and examples are as follows:

Step 1. Identify all elements, with the exception of H- and O-elements, on both reactant's side (left) and product's side (right).

Step 2. Choose a reactant on the left and identify all its non-H and non-O element(s).

Step 3. Link the reactant's element(s) on the left to product's element(s) on the right.

Step 4. Keep linking right-left-right…, until two half reactions are attained.

Example 1. Dividing an overall reaction, $Fe_3C + HNO_3 \rightarrow Fe(NO_3)_3 + CO_2 + NO_2$, into two half reactions.

The first half reaction (1st):

(1st i) Choose the first reactant on the left and identify all its non-H, non-O element(s):
Fe_3C: Fe and C elements

(1st ii) Link Fe and C on the left to $Fe(NO_3)_3$ and CO_2 on the right
$Fe_3C \rightarrow Fe(NO_3)_3 + CO_2$

(1st iii) Link N element on the right to HNO_3 on the left
$Fe_3C + HNO_3 \rightarrow Fe(NO_3)_3 + CO_2$

The second half reaction (2nd):

(2nd i) Choose the second reactant on the left and identify all its non-H, non-O element(s):
HNO_3: N element

(2nd ii) Link N on the left to NO_2 on the right
$HNO_3 \rightarrow NO_2$

an overall reaction:	$Fe_3C + HNO_3 \rightarrow Fe(NO_3)_3 + CO_2 + NO_2$
the first divided half reaction:	$Fe_3C + HNO_3 \rightarrow Fe(NO_3)_3 + CO_2$
the second divided half reaction:	$HNO_3 \rightarrow NO_2$

Example 2. Dividing an overall reaction, $P_2I_4 + P_4 + H_2O \rightarrow PH_4I + H_3PO_4$, into two half reactions.

The first half reaction (1st):

(1st i) Choose the first reactant on the left and identify all its non-H, non-O element(s):
P_2I_4: P and I elements

(1st ii) Link P and I on the left to PH_4I on the right
$P_2I_4 \rightarrow PH_4I$

(1st iii) The $P_2I_4 \rightarrow PH_4I$ half reaction cannot be balanced, then link to left side
$P_2I_4 + P_4 \rightarrow PH_4I$

The second half reaction (2nd):

(2nd i) Choose the second reactant on the left and identify all its non-H, non-O element(s):
P_4: P element

(2nd ii) Link P on the left to H_3PO_4 on the right
$P_4 \rightarrow H_3PO_4$

an overall reaction:	$P_2I_4 + P_4 + H_2O \rightarrow PH_4I + H_3PO_4$
the first divided half reaction:	$P_2I_4 + P_4 \rightarrow PH_4I$
the first divided half reaction:	$P_4 \rightarrow H_3PO_4$

Example 3. Dividing an overall reaction, $Pb(N_3)_2 + Cr(MnO_4)_2 \rightarrow Pb_3O_4 + NO + Cr_2O_3 + MnO_2$, into two half reactions.

The first half reaction (1st):

(1st i) Choose the first reactant on the left and identify all its non-H, non-O element(s):
$Pb(N_3)_2$: Pb and N elements

(1st ii) Link Pb and N on the left to Pb_3O_4 and NO on the right
$Pb(N_3)_2 \rightarrow Pb_3O_4 + NO$

The second half reaction (2nd):

(2nd i) Choose the second reactant on the left and identify all its non-H, non-O element(s):
$Cr(MnO_4)_2$: Cr and Mn elements

(2nd ii) Link Cr and Mn on the left to Cr_2O_3 and MnO_2 on the right
$Cr(MnO_4)_2 \rightarrow Cr_2O_3 + MnO_2$

an overall reaction: $Pb(N_3)_2 + Cr(MnO_4)_2 \rightarrow Pb_3O_4 + NO + Cr_2O_3 + MnO_2$
the first divided half reaction: $Pb(N_3)_2 \rightarrow Pb_3O_4 + NO$
the first divided half reaction: $Cr(MnO_4)_2 \rightarrow Cr_2O_3 + MnO_2$

H-atom method: procedures

When using the H-atom method, H, O, and H_2O are used as balancing devices. This method requires the use of a molecular chemical equation. If an ionic chemical equation is provided, it must be converted to a molecular chemical equation by adding proper spectator ions. H_2O can be omitted in the process optionally. When both half and overall chemical equations are balanced, H_2O will appear consequently through the working procedures to fulfill the conservational law of matter, which is one of the advantages of using the H-atom and O-atom methods. It is important to emphasize that these two methods are mathematically balancing methods. The H-atom and O-atom may not necessarily act as intermediates, and the H-atom and O-atom methods do not represent any reaction mechanisms.

Step 1. Divide into two half reactions

Step 2. Balance all atoms in the two half reactions
a) Balance all other atoms except H and O
b) Balance the oxygen atoms with O
c) Balance the hydrogen atoms with H
d) Add two H atoms for each O atom
e) Convert two H atoms and one O atom to one H_2O molecule

Step 3. Make the H-atom of the two half reactions equivalent

Step 4. Combine the two half reactions

Step 5. Simplify the overall chemical equation

Example 4. Given the following molecular chemical equation:
$C_6H_5CH_3 + KMnO_4 + H_2SO_4 \rightarrow C_6H_5COOH + K_2SO_4 + MnSO_4$
Convert to $C_7H_8 + KMnO_4 + H_2SO_4 \rightarrow C_7H_6O_2 + K_2SO_4 + MnSO_4$
Step 1. Divide into two half reactions
$C_7H_8 \rightarrow C_7H_6O_2$
$KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4$
Step 2. Balance all atoms in the two half reactions

$C_7H_8 \rightarrow C_7H_6O_2$
$C_7H_8 + 2O \rightarrow C_7H_6O_2$
$C_7H_8 + 2O \rightarrow C_7H_6O_2 + 2H$
$C_7H_8 + 2O + 4H \rightarrow C_7H_6O_2 + 2H + 4H$
$C_7H_8 + 2H_2O \rightarrow C_7H_6O_2 + 6H$
$KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4$
$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4$
$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8O$
$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 6H + 8O$
$2KMnO_4 + 3H_2SO_4 + 16H \rightarrow K_2SO_4 + 2MnSO_4 + 6H + 8O + 16H$
$2KMnO_4 + 3H_2SO_4 + 10H \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$

Step 3. Make the H-atom of the two half reactions equivalent (LCM = 30)
$(C_7H_8 + 2H_2O \rightarrow C_7H_6O_2 + 6H) \times 5$
$(2KMnO_4 + 3H_2SO_4 + 10H \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O) \times 3$

Step 4. Combine the two half reactions
$5C_7H_8 + 10H_2O \rightarrow 5C_7H_6O_2 + 30H$
$6KMnO_4 + 9H_2SO_4 + 30H \rightarrow 3K_2SO_4 + 6MnSO_4 + 24H_2O$

Step 5. Simplify the overall chemical equation
$5C_7H_8 + 6KMnO_4 + 9H_2SO_4 \rightarrow 5C_7H_6O_2 + 3K_2SO_4 + 6MnSO_4 + 14H_2O$

In this process, each H-atom is equivalent to the gain/loss of one electron. In example 4, $C_7H_8 + KMnO_4 + H_2SO_4 \rightarrow C_7H_6O_2 + K_2SO_4 + MnSO_4$, one half of the equation "$C_7H_8 + 2H_2O \rightarrow C_7H_6O_2 + 6H$" releasing six H-atoms represents the loss of six electrons, and the other half equation "$2KMnO_4 + 3H_2SO_4 + 10H \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$" obtaining ten H-atoms represents the gain of 10 electrons. $KMnO_4$ and C_7H_8 function as oxidizing agent and reducing agent respectively.

Example 5. Given the following ionic chemical equation:
$CH_3CH_2OH + Cr_2O_7^{2-} + H^+ \rightarrow CH_3COOH + Cr^{3+}$

Convert to $CH_3CH_2OH + K_2Cr_2O_7 + H_2SO_4 \rightarrow CH_3COOH + Cr_2(SO_4)_3 + K_2SO_4$
$C_2H_6O + K_2Cr_2O_7 + H_2SO_4 \rightarrow C_2H_4O_2 + Cr_2(SO_4)_3 + K_2SO_4$

Step 1. Divide into two half reactions
$C_2H_6O \rightarrow C_2H_4O_2$
$K_2Cr_2O_7 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4$

Step 2. Balance all atoms in the two half reactions
$C_2H_6O \rightarrow C_2H_4O_2$
$C_2H_6O + O \rightarrow C_2H_4O_2$
$C_2H_6O + O \rightarrow C_2H_4O_2 + 2H$
$C_2H_6O + O + 2H \rightarrow C_2H_4O_2 + 2H + 2H$
$C_2H_6O + H_2O \rightarrow C_2H_4O_2 + 4H$
$K_2Cr_2O_7 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4$
$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4$
$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7O$
$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 8H + 7O$
$K_2Cr_2O_7 + 4H_2SO_4 + 14H \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 8H + 7O + 14H$
$K_2Cr_2O_7 + 4H_2SO_4 + 6H \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$

Step 3. Make the H-atom of the two half reactions equivalent (LCM = 12)
$(C_2H_6O + H_2O \rightarrow C_2H_4O_2 + 4H) \times 3$
$(K_2Cr_2O_7 + 4H_2SO_4 + 6H \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O) \times 2$

Step 4. Combine the two half reactions
$3C_2H_6O + 3H_2O \rightarrow 3C_2H_4O_2 + 12H$

$2K_2Cr_2O_7 + 8H_2SO_4 + 12H \rightarrow 2Cr_2(SO_4)_3 + 2K_2SO_4 + 14H_2O$

Step 5. Simplify the overall chemical equation

$3C_2H_6O + 2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 3C_2H_4O_2 + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O$

In example 5, $C_2H_6O + Cr_2O_7^{2-} + H^+ \rightarrow C_2H_4O_2 + Cr^{3+}$, the ionic equation is converted to a molecular chemical equation, $C_2H_6O + K_2Cr_2O_7 + H_2SO_4 \rightarrow C_2H_4O_2 + Cr_2(SO_4)_3 + K_2SO_4$, by adding spectator ions K^+ and SO_4^{2-}. One half of the oxidation reaction "$C_2H_6O + H_2O \rightarrow C_2H_4O_2 + 4H$" releasing four H-atoms represents the loss of four electrons, and the other half reduction reaction "$K_2Cr_2O_7 + 4H_2SO_4 + 6H \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$" obtaining six H-atoms represents the gain of six electrons. $K_2Cr_2O_7$ and C_2H_6O act as oxidizing agent and reducing agent respectively.

Example 6. Given the following inorganic equation:

$P_2I_4 + P_4 + H_2O \rightarrow PH_4I + H_3PO_4$

Step 1. Divide into two half reactions

$P_2I_4 + P_4 \rightarrow PH_4I$

$P_4 \rightarrow H_3PO_4$

Step 2. Balance all atoms in the two half reactions

$P_2I_4 + P_4 \rightarrow PH_4I$

$2P_2I_4 + P_4 \rightarrow 8PH_4I$

$2P_2I_4 + P_4 + 32H \rightarrow 8PH_4I$

$P_4 \rightarrow H_3PO_4$

$P_4 \rightarrow 4H_3PO_4$

$P_4 + 16O \rightarrow 4H_3PO_4$

$P_4 + 12H + 16O \rightarrow 4H_3PO_4$

$P_4 + 12H + 16O + 32H \rightarrow 4H_3PO_4 + 32H$

$P_4 + 16H_2O \rightarrow 4H_3PO_4 + 20H$

Step 3. Make the H-atom of the two half reactions equivalent (LCM = 160)

$(2P_2I_4 + P_4 + 32H \rightarrow 8PH_4I) \times 5$

$(P_4 + 16H_2O \rightarrow 4H_3PO_4 + 20H) \times 8$

Step 4. Combine the two half reactions

$10P_2I_4 + 5P_4 + 160H \rightarrow 40PH_4I$

$8P_4 + 128H_2O \rightarrow 32H_3PO_4 + 160H$

Step 5. Simplify the overall chemical equation

$10P_2I_4 + 13P_4 + 128H_2O \rightarrow 40PH_4I + 32H_3PO_4$

In example 6, $P_2I_4 + P_4 + H_2O \rightarrow PH_4I + H_3PO_4$, one half of the reduction reaction "$2P_2I_4 + P_4 + 32H \rightarrow 8PH_4I$" gaining thirty-two H-atoms represents the gain of 32 electrons, and the other half oxidation reaction of "$P_4 + 16H_2O \rightarrow 4H_3PO_4 + 20H$" releasing twenty H-atoms represents the loss of 20 electrons.

Example 7. Given the following inorganic equation:

$Fe_3C + HNO_3 \rightarrow Fe(NO_3)_3 + CO_2 + NO_2$

Step 1. Divide into two half reactions

$Fe_3C + HNO_3 \rightarrow Fe(NO_3)_3 + CO_2$

$HNO_3 \rightarrow NO_2$

Step 2. Balance all atoms in the two half reactions

$Fe_3C + HNO_3 \rightarrow Fe(NO_3)_3 + CO_2$

$Fe_3C + 9HNO_3 \rightarrow 3Fe(NO_3)_3 + CO_2$

$Fe_3C + 9HNO_3 + 2O \rightarrow 3Fe(NO_3)_3 + CO_2$

$Fe_3C + 9HNO_3 + 2O \rightarrow 3Fe(NO_3)_3 + CO_2 + 9H$

$Fe_3C + 9HNO_3 + 2O + 4H \rightarrow 3Fe(NO_3)_3 + CO_2 + 9H + 4H$

$Fe_3C + 9HNO_3 + 2H_2O \rightarrow 3Fe(NO_3)_3 + CO_2 + 13H$

$HNO_3 \rightarrow NO_2$
$HNO_3 \rightarrow NO_2 + O$
$HNO_3 \rightarrow NO_2 + O + H$
$HNO_3 + H \rightarrow NO_2 + O + H + H$
$HNO_3 + H \rightarrow NO_2 + H_2O$

Step 3. Make the H-atom of the two half reactions equivalent (LCM = 13)
$(Fe_3C + 9HNO_3 + 2H_2O \rightarrow 3Fe(NO_3)_3 + CO_2 + 13H) \times 1$
$(HNO_3 + H \rightarrow NO_2 + H_2O) \times 13$

Step 4. Combine the two half reactions
$Fe_3C + 9HNO_3 + 2H_2O \rightarrow 3Fe(NO_3)_3 + CO_2 + 13H$
$13HNO_3 + 13H \rightarrow 13NO_2 + 13H_2O$

Step 5. Simplify the overall chemical equation
$Fe_3C + 22HNO_3 \rightarrow 3Fe(NO_3)_3 + CO_2 + 13NO_2 + 11H_2O$

In example 7, $Fe_3C + HNO_3 \rightarrow Fe(NO_3)_3 + CO_2 + NO_2$, one half of the oxidation reaction “$Fe_3C + 9HNO_3 + 2H_2O \rightarrow 3Fe(NO_3)_3 + CO_2 + 13H$” releasing 13 H-atoms represents the loss of 13 electrons, and the other half reduction reaction of “$HNO_3 + H \rightarrow NO_2 + H_2O$” gaining one H-atom represents the gain of one electron. Although example 7 contains uncertain oxidation numbers of a reactant Fe_3C, it can still be balanced by the H-atom method.

Stoichiometric number of transferred H-atoms in half redox reactions

For examples 4 through 7, the half redox reactions and their stoichiometric number of transferred H-atoms are presented and defined in Table 2.

According to the H-atom method, the gain/loss of one H is identical to the gain/loss of one electron ($H \rightarrow H^+ + e^-$). The number of transferred H-atoms (TH) is equal to the number of transferred electrons (Te^-) as shown in Table 3. TH can function as an electron-counting concept, $Te^- = 1 \times TH$.

The O-atom method: procedures

The procedures of the O-atom method are similar to that of the H-atom method. The O-atom, rather than the H-atom, acts as the dominant balancing device. The differences in their procedures are illustrated in Step 2d, Step 2e, and Step 3.

Table 2: Stoichiometric number of transferred H-atoms in half redox reactions.

Half reaction	TH	Half redox reaction
$C_7H_8 + 2H_2O \rightarrow C_7H_6O_2 + 6H$	Loss of 6H	Oxidation
$2KMnO_4 + 3H_2SO_4 + 10H \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$	Gain of 10H	Reduction
$C_2H_6O + H_2O \rightarrow C_2H_4O_2 + 4H$	Loss of 4H	Oxidation
$K_2Cr_2O_7 + 4H_2SO_4 + 6H \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$	Gain of 6H	Reduction
$P_4 + 16H_2O \rightarrow 4H_3PO_4 + 20H$	Loss of 20H	Oxidation
$2P_2I_4 + P_4 + 32H \rightarrow 8PH_4I$	Gain of 32H	Reduction
$Fe_3C + 9HNO_3 + 2H_2O \rightarrow 3Fe(NO_3)_3 + CO_2 + 13H$	Loss of 13H	Oxidation
$HNO_3 + H \rightarrow NO_2 + H_2O$	Gain of 1H	Reduction

Table 3: Stoichiometric TH and Te^- in half redox reactions.

Half reaction: TH	**Half reaction: Te^-**
$C_7H_8 + 2H_2O \rightarrow C_7H_6O_2 + 6H$	$C_7H_8 + 2H_2O \rightarrow C_7H_6O_2 + 6H^+ + 6e^-$
$2KMnO_4 + 3H_2SO_4 + 10H \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$	$2KMnO_4 + 3H_2SO_4 + 10H^+ + 10e^- \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$
$C_2H_6O + H_2O \rightarrow C_2H_4O_2 + 4H$	$C_2H_6O + H_2O \rightarrow C_2H_4O_2 + 4H^+ + 4e^-$
$K_2Cr_2O_7 + 4H_2SO_4 + 6H \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$	$K_2Cr_2O_7 + 4H_2SO_4 + 6H^+ + 6e^- \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$
$P_4 + 16H_2O \rightarrow 4H_3PO_4 + 20H$	$P_4 + 16H_2O \rightarrow 4H_3PO_4 + 20H^+ + 20e^-$
$2P_2I_4 + P_4 + 32H \rightarrow 8PH_4I$	$2P_2I_4 + P_4 + 32H^+ + 32e^- \rightarrow 8PH_4I$
$Fe_3C + 9HNO_3 + 2H_2O \rightarrow 3Fe(NO_3)_3 + CO_2 + 13H$	$Fe_3C + 9HNO_3 + 2H_2O \rightarrow 3Fe(NO_3)_3 + CO_2 + 13H^+ + 13e^-$
$HNO_3 + H \rightarrow NO_2 + H_2O$	$HNO_3 + H^+ + e^- \rightarrow NO_2 + H_2O$

Step 1. Divide into two half reactions

Step 2. Balance all atoms in the two half reactions

a) Balance all other atoms except H and O
b) Balance the oxygen atoms with O
c) Balance the hydrogen atoms with H
d) Add one O atom for two H atoms
e) Convert one O atom and two H atoms to one H_2O molecule

Step 3. Make the O-atom of the two half reactions equivalent

Step 4. Combine the two half reactions

Step 5. Simplify the overall chemical equation

The O-atom method: examples

Example 8. Given the following molecular chemical equation:

$C_6H_5CH_3 + KMnO_4 + H_2SO_4 \rightarrow C_6H_5COOH + K_2SO_4 + MnSO_4$

Convert to $C_7H_8 + KMnO_4 + H_2SO_4 \rightarrow C_7H_6O_2 + K_2SO_4 + MnSO_4$

Step 1. Divide into two half reactions

$C_7H_8 \rightarrow C_7H_6O_2$
$KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4$

Step 2. Balance all atoms in the two half reactions

$C_7H_8 \rightarrow C_7H_6O_2$
$C_7H_8 + 2O \rightarrow C_7H_6O_2$
$C_7H_8 + 2O \rightarrow C_7H_6O_2 + 2H$
$C_7H_8 + 2O + O \rightarrow C_7H_6O_2 + 2H + O$
$C_7H_8 + 3O \rightarrow C_7H_6O_2 + H_2O$
$KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4$
$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4$
$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8O$
$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8O + 6H$
$2KMnO_4 + 3H_2SO_4 + 3O \rightarrow K_2SO_4 + 2MnSO_4 + 8O + 6H + 3O$
$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5O + 3H_2O$

Step 3. Make the O-atom of the two half reactions equivalent (LCM = 15)

$(C_7H_8 + 3O \rightarrow C_7H_6O_2 + H_2O) \times 5$
$(2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5O + 3H_2O) \times 3$
Step 4. Combine the two half reactions
$5C_7H_8 + 15O \rightarrow 5C_7H_6O_2 + 5H_2O$
$6KMnO_4 + 9H_2SO_4 \rightarrow 3K_2SO_4 + 6MnSO_4 + 15O + 9H_2O$
Step 5. Simplify the overall chemical equation
$5C_7H_8 + 6KMnO_4 + 9H_2SO_4 \rightarrow 5C_7H_6O_2 + 3K_2SO_4 + 6MnSO_4 + 14H_2O$

In this process, each O-atom is equivalent to the gain/loss of two electrons. By using example 8, $C_7H_8 + KMnO_4 + H_2SO_4 \rightarrow C_7H_6O_2 + K_2SO_4 + MnSO_4$, as a demonstration, in the half oxidation reaction of "$C_7H_8 + 3O \rightarrow C_7H_6O_2 + H_2O$", the gain of three O-atoms represents the loss of six electrons. In the other half reduction reaction of "$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O$", the loss of five O-atoms represents the gain of 10 electrons.

Example 9. Given the following ionic chemical equation:
$CH_3CH_2OH + Cr_2O_7^{2-} + H^+ \rightarrow CH_3COOH + Cr^{3+}$
Convert to $CH_3CH_2OH + K_2Cr_2O_7 + H_2SO_4 \rightarrow CH_3COOH + Cr_2(SO_4)_3 + K_2SO_4$
$C_2H_6O + K_2Cr_2O_7 + H_2SO_4 \rightarrow C_2H_4O_2 + Cr_2(SO_4)_3 + K_2SO_4$
Step 1. Divide into two half reactions
$C_2H_6O \rightarrow C_2H_4O_2$
$K_2Cr_2O_7 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4$
Step 2. Balance all atoms in the two half reactions
$C_2H_6O \rightarrow C_2H_4O_2$
$C_2H_6O + O \rightarrow C_2H_4O_2$
$C_2H_6O + O \rightarrow C_2H_4O_2 + 2H$
$C_2H_6O + O + O \rightarrow C_2H_4O_2 + 2H + O$
$C_2H_6O + 2O \rightarrow C_2H_4O_2 + H_2O$
$K_2Cr_2O_7 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4$
$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4$
$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7O$
$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7O + 8H$
$K_2Cr_2O_7 + 4H_2SO_4 + 4O \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7O + 8H + 4O$
$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3O$
Step 3. Make the O-atom of the two half reactions equivalent (LCM = 6)
$(C_2H_6O + 2O \rightarrow C_2H_4O_2 + H_2O) \times 3$
$(K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3O) \times 2$
Step 4. Combine the two half reactions
$3C_2H_6O + 6O \rightarrow 3C_2H_4O_2 + 3H_2O$
$2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 2K_2SO_4 + 8H_2O + 6O$
Step 5. Simplify the overall chemical equation
$3C_2H_6O + 2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 3C_2H_4O_2 + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O$

By using example 9, $C_2H_6O + K_2Cr_2O_7 + H_2SO_4 \rightarrow C_2H_4O_2 + Cr_2(SO_4)_3 + K_2SO_4$, as a demonstration, in the half reaction of "$C_2H_6O + 2O \rightarrow C_2H_4O_2 + H_2O$", the gain of two O-atoms represents the loss of four electrons. In the other half reaction of "$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3O$", the release of three O-atoms represents the gain of six electrons.

Example 10. Given the following inorganic equation:
$P_2I_4 + P_4 + H_2O \rightarrow PH_4I + H_3PO_4$
Step 1. Divide into two half reactions
$P_2I_4 + P_4 \rightarrow PH_4I$

$P_4 \rightarrow H_3PO_4$

Step 2. Balance all atoms in the two half reactions

$P_2I_4 + P_4 \rightarrow PH_4I$

$2P_2I_4 + P_4 \rightarrow 8PH_4I$

$2P_2I_4 + P_4 + 32H \rightarrow 8PH_4I$

$2P_2I_4 + P_4 + 32H + 16O \rightarrow 8PH_4I + 16O$

$2P_2I_4 + P_4 + 16H_2O \rightarrow 8PH_4I + 16O$

$P_4 \rightarrow H_3PO_4$

$P_4 \rightarrow 4H_3PO_4$

$P_4 + 16O \rightarrow 4H_3PO_4$

$P_4 + 12H + 16O \rightarrow 4H_3PO_4$

$P_4 + 12H + 16O + 6O \rightarrow 4H_3PO_4 + 6O$

$P_4 + 6H_2O + 10O \rightarrow 4H_3PO_4$

Step 3. Make the O-atom of the two half reactions equivalent (LCM = 80)

$(2P_2I_4 + P_4 + 16H_2O \rightarrow 8PH_4I + 16O) \times 5$

$(P_4 + 6H_2O + 10O \rightarrow 4H_3PO_4) \times 8$

Step 4. Combine the two half reactions and simplify the overall chemical equation

$10P_2I_4 + 5P_4 + 80H_2O \rightarrow 40PH_4I + 80O$

$8P_4 + 48H_2O + 80O \rightarrow 32H_3PO_4$

Step 5. Simplify the overall chemical equation

$10P_2I_4 + 13P_4 + 128H_2O \rightarrow 40PH_4I + 32H_3PO_4$

By using example 10, $P_2I_4 + P_4 + H_2O \rightarrow PH_4I + H_3PO_4$, as a demonstration, in the half reduction reaction of "$2P_2I_4 + P_4 + 16H_2O \rightarrow 8PH_4I + 16O$", the loss of sixteen O-atoms represents the gain of 32 electrons. In the other half reduction reaction of "$8P_4 + 48H_2O + 80O \rightarrow 32H_3PO_4$", the gain of 80 O-atoms represents the loss of 160 electrons.

Example 11. Given the following inorganic equation:

$Pb(N_3)_2 + Cr(MnO_4)_2 \rightarrow Pb_3O_4 + NO + Cr_2O_3 + MnO_2$

Step 1. Divide into two half reactions

$Pb(N_3)_2 \rightarrow Pb_3O_4 + NO$

$Cr(MnO_4)_2 \rightarrow Cr_2O_3 + MnO_2$

Step 2. Balance all atoms in the two half reactions

$Pb(N_3)_2 \rightarrow Pb_3O_4 + NO$

$3Pb(N_3)_2 \rightarrow Pb_3O_4 + 18NO$

$3Pb(N_3)_2 + 22O \rightarrow Pb_3O_4 + 18NO$

$Cr(MnO_4)_2 \rightarrow Cr_2O_3 + MnO_2$

$2Cr(MnO_4)_2 \rightarrow Cr_2O_3 + 4MnO_2$

$2Cr(MnO_4)_2 \rightarrow Cr_2O_3 + 4MnO_2 + 5O$

Step 3. Make the O-atom of the two half reactions equivalent (LCM = 110)

$(3Pb(N_3)_2 + 22O \rightarrow Pb_3O_4 + 18NO) \times 5$

$(2Cr(MnO_4)_2 \rightarrow Cr_2O_3 + 4MnO_2 + 5O) \times 22$

Step 4. Combine the two half reactions and simplify the overall chemical equation

$15Pb(N_3)_2 + 110O \rightarrow 5Pb_3O_4 + 90NO$

$44Cr(MnO_4)_2 \rightarrow 22Cr_2O_3 + 88MnO_2 + 110O$

Step 5. Simplify the overall chemical equation

$15Pb(N_3)_2 + 44Cr(MnO_4)_2 \rightarrow 5Pb_3O_4 + 90NO + 22Cr_2O_3 + 88MnO_2$

By using example 11, $Pb(N_3)_2 + Cr(MnO_4)_2 \rightarrow Pb_3O_4 + NO + Cr_2O_3 + MnO_2$, as a demonstration, in the half oxidation reaction of "$3Pb(N_3)_2 + 22O \rightarrow Pb_3O_4 + 18NO$", the gain of 22 O-atoms represents the loss of 44 electrons. In the other half reduction reaction of "$2Cr(MnO_4)_2 \rightarrow Cr_2O_3 + 4MnO_2 + 5O$", the loss of five O-atoms represents the gain of 10 electrons. Although example 11 contains multiple redox couples, it can still be balanced by the O-atom method.

Stoichiometric number of transferred O-atoms in half redox reactions

For examples 8 through 11, the half redox reactions and their stoichiometric number of transferred O-atoms are summarized and defined in Table 4.

According to the O-atom method, the gain/loss of one O is identical to the loss/gain of two electrons ($O + 2e^- \rightarrow O^{2-}$). The number of transferred O-atoms (TO) can be represented by Te^- as shown in Table 5. TO acts as an electron-counting concept, $Te^- = -2 \times TO$.

Electron-counting concepts: ΔON, TH, and TO

The notion of electron transfer is the core of redox reactions. The mathematical relationship of $Te^- = n \times \Delta ON$ has been established and ΔON acts as an electron-counting concept in a half redox reaction (Yuen & Lau, 2022). TH and TO are demonstrated as electron-counting concepts by the H-atom and O-atom methods. The relationships among TH, TO, and ΔON are centered around Te^- as shown in Figure 1. The nature of the electron-counting concepts of TH, TO, and ΔON are summarized in Table 6.

TH, TO, Te^-, and ΔON in molecular and ionic chemical equations

The balanced half reduction reaction in molecular chemical equation (from example 4, H-atom method) is converted to ionic chemical equation as follows:

Table 4: Stoichiometric number of transferred O-atoms in half redox reactions.

Half reaction	TO	Half redox reaction
$C_7H_8 + 3O \rightarrow C_7H_6O_2 + H_2O$	Gain of 3O	Oxidation
$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$	Loss of 5O	Reduction
$C_2H_6O + 2O \rightarrow C_2H_4O_2 + H_2O$	Gain of 2O	Oxidation
$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3O$	Loss of 3O	Reduction
$8P_4 + 48H_2O + 80O \rightarrow 32H_3PO_4$	Gain of 80O	Oxidation
$2P_2I_4 + P_4 + 16H_2O \rightarrow 8PH_4I + 16O$	Loss of 16O	Reduction
$3Pb(N_3)_2 + 22O \rightarrow Pb_3O_4 + 18NO$	Gain of 22O	Oxidation
$2Cr(MnO_4)_2 \rightarrow Cr_2O_3 + 4MnO_2 + 5O$	Loss of 5O	Reduction

Table 5: Stoichiometric TO and Te^- in half redox reactions.

Half reaction: TO	Half reactions: Te^-
$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$	$2KMnO_4 + 3H_2SO_4 + 10e^- \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O^{-2}$
$C_7H_8 + 3O \rightarrow C_7H_6O_2 + H_2O$	$C_7H_8 + 3O^{-2} \rightarrow C_7H_6O_2 + H_2O + 6e^-$
$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3O$	$K_2Cr_2O_7 + 4H_2SO_4 + 6e^- \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3O^{-2}$
$C_2H_6O + 2O \rightarrow C_2H_4O_2 + H_2O$	$C_2H_6O + 2O^{-2} \rightarrow C_2H_4O_2 + H_2O + 4e^-$
$8P_4 + 48H_2O + 80O \rightarrow 32H_3PO_4$	$8P_4 + 48H_2O + 80O^{-2} \rightarrow 32H_3PO_4 + 160e^-$
$2P_2I_4 + P_4 + 16H_2O \rightarrow 8PH_4I + 16O$	$2P_2I_4 + P_4 + 16H_2O + 32e^- \rightarrow 8PH_4I + 16O^{-2}$
$3Pb(N_3)_2 + 22O \rightarrow Pb_3O_4 + 18NO$	$3Pb(N_3)_2 + 22O^{-2} \rightarrow Pb_3O_4 + 18NO + 44e^-$
$2Cr(MnO_4)_2 \rightarrow Cr_2O_3 + 4MnO_2 + 5O$	$2Cr(MnO_4)_2 + 10e^- \rightarrow Cr_2O_3 + 4MnO_2 + 5O^{-2}$

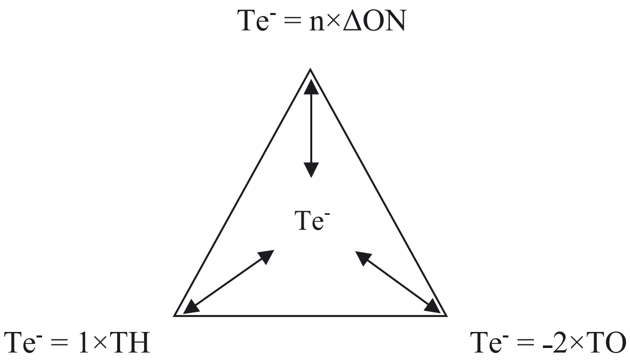

Figure 1: Mathematical relationships among Te^-, ΔON, TH, and TO.

Table 6: Nature of electron-counting concepts.

e^- counting concept	$Te^- = 1 \times TH$	$Te^- = -2 \times TO$	$Te^- = n \times \Delta ON$
$Te^- > 0$ (positive); Loss of electron	$TH > 0$ (positive); Loss of H-atom	$TO < 0$ (negative); Gain of O-atom	$\Delta ON > 0$ (positive); Increase in ON
Loss: + or positive Gain: − or negative	Loss of 1 H-atom = Loss of 1 electron	Gain of 1 O-atom = Loss of 2 electrons	Increase in ON; Loss of $n \times \Delta ON$ electrons
$Te^- < 0$ (negative); Gain of electron	$TH < 0$ (negative); Gain of 1 H-atom	$TO > 0$ (positive); Loss of O-atom	$\Delta ON < 0$ (negative); Decrease in ON
Gain: − or negative Loss: + or positive	Gain of 1 H-atom = Gain of 1 electron	Loss of 1 O-atom = Gain of 2 electrons	Decrease in ON; Gain of $n \times \Delta ON$ electrons

$$2KMnO_4 + 3H_2SO_4 + 10H \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$$
$$2K^+ + 2MnO_4{}^- + 6H^+ + 3SO_4^{-2} + 10H^+ + 10e^- \rightarrow 2K^+ + SO_4^{-2} + 2Mn^{2+} + 2SO_4^{-2} + 8H_2O$$
$$2MnO_4{}^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$

The balanced half reduction reaction in molecular chemical equation (from example 8, O-atom method) is converted to ionic chemical equation as follows:

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$2K^+ + 2MnO_4{}^- + 6H^+ + 3SO_4^{-2} + 10e^- \rightarrow 2K^+ + SO_4^{-2} + 2Mn^{2+} + 2SO_4^{-2} + 3H_2O + 5O^{-2}$$
$$2K^+ + 2MnO_4{}^- + 6H^+ + 3SO_4^{-2} + 10e^- + 10H^+ \rightarrow 2K^+ + SO_4^{-2} + 2Mn^{2+} + 2SO_4^{-2} + 3H_2O + 5O^{-2} + 10H^+$$
$$2K^+ + 2MnO_4{}^- + 6H^+ + 3SO_4^{-2} + 10e^- + 10H^+ \rightarrow 2K^+ + SO_4^{-2} + 2Mn^{2+} + 2SO_4^{-2} + 3H_2O + 5H_2O$$
$$2MnO_4{}^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$

Table 7: Comparison of TH, TO and ΔON in half reduction chemical equations.

Equation	Balanced half reduction reaction	Nature	e^- counting concept
Molecular chemical equation	$2KMnO_4 + 3H_2SO_4 + 10H \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$	Gain of 10 H ($TH < 0$)	$TH = -10$ $Te^- = 1 \times TH$ $Te^- = -10$
Molecular chemical equation	$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$	Loss of 5 O ($TO > 0$)	$TO = +5$ $Te^- = -2 \times TO$ $Te^- = -10$
Ionic chemical equation	$2MnO_4{}^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$	Gain of 10 e^-($Te^- < 0$)	$Te^- = -10$
Ionic chemical equation	$2MnO_4{}^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$	Decrease in ON ($\Delta ON < 0$)	$Te^- = -10$; $n_{(Mn)} = 2$ $Te^- = n \times \Delta ON$ $\Delta ON_{(Mn)} = -5$

The reduction reaction of "$KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4$" can be balanced by having a gain of ten H-atoms, a loss of five O-atoms, or a gain of 10 electrons. In Table 7, the half reduction molecular chemical equations are demonstrated by using either TH or TO as an electron-counting concept, and then Te^- can be calculated; the converted ionic chemical equation are exhibited by using Te^-, and then ΔON can be calculated.

Conclusion

Redox reactions can be defined by four different models: electron transfer, oxidation number, H-atom transfer, and O-atom transfer. Currently, the determination of oxidation number is a prevalent tool for calculating the number of transferred electrons, defining redox terms, and balancing redox equations. Nevertheless, it is not always easy to assign oxidation number. Without the assignment of oxidation number of atoms, the use of the ON method for balancing redox reactions is restricted. To overcome this problem, this article explores the H-atom and O-atom methods, When compared to the conventional ON method, these two methods work in a reversed direction. They operate by balancing atoms first, then counting TH or TO, and finally determining Te^-. Triangular relationships among TH, TO, and Te^- are established in the balanced redox reaction. Consequently, TH and TO are demonstrated as electron-counting concepts for balancing redox reactions. In addition, the electron transfer, oxidation number, H-atom transfer, and O-atom transfer models are integrated through the establishment of mathematical relationships among Te^-, TH, TO, and ΔON.

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