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Aggregate Redox Species Method - An Improved Oxidation Number Change Method for Balancing Redox Equations

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Abstract

This paper presents a variation of the oxidation number change method for balancing redox equations that is applicable to any type of redox reaction including ionic and molecular reactions. The Aggregate Redox Species (ARS) method is particularly suitable for reactions that cannot be "cleanly" separated into partial reactions of oxidation and reduction. This method solves the problem by aggregating all species with redox atoms into one equation, balancing the redox atoms in them and "freezing" their stoichiometric coefficients. Non-redox species are added to the "frozen" equation (ARS equation), after which all other atoms and charges are balanced. A program developed based on the suggested method proved to be successful at solving a large variety of redox equations, thus demonstrating that the oxidation number change method is a systematical and highly applicable method for balancing redox equations.

Keywords

Balancing Chemical Equation, Oxidation Numbers Change Method, Redox Reaction, Oxidation State, Stoichiometry, Computer-Based Learning

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1. Introduction

All chemical equations must be balanced for both mass and charge. The most common method for balancing chemical equations is by inspection. Although Toth [1] has shown that balancing chemical equations by inspection is not a trial-and-error process, this method is not suitable for balancing redox equations. The reason is that the redox equations have an additional requirement - the number of electrons gained in the reduction must be equal to the number of electrons lost in the oxidation. Out of all the specialized approaches for balancing redox equations [2-6], there are three main ones: (3) algebraic method, (2) ion-electron method, also called the half-reaction method, and (1) oxidation number change method.

The idea behind the algebraic method of balancing chemical equations is to translate the conservation of mass and charges in chemical reactions into a system of linear equations. The system is then solved by using the Gauss or Gauss-Jordan elimination methods. After Olson [7] introduced an additional equation for oxidation-reduction balance the algebraic method satisfied all three general conditions of a balanced reaction: electron balance, atom balance and charge balance. Although Charnock [8] underlines that in secondary chemistry education the linear algebraic method is the predominant method, it is less popular among chemists since the corresponding sets of linear equations are often tedious to equate. Even mathematicians have problems balancing redox equations because they need to know the oxidation numbers in order to set the equation for electron balance.

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University textbooks of general chemistry commonly support the ion-electron method as a basic procedure for balancing redox equations [9, 10]. In this method the overall reaction is divided into two half-reactions, one involving oxidation and the other reduction. Each half-reaction is balanced separately according to mass and charge. The final balanced ionic equation is obtained by multiplying each half-reaction with an appropriate constant and adding them together so that the free electrons cancel out. Although there is no need to calculate oxidation states in this method, separating complex redox equations into half-reactions without knowing the oxidation numbers can be a formidable task.

Despite the oxidation number change method being the oldest of these three methods, today both students and teachers only partially understands this method of balancing chemical equations [11]. It is a pity because the oxidation number change method often not only proves to be the simplest method for balancing redox equations, but also the fastest one. The aggregate redox species method, abbreviated as ARS method, is a variation of the oxidation number change method for balancing redox equations. The difference between them is the order in which the balancing process is performed, though all procedures that are applicable to one method are applicable to the other as well.

Šima [12] in his article proposes to characterize redox reactions "as the processes involving a change in the oxidation number of atoms of one or more elements." The oxidation state is a simple numerical attribute of an atom in a compound and is a key component when tracking the course of chemical equations. According to the Comprehensive definition of oxidation state, the oxidation state of an atom is the charge of this atom after ionic approximation of its heteronuclear bonds [13]. The alternative term "oxidation number" is largely synonymous with oxidation state. The origin of the oxidation state concept was given by Jensen et al. [14]. Nowadays it is common for students to determine oxidation numbers by following a list of rules despite the fact that its determination from the Lewis structure is even easier than deducing it from the molecular formula, as shown by Kauffman back in 1986 [15]. Determination of the oxidation state from the Lewis structure was explained in detail, as well as illustrated with examples, by Karen et al [16].

2. Research Significance

The aim of this paper is to revitalize the oxidation number change method for balancing redox equations, and through simple steps help teachers, students and scientists quickly solve both simple and complex redox equations. Since many popular textbooks lack adequate guidance for balancing complex redox equations, detailed steps for aggregating redox species are provided.

These steps are also useful for the ion-electron and the classic oxidation number change method, but for the ARS method they are essential. Each step will be accompanied by equations demonstrating its use.

3. Methodology and Discussion

The novelty of the proposed method is that it can be used for both redox and non-redox reactions. Similarly, when using the ARS method, equations can be written in both the ionic and molecular form. While balancing reactions with the ARS method it is unnecessary to introduce "alien" species into the reaction. If water is being added to balance hydrogen and/or oxygen atoms, then that water also participates in the reaction.

The following definitions are provided in order to help the reader in understanding the proposed methods described in this paper:

redox atom means an atom of an element whose oxidation number changes in the reaction,

redox species means a compound or ion which comprises at least one redox atom,

non-redox atom means an atom of an element that has not been oxidized or reduced,

non-redox species means a compound or ion that does not comprise even a single redox atom.

An atom of an element with a specific oxidation number can simultaneously be a redox and non-redox atom. In this work a partial reaction is a synonym for a half-reaction used in the oxidation number change method.

In any oxidation-reduction reaction it is imperative that oxidation and reduction must occur together and to the same extent. By writing the oxidation and reduction reactions separately and multiplying each one so that the electrons lost and gained are equal, there's no consistent way to obtain the final equation by simply adding these two equations together. This is because an equation cannot be "cleanly" separated into partial reactions of oxidation and reduction. The ARS method solves this problem by aggregating all species with redox atoms into one equation in such a way that all redox atoms are balanced.

The first and most important step is to assign oxidation numbers to each atom in the equation. When the oxidation numbers of atoms in an equation are known, it is simple to identify which atoms are being oxidized (the oxidation number increases) and which are being reduced (the oxidation number decreases). Take a look at a titration of potassium dichromate with Mohr salt in an acidic medium:

$$K_2Cr_2O_7 + (NH_4)_2Fe(SO_4)_2{\cdot}6H_2O + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + K_2SO_4 + (NH_4)_2SO_4 + H_2O$$

This huge reaction looks pretty intimidating, but once the oxidation numbers are determined it becomes evident that this is a simple redox reaction in which the chromium (VI) is reduced to chromium(III) and the iron(II) is oxidized to iron(III).

3.1. Aggregating Redox Species

After discovering what is oxidized and what is reduced, all redox couples that can be formed are written down. The following steps have two goals: (1) aggregate redox couples into two partial reactions, and (2) balance all redox atoms in them. These steps are universal and can also be used to determine half-reactions in the ion-electron method and to obtain partial reactions in the classic oxidation number change method.

1 Removing unnecessary redox couples

Some elements have atoms with different oxidation numbers on the left and right sides of the equation, but they do not participate in the electron transfer, thus they are non-redox atoms. Similarly, some elements have atoms which play a dual function, partly behaving as a redox and partly as a non-redox atom. Here are some rules to help you recognize such atoms:

Rule 0: Whatever you do, there must always remain at least one oxidation reaction and at least one reduction reaction.

Rule 1: If some element has atoms with identical oxidation numbers on both sides of the skeleton equation, it is a non-redox element and all redox couples in which they appear as redox atoms should be removed. For example:

$$FeSO_4 + Br_2 + KSCN \rightarrow K_3[Fe(SCN)_6] + KBr + K_2SO_4$$

$$FeSO_4 + (NH_4)_2Ce(NO_3)_6 \rightarrow Fe_2(SO_4)_3 + Fe(NO_3)_3 + Ce(NO_3)_3 + NH_4NO_3$$

In the first equation sulfur has the same oxidation numbers on both sides of the equation (+6 and -2). Similarly, nitrogen in the second equation has the same oxidation numbers on both sides of the equation (+5 and -3).

Rule 2: If an element has atoms with different oxidation numbers on the left and right side of the skeleton equation, but the atom with a specific oxidation number does not participate in the electron transfer (it is a non-redox atom), all redox couples in which this atom appears as a redox atom are to be removed. For example:

$$N_2H_4 + Fe(CN)_6^{3-} + OH^- \rightarrow N_2 + Fe(CN)_6^{4-}$$

$$Ag(NH_3)_2^+ + N_2H_4 \rightarrow Ag + N_2 + NH_3 + H_2O$$

In these reactions the cyanide ion and ammonium are spectators. Nitrogen from the cyanide ion and ammonium do not participate in the electron transfer so it is necessary to remove all redox couples in which they appear as a redox atom.

Rule 3: If an atom with a specific oxidation number is found in a non-redox species on the left side and appears as a redox atom in one or more redox species on the right side of the skeleton equation, all redox couples leading to that oxidation number, except the one with the simplest redox species, should be removed. The simplest redox species is the one that contains only one redox atom. That redox atom does not need to be balanced in the redox couple. The number of redox atoms on the left side determines how many electrons will be exchanged, while the right side can have more or less of these atoms. For example:

$$Ca(ClO)_2 + KI + HCl \rightarrow I_2 + CaCl_2 + H_2O + KCl$$

$$K_4[Fe(SCN)_6] + K_2Cr_2O_7 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + CO_2 + H_2O + K_2SO_4 + KNO_3$$

In the first reaction it does not matter which species with chloride is chosen, because neither contains other redox atoms. In the second reaction only K_2SO_4 is retained as that is the only species that contains sulfur(VI) without other redox atoms.

Rule 4: If multiple different species containing redox atoms with the same oxidation number are oxidized (or reduced) to the same oxidation state, and if there is a species containing an atom with that oxidation number on the right side of the skeleton equation, it is possible to choose which species will be oxidized (or reduced) and which will be the non-redox species. All reactions, except the simplest one, need to be removed. For example:

$$Fe(NO_3)_2 + HNO_3 \rightarrow Fe(NO_3)_3 + NO + H_2O$$

$$(NH_4)_2S_2O_8 + NH_3 \rightarrow N_2 + (NH_4)_2SO_4$$

Since it is possible to choose which species with a nitrogen(V) atom is going to get reduced, HNO_3 should be chosen because it contains only one redox atom, unlike $Fe(NO_3)_2$.

Rule 5: If a redox atom with the same oxidation number is found on the left side of one redox couple and on the right side of another, one of the redox couples needs to be removed. It is necessary to understand the chemical reaction in order to choose which redox couple has to be removed. For example:

$$KClO_3 + HCl \rightarrow KCl + H_2O + Cl_2$$

In this reaction it is obvious which redox couple needs to be removed - the reduction of chlorate to chloride.

In the case of oxidation of hydrogen sulfide by potassium permanganate the situation is much more complex. In redox processes with weaker oxidizing agents H_2S is oxidized to elemental sulfur, while with stronger oxidizing agents the oxidation of the sulfide proceeds until the +4 or +6 oxidation state [17]. Depending on the conditions this reaction can be run in two ways:

a) The sulfide ion oxidizes into elemental sulfur. In this case the sulfate ion is a spectator ion so the use of Rule 3 is required. The balanced reaction is:

$$2KMnO_4 + 5H_2S + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5S$$

b) The sulfide ion is partially oxidized into elemental sulfur and partially into sulfate ions. In this case sulfuric acid is added to make the solution acidic so the use of Rule 2 is required, and since the reduction of sulfate to sulfur is unlikely it is required to also use Rule 4. The balanced reaction is:

$$2KMnO_4 + 2H_2S + 2H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 4H_2O + S$$

2 Balancing redox atoms that are not a part of a redox couple

When more than one atom of an element that changes its oxidation number is present in a formula, it is necessary to calculate the number of electrons transferred per formula unit. Therefore, it is necessary to combine all redox couples that have species with multiple different redox atoms into one equation. The combined equation is then added to either the oxidation or reduction reactions depending on whether it is losing or gaining electrons.

Combining equations is not the same as summing equations. The two cases differ depending on whether the combined equations contain a shared species with multiple redox atoms: (1) If there are no such species then combining the equations is the same as summing them, or (2) if the combined equations have a shared species with multiple redox atoms it is necessary to ensure that their stoichiometric factor is the same in both equations. The equations are then combined by copying the shared species and summing the rest. For example, by combining the two oxidation equations for the reaction $Sb_2S_3 + NO_3^- \rightarrow Sb_2O_5 + HSO_4^- + NO$ only one molecule of Sb_2S_3 is obtained instead of two:

$$Sb_2S_3 \rightarrow Sb_2O_5 + 4e^-$$

$$Sb_2S_3 \rightarrow 3HSO_4^- + 24e^-$$

$$Sb_2S_3 \rightarrow Sb_2O_5 + 3HSO_4^- + 28e^-$$

One equation can be combined with many others. If necessary, i.e. the equation is the only member of the oxidation or reduction and cannot be moved, the equation can be duplicated in order to combine it with the others. For example:

$$Na_2CO_3 + C + N_2 \rightarrow NaCN + CO$$

$$Na_3[Co(NO_2)_6] + HCl \rightarrow CoCl_2 + NO + NO_2 + NaCl + H_2O$$

In the first reaction there are three redox couples containing species with two redox atoms on the right side. This can be solved by combining the nitrogen reduction with carbon oxidation as well as carbonate reduction. In the second equation the disproportionation of $Na_3[Co(NO_2)_6]$ produces three redox couples, so it is necessary to combine the reduction to $CoCl_2$ with the remaining two equations in order to balance all redox atoms. Depending on the position of the species with multiple redox atoms there are two possible scenarios:

a) The species with multiple redox atoms is on the left side

$$MnO_4^- + SCN^- \rightarrow Mn^{2+} + HSO_4^- + NO_3^- + CO_2$$

$$Ce^{4+} + Fe(CN)_6^{4-} \rightarrow Ce(OH)_3 + Fe(OH)_3 + CO_3^{2-} + NO_3^-$$

A special case of a species with multiple redox atoms on the left side is disproportionation

$$Ca(OCl)_2 \rightarrow Ca(ClO_3)_2 + CaCl_2$$

$$(NH_4)_2Cr_2O_7 \rightarrow NH_3 + H_2O + Cr_2O_3 + O_2$$

b) The species with multiple redox atoms is on the right side

$$FeTiO_3 + Cl_2 + C \rightarrow TiCl_4 + FeCl_3 + CO$$

$$KSCN + I_2 + H_2O \rightarrow KHSO_4 + HI + ICN$$

3 Balancing non-redox atoms that are present only in redox species

When the non-redox atom is found only in redox species it must be balanced before the electron transfer is equalized. Since the redox atoms are already balanced, non-redox atoms can only be balanced by multiplying the entire equation by some factor and then summing it with another oxidation or reduction equation. If possible, all equations that have a different number of non-redox atoms on the left and right side should be together in either oxidation or reduction reactions. Non-redox atoms that are already balanced do not affect the result and should not be touched.

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

$$Na_2S_4O_6 + H_2O_2 \rightarrow Na_2SO_4 + H_2O + H_2SO_4$$

4 Combining the remaining redox reactions into two the partial reactions

The remaining reactions are combined into two partial reactions: one for oxidation and one for reduction. When reactions are being combined special care must be taken to ensure that the balance of non-redox atoms is not disrupted.

At this point there is a divergence between the ARS and classic oxidation number change methods. In the ARS method only the redox atoms in partial reactions are balanced, while in the classic method all atoms must be balanced. As described, the classic oxidation number change method will continue balancing each partial reaction individually by moving the following two steps to the end of procedure. Since aggregating redox couples ensures that all redox atoms in partial reactions are balanced, the next step of the ARS method is to equalize the transfer of electrons.

5 Equalizing the number of electrons transferred in the partial reactions

The number of electrons in the two partial reactions can be equalized by multiplying one or both partial reactions with appropriate coefficients. The balance of redox atoms will not change by multiplying the partial reactions with some constant.

6 Adding the partial reactions

The last step in aggregating redox species is to add the two partial reactions together to create an ARS equation. The electrons are cancelled. Sometimes, if there is a species with multiple redox atoms in which it is not possible to balance all redox atoms in Step 2 because of Rule 0, the partial reactions need to be combined and not summed.

$$NH_4NO_3 \rightarrow N_2O + H_2O$$

$$CO + Cl_2 \rightarrow COCl_2$$

In the ARS equation all redox and non-redox atoms that appear only in redox species must be balanced. If they are not, it is necessary to choose a new route to the ARS equation, i.e. to combine the redox couples in a different way. The stoichiometric coefficients of redox species in the balanced ARS equation are "frozen". The only way to change the coefficients of a specific redox species is to multiply the entire ARS equation with some constant.

$$NaBO_3 + KI + H_2SO_4 \rightarrow H_3BO_3 + I_2 + Na_2SO_4 + K_2SO_4$$

$$LiBr + NaBrO_3 + H_3PO_4 \rightarrow Li_3PO_4 + Na_3PO_4 + Br_2 + H_2O$$

The exceptions are stoichiometric coefficients of species that have redox atoms with the same oxidation numbers on both sides of the equation. Such species have a dual role - as a redox and non-redox species. Its coefficients can be changed independently of other species in the ARS equation.

$$Ag_2S + HNO_3 \rightarrow AgNO_3 + NO_2 + S + H_2O$$

$$KMnO_4 + H_2SO_4 + FeSO_3 \rightarrow K_2SO_4 + MnSO_4 + Fe_2(SO_4)_3 + H_2O$$

Freezing the stoichiometric coefficients of redox species in the ARS equation satisfies the first general condition of a balanced reaction: electron balance, i.e. the sum of changes of the oxidation number in a balanced equation is equal to zero.

3.2. Balance the Rest of the Atoms and Charges

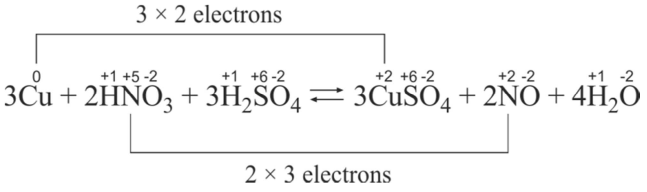
The next step is to add the non-redox species to the equation and balance all atoms except oxygen and hydrogen. This step, which in the ARS method is a trivial task, can become highly complicated in the classic oxidation number change method.

$$SO_2 + Na_2Cr_2O_7 + H_2SO_4 \rightarrow Na_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

$$U(SO_4)_2 + KMnO_4 + H_2O \rightarrow UO_2SO_4 + MnSO_4 + K_2SO_4 + H_2SO_4$$

Then, depending on the medium, the charges are balanced by adding H^+ or OH^- ions. After the oxygen atoms are balanced by adding H_2O, two general conditions of a balanced reaction are satisfied: atom balance and charge balance.

If the ARS method appears familiar to the reader, it is because anyone who has any experience with balancing redox reactions with the oxidation number change method has used some form of the ARS method. Skilled chemists can, after determining the oxidation number of redox atoms, equalize the transfer of electrons and balance redox species directly in the skeleton equation, thus reaching the ARS equation in one single, experienced leap (Figure 1). Easy steps for balancing redox equations directly in the skeleton equation are: 1) assign the oxidation numbers, 2) determine the transfer of electrons, 3) equalize the transfer of electrons, 4) determine the stoichiometric factors of the redox species, 5) balance the non-redox atoms without touching the redox species, 6) balance the charges with H^+ or OH^-, 7) balance the oxygen atoms with H_2O. Neither the ion-electron nor the algebraic methods offer any shortcuts for balancing redox equations.



$$3\overset{0}{\mathrm{Cu}} + 2\overset{+1}{\mathrm{H}}\overset{+5}{\mathrm{N}}\overset{-2}{\mathrm{O}}_3 + 3\overset{+1}{\mathrm{H}}_2\overset{+6}{\mathrm{S}}\overset{-2}{\mathrm{O}}_4 \rightleftarrows 3\overset{+2}{\mathrm{Cu}}\overset{+6}{\mathrm{S}}\overset{-2}{\mathrm{O}}_4 + 2\overset{+2}{\mathrm{N}}\overset{-2}{\mathrm{O}} + 4\overset{+1}{\mathrm{H}}_2\overset{-2}{\mathrm{O}}$$

Figure 1. How skilled chemists balance redox equations directly in the skeleton equation.

3.3. Steps for Balancing a Redox Reaction with the ARS Method

Based on the rules above, the following steps for balancing chemical reactions with the aggregate redox species method can be suggested:

Step 1: Write an unbalanced (skeleton) reaction

Step 2: Identify the redox couples in the reaction

a) Assign oxidation numbers to each atom

b) Identify and write out all redox couples

c) Remove unnecessary redox couples

Step 3: Aggregate redox species

a) Balance redox atoms that are not a part of a redox couple

b) Balance non-redox atoms that are present only in redox species

c) Combine the remaining redox reactions into two partial reactions

d) Equalize the number of electrons transferred in the partial reactions

e) Add or combine the partial reactions

Step 4: Balance the rest of the atoms and charges

a) Add non-redox species and balance all other atoms except hydrogen and oxygen

b) Balance the charges with H^+ or OH^- (depending on medium)

c) Balance the oxygen atoms with H_2O

Step 5: Simplify the reaction

Step 6: Check that the elements and charges are balanced.

3.4. Testing the Method

A computer program for balancing redox reactions has been developed based on the Aggregate Redox Species method [18]. The program follows the above-mentioned rules step by step, all the while showcasing the full procedure for balancing the reaction. Every step of the procedure is explained in detail.

The program has been tested on over 200 typical redox reactions and found to be very successful in almost all cases, regardless of whether the reaction has been written in molecular or ionic form. The reactions that the developed program cannot solve (or fails to solve correctly) are more a limitation of the program than the ARS method. For example:

$$CuSO_4 + KSCN + H_2SO_3 + H_2O \rightarrow CuCN + K_2SO_4 + H_2SO_4$$

The only way to obtain the ARS reaction from this reaction is to first combine the reduction reactions in order to balance both redox atoms in CuCN. The resulting reaction is then duplicated and combined with the first oxidation reaction in order to balance both redox atoms in KSCN.

4. Conclusions

The results demonstrate that with the knowledge of the nature of the reaction and the oxidation state of elements, as well as the application of the ARS method, it is possible to solve almost any redox reaction. By adopting the ARS method students will learn effective strategies for balancing redox equations as it offers a structured approach which can be systematically applied to all types of equations written in ionic or molecular form.

The suggested steps for obtain partial reactions are not specific to the ARS method alone. They can also be used to determine half reactions in the ion electron method and to obtain partial reactions in the classic oxidation number change method, thus reducing the number of unsolvable equations caused by the inability to separate equations into independent oxidation and reduction reactions.

Mastery over the ARS method gives students another valuable gift - a shortened procedure for balancing redox equations. Through a bit of practice the ARS method allows the majority of redox equations to be solved directly in the skeleton equation in only two steps: first the ARS equation is balanced (Step 3), and then all other atoms and charges are balanced (Step 4).

Despite being developed primarily as a method for balancing redox reactions, the ARS method is universally applicable and can be used for non-redox reactions as well.

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