Oxidation and Reduction: Too Many Definitions?

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In a fascinating recent article in this journal on fireworks and pyrochemistry (1), Steinhauser and Klapotke referred to the oxidizer as the reactant that “provides the oxygen” or “produces oxygen when decomposed”. As a biochemist and an introductory chemistry instructor, my operating definition of oxidant had always been “the compound that accepts electrons”. Since discussing this topic with Steinhauser and Klapotke, I have discovered that their definition is in fact fairly common.1 As Vitz (2) pointed out recently, the IUPAC Compendium of Chemical Terminology, the “Gold Book” (3) defines oxidation as a process wherein (I) an atom within a “molecular entity” loses electrons; (II) an atom within a “molecular entity” increases in oxidation state; or (III) an organic substrate either gains oxygen or loses hydrogen. Jensen, in his “Ask the Historian” column in this journal (4), recently pointed out that these three definitions actually arose in reverse chronological order: definition III first in the mid-19th century and definitions II and I in the 1920s. Vitz (2) and Lockwood (5) have both stressed that definition II, the increase in oxidation state, is the only one that is universal to all oxidations.

Definition I, loss of electrons, is the most common definition taught in undergraduate chemistry, and clearly this does indeed occur at the anode of a galvanic cell. However, as Vitz (2) and Lockwood (5) discuss, electrons are not always literally exchanged in redox reactions. For some redox reactions, especially those involving nitrogen, sulfur, halogens, or carbon (see definition III above), mechanisms can involve nucleophilic displacement or free radical intermediates, and electron transfer can be virtual, not literal. That is, oxidation states change, but this is a bookkeeping device and is not meant to imply that the transfer of real electrons necessarily takes place in the reaction mechanism (2, 5), as it would in a galvanic cell.

Two examples help to clarify the problem. Magnesium metal is readily oxidized by hypochlorous acid, either directly in acidic solution:

\[ \text{Mg}(s) + \text{HOCl}(aq) + \text{H}^+(aq) \rightarrow \text{Mg}^{2+}(aq) + \text{Cl}^-(aq) + \text{H}_2\text{O}(l) \]  

or at the anode of a galvanic cell:

anode : \( \text{Mg}(s) \rightarrow \text{Mg}^{2+}(aq) + 2e^- \)  

cathode : \( \text{HOCl}(aq) + \text{H}^+(aq) + 2e^- \rightarrow \text{Cl}^-(aq) + \text{H}_2\text{O}(l) \)  

In this reaction, magnesium is oxidized, losing two electrons, both in the literal mechanistic sense at the anode and also in the figurative bookkeeping sense as its oxidation state increases from 0 to +2.

However, the oxidation of nitrite by hypochlorous acid can occur only directly in solution and not in an uncatalyzed galvanic cell:

\[ \text{NO}_2^-(aq) + \text{HOCl}(aq) \rightarrow \text{NO}_3^-(aq) + \text{Cl}^-(aq) + \text{H}^+(aq) \]  

The reaction above occurs by a nucleophilic attack by the central N atom in nitrite on the O atom of hypochlorite (2, 6) forming the transition-state complex: \( [\cdot \text{O}+\cdot \text{N} \cdots \text{O}(\cdot \text{H}^+) \cdots \cdot \text{Cl}] \) (Scheme 1). From this adduct, Cl\(^{-}\) leaves by displacement, and the resulting product HNO\(_3\) deprotonates.

One can legitimately write oxidation and reduction half-reactions for this reaction (2):

anode : \( \text{NO}_2^- (aq) + \text{H}_2\text{O}(l) \rightarrow \text{NO}_3^- (aq) + 2\text{H}^+(aq) + 2e^- \)  

cathode : \( \text{HOCl}(aq) + \text{H}^+(aq) + 2e^- \rightarrow \text{Cl}^-(aq) + \text{H}_2\text{O}(l) \)  

These half-reactions show that the N atom in nitrite is oxidized from the +3 to the +5 oxidation state, whereas the Cl atom in hypochlorite is reduced from the +1 to the −1 oxidation state. However, in this particular reaction, the nitrite polyatomic anion must collide with a hypochlorite anion to foster nucleophilic displacement (Scheme 1); hence, nitrite cannot be oxidized at the anode of the uncatalyzed galvanic cell described in eq 2a. Furthermore, the electron pair is not transferred directly from the N in nitrite to the Cl in hypochlorite. Instead, as depicted in Scheme 1, the nitrite polyatomic anion enters an adduct with Cl\(^{-}\), with concomitant increase in N’s oxidation state by 2; also, the O−Cl bond in hypochlorite becomes, upon displacement of chloride, a lone pair on Cl\(^{-}\), with concomitant decrease in Cl\(^{-}\)’s oxidation state by 2. An electron pair is transferred from N to Cl through the bridging O atom in the transition state.

Others have noted that oxidation states are independent of formal charge, valence, or bonding (2, 3, 5). The nitrite oxidation above is a good example of this: When the nitrogen lone pair turns into an N−O bonding pair in nitrate, with concomitant increase in N’s oxidation state by 2; also, the O−Cl bond in hypochlorite becomes, upon displacement of chloride, a lone pair on Cl\(^{-}\), with concomitant decrease in Cl\(^{-}\)’s oxidation state by 2. In other words, in terms of oxidation state, both of the lone pair electrons on N

Scheme 1. Oxidation of Nitrite by Hypochlorous Acid

\[ \text{NO}_2^- + \text{HOCl} \rightarrow \text{NO}_3^- + \text{H}^+ + \text{Cl}^- \]
are assigned to the newly bonded more electronegative oxygen, so the N “loses” two electrons and its oxidation state goes up by two. Of course the nitrogen oxidation state of +5 in nitrate does not correspond to a formal charge of 5+(2,5). The electrons lost are “virtual”, and counted according to the formalism of oxidation state rules. Although nitrogen has five valence electrons, they are in shell number two, so nitrogen can only use them to make a maximum of four bonds (not five). Furthermore, even though nitrogen is more oxidized in nitrate than in nitrite (+5 vs +3 oxidation state), nitrate is the poorer oxidant, both kinetically (7) and thermodynamically ($E^\circ(\text{NO}_3^-/\text{NO}) = +0.96 \text{ V}$; $E(\text{NO}_2^-/\text{NO}) = +1.10 \text{ V}$). Thus, the +5 oxidation state of nitrogen in nitrite signifies neither formal charge, bonding ability, nor oxidizing power. Instead, oxidation state is a simple (and powerful!) formalism that allows chemists unambiguously to identify redox reactions and count the number of electrons transferred.

As implied by the IUPAC definitions of oxidation given above, there are three main types of oxidation: (i) loss of electrons to an oxidant, either via anodic electrode or by direct collision (cf. IUPAC definition I); (ii) loss of electrons as hydrogen (IUPAC definition III); or (iii) loss of electrons by gain of oxygen (IUPAC definition III). It is interesting to note that these can in turn be broken down into a number of different reaction subtypes.

Consider two examples of “loss of hydrogen”; (a) The dehydrogenation of methanol (CH$_4$OH) to formaldehyde (H$_2$C=O + H$_2$) features the heterolytic loss of a pair of electrons, as an H$_2$ leaving group, from the carbon. This methanol oxidation reaction actually conforms to all three of the IUPAC definitions! (b) On the other hand, the chlorination of methane (CH$_4$ + Cl$_2$) to chloromethane (CH$_3$Cl + HCl) occurs via a homolytic free radical mechanism, and real electrons are not actually transferred, just chlorine and hydrogen atoms; this is considered a redox reaction because H and Cl are assigned +1 and −1 oxidation states, due to their respective electronegativities.

Now consider two “gain of oxygen” examples: (a) The oxidation of carbon monoxide by NO$_3$,

$$\text{CO} + \text{NO}_3 \rightarrow \text{CO}_2 + \text{NO}_2$$

(3)

is known to occur by atom transfer (2), so here as well, real electrons are not transferred, just the oxygen atom; it is a redox reaction because the more electronegative O is assigned a 2− charge in its compounds. (b) Real electrons are transferred in the nitrile oxidation (eq 2), from the N in nitrile to the Cl in hypochlorite through the bridging O, which remains in the −2 oxidation state at all times (Scheme 1). In both of these cases, although an oxygen atom is “provided” by the oxidant and transferred to the reductant, the oxygen atom is not the ultimate electron acceptor. Vitz (2) and Lockwood (5) give a number of other examples of this type of oxidation in which a “virtual” pair of electrons is transferred from the reductant to the oxidant through a bridging atom (O, N, Cl, or I) in the transition state.

Summing up, although calculating oxidation states allows us to write out oxidation and reduction half-reactions, to balance redox equations, and to count the number of electrons transferred, it tells us nothing about the reaction mechanism (2,5). On the other hand, one thing that all redox reactions have in common is that oxidation states do change: Oxidants contain an atom whose oxidation state increases, whereas reductants contain an atom whose oxidation state decreases.

So where do we stand in terms of redox terminology? As students and faculty, we do love our anagrams: In LEO the lion says GER, loss of electrons is oxidation, gain of electrons is reduction; in OIL RIG, oxidation is loss of electrons, reduction is gain of electrons. This of course is IUPAC definition I, but as we have seen, oxidation does not always involve the loss of real electrons, and even when it does, the number lost must be calculated using oxidation states and not formal charges.

Furthermore, IUPAC definition III applies only to redox reactions in which an “organic substrate gain(s) oxygen or lose(s) hydrogen”. But note the ambiguity in definition III: What do we mean by “hydrogen” and “oxygen”? Loss of “hydrogen” as H$_2$ or H$^+$ is clearly oxidation, whereas loss of H$^+$ is clearly not. But what about loss of an H atom, H?: On the basis of the rules for assigning oxidation states, this depends on the electronegativity of the replacing atom. In halogenation reactions, the H atom is replaced by an electropositive halogen atom, for example, in

$$\text{NH}_3 + \text{F}_2 \rightarrow \text{NH}_2\text{F} + \text{HF}$$

(4)

the N− electron is assigned to F in the new N–F bond, so N is oxidized from oxidation state −3 to −1. This is another example of a redox reaction that involves atom transfer rather than electron transfer. However, in the preparation of boron nitride,

$$\text{NH}_3 + \text{B(OH)}_3 \rightarrow \text{B} = \text{N} + 3\text{H}_2\text{O}$$

(5)

the three hydrogens bonded to nitrogen are replaced with a boron, which is less electronegative than nitrogen; hence, the oxidation state of nitrogen remains at −3. This is essentially an acid−base reaction in which the ammonia nucleophile also serves as the acid, and hydroxide the base. The key point here is that for hydrogen atoms, gain or loss tells you nothing about whether the central atom is reduced or oxidized; this can only be done by comparing electronegativities and determining oxidation state changes.

The same ambiguity applies to characterizing oxidation as gain of “oxygen”. It has been pointed out$^2$ that what is really meant (but not specifically stated) in IUPAC definition III is gain of oxygen $\text{with no other accompanying change}$. Hence, in the Schiff’s base reaction

$$\text{CH}_2\text{O} + \text{NH}_3 \rightarrow \text{CH}_2\text{NH} + \text{H}_2\text{O}$$

(6)

the C=O carbon in formaldehyde loses an oxygen, but it gains a similarly electronegative nitrogen in the imine C=NH. Hence, this nuclophilic substitution reaction can also be thought of as an acid−base reaction in which the ammonia nucleophile is again the acid, donating two H$^+$ to the C=O oxygen base to make H$_2$O.

The bottom line is that IUPAC definition II of oxidation as the increase in oxidation state applies to all oxidations; therefore, this should be the primary definition of oxidation in introductory or general chemistry courses; it has the added advantage that it allows calculation of the number of electrons lost. If we focus the minds of first-year students on using oxidation states (rather than oxygen or hydrogen atoms) to follow electrons, this could simplify how students recognize redox reactions.

Note that I have focused this suggestion specifically on the first-year introductory or general chemistry course. The point has been made$^3$ that in other courses, there are easier ways of recognizing oxidation reactions without resorting to the calculation of oxidation states. For example, in pyrochemistry (1), the oxidant almost always transfers oxygen atoms to the reductant;
hence, the transfer of oxygen is a key hallmark of a combustion redox reaction, one that is easy for students to see. Qualitative recognition of a redox reaction is thus served by definition III, the gain of oxygen atoms; to quantitatively characterize the cell potential and free energy of these reactions, oxidation states must be determined.

Similarly, in organic chemistry, it is often much easier to identify oxidation by loss of hydrogen (i.e., H\(^-\) or H\(_2\)) or gain of oxygen, with no other accompanying change. For example, in the oxidation of benzyl alcohol \(\text{C}_7\text{H}_8\text{O}\) to benzaldehyde \(\text{C}_7\text{H}_6\text{O}\), it is much easier to recognize the loss of H\(_2\) than it is the increase in carbon oxidation state from \(-6/7\) to \(-4/7\). The same can be said for the gain of oxygen in the oxidation of benzaldehyde \(\text{C}_7\text{H}_6\text{O}\) to benzoic acid \(\text{C}_7\text{H}_6\text{O}_2\). Because organic chemists are rarely concerned with the cell potentials, free energy changes, or half-reactions involved in their redox reactions, the identification of oxidation state changes is generally less useful in this field.

In conclusion then, as one colleague has stated,\(^2\) “different definitions of oxidation can be appropriate in different contexts”. Certainly, loss of electrons or hydrogen or gain of oxygen are convenient in some cases; on the other hand, exceptions are numerous. Accordingly, for a beginning chemistry student, the very first thing to do in seeking to identify a redox reaction is to determine if any oxidation states change. If none do, then the reaction is not redox. If on the other hand one or more atoms are oxidized (increasing oxidation state), then others must be reduced. Identifying these changes of oxidation state subsequently allows the student to balance the redox equation. The oxidation state should therefore be the central pedagogic focus of discussions of redox reactions in introductory or general chemistry.

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Notes

1. For example, it is the first definition given in the Merriam—Webster Dictionary and also in Wikipedia.
2. Thanks to reviewer #1 for this clarification.
3. Again, thanks are due to reviewer #1 (organic chemistry) and also to Georg Steinhauser (pyrolysis reactions).

Literature Cited