ELECTRONS AND REDOX EQUATIONS

C. W. BENNETT
Western Illinois State Teachers College, Macomb, Illinois

We are told that electrons are real entities but of such nebulosity that they can best be characterized by a mathematical equation. Yet we grass-roots chemists glibly talk of electrons as if they were little hard particles with a definite volume, shape and smooth surface. In fact it seems to me that we use them about like one would a coinage of negative pennies for settling inter-atomic debts. With such usage a few errors have crept in which I should like to point out.

It is commonly taught and correctly so, I believe, that oxidation represents a loss of electrons while reduction represents a gain. This is obvious in the case of a piece of zinc metal used as the negative pole of voltaic cell:

$$Zn \longrightarrow Zn^{++} + 2e.$$

The zinc metal gains two points in valence and loses two electrons. While at the positive pole, let us assume that cupric ions are accepting electrons to form copper metal:

$$Cu^{++} + 2e \longrightarrow Cu.$$

(Of course, in this day and age of precise formulation we understand that all ions in solution are solvated and that $Zn(H_2O)_4{}^{++}$ and $Cu(H_2O)_4{}^{++}$ would more correctly express the cations involved.)

The ion-electron method of balancing redox equations has been widely accepted. We shall use this method to trace the migration of electrons during the oxidation of hydrochloric acid by $KMnO_4$. The unbalanced orthodox equation is:

$$KMnO_4 + HCl \longrightarrow KCl + MnCl_2 + Cl_2 + H_2O.$$

The ion-electron method recognizes that any permanganate and any soluble chloride in the presence of acid will react in a similar fashion. Therefore it is actually a reaction of the MnO_4 ion, the H^+ ion and the Cl^- ion. The K^+ ion is an innocent bystander and may be omitted from such an equation. The permanganate ion is obviously the oxidant and obviously forms manganous ions:

$$MnO_4^- \longrightarrow Mn^{++}.$$

The oxygen in the MnO_4^- must form H_2O which accounts for the need of acid or H^+. In the absence of acid, MnO_2 is formed, showing the importance of H^+ in the equation. (Of course H^+ is more correctly written H_3O^+ but H^+ is used for simplicity.) Now we are ready to continue with our balancing:

$$H^+ + MnO_4^- \longrightarrow Mn^{++} + H_2O$$

The four oxygens would yield $4H_2O$ which would call for $8H^+$:

$$5e + 8H^+ + MnO_4^- \longrightarrow Mn^{++} + 4H_2O$$

The reductant equation is much simpler:

$$2Cl^- \longrightarrow Cl_2 + 2e.$$

Here we have added two electrons to the right to make that side have two minus charges as the left already had.

Next, since electrons obey the law of conservation of matter we must have the same number of electrons leaving the reductant as are taken up by the oxidant. The lowest common multiple of 2 and 5 is 10. The oxidant equation is multiplied by 2 and the reductant by 5:

$$2\ (5e + 8H^+ + MnO_4^- \longrightarrow Mn^{++} + 4H_2O)$$

$$5\ (2Cl^- \longrightarrow Cl_2 + 2e)$$

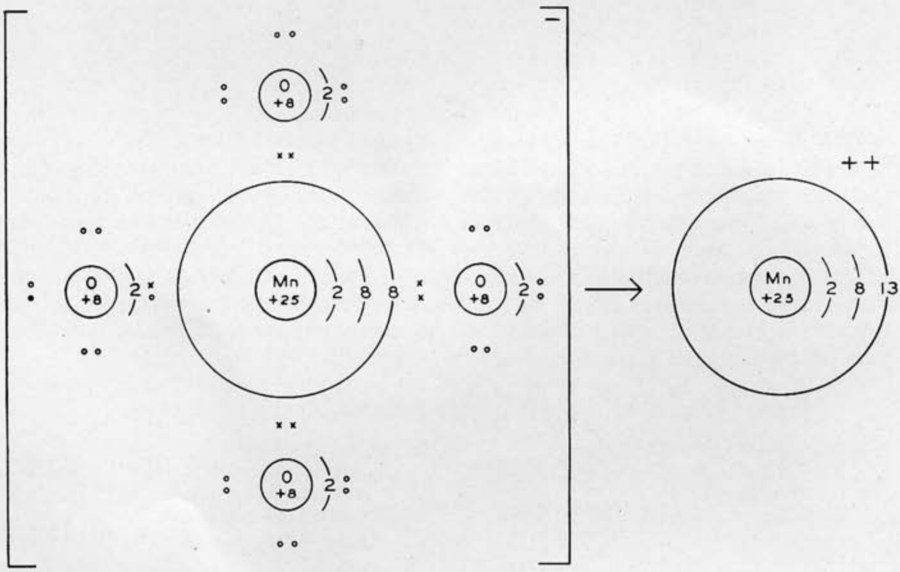
or

$$10e + 16H^+ + 2MnO_4^- \longrightarrow 2Mn^{++} + 8H_2O$$

$$10Cl^- \longrightarrow 5\ Cl_2 + 10e$$

$$16H^+ + 10Cl^- + 2MnO_4^- \longrightarrow 2Mn^{++} + 5Cl_2 + 8H_2O$$

When this same equation is balanced by the valence change method one finds that Mn loses 5 points of valence, going from +7 in $KMnO_4$ to +2 in $MnCl_2$ and that the 5 points loss is numerically equal to the number of electrons gained BY THE OXIDANT in the ion-electron method just shown. Also each Cl gains one point in valence. Now some teachers and some texts* argue that a loss in valence is a gain of electrons so that we can say if the Mn loses 5 points of valence it thereby gains 5 electrons. However our ion-electron oxidant equation shows that *the* MnO_4^- *ion in the presence of the* H^+ gains the 5 electrons and *not just the manganese atom.* Let us study the electronic structure of the two ions involved:



One can see that the Mn nucleus in the permanganate ion is surrounded by shells of 2, 8, and 8 electrons and is sharing 8 more with 4 oxygens making a total of 26 electrons while the manganous ion has shells 2, 8, and 13 electrons making a total of 23 (it having become deficient two electrons from a metallic manganense atom with 25 electrons and so has a charge of +2). It is therefore difficult to see how anyone can say that the Mn, itself, gains 5 electrons but it is easy to demonstrate that if each pair of H^+ ions removes an oxygen from the permanganate, 8 valence electrons will be required for each of the four H_2O molecules

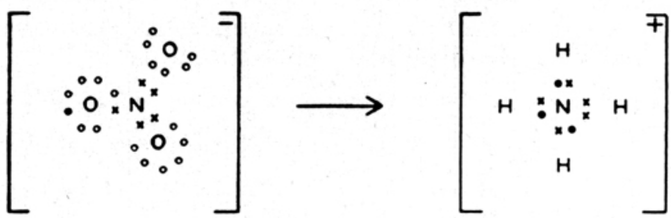
*See reference No. 4a for an example of this misconception.

formed as well as 2 each for the inner shell. With the original 26 electrons surrounding the Mn nucleus and the 6 valence electrons of each of the 4 oxygen (and the 2 inner shell electrons of the oxygens) we have 26 + 32 or 58 electrons supplied by the MnO_4^- but the $4H_2O$ required 10 each and the Mn^{++} ion 23 or a total of 63. Thus 5 electrons must be added from an outside source (reductant.) But the 5 electrons are used up by the reactants on the left working together and not by the manganese alone.

A simpler but just as interesting case is the reduction of nitrate ion in acid solution to ammonium ion:

$$8 + 10H^+ + NO_3^- \longrightarrow NH_4^+ + 3H_2O$$

The electronic configuration here can be limited to the valence electrons since no transition element is involved:



It will be seen that in each case the N atom is surrounded by 8 electrons. The ion-electron equation shows that 8 electrons are gained by the *10 H^+ and the NO_3^-* and the valence change method will show that 8 points in valence are lost by the nitrogen atom, which careless ones translate into a gain of 8 electrons *by the nitrogen*.

Therefore we should reject the method sometimes taught of balancing Redox equations which leads one to say "N loses 8 points in valence so it gains 8 electrons." One should not mix up valence-change, an 1880 concept, with a modern concept like electrons.

PERTINENT REFERENCES

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