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ELECTRONIC READJUSTMENTS IN OXIDATION-REDUCTION REACTIONS

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From the standpoint of the electron theory of matter, valence may be defined as follows: positive valence is the number of electrons in the outer valence orbit of an element; negative valence is the number of electrons necessary to fill the valence orbit to its maximum capacity, eight. In any chemical reaction involved in forming molecules, all the valence electrons of the element of positive valence are shared with the element of negative valence filling its valence shell to its maximum capacity of eight. Or, the octet theory of valence is here assumed to be adequate if entirely understood to explain all valence phenomena except the Werner supplemental valence. And ionization consists in the separation of a molecule so that the part of the molecule having positive valence contributes all its valence or shared electrons to the part of the molecule having negative valence. This action leaves the parts into which the molecule has divided electrically charged by the number of valence electrons contributed by the cation, and the number of valence electrons received by the anion. Hence the necessary operation of Faraday's law in electrolysis.

Having now affirmed the universality of the law of octets as related to valence it is now possible to explain the necessary readjustments in oxidation-reduction reactions.

The elements most involved in such reactions are the elements of the transition groups, those preceding or following these transition groups, and the elements of the (b) section of the periodic table having either a positive or a negative valence, depending upon the kind of elements associated with them in the molecule.

Let us now examine the transition elements and those adjacent them of group IV from Cr to Cu inclusive. The elements Fe, Co and Ni have regular low valences of two and high valences of three. The oxidation of Fe from two to three valence is accounted for thus: reduced structure 2-8-14-2, oxidized structure 2-8-13-3. The oxidized and reduced structure of Co and Ni are exactly analogous; as are also those of Ru, Rh, and Pd. Cu is in the group most closely associated with a positive valence of one due to its one valence electron. However, its more usual valence of two would be accounted for by its related symmetery in structure with Fe, Co and Ni. Cu in its reduced structure is 2-8-18-1 and in its oxidized structure is 2-8-17-2. Its more usual behavior is best accounted for by the oxidized structure but its position in the series demands that Cu be assigned its reduced structure which places it in group 1b. Cr has valences from two to six; the reduction from the six valence to the three valence would be accomplished by the transfer of three valence electrons to the orbit beneath the valence orbit making its structure 2-8-11-3; likewise Mn may be reduced from its seven valence to its two valence by the following readjustment 2-8-8-7 to 2-8-13-2.

This illustration might be lengthened without limit. Let us illustrate with an example:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

Fe-	Mn-	Fe-	Mn-
2-8-14-2	2-8-8-7	2-8-13-3	2-8-13-2
change 1	change 5		

Fe had one valence electron transferred from the next to outer shell to outer.

Mn has five valence electrons transferred from outer to next to outer shell.

The transfer from the outer to the inner equals that from an inner to an outer. Therefore these molecules must be taken in number proportional to their change in the valence orbit. Thus these equations are written as in the past but the change taking place leaves each atom having the same number of electrons in its outer shells as protons in the nucleus. A change of number of electrons in a radioactive element leaves the element with a marked change in its properties; an oxidation-reduction reaction changes principally only the valence. Therefore the shift of valence electrons is more in accord with the observed phenomena than a gain or loss of electrons.