

THE ROLE OF VALENCE AND ELECTRONS IN THE
TEACHING OF GENERAL CHEMISTRY.

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In the history of every science there comes from time to time some epochal discovery or some novel interpretation of phenomena that marks the beginning of a new era. The development of chemistry has been particularly marked by these epochal discoveries and unfoldings of new ideas, many of them, it is only fair to say, having had their birth in the sister science of physics.

Priestley discovers or, more accurately, rediscovers oxygen, and soon Lavoisier sweeps away the old phlogiston theory and sets the new science upon solid foundations. Dalton pierces the hazy dreams of ancient philosophers and visions for the chemical world a practical theory of atoms,—and again the infant science moves a step forward. Davy finds an effective tool in the newly discovered galvanic current, splits asunder the hitherto resistant alkalis, and opens the way for Berzelius's theory of dualism, an electrochemical theory that dominated the minds of chemists for more than a quarter of a century. Wöhler's synthesis of urea marked the beginning of another epoch and for another quarter of a century the open sesame in every chemical laboratory of Europe was synthetic chemistry. Kekulé's linking of atoms and the benzene ring led to the innumerable novelties of structural chemistry and maintained the chemist's enthusiasm at fever heat for some decades longer. Suddenly Arrhenius stepped into the limelight with his theory of ionization in salt solutions and from that time down to very recent years chemistry has fairly leaped forward under the magic power of ions. Radioactivity, cathode rays, and the electronic conception of atoms, discovered and fashioned for the most part in the workshop of the physicist, have been of incalculable value in extending the domains of chemistry in our own day.

It is the purpose of this paper to attempt to add a little impetus to the present tendency to interpret the reactions of general chemistry in the light of the newer ideas of atoms and electrons, coupled up with the older inadequate conceptions of valence, as we endeavor to introduce students to an increasingly popular and practical science.

For many years it has been quite the common custom to classify chemical reactions, more accurately chemical action, from a material standpoint under six heads: combination, decomposition, double decomposition, displacement, substitution, and internal rearrangement, the last two finding a prominent place in organic chemistry. Double decomposition reactions have been explained for some time on the basis of the law of mass action and ion product constant. We now have a

single viewpoint from which to interpret the other three classes of chemical action and we need no longer regard them as individual types. They are simply valence changes and a valence change merely involves the transfer of one or more electrons from one atom to another. This involves the conception of positive and negative valence and of course the idea of neutral valence, also designated as zero valence.

Four simple assumptions, which we may no longer regard as assumptions but as well-established facts, form the basis of these interpretations:

1. Each element in the uncombined state has a valence of zero.
2. Hydrogen in combination has a positive valence of one; that is to say, each hydrogen atom in entering into combination with some other atom has lost one electron.
3. Oxygen in combination has a negative valence of two, which means that in entering into combination with some other element each oxygen atom has gained two electrons. In peroxides, however, we must assume for oxygen a negative valence of one.
4. In every compound there is a neutrality of valence; in other words, an exact balance between the total positive and negative electrical forces in the molecule of the compound.

With the exception of double decomposition reactions, chemical action in general may now be interpreted as merely an oxidation-reduction process, oxidation taking place where an atom is losing electrons, reduction where an atom is receiving electrons. Obviously there cannot be one without the other.

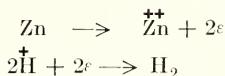
The modern theory of the atom and the further light thrown upon the Periodic Law by the derivation of Atomic Numbers give us a rational explanation of why the maximum change in the valence of any element should be eight. In some elements the tendency to lose electrons is greater than the tendency to acquire them; in others the tendency to acquire electrons is greater than the tendency to lose them; while in still others the tendency in either direction appears to be more nearly equalized.

Chlorine, of the seventh group of the periodic system, for example, shows a marked tendency to acquire one electron although under proper conditions it may lose one, three, five, or seven, the total range being eight. Sulphur, of the sixth group, may gain two electrons but on the other hand it may lose two, four, or six, the total range being eight. Nitrogen, of the fifth group, may receive three electrons or lose two, three, four, or five, the total range once more being eight. Carbon, of the fourth group, may gain four or lose two or four; again the range is eight. Boron, of the third group, may lose three but may not acquire any, unless possibly it be three in boron nitride. Beryllium, of the second group, may lose two but not receive any; the same is true of magnesium, cadmium, zinc, and others. Copper, of the first group, may lose one or two but acquire none, while gold may give up one or three but gain none. Lithium and the other alkali metals may lose only one and receive none. Note exceptions in metallic hydrides.

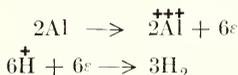
With this idea in mind, therefore, that chemical action is primarily

an electronic transfer, this transfer affecting only two elements in the interacting substances, or in the single substance if it is what is ordinarily called decomposition, let us examine several common reactions and note how they illustrate the principle that has been stated.

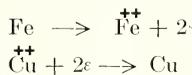
The typical reaction between an acid and a metal, zinc and sulphuric acid for example:



Or aluminium reacting with hydrochloric acid:

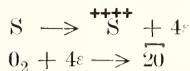


Or the displacing of a metal in a salt by another metal:



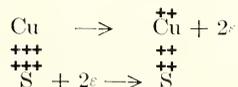
Here zinc, aluminium, and iron are oxidized while hydrogen and copper or, to speak more accurately, hydron and cupron are reduced.

Let us consider another example, the preparation of sulphur dioxide. We may readily prepare the gas by two methods; by the combustion of sulphur in air or oxygen, or by what is commonly called the reduction of sulphuric acid. In the first case we have sulphur and oxygen each with a valence of zero, the atoms of each element having their normal number of electrons. But at the proper temperature there is a rapid transfer of electrons from sulphur to oxygen, four from each atom of the former to two atoms of the latter, with the resultant formation of sulphur dioxide.

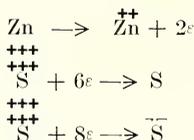


In sulphur dioxide the sulphur has a positive valence of four while the oxygen has a negative valence of two; the sulphur has been oxidized and the oxygen reduced.

In the preparation of the gas from sulphuric acid we have the opposite change so far as the sulphur is concerned. In the acid we have hexavalent sulphur, sulphur with a positive valence of six. This must be reduced to four before we can have sulphur dioxide. To make this reduction requires the presence of some element that will readily give up electrons but not with too great a facility or else the sulphur atom may be given six electrons and brought to free sulphur or even eight electrons and reduced to hydrogen sulphide. We select copper and bring the substances to the proper temperature:



If zinc be substituted for the copper, the greater tendency of this metal to lose electrons may reduce the sulphur to its normal electronic state or even transfer to its atoms an excess of two electrons:

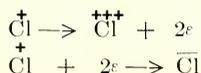


It is interesting to note that in some cases the same element may play a double rôle, some of the atoms giving electrons to or taking electrons from atoms of its own kind. An interesting illustration is afforded in the formation of the higher oxygen acids of the halogens by the process known as self-oxidation.

Even in the formation of the lowest oxygen acid of the series, hypochlorous acid for example, we have the phenomenon illustrated. As we all know, when chlorine is dissolved in water we have in solution not only molecules of chlorine but also molecules of each of the acids, hydrochloric and hypochlorous. In hydrochloric acid we find chlorine with a negative valence of one; it has gained one electron. In hypochlorous acid chlorine has a positive valence of one; the chlorine has lost one electron. In other words, in the reaction one atom of chlorine has given one electron to a second atom of chlorine, resulting in the formation of two distinct compounds of this element. When the element is run into a solution of a base, we have the corresponding salts of these acids. When the salts are heated, the valence of the halogen in some of the molecules of the oxygen acid falls as that in other molecules rises, thus yielding successively the salts of the higher acids. Potassium hypochlorite, for example, when heated yields the chlorate and at higher temperature the perchlorate. Assuming what seems fully warranted, the formation first of the chlorite, we have as ordinarily written:

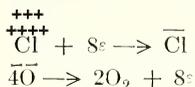


We start with a compound in which chlorine has a positive valence of one, each atom having one electron less than when it is in the uncombined state. On raising the temperature, the atom of chlorine in one molecule of the salt takes two electrons from the atom of chlorine in a second molecule and we have the formation of potassium chlorite with chlorine having a positive valence of three, and potassium chloride with this element having a negative valence of one:



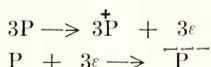
The same interesting phenomena are observed in the two other stages, the final result being positive heptavalent chlorine on the one hand and negative monovalent chlorine on the other. If the tempera-

ture is raised sufficiently, the heptavalent chlorine becomes negative monovalent chlorine with the escape of oxygen:

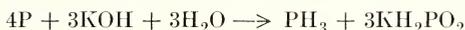


In bleaching powder, whether we accept the evidence in support of the contention that the material is a single substance and assign it the formula, CaOCl_2 , or assume that we have a mixture of hypochlorite and chloride, the conclusion is the same so far as the electronic changes in the chlorine are concerned; one atom of chlorine has given one electron to a second atom of chlorine. If we call the material calcium oxychloride and express it as CaOCl_2 , we must recognize chlorine as playing a double rôle in the molecule; one atom has a positive valence of one, the other a negative valence of one. In the upheaval arising from the treatment of this material with an acid accompanied by the liberation of chlorine, we have the reverse electronic changes; uncombined chlorine with a valence of zero is obtained.

Another interesting example of self-oxidation is presented in the formation of phosphine and potassium hypophosphite from the action of potassium hydroxide and water on phosphorus. Starting with phosphorus with a valence of zero, each atom with its normal number of electrons, we obtain two phosphorus compounds: in one the phosphorus atom has a negative valence of three, it has received three electrons; in the other compound the phosphorus atom has a positive valence of one, it has lost one electron. It is quite evident, therefore, that three phosphorus atoms have each lost one electron to a fourth atom:

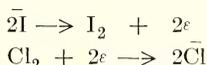


The reaction is commonly written:



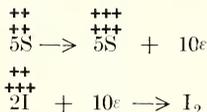
The preparation of iodine from either an iodide or an iodate, the sodium salts for example, furnishes another good illustration of the truth of the statement that with the exception of double decomposition reactions our reactions in general chemistry are essentially electronic changes, commonly known as valence changes, and may be brought under the general classification of oxidation-reduction reactions.

In sodium iodide we have iodine with a negative valence of one, the iodine atom has one electron more than its normal quota. To secure the elementary iodine we must introduce an element that readily receives electrons, chlorine for example. Chlorine run into a solution of sodium iodide liberates iodine with the formation of sodium chloride:



On the other hand, in sodium iodate we have positive pentavalent iodine, iodine atoms that have lost five electrons each from their normal

supply. To set the element free there must be added some compound containing an element that will readily give up electrons. Sulphurous acid suggests itself. Here we have positive tetravalent sulphur, sulphur atoms with a deficiency of four electrons each. But sulphur can lose comparatively readily a total of six electrons per atom, hence the sulphur atom in sulphurous acid has two electrons yet to spare. It is evident that we must have five atoms of this tetravalent sulphur for every two atoms of the pentavalent iodine:

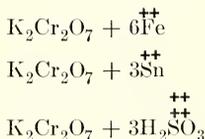


The reaction is commonly written:



A compound containing any element that may lose or gain more than some specific number of electrons, in other words change its valence, may be designated an oxidizing or reducing agent according to whether this element gains or loses electrons in the course of the reaction. Potassium dichromate, potassium permanganate, and nitric acid are common oxidizing agents. The capacity of these compounds to "oxidize" some other substance lies in the chromium, the manganese, and the nitrogen just as the reducing action of sulphurous acid, hydrogen sulphide, hydriodic acid, and stannous chloride lies in the sulphur, the iodine, and the tin.

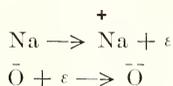
In potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, for example, we have positive hexavalent chromium, chromium atoms with six less electrons than are found in the uncombined element. It readily takes up three, giving trivalent chromium, provided there is an element to supply these electrons. Such an element is found in iron, tin, sulphur, etc., in a ferrous salt, a stannous salt, sulphurous acid, or a sulphite. Bivalent iron loses an electron and passes into trivalent iron—a ferrous to a ferric salt. Bivalent tin loses two electrons, passing into quadrivalent tin—a stannous into a stannic salt. Quadrivalent sulphur loses two electrons and passes into hexavalent sulphur—sulphurous into sulphuric acid, a sulphite into a sulphate. It is a matter, therefore, of balancing the chromium against the iron, the tin, or the sulphur. Each two atoms of the chromium must oxidize six atoms of iron, or three of tin, or three of sulphur:



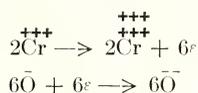
An interesting question arises just here: What would be the order of transition if the dichromate were added to a solution of ferrous sulphite or stannous sulphite? Would the electrons be supplied to the chromium simultaneously by the iron and the sulphur, or first by one and then by the other? If the latter is the rule, which would dis-

appear first, ferrous ion or sulphite ion? In other words, would the dichromate convert ferrous sulphite first into ferric sulphite and this then into ferric sulphate, or would ferrous sulphate be first formed and this then converted into ferric sulphate? Or would the two elements, iron and sulphur, act simultaneously, giving rise *pari passu* to ferric sulphate?

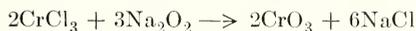
The reverse process, the loss of electrons by chromium when in contact with sodium peroxide, raises an interesting question. As is well known, if sodium peroxide is added to a solution of a chromic salt, chromic chloride for example, sodium chromate is formed; trivalent chromium is converted into hexavalent chromium. In other words, each atom of chromium has lost three electrons. What element in the sodium peroxide has received them? Surely not the sodium; then it must be the oxygen. As was said in a former paragraph, in peroxides oxygen must be regarded as having a negative valence of only one; each atom has received from some other element one electron only. So far as its chemical activity is concerned, sodium peroxide might be assigned the formula, NaO; the oxygen has received one electron from the sodium. To become the constituent of an ordinary oxide it must receive an additional electron. Under suitable conditions it may receive this from metallic sodium:



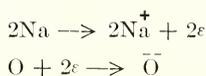
In the reaction of the peroxide with potassium dichromate the oxygen receives the electrons from chromium:



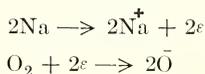
In the ordinary way the reaction is written:



It will be seen that sodium peroxide is of more than ordinary interest. When exposed to oxygen at ordinary temperature sodium is slowly converted into the monoxide, each oxygen atom taking one electron from each of two sodium atoms:

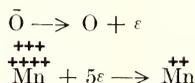


When the metal is brought in contact with the gas at a much higher temperature, each atom of the oxygen receives only one electron:



The attempt to explain the composition of sodium peroxide by a structural formula representing oxygen with a constant valence of two is inadequate.

Let us consider another interesting reaction, that between potassium permanganate and hydrogen peroxide in acid solution. Here positive septavalent manganese is reduced to bivalent manganese—a manganese salt—hydrogen peroxide is converted into water, and at the same time oxygen is evolved. We have the interesting phenomenon of two so-called oxidizing agents each reducing the other. In looking at the reaction from the standpoint of electronic transfer we are consistent in stating that reduction takes place in the manganese—the permanganate acts as the oxidizing agent. But how about the hydrogen peroxide? In this case there is oxidation in the oxygen—the hydrogen peroxide in this reaction is a reducing agent. The manganese atom has received five electrons. In hydrogen peroxide each atom of oxygen has one electron more than its normal quota and this it gives to the manganese. It is readily seen that this will require one molecule of the permanganate for each of the peroxide if the latter is written HO, or two if the peroxide is written H_2O_2 :



Is there any inconsistency in regarding hydrogen peroxide an oxidizing agent in its reaction with a chromic salt and a reducing agent in its reaction with potassium permanganate? There is none, any more than there is in designating zinc electronegative towards magnesium and electropositive towards copper.

To regard oxygen in peroxides as having a negative valence of one on the ground that its atom has received one electron from an atom of another kind, just as we ascribe to it a negative valence of two in ordinary oxides on the ground that its atom has received two electrons from one or more atoms of another element, is consistent with the view that elements in the uncombined state have a valence of zero on the ground that their atoms have neither given electrons to nor received electrons from atoms of another element, whatever forces may have come into play in the union of atoms of the same kind to form elementary molecules.

No one has yet offered a generally acceptable explanation of the fact that uncombined hydrogen and chlorine are found in the form of molecules of two atoms each, combinations, if we choose to call them such, of great stability, and yet when a mixture of equal volumes of the two gases is subjected to an electric spark or exposed to direct sunlight, hydrogen leaves hydrogen, chlorine leaves chlorine, and hydrogen and chlorine combine with tremendous vigor.

While persistent efforts have been made to demonstrate the existence of two distinct kinds of chlorine atoms, it cannot be said that these efforts have met with success. Should such a demonstration be made, we should be induced to believe that there must be two kinds of hydrogen atoms of opposite electrical properties, two kinds of oxygen atoms, two of nitrogen, and so on throughout the entire range of those elements whose properties are manifested by molecules of two atoms each.

And what shall we say of those elements whose molecules consist of four atoms or six or perhaps even more according to conditions? It is not only in elements but also in compounds that we find this inexplicable capacity of particles of the same kind to become associated in what is evidently some other manner than mere physical juxtaposition. The application of X-rays has radically changed our former conception of crystalline structure, as is beautifully illustrated in such an apparently simple substance as sodium chloride. We think of this salt as a combination of one atom of sodium with one of chlorine, the molecule of two atoms being formed in some way by the transfer of one electron from the sodium atom to the chlorine atom, and we speak of the atom of sodium as now having a positive valence of one and the atom of chlorine as having a negative valence of one. When, however, we undertake to account for the currently accepted structure of crystalline sodium chloride, we find our efforts so far unsuccessful.

Let us conclude, therefore, that until we find more light on the nature of the forces operating between atoms of the same element and the relation between these inter-atomic forces and the electrons involved, we might do well to content ourselves with the interpretation of chemical action on the basis of the apparent transfer of electrons from one atom to another of different kind. The simple principles laid down in a former paragraph will serve as a guide and the application of these principles should give our students a clearer conception of the significance of chemical action than the meticulous care with which we are in the habit of presenting reactions in the form of balanced equations. We recognize the importance of chemical equations as ordinarily expressed but we are convinced that the deeper meaning of chemical action will become more apparent if attention is focused upon the valence changes and these are interpreted in terms of electronic transfer.

