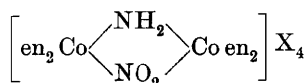


XIV.—*Polar and Non-polar Valency.*

By RAJENDRALAL DE.

IN a paper recently published, Briggs (T., 1917, 111, 267) asks: "What is the valency of cobalt in chloropentammine cobaltic chloride, $(\text{Co}_{\text{Cl}}^{\text{5NH}_3})\text{Cl}_2$?" This question has suggested the view set forth in the present paper.

From the study of the optical properties of the tetraethylene-diammine- μ -aminonitrodicobaltic salts,



Werner (*Ber.*, 1913, 46, 3674) concludes that there is no essential difference between the principal and auxiliary valency bonds. Evidently this conclusion may be applicable only to the bonds within the complex radicle (that is, bonds employed in uniting radicles co-ordinated with the cobalt atom). The bonds outside the complex radicle are employed in combining radicles which exist as ions. Their nature is thus entirely different from that of the former ones. A distinction ought therefore to be maintained between the bonds outside the complex radicle and those within it.

We can find an explanation of the valency outside the complex radicle, which is polar in type, from Sir J. J. Thomson's theory of valency. To understand the mechanism of it, let us picture the structure of an atom derived by Thomson. According to him, the atom consists of corpuscles moving in a sphere of uniform positive electrification, and its valency depends on the ease with which corpuscles can escape from, or be received by, the atom. Difficulties, however, arise in explaining the valencies within the complex radicle in the above manner, they being non-polar in type.

During the disintegration of radioactive substances, the negative charges of electricity are carried by β -rays and the positive charges by α -rays. The β -rays consist of expelled particles—not atoms of matter, but free atoms of negative electricity or "electrons." An α -particle, however, consists of two atomic charges of positive electricity combined with a helium atom—a substance inert in the chemical sense. It may therefore be assumed that the positive electricity can have an attraction for the mass itself, even if there be no charge of negative electricity on it. Thomson ("Rays of Positive Electricity and their Application to Chemical Analysis," p. 40) also observes that molecules with positive charges are quite

common, whilst those with negative charges of electricity are very rare. This property which the positive electricity possesses affords an explanation of the phenomena of the valencies inside the complex radicle of a complex salt.

In order to explain the phenomena of the above valencies, we shall consider Rutherford's view as regards the constitution of an atom. According to him, a positive nucleus is situated in the centre, whilst electrons move around it in various concentric rings. We shall conceive this nucleus as having a binding capacity for the radicles which are co-ordinated with a metallic atom in the case of complex salts. It is significant that no positive radicles, such as ammonium, tetramethylammonium, etc., which can exist as cations, have been observed to combine with a metallic atom forming a complex radicle. Negative radicles, such as Cl (chloro-), NO_2 (nitro-), etc., however, do form a complex radicle with a metallic atom. These negative radicles also carry negative charges of electricity when they exist as anions.

Let us form a picture of the mechanism as conceived above. We have the positive nucleus of the metallic atom (capable of forming a complex radicle) in the centre, and around it there are various concentric rings along which the electrons move. We may assume that adjacent to the outermost ring of electrons constituting the atomic structure there are the neutral molecules, for example, NH_3 , H_2O , etc., or the negative radicles, for example, Cl, NO_2 , etc., or both these neutral and negative radicles, held by the influence of the positive nucleus of the metallic atom concerned.

Accordingly, in the case of tetraethylenediammine- μ -aminonitrodicobaltic salts, radicles within the complex radicle may be supposed to be attached to the positive nuclei of its cobalt atoms, and thereby, the valencies within the complex radicle being taken to be all alike, the two cobalt atoms become linked to the two groups in the middle, namely, NO_2 and NH_2 , in a similar way.

The conditions favourable to the formation of complex salts may now be stated. The number of concentric rings in the structure of an atom grows large as the atomic weight increases, and, thereby, the structure also becomes more complex. According to Rutherford, however (Soddy, "The Chemistry of the Radio-elements," 1914, Part II, p. 39), the mass of an atom is concentrated in an exceedingly small central nucleus. Hence, with the decrease in the atomic volume, only the rings will decrease in size, and the outermost ring will approach nearer to the nucleus. We have already supposed the radicles, co-ordinated with a metallic atom, to be placed adjacent to its outermost ring of electrons and also bound by its nucleus. Evidently, the attraction of the nucleus

for the mass of the radicles would increase where there are possibilities of their being placed near to the nucleus, that is to say, where the atomic volume is small. In fact, metals that are capable of forming complex salts, as, for example, chromium, iron, manganese, cobalt, nickel, copper, ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, etc., are situated on the troughs of Lothar Meyer's atomic volume curve. Here it may also be mentioned that Ephraim (*Ber.*, 1912, **45**, 1322; 1913, **46**, 3103; 1914, **47**, 1828; *Zeitsch. physikal. Chem.*, 1913, **81**, 513, 539; **83**, 196), from his study of the strength of the auxiliary valencies of various metals, has drawn the conclusion that the strength of the auxiliary valencies falls with the increase of the atomic volume of the metal concerned. We thus find a further support for the above assumption.

It will be observed that the metals which form complex salts are mostly found both in the "ous" and the "ic" state of their ionic condition, as, for instance, we have Cr^{++} (chromous), Cr^{+++} (chromic), Co^{++} (cobaltous), Co^{+++} (cobaltic), etc. It may also possibly be that the "ous" condition of the metallic ion is more favourable to the formation of a complex radicle. During the reduction of a metallic ion from the "ic" to the "ous" state, there is an alteration in the electric charge of its rings, and the probability is that this alteration is confined to the outermost ring (Soddy, *ibid.*). Evidently, in the "ous" condition of the metallic atom, there is a less number of electrons in its outermost ring. Keeping in view the structure of an atom, it would be natural to expect that, ordinarily, the outer rings of electrons would offer themselves as a shield against the attraction of the positive nucleus for the radicles which may be co-ordinated with a metallic atom. The case is, however, different in its "ous" state, for, there being produced a weakness in the shield, due to a less number of electrons in the ring, the attraction of the nucleus will obtain an opportunity of manifesting itself by forming a complex radicle. It is known that chromic chloride has to be reduced to the chromous state for the preparation of chrom-ammonia salts (Christensen, *J. pr. Chem.*, 1881, [ii], **23**, 54). Similarly, in the preparation of cobalt-ammonia and platinum-ammonia compounds (Gerhardt, *Annalen*, 1850, **76**, 307), the starting materials are the "ous" salts of the metal concerned.

Lastly, it is found that the formation of a complex anion is a more general phenomenon than the formation of a complex cation; for example, there are compounds of the type $[\text{M}(\text{C}_2\text{O}_4)_3]\text{R}_3$, where M may be Vd, Cr, Mn, Fe, Co, Rh, Al, As, Sb, or Bi (Werner, "New Ideas on Inorganic Chemistry," p. 115, ed. 1911). It

seems possible that there is a connexion between the increase of attraction of a metallic atom for these negative radicles (co-ordinated with it) and the cause which occasions the presence of negative charges of electricity on them when they exist as anions.

We have already supposed that the valencies outside the complex radicle are caused by electrons of the outermost ring constituting the atomic structure. These electrons may therefore be termed *valence-electrons*. Obviously, the number of the valence-electrons of a metallic atom corresponds with that of its maximum valencies outside the complex radicle. In the case of the complex metal-ammonia compounds, this maximum valency is exhibited when all the radicles co-ordinated with the metallic atom are NH_3 or H_2O , and when a negative radicle is introduced into the above complex radicle the number of valencies outside the complex one is decreased (that is, the number of valence-electrons appears to become less). We may call those valence-electrons which seem to have vanished in this way *bound valence-electrons*, and those which have caused the appearance of valencies outside the complex radicle *free valence-electrons*. We may also notice that the maximum number of free valence-electrons (that is, electrons which can escape from a metallic atom, forming a complex cation) is the same as the maximum number of electrons which can be received by the atom in addition to its own valence-electrons, when it forms a part of a complex anion. For illustrating this point, we may cite the compounds: (i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, where the complex radicle is a trivalent cation, (ii) $\text{K}_3[\text{Co}(\text{NO}_2)_6]$, where the complex radicle is a trivalent anion, and (iii) $[(\text{NH}_3)_3\text{Co}(\text{NO}_2)_3]$, a non-electrolyte. In the third compound, no electron has escaped or been received by the metallic atom, but all the three valence-electrons, along with the three univalent negative radicles, have been bound by its positive nucleus. Regarding the question at hand, namely, that of the number of valencies in chloropentamminecobaltic chloride, it may be said that here the cobalt atom contains three valence-electrons—one is bound along with the univalent chloro-radicle co-ordinated with cobalt, and the remaining two have caused the appearance of valencies of polar type outside the complex radicle. Besides these three valence-electrons, the metallic atom possesses six valency bonds of non-polar type caused by the attraction of its positive nucleus.

The structure of the complex radicle as conceived above explains also the phenomenon of the directional nature of the auxiliary valency bonds, indicated by the stereoisomeric compounds of complex metal-ammonia salts, for the nucleus, being centrally placed in the structure of an atom (metal), has an advantage in exerting

its attraction along different directions, which the electrons moving in their orbits cannot possibly have. The assumption of the nuclear attraction, however, need not be confined to these cases of complex derivatives alone. The phenomena of non-polar valency may, in general, be considered to have arisen from this attraction.

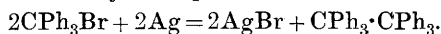
The kind of valency exhibited in organic compounds is a typical non-polar one. If we compare the valencies of the carbon atom with those of metallic ones, employed in co-ordinating radicles with them, we find that both these two kinds are non-polar and directional in nature (shown by the stereoisomerides of the carbon compounds and those of complex metal-ammonia derivatives). This similarity in their character may indicate the probability of their being brought about by the same cause, namely, by the attraction of the positive nucleus of an atom. The assumption receives further support from the small atomic volume of carbon (as shown in Lothar Meyer's atomic volume curve). It has already been supposed that the attraction of the nucleus for radicles should increase as the atomic volume decreases, and this should tend to a maximum when the volume becomes very small.

Nernst is of opinion that the forces by which the carbon atoms in a crystal of diamond are held together are identical with the attraction of its four valencies called into play in the formation of organic compounds, that is to say, "the forces of cohesion are identical in nature with the forces of chemical affinity" ("The Theory of Solid State," p. 6). The cohesive forces are found to increase with the decrease of the atomic volume of elements. They may therefore arise from the very same nuclear attraction of atoms mentioned before. An inspection of the behaviour of carbon and its compounds might help in giving some light in this direction.

In the process of the synthesis of diamond, an immense pressure is brought about by the contraction of iron in which carbon has been dissolved. Evidently, for effecting union (that is, saturation of the valencies of carbon atoms), the atoms are required to be brought very near to one another. It may also be noted that in the case of the carbides of metals, the carbides Li_2C_2 , CaC_2 , etc., where the metals are of large atomic volumes, are decomposed by water, whilst the carbides Cr_3C_2 , Cr_4C , etc., where the metals in combination are placed on a trough in the atomic volume curve (that is, are of small atomic volumes), form stable compounds. Taking into consideration that the mass of an atom is concentrated in an exceedingly small central nucleus in the structure, it seems possible that carbon atoms would exert only a very feeble attraction when placed a little apart or when combined with metals of large atomic volumes. The various rings of electrons around the

nucleus, which have already been compared to shields, may also occasion a further hindrance in their union.

Further light will be thrown on the above if the following view is taken of the constitution of triphenylmethyl. It is found that in solution triphenylmethyl has a molecular weight corresponding with the formula $(\text{CPh}_3)_2$ (Gomberg and Cone, *Ber.*, 1904, **37**, 2033). This is what may be expected from its mode of preparation :



As the compound is very reactive, even at a low temperature, it has been assumed that it is rather a derivative of tervalent carbon. Exposure to the air, even for a very short time, is sufficient to transform it into a peroxide of the constitution $\text{CPh}_3 \cdot \text{O} \cdot \text{O} \cdot \text{CPh}_3$.

We may, however, represent the constitution of triphenylmethyl as $\text{CPh}_3 \dots \text{CPh}_3$. The weak attraction between the two carbon atoms is shown by the dotted line. The feebleness of their attraction may be due to the inability of the carbon atoms to approach very near to each other on account of the hindrance caused by the large phenyl groups attached to them. The hindrance referred to may be of the type similar to that of steric hindrance (Wegscheider, *Monatsh.*, 1895, **16**, 148), and their reactivity may be due to the possibility of their drawing small atoms very near to them. Viewing the constitution given for the oxidation product, it is seen that by the intervening of two oxygen atoms the large radicles have been placed apart, and by the union of the two carbon atoms with two oxygen atoms (small indeed compared with the triphenylmethyl radicle) a stable compound has been formed.

According to our assumption, radicles bound by the positive nucleus should not show any polar character. Although the valency of carbon is ordinarily non-polar, there are a few organic compounds where it seems to function as polar, as, for instance, in hydrogen cyanide and in organic acids, where we have the radicles $\cdot \text{C} \vdots \text{N}$ or $\cdot \text{N} \vdots \text{C}$ and $\text{R} \cdot \text{CO}_2 \cdot$ respectively, besides hydrion. There are also sodium acetylide, $\text{CH} \vdots \text{CNa}$, silver acetylide, C_2Ag_2 , and cuprous acetylide, C_2Cu_2 , where the hydrogen atoms of acetylene have been displaced by metallic atoms. In order to explain this anomaly, we may consider Sir J. J. Thomson's observation that "when the discharge tube contains such gases as CH_4 , CO_2 , CO , where there are no bonds between two carbon atoms in the molecule, we find negatively charged carbon atoms, but no negatively charged molecules. When, however, we use compounds such as acetylene, $\text{HC} \vdots \text{CH}$, ethylene, $\text{H}_2\text{C} \vdots \text{CH}_2$, or ethane, $\text{H}_3\text{C} \cdot \text{CH}_3$, where, according to the usual interpretation of the constitution of these substances, there are bonds between carbon atoms in the molecule, then we find molecules as well as atoms of carbon with the negative

charge" (*loc. cit.*). He is also of the opinion that on account of the unsaturated valencies of the carbon atoms in the molecule, it has been possible for the negative corpuscles to become attached to them (*ibid.*). A similar explanation may be applicable in the above cases. In them, more than one bond of carbon has been occupied with the other element combined with it, and a corpuscle received from an adjacent hydrogen atom may become attached to the remaining part of the compound, thus giving rise to their polar character.

Compounds such as LiH , H_2O , NH_3 , etc., $\text{Ni}(\text{CO})_4$, $\text{Co}_2(\text{CO})_8$, etc., and also groups of atoms forming radicles, such as CO_3 , NO_3 , SO_4 , etc., being formed by non-polar valencies, may have their origin in the nuclear attraction. We may also ascribe the forces by which atoms and molecules in a crystal are held together to the same attraction. These forces have been supposed to be caused by residual valency, which has also been assumed to bring about the solution of a substance in a solvent (Baly, "Spectroscopy," 1912, p. 487). The phenomena of solution should necessarily be considered to be due to the same attraction of the nucleus. In these cases, the size of the molecules may account for the feeble character of their binding. Lastly, all catalytic substances which are employed in gaseous reactions may be supposed to owe their catalytic action to the positive nuclei of the atoms in them. Indeed, the study of the dissociation of the hydrogen molecule into atoms, and other similar studies, have convinced Langmuir (*J. Amer. Chem. Soc.*, 1916, **38**, 2221) that prior to the dissociation, absorption of hydrogen by tungsten wire, due to its secondary valency, does take place. We see, therefore, that the nuclear attraction plays a great part in all chemical phenomena.

Regarding the number of valencies of the non-polar type for different elements, it may be noted that carbon (placed in the first trough of Lothar Meyer's atomic volume curve) has four valencies, whilst other elements (placed in subsequent troughs of the curve) generally have six. In the case of the complex platinum-ammonium salts, however, the derivatives of the platinous salts, for example, $[(\text{NH}_3)_4\text{Pt}]\text{Cl}_2$, tetra-amminoplatinous chloride, show the number of auxiliary (non-polar) valencies to be four, whilst those of the platonic salts, for example, $[(\text{NH}_3)_6\text{Pt}]\text{Cl}_4$, hexa-amminoplatinic chloride, the number is six. The increase of two non-polar valencies in the latter case has been attended with an increase of two polar ones. Also the directions of these valencies, in the former case, lie in a plane, whilst in the latter case there are two additional directions lying in the same line perpendicular to the above plane. Whether and how the electrons constituting

the atomic structure influence the number and directions of the non-polar valencies of different elements awaits further study.

My best thanks are due to Prof. P. C. Rây for his kind help and encouragement.

PRESIDENCY COLLEGE, CALCUTTA.

ISLAMIA COLLEGE, PESHAWAR, INDIA.

[*Received, October 2nd, 1917.*]
