The Modern Theory of Valency.

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NEARLY 100 years ago, in 1852, it was stated for the first time, by E. Frankland, that atoms have a definite combining power, which determines the formulas of compounds. Then in 1858 Archibald S. Couper introduced the idea of the valency bond and drew the first structural formulas, and August Kekulé showed that carbon is quadrivalent. This simple valency-bond theory permitted great progress to be made in structural organic chemistry, but structural inorganic chemistry remained largely undeveloped until the present century. With the discovery of the electron and the elucidation of the electronic structure of atoms, it became possible for Gilbert Newton Lewis in 1916 to identify the covalent bond with a pair of electrons shared by two atoms and counting as part of the outer shell of each, and thus to lay the basis for the development of the modern theory of valency, to which Sidgwick, Robinson, and many other chemists have contributed.

The modern theory of valency is not simple—it is not possible to assign in an unambiguous way definite valencies to the various atoms in a molecule or crystal. It is instead necessary to dissociate the concept of valency into several new concepts—ionic valency, covalency, metallic valency, oxidation number—that are capable of more precise treatment; and even these more precise concepts in general involve an approximation, the complete description of the bonds between the atoms in a molecule or crystal being given only by a detailed discussion of its electronic structure. Nevertheless, these concepts, of ionic valency, covalency, etc., have been found to be so useful as to justify our considering them as constituting the modern theory of valency.

Ionic Valency.

It is customary to describe a crystal of cæsium fluoride as a regular arrangement of ions Cs^+ and F^-, held together in a stable equilibrium between the Coulomb forces of electrostatic attraction and the characteristic repulsive forces of closed shells of electrons. The loss of an electron by an atom of cæsium and its gain by an atom of fluorine may be said to be due to the striving of the atoms to achieve the stable electronic structure of the neighbouring noble gases, xenon and neon, respectively. The crystal barium oxide may be similarly described as an arrangement of ions Ba^{++} and O^{--}, with the same noble-gas structures. These considerations lead to the assignment of the ionic valencies $+ 1$, $+ 2$, $+ 3$ to elements of the first, second, and third, and $- 1$, $- 2$, $- 3$ to elements of the seventh, sixth, and fifth periods of the periodic table. In addition, there are ions, existing in aqueous solution, which do not correspond to noble-gas structures, such as the ferrous ion and the ferric ion. The existence of these ions is usually attributed to the relative ease of removing two or three of the outer electrons of the atoms of the transition elements.

This concept of ionic valency, useful as it is, must be considered only as an approximation to the truth. In a gaseous molecule CsF the electronic structure is not so well described by a wave function corresponding to a cæsium cation and a fluoride anion held together by electrostatic attraction as by a wave function describing a hybrid of this structure and a covalent structure, in which one pair of electrons is shared in the normal way between a cæsium atom and a fluorine atom. The difference in electronegativity, 3·3, of cæsium and fluorine permits the amount of covalent character of the cæsium–fluorine bond in this molecule to be estimated as 9%. It is only to this degree of approximation, then, that the bond in the cæsium fluoride molecule can be described as an ionic bond. In the cæsium fluoride crystal each cæsium atom is surrounded octahedrally by six fluorine atoms. If each of these bonds had 9% covalent character, the total covalency of cæsium and of fluorine would be 0·54, and the crystal could be described as involving, for each atom, a single bond, about 50% covalent and 50% ionic, resonating among the six positions connecting the atom with its six ligates.

This description would assign to the cæsium atom in the cæsium fluoride crystal a resultant charge $+ \frac{1}{2}$, and to the fluorine atom a charge $- \frac{1}{2}$. It has seemed to me likely that in general all of the atoms in the complexes that constitute stable chemical substances have resultant electrical charges smaller than those shown by these most electropositive and electronegative atoms in their compounds with one another, and I have accordingly formulated the *postulate of the essential electrical neutrality of atoms*: namely, that the electronic structure of substances is such as to cause each atom to have essentially zero resultant electrical charge, the amount of leeway being not greater than about $\pm \frac{1}{2}$, and these resultant charges are possessed mainly by the most electropositive and electronegative atoms, and are distributed in such a way as to correspond to electrostatic stability.

According to this postulate the description of the barium oxide crystal as consisting of an arrangement of ions Ba^{++} and O^{--} would be a poorer approximation to reality than its description as a regular arrangement of atoms Ba and O, with each atom forming two covalent bonds, which resonate among the positions to the six surrounding atoms. These bonds have enough ionic character to give a small positive charge to each barium atom and a small negative charge to each oxygen atom.

I doubt whether the ferrous ion and ferric ion, and similar ions of the transition elements, exist in chemical substances. I think instead that the atoms of iron in all ferrous and ferric compounds form covalent bonds in such a way as to remain essentially neutral. The postulate of neutrality of all atoms permits one to understand why the transition elements tend to form hydrated ions that carry two or three positive charges, rather than a smaller or larger number, and thus accounts for the observed bivalency and tervalency of these elements.* Let us consider a hexahydrated ion $M(OH_2)_6{}^{v+}$. The transition metals have electronegativity values lying between 1·5 and 2·0, corresponding to bonds with oxygen having between 37% and 57% of covalent character. The sizes of these atoms are such as to permit them to co-ordinate six water molecules about them, and the six bonds with the oxygen atoms of the water molecules would accordingly transfer a negative charge of between 2·2 and 3·4 units to the metal atom. This would neutralise the positive charge of the metal atom if two or three electrons were to be removed from it. For example, a ferric ion Fe^{+++} could have its charge exactly neutralised by forming bonds with 50% covalent character with the oxygen atoms of six water molecules co-ordinated about it. The charge of $+ \frac{1}{2}$ would not, moreover, remain on the oxygen atoms of these water molecules, but would be transferred to the hydrogen atoms, since each O–H bond has enough ionic character (32%, as indicated by its electric dipole moment) to transfer $+ \frac{1}{4}$ charge to itself. Thus the total positive charge of the complex ion $Fe(OH_2)_6{}^{+++}$ is distributed over the twelve hydrogen atoms on its periphery, this distribution being that which is favoured by the electrostatic forces. It is seen from this example that the bivalency and tervalency shown by the transition elements is not the result of the ease of removal of two or three electrons from the atoms, but is rather a consequence of the electronegativity of these elements relative to the non-metallic elements, together with the tendency of atoms to remain electrically neutral.

Covalency.

A covalent bond between two atoms requires two electrons and two orbitals, one for each atom.† The factors determining the properties of the covalent bonds formed by an atom are primarily the number and nature of the orbitals (hybridised bond orbitals) available to the atom, and the number of electrons that it can use in bond formation without losing its electrical neutrality. The opportunities for stabilisation through resonance of covalent bonds among alternative positions are also important.

For elements adjacent to the noble gases the principal orbitals used in bond formation are those formed by hybridisation of the *s* and *p* orbitals. For the transition elements there are nine stable orbitals to be taken into consideration, which in general are hybrids of five *d* orbitals, one *s* orbital, and three *p* orbitals. An especially important set of six bond orbitals, directed toward the corners of a regular octahedron, are the d^2sp^3 orbitals, which are involved in most of the Werner octahedral complexes formed by the transition elements.

I feel that it is necessary to clarify the interpretation of the magnetic criterion for bond character.‡ It has been customary to describe the results of the application of this criterion by saying that the bonds in a complex are either essentially covalent or essentially ionic. For example, the bonds in the cobaltic hexammoniate complex, $Co(NH_3)_6{}^{+++}$, are said to be shown to be essentially covalent by the diamagnetism of the substance, and the bonds in the hexahydrated cobaltic ion, $Co(OH_2)_6{}^{+++}$, are said to be shown to be essentially ionic by the possession by this complex of a magnetic moment of about 5·3 Bohr magnetons. The diamagnetism of the first substance does in fact show that the six outer electrons of the cobalt atom not involved in the formation of single bonds with ammonia are forced in pairs into three of the 3*d* orbitals, showing that the remaining two of the 3*d* orbitals are used in bond formation.

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* See Pauling, Victor Henri Memorial Volume.

† Heitler and London, *Z. Physik*, 1927, **44**, 455.

‡ Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367.

With the sp^3 orbitals, these two orbitals permit the formation of six d^2sp^3 octahedral hybrid orbitals, which would permit the formation of a normal covalent bond between cobalt and each of the six nitrogen atoms. However, the six bonds that are formed by a cobalt atom with the nitrogen atoms have only about 50% covalent character, the amount required to neutralise the charge of a cobaltic ion. This amount of covalent character could be achieved with the use of only three orbitals, resonating among the six positions, and accordingly it is not necessary to have use of the two 3*d* orbitals in order to form six bonds with 50% covalent character. With the other complex, the hexahydrated cobaltic ion, the six outer electrons of the cobalt atom occupy all five of the 3*d* orbitals, leaving the four sp^3 hybrid orbitals for bond formation. By resonating among the six positions, these four orbitals could permit the formation of six bonds with as much as $\frac{2}{3}$ covalent character, and hence could provide the amount, 50%, required to make the central atom electrically neutral.

It now seems to me that there are two ways in which the bonds in the first complex differ from those in the second, and two mechanisms for providing the extra energy required to force the six outer electrons of the cobalt atom from five 3*d* orbitals into three 3*d* orbitals, with the accompanying decrease in stability indicated by Hund's rule of maximum multiplicity for electrons in a sub-shell of oribitals. In the first place, the d^2sp^3 orbitals have a larger bond strength than the sp^3 orbitals, 3 instead of 2, and the bonds that they form should accordingly be 50% stronger. Secondly, a greater amount of resonance stabilisation through ionic–covalent resonance is to be expected for six bonds if an orbital is at hand for each of them, permitting the resonance to be unsynchronised, than if there are only four orbitals available for the six bonds, requiring some synchronisation of the covalent phases of the resonating bonds. We conclude accordingly that the magnetic criterion distinguishes, not between essentially covalent bonds and essentially ionic bonds, but between strong covalent bonds, using good hybrid bond orbitals and with the possibility of unsynchronised ionic–covalent resonance, and weak covalent bonds, using poor bond orbitals, and with the necessity for synchronisation of the covalent phases of the bonds. In a complex of the first sort the stability of the complex is due in larger part to the bonds themselves and in smaller part to the atomic electrons, and in a complex of the second sort the situation is reversed.

It is interesting to note that as many as all nine of the d^5sp^3 hybrid bond orbitals may be involved in bond formation in complexes formed by the transition elements.* In the ferrocyanide ion, $Fe(CN)_6^{----}$, the distance between the iron atom and the carbon atoms shows that the bonds have a large amount of double-bond character. This could be achieved by using the nine outer orbitals of the iron atom and the appropriate electrons in the formation of three double bonds and three single bonds with the six surrounding carbon atoms. If these bonds were all normal covalent bonds the iron atom would have a resultant charge -1; but carbon is slightly more electronegative than iron, which permits this charge to be drained off into the carbon atoms, and from them to the nitrogen atoms, in such a way that the entire charge 4– of the ion is distributed over the six nitrogen atoms. The complex is thus stabilised not only through the formation of these covalent bonds, in a way compatible with the postulate of electrical neutrality of the atoms, but also by the resonance energy of the single and double bonds among the alternative positions.

The interesting fact that the ferrocyanide ion is less easily oxidised to the ferricyanide ion than is the hydrated ferrous ion to the hydrated ferric ion can now be explained. The ferricyanide ion, with one odd electron occupying one of the nine orbitals of the iron atom, contains only two double bonds between iron and carbon, resonating with four single bonds. However, there is a smaller amount of resonance energy associated with the resonance of two double bonds among six positions than of three double bonds among six positions (there being, respectively, 15 and 20 ways of arranging the bonds), and accordingly this ion is not stabilised so greatly by resonance as is the ferrocyanide ion. The same argument explains the stability of the ions $Mn(CN)_6^{-----}$ and $Co(CN)_6^{---}$, which are similar in electronic structure to the ferrocyanide ion.

The stability of sexivalent chromium, in the chromate ion and related ions, can also be understood. The chromic complexes, involving tervalent chromium, make use of d^2sp^3 bond orbitals, the three remaining outer electrons of the chromium atom being in three of the 3*d* orbitals, with parallel spins. The resonance energy of these three atomic electrons in a quartet state helps to stabilise the chromic compounds. However, if all of the nine outer orbitals of the chromium atom were available for bond formation, stable compounds might also be expected

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* Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., Second Edition, 1940, p. 255.

to be formed. In the chromate ion, CrO_4^{--}, each of the oxygen atoms might use one of its σ orbitals and two of its π orbitals (relative to the axis connecting it with the chromium atom) for the formation of covalent bonds with that atom, the outer σ orbital not being suitable to bond formation, and being occupied by an unshared pair. The total of twelve bonds formed by the chromium atom (four triple bonds with the four oxygen atoms) would, with 50% covalent character per bond, lead to zero charge for the chromium atom, placing the charge $-\frac{1}{2}$ on each oxygen atom. The resonance of the bonds between covalent and ionic aspects (that is, between single, double, and triple bonds with oxygen) could not take place in a completely unsynchronised way, because chromium has only nine orbitals available; but the availability of as many as nine orbitals would lead to a large amount of resonance stabilisation.

The complex might be best described by saying that each oxygen atom could form a double bond with the chromium atom with the use of either one of its two π orbitals and the accompanying pair of electrons, extra stability being achieved through the resonance between the two kinds of double bonds.

Metallic Valency.

In most substances the phenomenon of quantum mechanical resonance of valency bonds among alternative positions is important for the stability and physical and chemical properties of the substances, but not directly for the valency of the elements. Thus the quadrivalency of carbon is not affected by the Kekulé resonance in benzene or the conjugation resonance in the polyenes, which instead affect principally the distribution of the four covalencies of each carbon atom among the bonds to its neighbours. The hydrocarbon free radicals constitute an exceptional case, in which the stabilising effect of the resonance of the odd electron among various carbon atoms is sufficiently great to cause one covalency—not, however, rigorously associated with one carbon atom—to become ineffective.

In recent years it has become clear that the structure of metals and alloys may be described in terms of covalent bonds that resonate among the alternative interatomic positions in the metals, and that this resonance is of greater importance for metals than for substances of any other class, including the aromatic hydrocarbons. Moreover, the phenomenon of metallic resonance of the valency bonds must be given explicit consideration in the discussion of metallic valency: it is necessary in deducing the metallic valency from the number of available electrons and bond orbitals to assign to one orbital a special rôle in the metallic resonance.

A few years ago, while examining the consequences of the concept that in a metal, in which each atom is surrounded by a large number of neighbours, the valency bonds that it is permitted to form by its numbers of outer electrons and bond orbitals resonate among the positions connecting it with its ligates, I concluded from the examination of the magnetic properties and mechanical properties of the transition elements that the nine outer orbitals may be divided into three classes: *viz.*, a class of stable bond orbitals, consisting of 5·78 orbitals per atom; a class of stable atomic orbitals, essentially *d* in character, consisting of 2·44 orbitals per atom; and the remaining 0·78 orbital per atom, with no apparent use, which was then designated as the unstable orbital.* It has now become evident that the characteristic nature of metals is determined by the unsynchronised resonance of individual valency bonds in the metal, and that the existence of this resonance depends upon the possession by each atom in the metal, or by a large number of the atoms, of an extra orbital, in addition to those normally occupied by unshared electrons or bonding electrons. The number 0·78 may be interpreted as showing that about three quarters of the metal atoms in the structures to which this number applies possess this extra orbital, the *metallic orbital*.

The significance of the metallic orbital to metallic valency may be illustrated by the example of the element tin. Tin has fourteen electrons outside of its completed krypton shell. These fourteen electrons might be introduced into the nine outer orbitals by placing pairs of electrons in five of the orbitals (presumably largely *d* and *s* in character, in order that the atomic energy might be minimised by the introduction of two electrons in each of these more stable 4*d* and 5*s* orbitals, rather than the less stable 5*p* orbitals), leaving the four remaining electrons to occupy four bond orbitals. This quadrivalent tin atom could then form covalent bonds, which might resonate among alternative positions in the crystal, but only by a process of synchronised resonance, similar to that between the Kekulé structures in benzene. The amount of resonance energy that could be achieved by this synchronous resonance might not be great enough to overcome the repulsive energy between non-bonded atoms, and thus to permit the increase in the co-ordination number of each tin atom above the covalency four. This is, in fact, true—

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* Pauling, *Physical Rev.*, 1938, **54**, 899; *J. Amer. Chem. Soc.*, 1947, **69**, 542.

quadrivalent tin forms the essentially non-metallic crystalline modification of the element called grey tin, in which each tin atom is bonded by single covalent bonds to four atoms that surround it tetrahedrally, in the same way that the carbon atom expresses its quadrivalency in diamond. On the other hand, if the fourteen outer electrons of the tin atom are introduced into eight of the nine orbitals, by placing six pairs in six orbitals (essentially hybrids of the three $4d$ orbitals and the single $5s$ orbital) and the two remaining electrons in two orbitals, the resulting bivalent tin can form a crystal in which each atom has co-ordination number larger than the covalence 2; in particular, it can have co-ordination number 6, which is observed in the metallic form of tin, white tin. The bonds present in this metallic tin do not need to resonate among the various positions synchronously, because the presence of an additional orbital, the metallic orbital, permits a tin atom to assume the covalency 3, by accepting an additional electron from a neighbouring tin atom, which would itself be reduced to covalency 1. This metallic resonance thus leads to the presence in the white tin crystal of neutral bicovalent tin atoms, tercovalent tin atoms with a negative electrical charge, and unicovalent tin atoms with a positive electrical charge. The amount of stabilisation by this resonance and the extra atomic energy resulting from changing one electron from a p orbital to the more stable s orbital are great enough to give to the crystal essentially the same stability as that of grey tin, in which each atom forms a larger number of covalent bonds. Approximate calculations of the resonance energy indicate that the energy of the system is minimised when the metallic crystal contains about 50% neutral atoms, 25% negatively charged atoms, and 25% positively charged atoms. The electrical conductivity of metals may be described as resulting from the motion of these negative and positive charges through the crystal.

In this way the conclusion is reached that the metallic valency of the transition metals is not the number of unpaired electrons obtained by distributing the outer electrons among the nine stable outer orbitals (valency 4 for germanium, 5 for gallium, 6 for zinc, 7 for copper, and 8 for nickel), but is, rather, a number 2 less than this, obtained by distributing the electrons among eight orbitals, and leaving the ninth for use as the metallic orbital (valency 2 for germanium, 3 for gallium, 4 for zinc, 5 for copper, and 6 for nickel). Thus metallic zinc in the elementary state seems to be quadrivalent; each zinc atom uses three of its covalencies in forming half-bonds with six ligates, and the remaining single covalency in forming one-sixth bonds with six somewhat more distant ligates.

Variability in metallic valency is also made possible by the resonance of atoms among two or more valence states. In white tin the element has valency approximately 2·5, corresponding to a resonance state between bicovalent tin, with a metallic orbital, and quadricovalent tin, without a metallic orbital, in the ratio 3 to 1; and copper seems similarly in the elementary state to have metallic valency 5·5.

The close relation between metallic valency and the valency operative in ordinary compounds between metals and non-metallic elements may be illustrated by chromium. This element occurs in two metallic forms, in which its valency is shown by the observed interatomic distances to be, respectively, 6 and 3. These two forms of the metal are accordingly analogous to the chromate ion and other ordinary compounds of sexivalent chromium, on the one hand, and, on the other, to the hexahydrated chromic ion and other chromic compounds. The stability of the two metallic forms may also be attributed to the same effects, described above, as for ordinary compounds of sexivalent chromium and tervalent chromium: namely, for sexivalent chromium the stabilising bond energy and resonance energy result from use of all six electrons and all available orbitals in forming bonds, and for tervalent chromium, with a decreased amount of bond energy and resonance energy, the extra atomic stability results from the presence of three unpaired electrons with parallel spin in stable atomic orbitals.

Oxidation Number.

One important use of the concept of valency is in the discussion of oxidation–reduction reactions. The assignment of positive and negative valencies to the elements in their various compounds and the consideration that in the processes usually classified as oxidation–reduction reactions electrons are transferred from the atoms of one element to those of another, causing an increase and decrease, respectively, in their positive valencies, have been found to be a useful part of chemical theory. With the development of a sound understanding of the electronic structure of molecules it has been recognised that this transfer of electrons to or from a single atom in a complex is not complete, and that the positive and negative valencies customarily used in the discussion of these reactions may be assigned in an arbitrary manner.

The special nature of these valencies has been indicated by designating them by the name oxidation number, and their values, agreeing for the elements in most substances with the values used by chemists of past generations, may be taken to be given by rules such as the following : *

1. The oxidation number of a monatomic ion in an essentially ionic substance is equal to its electrical charge.
2. The oxidation number of atoms in an elementary substance is zero.
3. In a covalent compound of known structure, the oxidation number of each atom is the charge remaining on the atom when each shared electron pair is assigned completely to the more electronegative of the two atoms sharing it. A pair shared by two atoms of the same element is split between them.
4. The oxidation number of an element in a compound of uncertain structure may be calculated from a reasonable assignment of oxidation numbers to the other elements in the compound.

Thus in the hexahydrated ferric ion hydrogen and oxygen are assigned their normal oxidation numbers + 1 and — 2, respectively, and the total charge of the complex ion, + 3, is assigned to the iron atom as its oxidation number. The same oxidation number would result from assigning the bonding electron pairs with hydrogen and iron to the oxygen atom, which is more electronegative than either hydrogen or iron. The fact that the electrical charge of the hexahydrated ferric ion is distributed among the twelve hydrogen atoms rather than being resident on the iron atom emphasises the artificiality of this assignment of oxidation numbers; but the fact that it is the iron atom which undergoes a significant change in electronic structure (the replacement of an unshared and unpaired electron by an unshared electron pair) when the hexahydrated ferric ion is reduced to the hexahydrated ferrous ion, the approximation to electrical neutrality being achieved by small changes in the amounts of partial ionic character of the bonds from iron to oxygen and from oxygen to hydrogen, validates the selection of iron as the element that undergoes the change in valency (oxidation number) during this process.

The rules that are given above permit the reasonable assignment of oxidation numbers to the elements in most substances, but occasionally are found to be insufficient or ambiguous. Thus in our description of the electronic structure of the ferrocyanide ion it has been said that the iron atom forms three single bonds and three double bonds with the surrounding carbon atoms, all of its electrons outside of the completed argon shell being used in bonding. Carbon is more electronegative than iron, and the application of Rule 3 would lead to the assignment of oxidation number + 8 to iron in the ferrocyanide ion. This is, however, unreasonable; the more reasonable oxidation number + 2 results from assigning to the iron atom two of the four electrons involved in each of the double bonds with carbon, and to the carbon atom two of the electrons involved in each double bond and each single bond. This procedure might be justified by showing that the carbon atom is more electronegative than iron with respect to the electrons used in the σ bonds, and less electronegative with respect to the electrons used in the π half of the double bonds.

Now that the general concept of valency has been divided into several concepts capable of more precise formulation we may ask whether the word valency, without qualification, need ever be used. I think that it may be used as a synonym for one of the more precise concepts when its meaning is clear from the context. Thus in the classification of the compounds of iron we may include the ferrocyanides among the compounds of bivalent iron. We might say that in the ferrocyanide ion the iron atom is sexiligant (has co-ordination number 6), is enneacovalent, and has oxidation number + 2. In the compound FeSi each silicon atom uses its four valencies in forming a single bond with one iron atom, three two-thirds bonds with iron atoms, and three one-third bonds with iron atoms, and each iron atom forms similar bonds with seven silicon atoms and in addition forms six one-third bonds with iron atoms. Thus iron in this compound is sexicovalent, and may be assigned oxidation number + 4, if silicon is assumed to be more electronegative than iron—actually the elements are essentially equal in electronegativity, and the assignment of oxidation numbers + 4 and — 4 to silicon may be less reasonable than that of oxidation number 0 for each element.

The Future of the Theory of Valency.

The theory of valency is equivalent to the theory of structural chemistry. This theory has now passed through the first stage of its modern development, that of the formal assignment of structures to chemical substances, and is entering upon its second stage, the development of a system permitting the prediction of the approximate thermodynamic stabilities corresponding

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* See Pauling, " General Chemistry ", W. H. Freeman and Co., San Francisco, Calif., 1947, Chap. 10.

to alternative structures. I believe that, despite the complexity of the problem, it will become possible to make reliable (but not precise) predictions of the free energy of substances, even before they have been synthesised, and that in this way the theory of valency will come to have far greater value than at present. A start has already been made on this programme—the discussion of the stabilising influence of the resonance corresponding to partial ionic character of single covalent bonds and of resonance of valence bonds among alternative positions in a molecule or crystal has aided in the systematisation of inorganic chemistry and of organic chemistry. The postulate of the electrical neutrality of atoms, discussed above, has provided us with a general explanation of the tendency of the transition elements to assume the valencies 2, 3, and 6. Professor Ingold has pointed out to me that this postulate also explains why it is that the cations stable in solution are in general complexes in which the outer layers of atoms consist of hydrogen atoms attached to electronegative atoms, so that the partial ionic character of the bonds leads to the production of a resultant positive charge on the peripheral hydrogen atoms, the charge of the cation thus being distributed in an electrostatically favourable manner. This explains the stability of the complexes with water and ammonia, as compared with complexes with dimethyl ether, trimethylamine, and phosphine. In a similar way the outermost atoms in the anionic complexes tend to be oxygen atoms, or atoms of another strongly electronegative element. The use of structural arguments to explain the relative stabilities of substances has also been illustrated in the discussion of the relative ease of oxidation of the ferrocyanide ion and the hexahydrated ferrous ion.

The progress that has been made during the last few decades has been the result of the development of the theory of quantum mechanics, and of the application of experimental methods of determining the structure of molecules and crystals, especially the methods of *X*-ray diffraction by crystals and of the diffraction of electrons by gas molecules. Much valuable information has been provided by the techniques of molecular spectroscopy, and by the measurement of electric and magnetic dipole moments. We may be assured that the continued application of these techniques will provide us with much more knowledge, and that in addition other methods of experimental investigation will be found. Perhaps microwave spectroscopy and the more complex electrical and magnetic phenomena (Kerr effect, magnetic birefringence, etc.) will be found to be very useful—and we may hope that powerful methods of investigation that are not yet known will be discovered. If scientific progress continues, the next generation may have a theory of valency that is sufficiently precise and powerful to permit chemistry to be classed along with physics as an exact science.