1913. "Studies of the Electrical Conductance of Nonaqueous Solutions," Shaw, *J. Phys. Chem.*, **17**, 162.

1913. "The Dielectric Constants of Dissolved Salts," Walden, THIS JOURNAL, **35**, 1649.

1914. "Conductance and Viscosity of Electrolytic Solutions," Kraus, *Ibid.*, **36**, 35.

1914. "Einige Lösungsmittel mit kleinen Dielektrizitätskonstanten," Sachanov and Prscheborowsky, *Z. Elektrochem.*, **20**, 39.

1914. "Verbindung des gelösten Körpers und des Lösungsmittels in der Lösung." Dhar, *Z. Elektrochem.*, **20**, 57.

Ionic Velocities.

1888. "Ueberführungszahlen und Leitvermögen einiger Silbersalze," Loeb and Nernst, *Z. physik. Chem.*, **2**, 948.

1894. "Der Einfluss der Lösungsmittel auf die Beweglichkeit der Ionen," Campetti, *Nuovo Cimento*, [3] **35**, 225.

1901. "A New Apparatus for Determining the Relative Velocity of Ions; with Some Results for Silver Ions," Mather, *Am. Chem. J.*, **26**, 473.

1902. "On the Relative Velocities of the Ions in Solutions of Silver Nitrate in Pyridine and Acetonitrile," Schlundt, *J. Phys. Chem.*, **6**, 159.

1904. "Determination of the Relative Velocities of Ions of Silver Nitrate in Mixtures of Alcohol and Water," Jones and Bassett, *Am. Chem. J.*, **32**, 409.

1904. "Über die Verbindung der Lösungsmittel mit den Ionen," Morgan und Kanolt, *Z. physik. Chem.*, **48**, 365.

1906. "The Compounds of a Solvent with the Ions," Morgan and Kanolt, *J. Chem. Soc.*, **28**, 572.

1906. "The Relative Migration Velocities of the Ions of Silver Nitrate in Water, Methyl Alcohol, Ethyl Alcohol, and Acetone, together with the Conductivity of Such Solutions," Jones and Rouiller, *Am. Chem. J.*, **36**, 427.

1912. "Calculation of Ionic Velocities of Silver Nitrate in Acetone Solutions," Roshdestwensky and Lewis, *J. Chem. Soc.*, **101**, 2097.

Molecular Weight.

1897. "Molekulargewichtsbestimmungen in Pyridin," Werner und Schmujlow, *Z. anorg. Chem.*, **15**, 18.

1902. "The Molecular Weights of Certain Salts in Acetone," H. C. Jones, *Am. Chem. J.*, **27**, 16.

1902. "Elektrolyse einiger anorganischen Salze in organischen Lösungsmitteln," Speransky und Goldberg, *Z. physik. Chem.*, **39**, 369.

1905. "Verhalten von Silbersalzen in Pyridin," Schroeder, *Z. anorg. Chem.*, **44**, 20.

1908. "Equilibrium in the System Silver Nitrate and Pyridine," Kahlenberg and Brewer, *J. Phys. Chem.*, **12**, 283.

A THEORY OF VALENCY AND MOLECULAR STRUCTURE.

BY WILLIAM C. ARSEM.

Received May 28, 1914.

Introduction. Historical. Outline of Theory: (*a*) Structure of Molecules; (*b*) Multiple Valency; (*c*) Valency Relations in the Periodic System. Applications of the Theory: (*a*) Mechanism of Reactions; (*b*) Tautomerism; (*c*) Conduction in Metals; (*d*) Association; (*e*) Dissociation and Conduction in Electrolytes; (*f*) Dissociation and Conduction in Gases; (*g*) The Charge and Apparent Mass of an Electron.

Introduction.

The purpose of this paper is to advance a theory of molecular structure and valency and to attempt to explain certain phenomena by means of it. The main features of the theory were conceived about ten years ago, and have been in process of development and extension since that time. Recently, however, some papers have appeared which contain ideas somewhat similar to my own. Among these was a paper by Sir William Ramsay,[1] in which he advanced the view that an electron may serve as a bond between the atoms in a compound, and that the electron behaves like an atom of an element. On this basis he gave explanations of certain chemical and electrochemical phenomena.

Practically the same idea has been used by P. Achalme,[2] to explain the formation of neutral molecules at the electrodes during electrolysis, and to show the mechanism of one type of gaseous ionization.

I have, therefore, ventured to present my views at this time with a feeling that they are in harmony with the present trend of scientific speculation.

Any theory of the nature of valency, or of the forces which hold atoms together in a molecule, should explain a number of facts, such as are here briefly summarized:

1. The combination of a "positive element" and a "negative element," to produce a stable compound.
2. The union of two atoms of a "positive" element, such as hydrogen, with each other, or the combination of two atoms of a "negative element," such as chlorine, with each other.
3. The formation of double salts and salts with water of crystallization.
4. The existence of monatomic molecules.
5. The absence of chemical affinity in the gases of the helium group.
6. Ionization and conduction in gases.
7. The mechanism of chemical reactions.
8. The phenomena of electrolysis and dissociation.

Valency is ordinarily assumed to be a property of free atoms; that is, we say the hydrogen atom is univalent, or that the aluminium atom is trivalent; but it seems to me more logical to consider valency as a property of atoms in a state of combination, since we know very little about free atoms, except in the case of the monatomic gases.

For example, in considering the combination of hydrogen and chlorine, we should attempt to find an explanation, not for the *union* of *atoms* of hydrogen and chlorine, but for the existence and stability of the *molecules* of these elements, and for reactions which take place between the *molecules*. The meaning of this statement will become clearer after the explanation of the theory has been read.

---

[1] *Trans. Chem. Soc.*, 93, I, 774 (1908).

[2] *Compt. Rend.*, 134, 647 (1912).

Historical and Critical.

The history of the electron conception of valency really began with the attempts of Davy and of Berzelius to explain chemical affinity by assuming that electric charges were associated with the atoms. This theory required that the atom of a given element should possess a charge of the same sign in all its compounds, but when it was discovered that a great many compounds could be made, whose very existence would seem to be contrary to these views, the theory of Berzelius, in its original form, lost the enthusiastic support which it had received at first.

The development of the electron theory has recently led to a revival of the views of Berzelius in a modified form. J. J. Thomson[1] has advanced the idea that an atom is a system of revolving electrons, of greater or less stability, capable of gaining or losing a certain number of electrons without sensibly changing its configuration. He uses the terms "positive valency" and "negative valency," and explains positive valency as the ability of an atom to lose electrons, and negative valency as the power to gain electrons. He regards the combination between two atoms as involving a permanent transfer of one or more electrons from one atom to the other, the atom which gains electrons becoming negative, while the one which loses electrons becomes positive. The direction of the electric force between two atoms in a compound will then depend upon the direction in which the transfer has taken place. This assumption requires, as J. J. Thomson points out, that the bond should have direction.

Thomson's conception of valency as a vector phenomenon has been developed at considerable length by Falk and Nelson,[2] and by Fry[3] in connection with some organic compounds and reactions.

Thomson, and also Falk and Nelson, take some hypothetical free atoms, having no charges, then proceed to combine them and assume that an electron is permanently transferred. This would seem to be an inverted method of constructing a theory. We deal almost entirely with molecules, and know very little about free atoms, certainly not enough to postulate the existence of uncharged free atoms of elements like hydrogen and chlorine. The idea that a bond is formed by the permanent transfer of an electron, involves numerous difficulties, one of which is that the separate atoms in a compound should be charged. I know of no experimental evidence showing that portions of a saturated molecule are charged differently. The fact that many substances can be dissociated into oppositely charged atoms or groups does not prove that these atoms or groups are permanently charged in the same way when in the undissociated compound.

---

[1] "Corpuscular Theory of Matter."

[2] *School of Mines Quarterly*, Columbia Univ., **33**, 179, 980; THIS JOURNAL, **32**, 1637 (1910).

[3] THIS JOURNAL, **36**, 248 and 262 (1914).

There is a difficulty in accounting, on the basis of Thomson's theory, for the existence of a hydrogen molecule made up of two positive atoms, or of a chlorine molecule with two negative atoms, and it is hard to see why two neutral atoms or two atoms having equal valency of the same sign should combine to form a stable molecule. In general, it seems as though binary elementary molecules should be incapable of existence on the basis of this theory.

Bray and Branch[1] find difficulties in the application of Falk and Nelson's conception of valency and introduce the ideas of polar and non-polar valency according to which an "electron passes completely or does not pass from one atom to the other."

Lewis[2] adopts their terms "valence number" and "polar number," the former a pure integer, the latter a positive or negative integer, and assumes three types of chemical compound; the polar type, in which the electrons occupy fixed positions within the atom; the non-polar type, in which the electrons move freely from atom to atom within the molecule; and the metallic type, in which the electron is free to move even outside the molecule. He criticizes the structural formulas of Falk and Nelson and of Bray and Branch, showing that, in certain cases such as

$$H \longrightarrow O \rightleftarrows O \longleftarrow H,$$

they either have no meaning or that the atoms are not bonded together where the arrows have opposite directions.

Some of the objections to Thomson's theory and Falk and Nelson's extension of it have been outlined in a recent article by Bates.[3]

Stark's theory[4] like Ramsay's, assumes that chemical combination between two atoms represents "a simultaneous attraction of both atoms for the same electron, which thus forms a bond between them." He supposes that a monovalent electropositive atom can be neutralized by a single valence-electron which is at an appreciable distance from the atom. The objection to this view is that it assumes that monovalent atoms in the free state may be neutral, whereas, to my knowledge, this has never been shown to be the case.

Outline of the Theory.

(*a*) *Structure of Molecules.*—Regarding molecules and atoms as systems of moving electrons, I shall treat valency as a consequence of the relative stability of these systems. An attempt will be made to apply the theory to explain certain phenomena, and to show that it is consistent with the observed facts.

Considering the simple case of a binary molecule in which the atoms are

---

[1] THIS JOURNAL, 35, 1440 (1913).

[2] *Ibid.*, 1448 (1913).

[3] THIS JOURNAL, 36, 789 (1914).

[4] Campbell's Modern Elect. Theory, 2nd. Ed., March, 1913.

monovalent, the theory supposes that the molecule is a stable system composed in turn of two systems or sub-groups of moving electrons which we call atoms, the dynamic equilibrium being such that one electron oscillates periodically from one system to the other, and is common to both systems, neither of which is complete in itself. This oscillating electron I shall call the valence-electron, since this term has come into use.

Although I speak of the valence-electron as oscillating, it might have any kind of motion such as revolution in an orbit or motion in a complex curvilinear path. It can be considered as forming a connecting link between the two atoms, being an integral part of each atom in turn. I have developed the theory as though each bond corresponded to a single valence-electron. It is, of course, conceivable that a group or system of electrons might perform the same function.

Valency is the property, or power, which an atom possesses of sharing a certain number of electrons with one or more other atoms, in such a way that the atoms so united form a *complete* or *perfect* electron system which is electrically neutral.

If a single valence-electron be assumed to be characteristic of a monovalent union, unit valency of an atom or radical in a compound may be defined as the power or property of sharing one oscillating electron with another atom or radical.

The hydrogen molecule, for example, can be represented as in Fig. 1, the black dot indicating the valence-electron, and the dotted line its path of oscillation. For convenience, the atoms in the molecule are represented as spheres in contact at a single point because, in the present state of our knowledge, this kind of a mental picture answers the purpose perhaps as well as any other. Very probably the method of union is much more intimate than such a diagram indicates. The separate atoms may even lose their identity when combined to form a molecule as suggested by A. A. Noyes.[1]

It is evident that the molecule cannot be *symmetrically* divided into two equivalent parts. If it is divided, one of the atoms will retain the valence-electron, and the other will be without it, and the two will become oppositely charged ions. (See Fig. 18.) In an ion therefore, unit valency corresponds to an excess or deficiency of half an electron.

A *free* hydrogen atom will, therefore, be either negative or positive, according as it does, or does not, retain the valence-electron, and its charge will be $^1/_2$ the charge of an electron, or $\epsilon/2$. (The symbol ϵ, used in this paper for the charge of an electron, is not to be confused with the charge of a univalent ion, which I have denoted by e. The relation between these quantities is discussed below.)

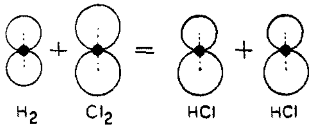
The hydrogen molecule can also be considered as two "partial atoms,"

---

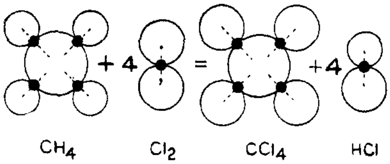
[1] THIS JOURNAL, 30, 351–2 (1908).

or "incomplete systems," both positive, held together by a negative valence-electron, and thus forming a "complete" or perfect system. The

1

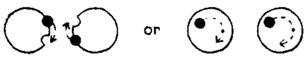


2

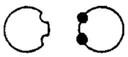


3

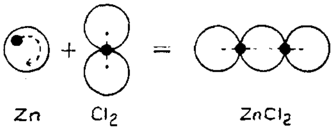
4



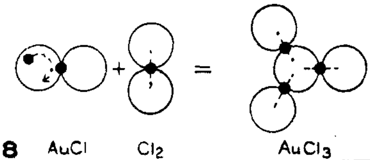
5



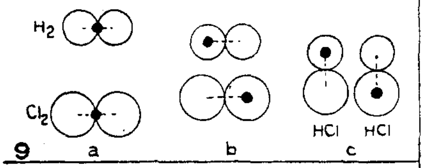
6



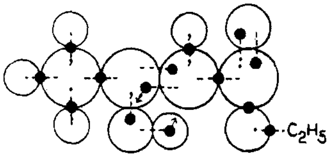
7



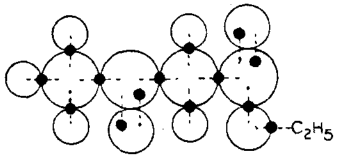
8



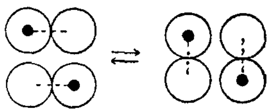
9



10



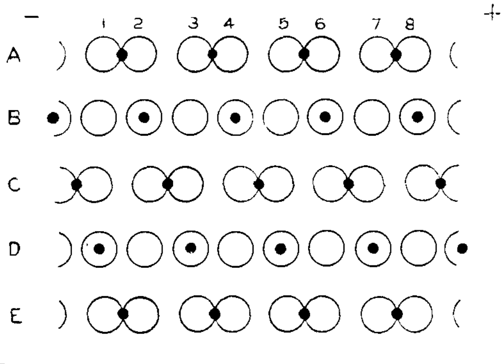
11



12

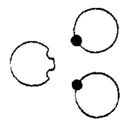
Fig. 1.—Hydrogen molecule.
Fig. 2.—Formation of hydrochloric acid.
Fig. 3.—Chlorination of methane.
Fig. 4.—Oxygen molecule.
Fig. 5.—Dissociated oxygen, not ionized.
Fig. 6.—Dissociated oxygen, ionized.
Fig. 7.—Formation of zinc chloride.
Fig. 8.—Formation of auric chloride.
Fig. 9.—Formation of hydrochloric acid.
Fig. 10.—Enol form of acetacetic ester.
Fig. 11.—Keto form of acetacetic ester.
Fig. 12.—"Free electrons" in metals.

structure of binary molecules of other monovalent elements, such as chlorine and bromine, should be exactly similar to that of hydrogen.

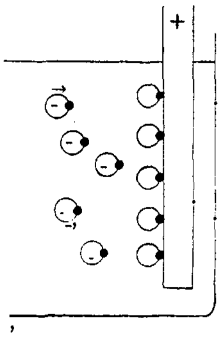


13

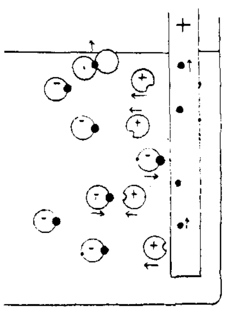
14



17



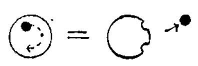
15



16

18

19



20

Fig. 13.—Conduction in metals.

Fig. 14.—Ionized hydrochloric acid.

Fig. 15.—Polarized anode.

Fig. 16.—Discharge of negative chlorine ions at anode, forming positive chlorine ions.

Fig. 17.—Ionized zinc chloride.

Fig. 18.—Partial dissociation of hydrogen.

Fig. 19.—Complete dissociation of hydrogen.

Fig. 20.—Ionization of helium.

Such a view of the relation of the atom to the molecule avoids the necessity of differentiating the elements as positive or negative. (An ion may be positive or negative, but an atom in a compound has no sign.) Its advantages will be illustrated by a few examples.

A molecule of hydrochloric acid is composed of a "partial atom" of hydrogen and one of chlorine, held together by a valence-electron, and the synthesis of hydrochloric acid from hydrogen and chlorine may be represented as in Fig. 2, the molecules of H_2, Cl_2 and HCl having similar structures.

A molecule of carbon tetrachloride is composed of a "partial atom" of carbon and four "partial atoms" of chlorine, held together by four valence-electrons. The substitution of hydrogen in methane by chlorine to form carbon tetrachloride takes place as shown in Fig. 3.

In this reaction, four "partial atoms" of chlorine exchange places with four "partial atoms" of hydrogen.

If considered apart from the valence-electrons, all atoms (partial atoms) will be positive.

A molecule of a divalent element, such as oxygen, containing two atoms, will have two valence-electrons, and may be represented as in Fig. 4. Such a molecule differs from one in which the atoms are monovalent, for in this case the molecule *can* be divided so that each atom retains one of the valence-electrons.

A molecule thus divided could be represented in either of two ways as in Fig. 5.

Each of these atoms is therefore electrically neutral, since it is at the same time positive by half an electron, and negative by half an electron. We should expect, therefore, to find that some *divalent* elements are stable in the monatomic condition, and we know this to be the case with zinc, cadmium and mercury.

If we exclude dissociation phenomena, we may deduce from the theory the general principle that only the elements of even valency—that is, elements of groups 0, 2, 4, 6, and 8 of the periodic system—should be capable of forming stable monatomic molecules.

A binary molecule of a divalent element will also have an alternative method of splitting, so that one of the atoms will have both of the valence-electrons. (See Fig. 6.) In this case, each atom will have a double charge or $2 \times \epsilon/2$, one atom having the charge $+ \epsilon$ and the other the charge $- \epsilon$.

Comparing the chief theories of valency with my own, it will be seen that Ramsay and Stark each assume that the valence-electron is attached in some way to both the atoms which it joins, but do not claim that it forms an integral part of each atom. Moreover, Stark's valence-electron is at some distance from both the atoms which it joins, and does not enter the atoms at all. J. J. Thomson, Falk and Nelson, H. S. Fry, and others assume that the valence-electron is permanently transferred in one or the other direction across the point of union of two atoms. My theory assumes that the valence-electron oscillates continually between the atoms which it joins and forms an integral part of each.

(b) *Multiple Valency.*—The valency of each element was at one time assumed to be constant, and in cases where two elements combined in more than one proportion, some of the molecular formulas were doubled to make them agree with the theory. This belief gradually lost ground, and it now appears to be generally admitted that most elements can exhibit multiple valency. Moreover, there is much evidence in support of the belief that in such cases the several valencies of an element will differ successively by two. This is in perfect agreement with the new theory, as will be shown.

Multiple valency may be explained by an example as follows: if we assume that a free zinc atom has zero valency, then when zinc combines with chlorine, one of the electrons of the zinc atom must become a valence-electron. But since this electron must oscillate so that it is out of the atom half of the time, another electron must be supplied to maintain equilibrium. This electron is supplied by the chlorine, the valence-electron which previously held the chlorine atoms together in the chlorine molecule now serving to unite the second atom of chlorine to the zinc. The reaction is illustrated in Fig. 7.

The net result of these changes is that the valency of zinc is increased from zero to 2. If another electron should become a valence-electron, the valency of the zinc atom would in the same way be increased to 4. An increase of valency, when it is originally *odd*, can occur in like manner; for instance, in aurous chloride, if another electron in the gold atom becomes a valence-electron, the valency will be increased by two, as in the case of zinc, so that when aurous chloride takes up more chlorine, the trichloride is formed. (See Fig. 8.)

The gold in aurous chloride can, therefore, be said to have a *latent valency* of *two.*

It will be seen from the foregoing examples that the theory requires that:

1. When an element exhibits multiple valency, the several values of the valency must differ successively by two.

2. When an additional electron in an atom becomes a valence-electron, the valency of the atom must increase by two.

3. A given element must have either even or odd valency consistently in all its compounds.

(c) *Valency Relations in the Periodic System.*—On the basis of this theory, it seems reasonable to assign valencies in the periodic system as follows:

Group 0	No valency, or even valency
Groups 2, 4, 6, 8	Even valency
Groups 1, 3, 5, 7	Odd valency

Many of the compounds whose molecular formulas are known with certainty, agree with this classification, but there are a number of elements which form compounds of two types, the valency being apparently odd in one and even in the other, if we represent these compounds by the simplest possible formulas which will correspond with the percentage composition, but which agree with the theory if the simple formulae of the compounds of one type are doubled. As the theory indicates that the valency of a given element should remain consistently odd or even in all its compounds, it becomes necessary in these cases to know the molecular weights of the compounds in question, in order to determine the correct molecular formulas. Among these apparent exceptions are the salts of copper and mercury, which will be especially discussed.

The helium group includes those elements, the atoms of which are "complete" or "perfect" electron systems and which are, therefore, capable of existing in the free or uncombined state, showing no tendency to form doubled systems.

If the elements of this group showed any tendency to combine with others, we might expect combination to occur with elements having even valency; most readily perhaps, with those which normally occur in the monatomic state, such as mercury, zinc and cadmium, and less readily with other elements of even valency. It is therefore an interesting fact that Cooke[1] has found some evidences of the combination of argon with zinc, mercury and selenium, and of helium with cadmium, mercury and selenium.

In Group 1, in which the theory requires that the valency should always be odd, we have the alkali metals, copper, silver and gold. The alkali metals appear to be univalent in all compounds; at least no difficulty arises from this assumption. Gold is either monovalent or trivalent.[2]

Silver seems to be monovalent in all its well known compounds. Silver iodide occurs in two allotropic forms which might correspond to any two of the formulas: $Ag\text{-}I$, $Ag \equiv I$, $Ag\text{-}I = I\text{-}Ag$.

Copper, however, offers some difficulties: Cuprous chloride, in the vapor state, has the formula Cu_2Cl_2, according to Biltz and V. Meyer[3] and V. Meyer and C. Meyer,[4] while Werner[5] found that the formula was $CuCl$ in organic solvents, and the same was found by Rugheimer and Rudolphi[6]

---

[1] *Z. physik. Chem.*, **55**, 537 (1906).

[2] Pope and Gibson, *Trans. Chem. Soc.*, **91**, 2061 (1907).

[3] Biltz and C. Meyer, *Ibid.*, **22**, 725 (1889).

[4] V. Meyer and C. Meyer, *Ibid.*, **12**, 609, 1112, 1185, 1292 (1879).

[5] Werner, *Z. anorg. Chem.*, **15**, 565 (1897).

[6] Rugheimer and Rudolphi, *Ann.*, **339**, 311 (1905).

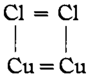
in solutions of cuprous chloride in fused bismuth chloride and by Beckmann and Gabel,[1] using quinoline as solvent.

The formulas for cuprous chloride in these two forms can be written:

$$\mathrm{Cu - Cl} \quad \text{or} \quad \mathrm{Cu - Cl = Cl - Cu}^{2}$$

copper being monovalent in both cases.

or

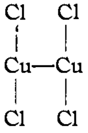


$$\begin{array}{ccc} \mathrm{Cl} & = & \mathrm{Cl} \\ | & & | \\ \mathrm{Cu} & = & \mathrm{Cu} \end{array}$$

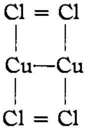
or $\mathrm{Cu{\equiv}Cl}$

in which copper is trivalent. (Two of these types may exist as allotropic modifications.)

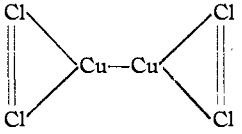
In cupric chloride, however, the usual formula, $CuCl_2$, would require that the valency of copper should be even, if that of chlorine remains odd; so that to make this compound conform to the new theory, which indicates that copper should have odd valency, the formula must be doubled, which may be done in various ways:

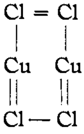


$$\begin{array}{ccc} \mathrm{Cl} & & \mathrm{Cl} \\ | & & | \\ \mathrm{Cu} & - & \mathrm{Cu} \\ | & & | \\ \mathrm{Cl} & & \mathrm{Cl} \end{array}$$



$$\begin{array}{ccc} \mathrm{Cl} & = & \mathrm{Cl} \\ | & & | \\ \mathrm{Cu} & - & \mathrm{Cu} \\ | & & | \\ \mathrm{Cl} & = & \mathrm{Cl} \end{array}$$





$$\begin{array}{ccc} \mathrm{Cl} & = & \mathrm{Cl} \\ | & & | \\ \mathrm{Cu} & & \mathrm{Cu} \\ \| & & \| \\ \mathrm{Cl} & - & \mathrm{Cl} \end{array}$$

There seems to be no evidence to support any of these formulas, but on the other hand, no definite experimental evidence was found to show that copper is ever bivalent, and we shall have to await the determination of the molecular formula of some cupric compound before we are able to decide the question.

On the basis of this theory, cupr*ic* compounds should have the general formula Cu_2X_4 in the undissociated state, if the valency of copper is odd.

In the second group, which should exhibit even valency, no special difficulties are encountered until we come to mercury. In mercur*ic* compounds there seems to be little doubt that the mercury is divalent, the best evidence being the formation of compounds of the type HgX_2 with the organic radicals. In regard to mercur*ous* compounds, there appears to be some doubt still, although much work has been done on the constitution of mercurous chloride. It was at one time supposed, on the basis of vapor density measurements, that calomel had the formula HgCl, but it was later shown that on vaporization the salt was decomposed into $HgCl_2$ and Hg, which gave a vapor density corresponding to HgCl. Baker,[3] however, showed that calomel vapor in the absence of water had the formula Hg_2Cl_2.

---

[1] Beckmann and Gabel, *Z. anorg. Chem.*, **51**, 536 (1906).

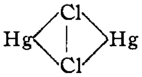
[2] J. Newton Friend, "Theory of Valency," p. 61 (1908).

[3] Baker, *Trans. Chem. Soc.*, **77**, 646 (1900).

With only these data, mercury in calomel can be represented as either monovalent[1] or divalent:

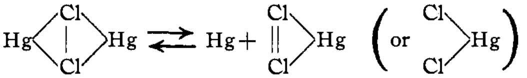
$$\underset{\text{(I)}}{\mathrm{Hg-Cl=Cl-Hg}} \quad \text{or} \quad \underset{\text{(II)}}{\mathrm{Cl-Hg-Hg-Cl}}$$

I am of the opinion that mercury in calomel is divalent and that the formula of calomel should be written



(III)

This formula would easily account for the decomposition of Hg_2Cl_2 into $HgCl_2$ and Hg, as an atom of mercury simply splits off, leaving $HgCl_2$, according to the equation:



Moreover, a molecule of Hg_2Cl_2 constituted according to Formula III could not readily split into 2 HgCl, which again agrees with experimental results.

There is, however, no evidence yet which will decide this question, but it may be said that our apparent inability to prepare mercurous salts or organic derivatives of the type HgX where X is a monovalent element or radical, is presumptive evidence that mercury does not have unit valency, and that we are justified in considering mercury no exception to the theory.

The other groups could be discussed in the same way and apparently show no special contradictions to the theory. In cases such as the halogen salts of gallium and indium, in which the evidence showing that the valency of the metal may be both odd and even, rests on vapor-density measurements, I think, in view of the work of Baker on mercurous chloride, that more remains to be done, before we can accept formulas derived in this way as evidence against the theory.

Applications of the Theory.

(*a*) *Mechanism of Reactions.*—Let us consider a simple reaction, such as the combination of hydrogen and chlorine. Reaction occurs only during collisions, or when the molecules come within a certain distance of each other, and may be conceived to occur in either of two different ways.

(1) The valence-electrons in two adjacent molecules may simultaneously shift their positions to form the new compound. The method by which the shifting could take place is illustrated in Fig. 9, *a*, *b*, and *c*.

Fig. 9*a* shows a hydrogen molecule with the valence-electron in the middle of its path of oscillation, and also a chlorine molecule of exactly similar structure. In Fig. 9*b* the valence-electrons are at opposite ends of

---

[1] J. N. Friend, "Theory of Valency," p. 67 (1908).

their paths, so that each hydrogen atom is adjacent to an oppositely charged atom. If the valence-electrons are in this relative position at the moment when a collision occurs, conditions are very favorable for combination, and, since hydrogen chloride is a more dynamically stable electron system than either hydrogen or chlorine, the valence-electrons will oscillate in new paths, as in Fig. 9*c*, thus forming the new compound, HCl.

The position illustrated in Fig. 9*a* is not the only one favorable for reaction, since any position in which both atoms of a chlorine molecule are in contact with the corresponding atoms of a hydrogen molecule would be favorable. Not every colliding pair of molecules will, at the instant of collision, be in the position most favorable for reaction, hence the number of collisions resulting in chemical combination would be only a certain percentage of the whole number of collisions.

The increase in the rate of reaction caused by raising the temperature would be due to an increase in the number of collisions per second. The increase in the reaction rate caused by light is perhaps due to a sort of polarization of the molecules which arrange themselves in similar positions along the direction of the light rays, or the valence-electrons may be constrained to move in a particular way which favors reaction during collision.

(2) Another explanation of the mode of reaction is the following: a certain number of the collisions between the molecules of a gas may result in dissociation, and in a mixture of hydrogen and chlorine the ions or partial atoms thus produced would recombine to form HCl. On this view, the effects of heat and light are merely to increase dissociation; the former by increasing the velocity, and hence the collision rate; and the latter by influencing the motion of the valence-electrons within the molecules.

A chemical reaction, then, is nothing more than the readjustment of the paths of oscillation of valence-electrons between the atoms of contiguous molecules.

(*b*) *Tautomerism.*—On this theory the "wandering" of hydrogen in an organic compound, and the equilibrium between tautomeric substances can be explained as a special kind of chemical reaction. As an example take the case of acetoacetic ester. This substance exists in two forms—the enol form:

$$CH_3 - C(OH) = CH - COOC_2H_5$$

and the keto form:

$$CH_3CO - CH_2 - COOC_2H_5$$

Writing these formulas with the valence-electrons indicated we have for the enol form, Fig. 10, and for the keto form Fig. 11. In the enol form the hydrogen of the hydroxyl group, and perhaps the hydroxyl group itself, has a certain freedom of motion, and at some particular instant the molecule will have the configuration shown in Fig. 10, in which the hydrogen is nearly in contact with the α-carbon atom. If now a readjustment of the motions of the valence-electrons should occur as indicated by the small arrows, so that the hydrogen becomes attached to the α-carbon atom, and the oxygen attached to the β-carbon becomes double-bonded, we should have the keto form, Fig. 11.

The reverse transformation could be explained in a similar way. According to this view, the wandering of hydrogen is simply a change of path of certain valence-electrons in the molecule. Other types of tautomerism could be explained similarly.

(*c*) *Conduction in Metals.*—Consider a solid mass of silver, and assume that its molecules are diatomic, two atoms of silver being connected by a single oscillating valence-electron.

If two molecules are close together we may conceive that a species of chemical reaction may occur, involving a shifting of valence-electrons, and forming new molecules as in Fig. 12.

If we consider a constant shifting and oscillation of valence-electrons to be taking place in this way in a mass of metal, we have an explanation of the freedom of electrons, upon which the conductivity of a metal is supposed to depend. According to this view, the number of "free" electrons will be of the same order as the number of molecules in unit volume, but the *time* that the electrons are actually free may be very small or zero. When a potential difference is applied to a piece of metal, the electrons are constrained to drift in one direction, and we have an electric current.

The way in which the electrons may drift in one direction in an electric field, while still functioning as valence-electrons is illustrated in Fig. 13, in which a chain of molecules is shown in five successive conditions.

In position A each of the molecules 1–2, 3–4, 5–6 and 7–8, has its valence-electron at the point of contact between the atoms as shown. In position B, the valence-electrons have moved toward the positive pole, and the atoms have become ions of opposite signs. The ions 1, 3, 5, and 7 are positive and drift toward the negative pole, or to the left in the diagram, while the ions 2, 4, 6 and 8 are negative and move to the right. The mean free paths of these ions are very short, and the ions 2 and 3 very soon come together as in C; and the valence-electron of 2, which continues to drift to the right, becomes the bond of the molecule 2–3. The other pairs of ions in the same way form the new molecules 4–5, 6–7, etc.

The motion of the valence-electrons toward the positive pole continues and we soon have the condition shown in D, in which the atoms 1, 3, 5 and 7 have now become negative ions, and started to move toward the positive pole. Finally, we have the condition shown in E, which is the same as in A except that the valence-electrons have each advanced a certain distance.

We see, therefore, that the electrons do not really have to be "free," in the sense of being outside of the molecules, in order that a substance should conduct. It is only necessary that their direction of movement be brought under control.

We have now gone through a complete cycle of changes in which each electron has moved toward the positive pole a distance equal to twice the diameter of an atom plus the mean distance between two molecules, and at the same time each atom has moved half the distance separating two molecules and back again.

Thus, a directional *drift* of the valence-electrons is accompanied by an oscillation of the atoms, and we can construct on this basis a more or less clear mental picture of the thermal phenomena accompanying the flow of electric currents in metals.

An electron probably encounters little or no resistance to its motion while inside of, or forming part of an atom, so that electrical resistance is due mainly to the molecules not being in contact, and thus being obliged to oscillate in order to allow a drift of the electrons in the manner illustrated. Cooling a metal lowers its resistance by bringing the molecules closer together and reducing the amplitude of oscillation of the atoms. At absolute zero, when there is no motion of the atoms, and they are very close together, the electrons can move in approximately straight lines without hindrance and the conductivity is very high.

Alloys present some interesting phenomena. If compounds are formed, the molecules are unsymmetrical and are consequently less often in positions favorable to an interchange of electrons, which presumably will seldom occur, except when the new molecules formed by the reaction are like the original ones. The small percentage of opportunities for the transfer of electrons, causes such an alloy to have a high resistance. The more complicated the molecule is, the higher the resistance should be. If the constituent metals form no compound, the conductivity of the alloy should be quite high, and should correspond approximately to that calculated from its composition.

The small temperature coefficient of resistance of alloys may be explained as follows:

The metallic compound dissociates with rise of temperature so that the alloy is a mixture of pure metals and a compound of them. As the temperature rises, the composition approaches that of a mixture of the two pure metals, which has a lower resistance than that of the compound. At the same time the resistances of the pure metals themselves are increasing, and this opposes the diminution of resistance due to dissociation, so that the net rate of change may be very small.

(*d*) *Association.*—Association may be defined broadly as a combination of two or more molecules to form a single complex molecule. In a general way, it includes not only the formation of complex molecules from organic hydroxyl compounds, the addition of water to salts as water of crystallization, the addition of halogen hydrides to ethers to form oxonium salts, all of which probably involve an increase in the valency of oxygen from two to four, but also the formation of double salts by the union of two or more single salts. The increase of valency can take place as illustrated in the case of formation of $ZnCl_2$ from Zn and Cl_2, or of $AuCl_3$ from AuCl and Cl_2.

The formation of "intermediate compounds" or addition products during a chemical reaction can be readily explained by assuming that extra valencies are momentarily brought into action to form unstable associated molecules.

(*e*) *Dissociation and Conduction in Electrolytes.*—Consider a solution of a simple binary compound; for example, hydrochloric acid. In aqueous solution the molecules are, according to the electrolytic dissociation theory of Arrhenius, largely dissociated into positive hydrogen ions and negative chlorine ions. These are considered to differ from the ordinary atoms only by being charged. When the charges are given up at the electrodes during electrolysis, the ions become converted to *uncharged atoms.* The electrolytic dissociation theory is somewhat vague as to the origin of the charges on the ions, as well as to the mode by which *molecules* are formed from uncharged atoms at the electrodes.

According to the new theory, the dissociation of the molecule is a division in such a way that the valence-electron forms part of the negative ion, while the positive ion consists of a partial or incomplete atom, as shown diagrammatically in Fig. 14.

The charge of a monovalent ion would therefore be $\epsilon/2$, or half the charge of a single free electron, while the charge of a divalent ion would be ϵ, etc.

Omitting, for the present, any speculation as to the primary cause of dissociation, the explanation of the phenomena at the electrodes is as follows:

The current in the hydrogen chloride solution consists of a stream of chlorine ions moving to the anode, and of hydrogen ions moving to the cathode. In order that molecular hydrogen may be formed and set free at the cathode, one electron must be supplied to every pair of hydrogen ions arriving at the cathode, and this is supplied from the stream of electrons which constitute the current in the wire leading to the cathode, thus liberating molecular hydrogen. At the anode, very similar phenomena occur; every pair of chlorine ions reaching the anode must lose one electron in the process of forming molecular chlorine, this electron passing into the conducting wire.[1]

The process of discharging ions at the electrodes and forming neutral

---

[1] Compare P. Achalme, *Compt. rend.*, **154**, 647–99 (1912).

molecules should be capable of explanation in such a way as to make clear the nature of polarization and of decomposition voltage, neither of which have yet had a wholly satisfactory explanation.

The following is an explanation of these phenomena by the new theory: In a hydrochloric acid solution the negative chlorine ions move toward the anode and, if the voltage is not too high and the material of the anode does not combine readily with chlorine, the surface of the anode soon becomes covered with a molecular layer of these ions, and is said to be polarized. To discharge these ions, the potential difference at the electrode must be great enough to pull the valence-electrons away from the atoms.

If a potential greater than this value (commonly called the "electrode single potential") be applied, the negative chlorine ions give up their valence-electrons, which then pass off into the wire leading from the anode, and the negative chlorine ions, upon losing valence-electrons, according to the theory become *positive* ions. The positive chlorine ions thus produced would immediately begin to move away from the anode, and would soon combine with approaching negative chlorine ions to form neutral molecules of chlorine gas.

At the surface of the anode during electrolysis, there would be a layer of ions undergoing a change of sign from negative to positive, while, at a short distance away from the surface of the anode, there would be an advancing layer of negative ions, and between them a reaction zone where neutral molecules are formed.

The phenomena at the cathode would be quite similar to those at the anode.

Fig. 15 shows a polarized anode covered with a molecular layer of negative chlorine ions.

Fig. 16 shows an anode at which the potential is high enough to remove electrons from the negative ions, and shows positive ions moving away from the electrode just after losing electrons, also a molecule of Cl_2 escaping.

The electrode single potential depends on the nature of the electrode material, and will be the algebraic sum of the potential representing the attraction of the electrode material for electrons, and of the force necessary to remove an electron from a negative ion at the anode, or to add an electron to a positive ion at the cathode,

Just as many electrons are passing into the solution at the cathode as there are leaving at the anode. Thus, the theory of the mechanism of conduction in electrolytes is in complete harmony with the theory of a current in a metallic conductor as a stream of electrons.

Let us now consider the special case in which the "positive" element of the compound forms monatomic molecules. If we take zinc chloride for an example; the salt, in solution dissociates as follows: $ZnCl_2 = Zn + 2Cl$

so that we have a divalent positive zinc ion and two negative chlorine ions, the valence-electrons remaining with the chlorine ions. At the anode, the chlorine ions combine in pairs to form chlorine molecules, and, for each molecule which is formed, one valence-electron is set free and passes into the metallic circuit. At the cathode the conditions are somewhat different. Each zinc ion has a double charge ($2 \times \epsilon/2 = \epsilon$) and hence requires one electron to convert it into a neutral atom. Each zinc ion, therefore, receives one electron at the surface of the cathode and becomes free metallic zinc in the monatomic state. If zinc in the free state were diatomic, then two zinc ions would unite with two electrons and form a binary molecule.

(*f*) *Dissociation and Conduction in Gases.*—In an undissociated gas, a free and continuous interchange of electrons between molecules, as in a metal, is impossible, because the molecules are too far apart, so that a gas or vapor is ordinarily non-conducting unless free ions are produced in it by Röntgen rays, ultraviolet light radiation from radioactive substances, or an electrostatic field.

Consider the ionization of a simple binary gas molecule, such as that of hydrogen. According to the new theory, two kinds of dissociation are possible, which I shall call partial and complete dissociation.

(*a*) Partial dissociation. The molecule can split into two "atomic ions," the positive ion being a "partial atom" *without* the valence-electron, and the negative ion being a partial atom *with* the valence electron. A hydrogen molecule which has undergone partial dissociation in this manner may be represented as in Fig. 18.

The charges on these atomic ions will be $+ \epsilon/2$ and $- \epsilon/2$, respectively, if ϵ is taken as the charge of a single free electron.

(*b*) Complete dissociation. The molecule can split into three ions, the two "partial atoms" of hydrogen becoming positive atomic ions, each having a charge of $+ \epsilon/2$, while the valence-electron becomes a negative ion with the charge $- \epsilon$. A molecule dissociated in this way can be represented as in Fig. 19.

What determines the type of dissociation which takes place when a gas is ionized? A somewhat analogous case is that of the dissociation of a dibasic acid in aqueous solution which forms first a single hydrogen ion, and a complex negative ion, which is itself further dissociated in more dilute solutions, both types obeying the law of mass action.

If we assume that a gas under the influence of an ionizing agent is subject to laws of equilibrium similar to those that apply to an electrolyte which is being ionized by the dissociating agent, water, the line of reasoning is as follows:

The two types of dissociation may be represented as reversible reactions, thus

$$\mathrm{H\epsilon H} \rightleftarrows \mathrm{H}^{\cdot} + \mathrm{H\epsilon}'$$
$$\mathrm{H\epsilon H} \rightleftarrows \mathrm{H}^{\cdot} + \mathrm{H}' + \epsilon''$$

The nature and extent of the ionization produced in a gas when it is in a steady state, under the influence of an ionizing agent, will depend upon the frequency with which collisions causing recombination occur, that is, upon the pressure of the gas. At extremely low pressures, dissociation should be complete and the negative ions should consist of electrons only, while at higher pressures partial dissociation will predominate, and the ions will be mostly "atomic ions"[1] of both signs.

Experimental evidence shows that positive and negative ions in a gas differ in size and that this difference becomes much greater for low pressures of the gas, and that at low pressures the negative ion is identical with the electron. The change in size of the negative ion is quite marked at 10 mm. pressure. The positive ion is always atomic in size, even at a low pressure of the gas.

The commonly accepted theory seems to be that at high pressures the negative ion is an electron to which a cluster of molecules has become attached, and that at low pressures the electron sheds the clusters, and the difference in size and velocity is supposed to be explained in this way, but I believe that the above explanation agrees with the facts just as well.

At moderate pressures, therefore, according to our theory, there should be, in an ionized gas, two kinds of negative ions, *viz.*, "atomic ions" and electrons, and consequently the experimentally determined values of e/m for the negative ion, being average values for all the ions present, should vary with the pressure of the gas between certain limits, which for hydrogen would be 1.7×10^7 and 10^4 (electromagnetic units). The charge on a gaseous ion should also appear to be a variable depending on the pressure, if determined from measurements on a large number of ions at once, as is done by the "cloud method."

At moderate pressures the velocities of positive and negative ions are found experimentally to be *nearly* equal. This agrees with the theory, since the two kinds of "atomic ions" should have the same mass. Since, however, a certain proportion of the negative ions will be electrons, with much higher velocity than the atomic ions, the *average* velocity of the negative ions should be somewhat greater than for the positive ions. Here again, experimental results agree with the theory.

Any element having odd valency should, in the gaseous state, show a perceptible increase in electrical conductivity when dissociated by heat, because the free atoms must necessarily be charged.

The elements of the helium group, which occur in the free state in the

---

[1] For the sake of clearness, the term "atomic ion" is proposed, to distinguish such ions as $\mathrm{H}^{\cdot}$ and $\mathrm{H\epsilon}'$ from electrons.

uncharged monatomic condition, would be expected to become divalent if ionized. Rutherford and Geiger's value of 9.3×10^{-10} E. S. U. for the charge on an α-particle is approximately twice Millikan's value for the unit ionic charge, and agrees with the theory. A neutral helium atom by losing a single electron would become a positive ion with a double charge (See Fig. 20), and *vice versa*, when an α-particle gains an electron it becomes an uncharged helium atom. This probably occurs during many radioactive changes.

(*g*) *The Charge and the Apparent Mass of an Electron.*—The charge on a negative ion in a gas at moderate pressures has been determined many times and in many different ways, but the charge on an *electron* has not yet been measured. It is commonly, but without warrant, assumed that the two are equal, and many workers who have determined simply the charge on a gaseous ion use the term *ionic charge*, *unit charge*, and *electron charge* as though they were synonymous. Some confusion exists because the same symbol is used both for the ionic charge and the electron charge, but, since these quantities are not known to be equal, I would urge that the symbol ϵ be used only for the charge of a single free electron.

My theory seems to require that the charge of an electron should be twice as great as that of an univalent ion, or if the electron charge be taken as a unit and represented by the symbol ϵ, the charge of a univalent ion will be $\epsilon/2$, or *half the unit charge.* Taking Millikan's value[1] for the *ionic charge*, e, we should have for the electron charge, $2 \times 4.774 \times 10^{-10} = 9.548 \times 10^{-10}$ E. S. U.

This point has an important bearing on the value of the apparent mass of an electron, which is usually calculated from the following considerations:

ϵ/m for cathode rays (free electrons) $= 1.7 \times 10^7$

E/M for hydrogen ions in electrolysis $= 10^4$

Now the relation of m to M depends on the relation of ϵ to E. The minimum charge on a negative ion in a gas at ordinary pressure seems, beyond doubt, to be equal to the charge on a hydrogen ion in electrolysis, but J. J. Thomson,[2] assumes that the charge on a cathode-ray particle (corpuscle) is equal to the charge on a negative gaseous ion, and that, therefore, $\epsilon = E$ which leads to the result that $m = 1/1700\ M$. According to my theory $E = \epsilon/2$, hence $2E/M\ .\ m/\epsilon = 1/850$, or $m = 1/850M$.

We have the following values:

ϵ, the electron charge $= 9.548 \times 10^{-10}$ E. S. U.

e, or E, the univalent ionic charge $= 4.774 \times 10^{-10}$ E. S. U.

m, the apparent mass of an electron in cathode rays $= 1.65 \times 10^{-24}/850 = 1.94 \times 10^{-27}$ gram.

---

[1] *Phys. Rev.*, [2] **2**, 109–43 (1913).

[2] "Conduction of Electricity through Gases," 2nd Ed., p. 160.

Summary.

The theory assigns to the "bond" a physical meaning, the oscillating valence-electron; and this idea is shown to be in harmony with recent theories of the structure of matter. It explains a number of phenomena in a fairly satisfactory way.

Valency is the property or power which an atom possesses of sharing a certain number of electrons with one or more other atoms in such a way that the atoms so united form a relatively stable, electrically neutral system.

The valence-electrons oscillate periodically between the atoms which they unite.

Valency is, therefore, a purely mechanical result of the dynamic relations between molecules and the atoms of which they are composed.

The valency of an atom in a state of combination with other atoms is simply a numerical quantity, neither positive nor negative, but the valency of a radical or an ion may be positive or negative.

Explanations are given of the mechanism of chemical reactions, tautomerism; conduction in metals; association; dissociation and conduction in electrolytes and gases. The following deductions from the theory are made:

Uncharged free atoms can exist only when the element belongs in an even group of the periodic system. Free atoms of elements of odd valency can exist only as ions having charges which are odd multiples of the unit *ionic* charge.

Elements belonging to odd groups of the periodic system will have odd valency, while elements of even groups will have even valency.

Valency varies in steps of two, being always even or always odd for the same element.

The unit electric charge or the charge of an electron is twice the ionic charge or 9.548×10^{-10} E. S. U.

The apparent mass of the electron in cathode rays is 1/850 of the mass of a hydrogen atom.

RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.,
SCHENECTADY, N. Y.

THE CHEMICAL SIGNIFICANCE OF CRYSTALLINE FORM.

BY WILLIAM BARLOW AND WILLIAM JACKSON POPE.

Received January 5, 1914.

In a recent paper,[1] Professor Theodore W. Richards criticizes adversely the work which we have done on the relationships existing between crystal structure and chemical constitution and arrives at the conclusion that many of our arguments are fallacious and that our theoretical deductions must be rejected. We welcome this criticism, not only because of its

---

[1] THIS JOURNAL, **35**, 381 (1913).