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THE VALENCE THEORY OF J. STARK FROM A CHEMICAL STANDPOINT.

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Since the publication in 1908 of J. Stark's first comprehensive paper "The Valence Theory on an Electroatomic Basis,"[2] there has been a constantly growing tendency to apply this theory to the interpretation of chemical phenomena. Pauly and Butler have used it to explain the reactivity of the aldehyde group,[3] and Ley has followed many of its assumptions in his interpretation of the relation existing between the color and constitution of organic compounds.[4] A recent treatise by Dr. Paul Ruggli[5] summarizes the later developments and applications of the theory.

Stark's theory attempts to solve the old problem of valence with the assistance of the new views regarding the atomic nature of electricity.

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[1] This manuscript was submitted to Dr. Ruggli and he has kindly suggested some changes, but the manuscript with his revision cannot be passed by the censor at the present time and Dr. Ruggli has very kindly given his consent to publication in the present form. We regret very much that his emendations cannot be secured for inclusion in the review.

[2] *Jahrb. Radioakt. und Elect.*, **5**, 125 (1908).

[3] *Ann.*, **303**, 254.

[4] "Farbe und Konstitution bei Organischen Verbindungen," Leipzig, **1911**.

[5] "Die Valenzhypothese von J. Stark von Chemischen Standpunkt," Stuttgart, **1912**.

The idea of applying the results of experiments in the field of electricity to chemical problems is not new, but goes back to Berzelius. In more recent times it finds supporters in A. Michael, H. Kauffmann, R. Abegg, W. Nernst, and many others, although it must be added that these names represent a very wide diversity of opinion. Stark seeks to avoid all distinctions between dualistic and unitary views by ascribing the variations (other than size, etc.) between atoms of different elements to a difference in the electric fields of force on the outer surfaces of the atoms. According to the theory, metallic elements appear positive because their atoms easily lose negative electrons, but the same theory makes possible the conception of molecules formed from the same kind of atoms. In general, the hypothesis possesses the advantage of being expressed in a form capable of being put to experimental proof, and has been already partially verified.

The essentials of the electroatomic theory are supplied by the new physical conception of the great difference in volume existing between the positive and negative units of electricity, and by the extended application of the conception of lines of force. The latter idea has been applied already to chemistry in Thiele's "Theory of Partial Valency," and has been helpful in establishing the conception of the divisibility of valence. The theory of partial valency becomes far more valuable when expressed in terms of the electroatomic theory.

The work of Faraday, Helmholz, and others has established the fact that electricity is not continuous, but has an atomic structure like that of matter. In 1891, J. Stoney suggested the name electron for this "elementar-quantum." As a result of experiments by Helmholz, Nernst, and Ramsay, we may now picture a negative electron as corresponding roughly in size to a monovalent chemical atom, about $^1/_{1800}$ the size of an atom of hydrogen. Similar calculations regarding positive electrical units have not yet been successful, and indeed a positive electron may not even be demonstrated with certainty. Observations up to the present time have merely seemed to indicate that the mass associated with a positive unit of electricity belongs to the same mathematical order as the mass of chemical atoms. (W. Wien, J. Stark, J. J. Thomsen, etc.) This *disparity in size* of the negative and the positive "elementar-quantum" *is emphasized by Stark.* Regarding negative electrons, it has been demonstrated further that they may be separated from chemical atoms by the expenditure of chemical energy, and that the remaining atom then shows a positive charge.

A close study by chemists and physicists of the association of atoms indicates that the chemical atoms in their combinations do not interpenetrate, but are bound together mainly by their outer surfaces. A conception of the nature of the mutual union of atoms to form molecules requires an investigation of the structure of the fields of force existing on the outer surfaces of the atoms; and an electroatomic study of chemical action shows that in, or on, the chemical atom positive and negative units of electricity are present as constituent parts. Physicists have even extended these conclusions and advance the hypothesis that the chemical atom is built up of positive and negative units of electricity and of nothing else. This hypothesis is assumed here, but all considerations as to the inner nature of the atom may, for the purposes of the present theory, be disregarded. It is supposed that the surface of a chemical atom may be adequately represented by a three dimensional arrangement of positive and negative electrical charges. If, then, the great difference in size between the fundamental units of positive and negative electricity is considered, the surface of an atom must be pictured as made up of extended zones or spheres (not necessarily spherical in shape) of positive electricity, and between or even above these the comparatively small, point-like, negative electrons. These negative electrons, for reasons which will follow, are to be regarded as valence electrons. Further, since the structure of an electric field is usually represented by the course and density of lines of force which originate at positive charges and end at equally great negative charges, we must imagine a system of lines of force radiating in all directions from the point-like negative electrons, many of them terminating in the extended positive zones on the atom.

The point-like origin and the diverging course of the lines of force are important facts to be remembered in considering the union between one atom and another; for the disparity in the size of the positive and negative units of electricity must be regarded as the determining factor in establishing simple relationships between atoms, such as are expressed, for example, in the fundamental laws of chemistry.

The discrete positive units of electricity situated upon the surfaces of the atoms must not be regarded as consisting of uniformly charged positive zones, but as presenting a concentration of positive electricity at certain points. The neutralizing valence electrons are bound most strongly at these points, and must be assigned, therefore, to quite definite positions on the surface of the atom. If they are pushed from these to neighboring places on the surface, a definite expenditure of energy is necessary. If a valence electron is pushed away from the surface of the atom to a very great distance from it, much more energy must be employed. The maximal amount of this energy measures the strength of the union of the valence electron with the positive sphere of its own atom, and is different for different kinds of chemical atoms. Chemical union between two atoms results because some of the lines of force of a valence electron are detached from its own atom by the approach of the second atom, and become attached to the positive spheres of this atom. In so far as the negative electrons lying on the surface of the atom exercise those functions of the atom for which chemists have evolved the idea of valency, they may be called valence electrons. In terms of these fundamental conceptions, it is now possible to explain a great variety of individual phenomena.

In the static condition the resultant of all the lines of force between the negative electrons and the positive spheres in a compound is zero. If now a part of the system is deflected from its condition of equilibrium, energy is expended against the electric forces and these forces become active as a function of this deviation. Electrical potential energy is in this way created. It reaches the maximum when the individual atoms of the compound become so far separated that the electric force between them becomes very small. On the return of the atoms to the static arrangement these free potential energies, computed at a relatively great distance, are changed into heat, and in this form may be measured. A definite energy value, characteristic of every compound, *viz.*, the heat of formation of that compound, may be, therefore, referred to its dissociated atoms. This potential energy is a minimum in a chemical compound in the static condition. If the same number of chemical atoms is capable of arrangement in different configurations in a molecule, isomeric compounds result, and in such cases several minima are possible. The most stable isomer has a configuration which represents the least potential energy. The heat arising from chemical action may be regarded, therefore, as of electrical origin.

In the act of chemical union between atoms, the negative electron of one atom approaches the positive sphere of another atom, and this is attended by the shortening of the lines of force in the immediate neighborhood of each atom, or, in general, by a contraction of the field of force of the atoms. It therefore follows that chemical reactions are accompanied by changes in volume. This is corroborated by the work of T. W. Richards[1] who has shown experimentally that positive heats of reaction (exothermic reactions) correspond to contractions of volume.

In chemistry it is customary to speak of the saturation or union of valencies. In terms of the electroatomic theory, a valence electron is not bound by another valence electron but by a positive sphere. There are three classes of valence electrons: unsaturated, saturated, and partially dissociated ("gelockert") valence electrons. If a negative electron is bound only to the positive sphere of its own atom, it is called unsaturated, and corresponds to an unsaturated valency in chemical phraseology. Such a condition is represented by Fig. I. By the potential energy, Vu, of an unsaturated valence electron is to be understood the work done when the electron is removed to a relatively great distance from

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[1] *Z. physik. Chem.*, 4, 169, 597 (1902).

its position of equilibrium on its atom. Unsaturated valence electrons may appear on single atoms or on atoms that are joined to other atoms. In the latter case more than one electron must be present on each atom. If a valence electron is bound by its lines of force to the positive sphere of another atom as well as to its own atom, it is called saturated. Such a condition is represented by Fig. II. From its nature, a saturated valence electron appears only in compounds. By the potential energy of a saturated valence electron, Vg, is to be understood the work done when its union with the positive sphere of the second atom is dissolved and the two atoms separated by a relatively great distance from each other. H. Kauffmann has expressed this relation in abbreviated form[1] by the symbols

Fig. I

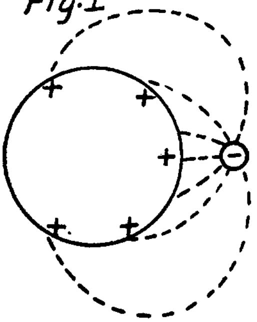
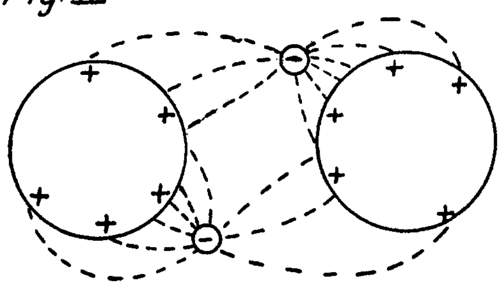
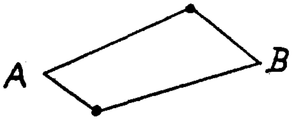
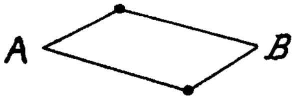


Fig. II





or



where A and B represent the reacting atoms. The conception of the third class, partially dissociated valence electrons, offers more difficulty because the idea is new. We must imagine an electron that is not bound to a second atom, yet forced away from its own atom. This might be caused by repelling forces, due to the approach of a second atom. Such a condition is represented by Fig. III. This figure shows schematically a compound, consisting of three divalent atoms, on which are present three saturated valence electrons, E_1, E_2, E_3 and three partially dissociated valence electrons, E'_1, E'_2, E'_3. By the potential energy, V_o, of a partially dissociated valence electron is to be understood the work done when such an electron is removed from its position of equilibrium with relation to its atom to a relatively great distance from its atom. It follows that V_o is smaller than Vu. The unsaturated and the partially dissociated valence electrons may be separated from their atoms in a

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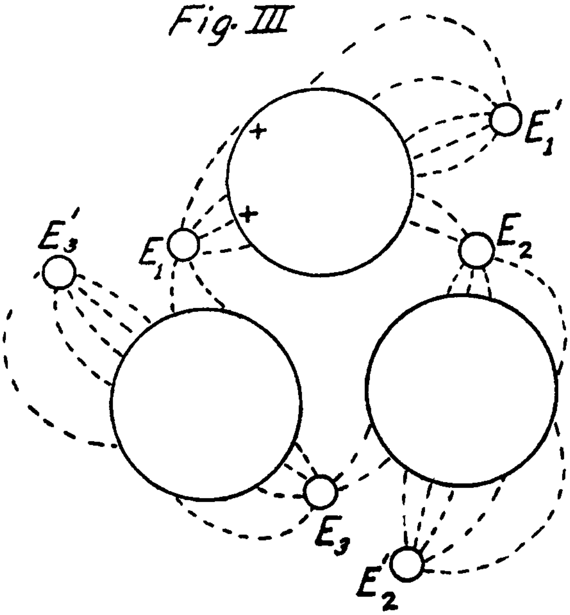
[1] *Physik. Z.*, 9, 312 (1908).

compound without destroying the compound. This is not true in the case of saturated valence electrons.

Fig. III



A valence electron bound to only one other atom besides its own represents a condition of *simple saturation*, while an electron bound to two or more other atoms represents a condition of *multiple saturation*. Simple saturation is the more important since it is the condition prevailing in most stable compounds. Under such circumstances the extended positive sphere of an atom, A, must be conceived as occupying a position directly opposite the valence electron of an atom, B, so that the positive sphere of A receives all the lines of force of the electron that radiate from the side turned away from its own atom. The nearness of the positive and negative charges in such a case make the value V*g* of saturation very high, and the union of the two atoms is very stable. The doctrine of valency in chemistry developed from data limited to this simplest type of combination between atoms. The development of this doctrine has been attended by many difficulties, among them the application of the conception to molecular compounds. In terms of the theory of valency it is customary to speak of the saturation of valencies and to represent such a condition schematically by a straight line, thus A——B, where A and B are monovalent atoms. In terms of the electroatomic theory, saturation implies the union of an electron with the positive sphere of another atom and must be represented schematically by a system of double lines as shown on p. 2615. Such a conception obviates many of the difficulties of the older theory. In terms of it, both molecular compounds and crystalline form may be explained readily by simply extending the idea of multiple saturation. Multiple saturation itself has not been carefully studied because this condition in its very nature implies great instability. Under such circumstances the valence electron of an atom, A, must be imagined as occupying a position opposite two positive spheres of A_2 and A_3, so that its lines of force pass simultaneously to the two atoms. It follows that the relatively great extension of the positive spheres hinders any real proximity of the positive charges to the electron attracting them. The value Vg of saturation therefore remains small, and the compound possesses only slight stability. The conception of multiple saturation may be extended to explain molecular compounds by supposing that at one or more points in a stable molecule some of the lines of force, emanating from saturated valence electrons or from positive spheres, may protrude beyond the contour of the molecule. If, now, from some part of a second like or unlike molecule similar lines of force protrude, combination between molecules might result, the positive part of one molecule taking a position opposite the negative part of another and an electrical union taking place. Since only a very small fraction of the lines of force of a saturated valence electron may be imagined as expended in this way, the resulting attraction of the two molecules will be slight. The difference between molecular compounds and crystalline structure is one only of degree. If electric fields of force exist on the surfaces of molecules as well as on the surfaces of the atoms, it may be conceived that, under the influence of these outer fields of electricity, adjacent molecules will seek to orientate in such a way that the negative and positive parts of one molecule shall lie opposite the positive and negative parts of another. If these forces of orientation overbalance in magnitude the energy of the thermic movements of the molecules, there will be established a regular arrangement in the aggregate of molecules, that is to say, crystalline form. In the restricted orientation of positive and negative spheres, within or outside the contour of the molecule, may be found the explanation of varied phenomena—among them the phenomena of tension in Baeyer's sense, and the phenomena of steric hindrance.

Electrical dissociation in metals, gases, and in solution is readily interpreted in terms of the electroatomic theory. It is necessary to distinguish between the movement of ions in solution, of electrons in metals, and of ions and electrons in gases. In all of these cases conceptions are vague regarding the process and the whole matter needs the closest study by both physicists and chemists. Ions may be defined as free moving fundamental units of electricity arising from the separation of electrons from the positive spheres of their atoms. In metallic dissociation, *e. g.*, an unsaturated or partially dissociated valence electron becomes detached from its atom, the residual atom either being isolated or remaining united to other atoms in a molecule. The dissociated electron may remain by itself or may attract to it an electrically neutral atom or molecule. The ease with which dissociation takes place depends upon the relative values of Vu and V_0. If Vu is small as compared with V_0 then even at ordinary temperatures the thermic energy may be sufficient to cause the dissociation of partially dissociated valence electrons. Equilibrium between the dissociated and undissociated phases depends upon the absolute temperature and upon the relation of Vu to V_o, the value V_o being a constitutive property of a compound. In this connection it is interesting to note that saturated compounds of carbon and hydrogen, *i. e.*, the methane and terpene derivatives, show only slight electrical dissociation even at 500°, while benzene, naphthalene, and anthracene, to which on spectro-analytic grounds partially dissociated valence electrons are assigned, show a measurable conductivity, increasing rapidly with increase in temperature. This dissociation is evidently of the same character as that which takes place in metals. Liquid mercury, *e. g.*, shows a noticeable electrical dissociation. It may be therefore multiatomic, with partially dissociated valence electrons. Amorphous carbon shows electrical dissociation while the diamond does not, from which we might infer the presence in the former of partially dissociated valence electrons. It may be added that the heat of combustion of amorphous carbon is greater than that of the diamond.

In electrolytic dissociation it is supposed that the dissociating electron becomes bound to another atom. Ions thus arise, differing as to chemical mass. Their ordered movements, under the influence of the electric current, give rise to the phenomena of electrolysis. In the case of fused salts, it is possible that dissociation limits itself in the sense that the electron of the metallic radical, which is attached also to the metalloid radical, becomes detached *only* from the former without disturbing the integrity of the molecule as a whole. This might happen as a result solely of thermic movements. In the case of dissociation in solution, it is probable that the molecule is broken down, and at the same time the electron of a metallic radical becomes separated from its own radical and attached to the metalloid. Although the reason for this is found in the fact that different chemical atoms bind their electrons with different degrees of force, it is probable that in the case of electrolytes in solution, other factors than thermic movements within the molecule are responsible for the separation. It is likely that the molecules of the solvent enter into reactions with the components of the electrolytes. An *ion* in this case represents a complex formed by components of the dissolved molecule and molecules of the solvent and may be imagined as built up in much the same way as molecular compounds.

The application of the electroatomic theory to phenomena in the field of light is especially interesting, because many of the deductions from theory are here capable of experimental verification. As is well known, a substance is colored if it absorbs light of wave lengths within the limits of the visible spectrum. The light emitted by a colored body may be analyzed by means of a prism and an absorption spectrum may be obtained which is characteristic of the particular substance, and intimately dependent upon its molecular constitution. Since many colorless bodies show light absorption in the ultraviolet and the ultrared, the photographic plate and other devices have been employed, and the absorption spectra of countless chemical compounds have been accurately determined. The application of these results to the determination of the molecular constitution of chemical compounds has been receiving greater and greater attention, especially in the field of organic chemistry, and the question which has arisen as to the cause of the emission and absorption of light has thus come to be of increasing importance. The theory of the electromagnetic origin of light is at present generally accepted, and Stark merely extends this idea when he says that the source of the emission and absorption of light lies in the electrons. As a result of extended experiment it seems probable that the line spectra of the gaseous elements proceed from positive electrical spheres, while the band spectra originate in the movement of negative valence electrons relative to their atoms. The applications of this conception in investigations of the Zeeman effect are interesting. Most striking, however, is the application of the theory to the quantitative determination of the position of the band spectra emanating from (*a*) unsaturated, (*b*) saturated, and (*c*) partially dissociated valence electrons.

(*a*) Stark calculates the value of the potential energy Vu of unsaturated valence electrons as the product of the electric charge and the ionization tension. Taking the ionization tension as 30 volts, this would bring the lower limit for band spectra of metalloids into the region of the impenetrable ultraviolet, $\lambda = 0.06\mu$. Recent investigations, however, seem to show an agreement even among metalloids of an ionization tension of 6 to 11 volts, which brings the band spectra of unsaturated valence electrons into the region of the ultraviolet. In harmony with these deductions from theory, W. Steubing has found examples of band spectra in the ultraviolet in the case of mercury vapor[1] and also of monatomic oxygen.[2]

(*b*) The agreement between fact and theory is even more remarkable, when methods for determining the position of the absorption bands of saturated valence electrons are considered. If the heat of formation of a simple chemical compound has been experimentally determined, it is possible to find the minimal wave lengths of the absorption bands of the substance by the application of Planck's law. Significant calculations have been made in the cases of carbon dioxide and water. If e equals the changed kinetic energy of an electron; c, the velocity of light; λ, the wave length of the emitted radiation, then, according to the fundamental

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[1] *Physik. Z.*, **10**, 787 (1909).

[2] *Ann. Physik.*, 33, 553 (1910).

relation discovered by Planck, $e = \frac{6.55 \times 10^{-27} \times c}{\lambda} = \frac{1.86 \times 10^{-6}}{\lambda}$.[1] If the quantity of energy capable of being transformed into light is known, a minimal value may be calculated for the emitted wave lengths. Since the emission of band spectra takes place as the result of the fact that the potential energy Vu, Vg, V_o, of an unsaturated, saturated, or partially dissociated valence electron, is changed into radiant energy on the reattachment of the electron to the atom, the value $V(Vu$, Vg or $V_o)$ may be substituted for the value e in the equation. But since Vg equals the maximal value of potential energy which is never completely transformed into light, the value actually substituted will be smaller than V and, therefore, the true value of λ will be greater than calculated. In other words the observed wave lengths should always be greater (*e. g.*, lie nearer the red) than the wave lengths calculated, and the truth of this has been experimentally demonstrated.

Carbon dioxide may be regarded as a saturated compound. It must then be assumed that in the carbon dioxide molecule the four negative valence electrons of carbon are saturated by the positive zones of oxygen, and the two pairs of valence electrons of oxygen are saturated by the positive zones of carbon. Eight saturated valence electrons are therefore present in a molecule of carbon dioxide. The molecular heat of formation of the substance from isolated atoms is represented by the energy $4n(Vg^C + Vg^O)$, where n equals the number of molecules. For the gram molecule it amounts to 161660 gram calories; for, according to J. Thomsen,[2] the heat of combustion of isolated carbon equals 135340 and the heat of formation of the oxygen molecule equals 26320 gram calories. If, now, the eight unions are assumed to be equivalent in value, it follows that $nVg = 20207$ gram calories, $= 20207 \times 4.2 \times 10^7$ ergs per gram molecule. And since a gram molecule at zero degrees and 760 mm. pressure contains $n = 1/1.2 \times 10^{-24}$ molecules, $\lambda = \frac{1.86 \times 10^{-16}}{20207 \times 4.2 \times 10^7 \times 1.2 \times 10^{-24}} = 1.93 \times 10^{-4}$ cm. $= 1.93\mu$. Experimental investigation shows that carbon dioxide possesses band spectra, the bands shading toward longer wave lengths, and the edges of the bands having wave lengths $\lambda = 2.6$, $\lambda = 4.3$, $\lambda = 12.5$–16μ. When it is remembered that according to Planck's law only a theoretical lower limit for the position of band spectra may be calculated, and that in reality band spectra must lie considerably above this theoretical limit,—the agreement between the observed and calculated values is indeed remarkable. A similar agreement exists between the theoretical and observed values for the position of the absorption bands of water. And since it is probable that the valence electrons contained in water

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[1] *Physik. Z.*, 9, 88 (1908).

[2] *Thermochem. Untersuch.*, IV, pp. 257, 316.

have the greatest energy of combination possible for saturated valence electrons in any compound ($\lambda = 0.73\mu$), it may be suspected that all band spectra of saturated valence electrons lie above the wave lengths $\lambda = 0.5\mu$, that is to say, in the ultrared. If a chemical compound, therefore, possesses a band spectra under $\lambda = 0.5\mu$, the presence of valence electrons other than saturated ones may be inferred.

In the case of saturated valence electrons Stark distinguishes between the bands of total and partial valence fields. The bands of a total valence field correspond to the rotation of the electron as determined by its position in the molecule relative to the positive zones of its own and another atom. Such bands are of short wave length, and lie for the most part in the ultraviolet spectrum. The bands of a partial valence field correspond to the rotation of the electron *together with its atom*, relative to another atom. Such bands are of long wave length and lie in the ultrared. It must be remembered that it is the acceleration of an electron at certain points in its sphere of rotation, that has as its result the emission of electromagnetic waves, in that the kinetic energy of the moving electron is changed into radiant energy. In order to avoid misunderstanding, attention is expressly called to the fact that the band spectra of saturated valence electrons are a constitutive property of the molecule. The band spectra of the same valence electrons of a given atom are, therefore, different in different chemical compounds; and this may be true even if the electrons are bound in these different compounds to the same kind of atoms. If the energy Vg of union is a constitutive property and dependent upon the configuration of the molecule, it follows that the heat of formation or the heat of combustion is also a constitutive property. This has been shown to be the case in a great number of instances—as, for example, the heat of combustion of propylene equals 492700 gram calories, and that of its isomer, trimethylene, equals 499400 gram calories. If, in a series of different compounds, the homologous combinations of the saturated valence electrons present in them are of equal energy values, it follows that the ultrared absorption spectra of these substances are identical. Experimental proof of this is given by J. Thomsen, who shows that the heats of formation of ethane, propane, butane, etc., are compounded additively of the combinations $H \longleftrightarrow C$ and $C \longleftrightarrow C$; and by W. W. Coblenz, who shows that the ultrared absorption spectra of hexane, octane, dodecane, tetracosane, etc., are identical. In the position of the principal bands, ethane and butane agree with them.

(*c*) It is not possible as yet to make quantitative determinations regarding the spectra of partially dissociated valence electrons. It may, however, be said in general that the potential energy of partially dissociated valence electrons, V_o, is less than the potential energy of unsaturated valence electrons, Vu; and that, therefore, the band spectra of the former should lie above greater minimal wave lengths than those of the latter. If the work done on the valence electron in changing it into a partially dissociated valence electron is equal to a Vu, where a signifies a number less than unity, then $V_o = Vu\ (1 - a)$, and accordingly a may be called the coefficient of the partial dissociation of an electron. From this it appears that the band spectra of partially dissociated valence electrons are pushed further towards the ultrared, the greater the value of the coefficient a. Since band spectra of saturated valence electrons lie above $\lambda = 0.5\mu$, the presence of partially dissociated valence electrons must be suspected in the molecule if a substance possesses a band spectra under $\lambda = 0.5\mu$, and if the substance is not known to be unsaturated. For example, benzene is a substance which according to Stark contains partially dissociated valence electrons, since its absorption bands have their edges at $\lambda = 0.233$, $\lambda = 0.268$. According to the electroatomic theory these bands should not be ascribed to the saturated valence electrons which unite C with C, and H with C, thereby holding together the parts of the molecule. If the symbol $\longleftrightarrow$ represents the union of two atoms by means of saturated valence electrons, and the symbol —o represents a partially dissociated valence electron, then on spectro-analytic grounds the following configurations may be assigned to the benzene molecule. The configuration of Fig. IV is open to the objection that in

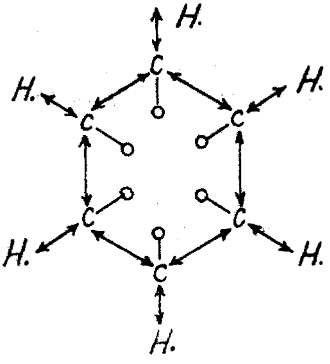

Fig. IV

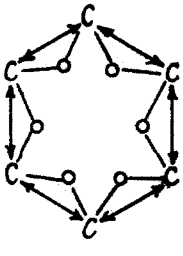

Fig. V

the case of ortho- and meta-substitution products of unlike groups optical isomers are expected. These have been long sought and never found. Kauffmann[1] meets this objection by the configuration represented in Fig. V, which suggests at the same time the formula advanced by Thiele for benzene on the basis of purely chemical investigations. By substitution or condensation the ultraviolet absorption bands of benzene are pushed in the direction of the red, and this, in harmony with the theory,

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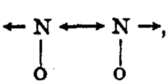
[1] *Physik. Z.*, 9, 318 (1908).

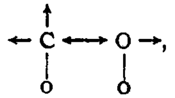
signifies a decrease in the potential energy of the partially dissociated valence electrons, or an increase in the coefficient of dissociation. If benzene is changed into hexahydrobenzene by the addition of hydrogen, the partially dissociated valence electrons become saturated valence electrons. As is to be expected, the characteristic bands in ultraviolet vanish, and absorption is limited to the ultrared.

The treatment of the chromophore theory and the theory of fluorescence from the standpoint of the electroatomic theory is very important, but can be suggested here only in outline. As is well known, the color in colored bodies is dependent upon the presence in the molecule of certain groups called chromophores. These groups are very reactive and are characterized by the properties of unsaturation. In terms of the present theory, they may be defined as groups that contain at least two multivalent atoms, each possessing a partially dissociated valence electron. Since the band spectra of such electrons lie in the visible or ultraviolet portion of the spectrum, color, in the larger significance of the term, must be associated with these groups; and in this sense, the benzene ring, because of its absorption in the ultraviolet, must be regarded as a chromophore as A. von Baeyer has shown.[1] The electroatomic configuration for benzene has been given: a few configurations for other chromophore groups follow:



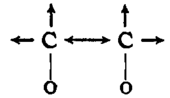
$$\leftarrow \underset{\substack{| \\ O}}{N} \longleftrightarrow \underset{\substack{| \\ O}}{N} \rightarrow ,$$

Azo group.



$$\leftarrow \overset{\uparrow}{\underset{\substack{| \\ O}}{C}} \longleftrightarrow \underset{\substack{| \\ O}}{O} \rightarrow ,$$

Carbonyl group.



$$\leftarrow \overset{\uparrow}{\underset{\substack{| \\ O}}{C}} \longleftrightarrow \overset{\uparrow}{\underset{\substack{| \\ O}}{C}} \rightarrow$$

Ethylene group.

The ethylene grouping is particularly interesting because the carbon atoms are not conceived to be joined by a double band, but by means of a saturated valence electron. The presence of a partially dissociated valence electron on each carbon atom conditions the reactivity of the group. Increase in dissociation of valence electrons increases the energy content of the molecule, so that in the case of stereoisomers, the labile form should give an absorption spectrum of the longer wave lengths. This, and other deductions from theory in this field, have received experimental verification. It would be interesting to consider the applications of the electroatomic theory to the phenomena of fluorescence, but this is not possible now for lack of space.

The subject of valency in the Periodic System forms the last topic for discussion. Proceeding from the idea that the forces of affinity or valency are located on the outer surfaces of the atoms, differences of structure must be assumed for the outer surfaces of the atoms of the different elements, depending upon their position in the Periodic System. Certain laws regarding both the value and quality of valency must be noted, in

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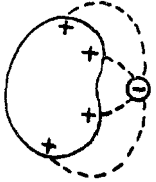
[1] *Z. angew. Chem.*, 19, 1227 (1908).

passing from elements of lower to elements of higher atomic weight. Since one valence electron must be assumed for every valence, the number of such electrons on the upper surfaces of the atoms must be constant for elements grouped together in a vertical series; while in a horizontal series, the number of valence electrons increases by whole units from one to four, and then decreases by whole units to zero. The quality of valency in a vertical series varies in such a way, that the substitution of one element for another in a compound alters the heat of formation of the compound. In terms of the theory the potential energy Vu decreases in any vertical series with increase in atomic weight—that is, the firmness of the union of an electron and its atom is weakened—and this is in harmony with the fact that the electrical dissociation of elements in a vertical series, increases with increase in atomic weight. It may not be decided as yet whether this variation in the strength of union is due to the fact that, with increasing atomic weight, the positive spheres opposite the negative electrons have greater extension, and are therefore a greater distance from the electron; or, whether the positive spheres have almost the same extension, but different inner properties. It should be noted that the strength with which a valence electron is bound to other atoms in the molecule depends not only upon the strength of its union to its own atom, but upon the fact that this union requires a certain volume. This fact alone conditions variations in the quality of valency. Space extension as a property of atoms in a vertical series plays a specially important role in the combinations of multivalent atoms. If a multivalent atom possesses a small volume and, therefore, its valence electrons lie closely together, its union with successive members of another multivalent series becomes more and more difficult, as the atomic weights of these elements increase. It thus becomes evident why, in certain cases, the valency number should not always remain constant in any given vertical series.

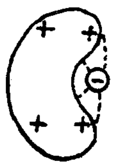
As regards variation of the quality of valency along horizontal series, the theory allows of the following interpretation. From one vertical series to another the strength of the union of a valence electron to its atom varies greatly; and for metallic elements in general, Vu is much smaller than for the metalloids. This is in harmony with observations on the ionization of gases. Thus in electrical dissociation electrons separate more readily from a metallic than from a nonmetallic radical, with the result that the one appears with a positive, the other with a negative charge. In passing from one vertical series to the following along a given horizontal series, the distance of the electron from the positive sphere may be imagined to decrease as new material is added to the atoms. It may even be pictured that to the right of carbon, valence electrons become actually embedded in the surfaces of their atoms. This may take place to such a degree that the neutralizing electrons become so deeply embedded that they no longer emit lines of force beyond the contour of their atoms to other atoms. Figs. VI and VII show atom models as represented in a recent publication.[1] The metal and metalloid elements show great similarity in structure, the difference being in the arrangement of the field of force on their outer surfaces. This conception avoids some of the difficulties of a unitary or a dualistic conception. The protrusion of the negative valence electrons from the surface in the case of the metallic elements, and the receding of valence electrons resulting in corresponding prominence of positive spheres in the case of metalloids, give the character of polarity to the mutual relations of these two groups of elements. Models of multivalent atoms are represented in Figs. VIII to XI. Fig. VIII shows a divalent electropositive atom, as, for example, magnesium; Fig. IX a divalent electronegative atom, as, for example, oxygen; and Fig. X, a trivalent atom, as, for example, nitrogen (the difference in the positions of the electrons may be used to account for the difference between syn- and anti-isomers containing nitrogen).

Fig. VI



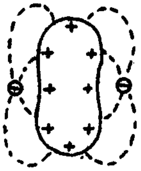
Monoatomic metal (Na).

Fig. VII



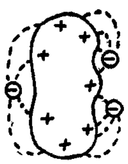
Monoatomic metalloid (Cl).

VIII



IX

X



XI

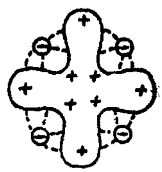


Fig. XI represents the extreme case of an atom, as, for example, of a noble gas, whose valence electrons are so deeply embedded in the positive spheres that their lines of force no longer have the power to unite with the positive spheres of other atoms to form chemical compounds, and the element appears thus to have a valency of zero. Stark has not discussed in this connection the amphoteric element carbon. On the analogy of what has been said, the assumption might be made that the outer surface of this atom presents conditions varying between the electronegative and the electropositive types recalling Michael's phrase "the plasticity of carbon."[2] Or, there might be a definite arrangement of

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[1] *Z. Elektrochem.*, 17, 515 (1911).

[2] *J. prakt. Chem.*, 60, 325 (1899).

the field of force midway between that of a positive and that of a negative element. The latter view would be in harmony with a continuous transition from the strongly electropositive to the strongly electronegative elements.

This paper can only suggest a few of the applications of the electroatomic theory of valence. It has been interesting to see the development of the theory during the past six years, to note its constant increase in scope and its ability to harmonize the most varied and complex phenomena in widely separated fields of science. In conclusion it may be said that none of the hypotheses here advanced claims acceptance without further verification. The aim of the theory is to develop gradually a precise and exact conception, which shall meet the fundamental needs of both physicists and chemists, and this end can be attained only by the earnest and critical coöperation of all investigators.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF JOHNS HOPKINS UNIVERSITY.]

CONDUCTIVITY AND DISSOCIATION OF SOME RATHER UNUSUAL SALTS IN AQUEOUS SOLUTION.[1]

BY CHARLES WATKINS AND HARRY C. JONES.

Received May 29, 1915.

This investigation is a study of the conductivity, temperature coefficients of conductivity and dissociation of electrolytes in aqueous solution. It is a continuation of work begun in this laboratory in 1905,[2] and which has been continued almost without interruption up to the present.

During the past ten years the following investigations bearing on this general problem have been carried out: Jones and Jacobson,[3] Jones and White,[4] Jones and Clover,[5] Jones and West,[6] Jones and Wightman,[7] Jones and Hosford,[8] Jones and Winston,[9] Jones and Wightman,[10] Jones and Springer,[11] Jones and Smith,[12] Jones and Howard,[13] and Jones and

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[1] The results of this investigation will appear in full in *Publ. Carnegie Inst. Wash.*, No. 230 (1915).

[2] *Am. Chem. J.*, 34, 357 (1905).

[3] *Ibid.*, 40, 355 (1908).

[4] *Ibid.*, 42, 520 (1909).

[5] *Ibid.*, 43, 187 (1910).

[6] *Ibid.*, 44, 508 (1910).

[7] *Ibid.*, 46, 56 (1911).

[8] *Ibid.*, 46, 240 (1911).

[9] *Ibid.*, 46, 368 (1911).

[10] *Ibid.*, 48, 320 (1912).

[11] *Ibid.*, 48, 411 (1912).

[12] *Ibid.*, 50, 1 (1913).

[13] *Ibid.*, 48, 500 (1912).