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THE THEORY OF CHEMICAL ACTION IN ELECTRICAL DISCHARGE[1]

THAT slow chemical action accompanies various types of electrical discharge in many gases has been long known. Berthelot[2] summarized and reviewed the earlier as well as his own work, in which the arc, spark or silent discharges were applied to a large number of gases or gaseous mixtures. At that time little or no attempt was made to find a general mechanism or theory. This is not surprising if we remember that almost nothing of our present ideas of discharge in gases was then known. While some of the early results have not been confirmed by later work, most of them have been, and many of the unusual products have also been found in other ways, for example, under *alpha* radiation, proving that the early work of Berthelot, Thenard, Brodie and their contemporaries offers many valuable leads and forms a basis for further progress.

Naturally the first attempts to find a theory for the electrochemical effects in gases were directed toward a correlation between the current flowing and the amount of action produced according to Faraday's law. The disagreement found in the exhaustive researches of Warburg and of others, while unexpected, was so unmistakable that these efforts had to be abandoned.

The theories advanced since then attribute the effects to one of the following agencies: (1) Photochemical; (2) Static ions; (3) Critical activation by kinetic ions. Upon failing to find a relation between current and chemical effect, Warburg quite early adopted the idea that ozone formation, for example, might be due to the ultra-violet light accompanying the discharge. In his review[3] of the subject in 1925 he still adhered to this hypothesis.

The equality of ozonization and ionization of oxygen by means of Tesla discharge convinced Krüger in 1912 of a static-ion theory of ozone formation. Simultaneously a study of ozonization under α radiation led me to the same conclusion, and to a generalization of this theory (as also Krüger) to explain all

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[1] The presidential address, presented at the fifty-third general meeting of the American Electrochemical Society at Bridgeport, Conn., April 26, 1928. Colin G. Fink in the chair.

[2] M. Berthelot, "Essai de Mécanique Chimique," Vol. II, Chap. 11 (Dunod, Paris, 1879).

[3] *Zeit. f. techn. Physik.*, 1925, p. 625.

cases of excess of chemical action over current prediction in gaseous discharge, which excess Warburg had shown might readily reach 1,000 fold.

The central hypothesis of the static-ion theory is that the chemical action is the direct result of recombination of positive and negative ions in the bosom of the gas, which never reach the electrodes and hence can have no relation to the current. In fact this represents in some respects a complete antithesis to the conditions of electrolytic reaction. In electrolysis it is the ions which conduct that react chemically, while in gaseous discharge it is the ions that recombine without conducting that react chemically; possibly the ions which conduct also react chemically at the electrodes, but their proportion is a negligibly small part of the total ionization under usual conditions of chemical action in gaseous discharge. In other words, an intensity of ionization that corresponds to measurable chemical action on a basis of equivalence is far outside the range in which saturation current can be produced or even approached. Any attempt to attain saturation by applying more voltage simply produces more ionization by electronic collision, and defeats its purpose by a yet wider margin.

Not only is it impossible to measure the total ionization accompanying electrical discharge through gases, but the theory of the discharge is so imperfectly understood that we are not able to calculate any comparison of the chemical yield with ionization in gaseous discharge.

The question must arise then: Is it important to establish this yield factor? The answer must be affirmative from several standpoints. The information gained about the chemical yield per ion in other types of ionization, especially by *alpha* radiation, has indicated that it is a fundamental constant for a given reaction. We also have much evidence, which is rapidly being strengthened, that the nature of the reaction and of the products is the same for different types of ionizing agencies. This is just what we should expect if the reactions are due to ionization, that the means of producing the ions ought to make no difference, or at least only secondary differences in the character of the reaction.

If this principle can be thoroughly established, then we can reverse the process and use a reaction of known chemical yield per ion to determine the ionization in electrical discharge. This suggestion applies equally well to the high-speed electrons from a Coolidge tube, or to any other ionizing agencies that produce chemical effects, excepting, of course, those types such as arc or spark discharge when temperature effects intervene. If the chemical yield per ion-pair remains constant for a given reaction, whether this ionizing agent be α rays, β rays, X-rays or heavy recoil atoms, there is no reason to foresee that it will not also be true in ionization by electronic discharge.

It has been quite certain for some time that chemical action produced by α rays is not only proportional to, but strictly equivalent to, the ionization. This equivalent is not equal to the Faraday equivalent, but greater within restricted limits. Since for nearly all α ray reactions the value of M/N[4] exceeds unity, usually having values between 2 and 20, we must assume some kind of multiplying process which acts either collectively or successively. The former seems more likely as a working hypothesis, so that we may assume ion clusters, for the existence of which there is also some physical evidence.

Unfortunately, the positive ray method, which gives us the most definite information about gas ions, is not applicable to the study of ion clusters, because it can be operated only at very low pressures, where the collisions necessary for clustering can not occur, and where the clusters if once formed would probably dissociate. Another general method, that of studying ions by means of their velocity of migration in a field, has not proved satisfactory in obtaining the mass of ions. Therefore the chemical method once firmly established may prove to be the best method of studying clustering.

The clustering hypothesis of mechanism of chemical action produced by gas ions may be briefly stated as follows: When a gas molecule is ionized by having one of its electrons removed, a minimum amount of work is required, which regarded thermally is very large, 10 to 20 electron-volts (or 230,000 to 460,000 calories per mole.) for different gases. This leaves a positive ion possessing a large amount of latent energy, and which owing to its charge will exert an induced attraction on neutral molecules that approach or collide with it, thus forming an ion cluster while still retaining its positive charge.

We do not know precisely the size of these clusters nor the efficiency of collision in clustering, but the chemical M/N ratios give a minimum—probably a critical—value for the portion which we may call the *chemical cluster;* while the physical cluster may be larger, and possibly is in dynamic (not kinetic) equilibrium with the colliding neutral molecules and is hence variable rather than critical in size. When the free electron or, in case a gas with electron affinity is present, the negative ion or cluster again unites with the positive cluster, the high energy of ionization is set free, and the cluster either dissociates to the original components (the energy being kinetically degraded to heat) or it may dissociate partly or wholly into the

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[4] M/N is the chemical yield per ion-pair, M being the number of molecules reacting for N ion-pairs produced.

elements or into new products of higher heat content, or may be largely stabilized to a product of high molecular weight. The heat of ion-recombination is either radiated[5] away or carried off by some of the molecules from the cluster.

The following empirical rules have been found for the size of that part of the cluster which reacts chemically, that is, for the M/N ratio. (1) In gaseous systems of one component with no affinity for free electrons, $M/N = 2$ (approximately), which means first a positive cluster of about two molecules, which reacts chemically upon being restored to electrical neutrality by the free electron. (2) In gaseous systems of two components one of which is oxygen and the other an oxidizable substance, $M/N = 2 \times$ (simplest stoichiometric reaction formula), one cluster belonging to the positive ion and the other to the negative (oxygen) ion. (3) In unsaturated compounds M/N is usually greater, lying in the region 5 to 20 molecules per ion-pair, the direct products being liquid or solid, confirming a high degree of clustering.

Recent work[6] on the effect of different kinds of electrical discharge, on ethane and on propane gases, has shown that the products both gaseous and liquid are quite similar to those obtained from the same gases by α radiation. Lower hydrocarbons are condensed to higher ones by the elimination of hydrogen or methane, with the formation of some liquid hydrocarbons. In the action on ethane in a Siemens tube, the ratio of methane to hydrogen liberated was quite close to that found for the condensation of ethane, propane, or butane under α radiation.

This makes it evident that the reaction has the same character and general mechanism in both cases, and if due to ionization, as is very probable for the α ray cases, then ionization must also be the primary step in chemical action under electrical discharge. Further we may predict that the character of the reaction should be more or less independent of the type of discharge, which we have found to be the case. Some secondary differences are found. For example, the more disruptive the type of discharge the more tendency there is for liberation of free carbon, and for the formation of insoluble solid hydrocarbons.

All of the predictions made from the α ray results, however, have been so thoroughly supported by the subsequent experiments in electrical discharge, that it seems safe to assume the same general kind of mechanism in both cases.

The acceptance of the static-ion mechanism of reaction in discharge has, however, not been general, perhaps mainly due to the lack of a knowledge of the ionization in order to evaluate the equivalence (M/N ratio). The conditions in electrical discharge are much more complicated than in ionization by radon, and suffer from the great disadvantage that the generation of ions is dependent on the field, and at any pressure above a few millimeters varies with it in a very complicated way.

Even in the α ray work some authorities have felt that it ought to be possible to demonstrate directly the chemical effect of ionization by diminishing or increasing in some independent way the number of ions, and correspondingly the number of molecules made to react. This is however quite impossible, because we have no means of adding more ions, from an independent quantitative source, to the intense ionization already necessary to produce a measurable rate of chemical action. Nor is it possible, as we have seen, to withdraw any considerable fraction of the ions, since such high fields must be applied that a larger but unknown quantity of new ions is at once produced.

The recent success of applying the quantum theory in various directions, especially to photochemistry, has frequently led to the belief that although the reactions under discussion are accompanied by and are proportional to ionization, they must, however, be directly caused by *excited* rather than by ionized molecules. It is sometimes lost sight of that ionization itself represents a wholly quantized as well as a highly energized state, and that there is every theoretical reason to believe that ions are equally if not more reactive chemically than excited molecules, because on account of the high electrical field of ions they exert a larger sphere of influence. We have then just as good reason to expect that the quantum law should apply to ionic-chemical as to photochemical reactions and, as a matter of fact, we have been successful in demonstrating its application in many cases, and without the prevalence of the marked exceptions which characterize the experimental tests of the Einstein Law.

The principle of a third theory, recently proposed from Prof. Donnan's laboratory by Elliott, Joshi and Lunt,[7] might be identified with excitation, though apparently it originated from analogy with a yet less energetic type of activation. They postulate that the concept of "critical activation" may be applied to chemical action in electrical discharge. They assume, as in the collision theory of chemical activation, that the reaction rate is a function of the kinetic energy of the constituent particles, and that it is im-

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[5] F. L. Mohler, *Phys. Rev.*, 31, 187 (1928).

[6] Lind and Glockler, *Trans. Am. Electrochem. Soc.*, 52, 37 (1927).

[7] G. A. Elliott, S. S. Joshi, and R. W. Lunt, Trans. Faraday Soc., 23, 57–60 (1927).

material whether the kinetic energy be of thermal or of electrical origin. According to this idea the activating energy might be the sum of kinetic energies of thermal and electrical origin. It would therefore be interesting to see whether reaction in electrical discharge has a positive temperature coefficient, as would be predicted by the theory. Many of the reactions under α radiation do not have, thus supporting a static rather than a kinetic-ion theory.

Based on the hypothesis of the kinetic action of ions, Elliott, Joshi and Lunt developed an equation which it seems would apply equally well for activation by either ions, excited molecules or kinetically activated molecules. Two kinds of experimentation might give a decision in the case of electrical discharge: evaluation of the proportionality factor, as in the determination of M/N or $M/h\nu$ values, or else by increasing the speed of homogeneous electrons until reaction begins. The difficulty of the former has been discussed. Work of the latter kind[8] on the reduction of CuO by H_2 gave no indication of reaction until the excitation potential of H_2 (11.4 volts) was reached, while Storch and Olson[9] and Andersen[10] found no synthesis of ammonia in low voltage arc until the ionization potential of nitrogen (17 volts) was reached.[11] Neither of these results supports the view that electrons produce chemical activation at low speed corresponding to critical activation potential—about 2 volts or 45,000 cal.

Hutchinson and Hinshelwood[11] have also recently investigated in a different way the possibility of a parallelism between electrical and thermal reaction mechanisms. They determine the relative decomposition of N_2O and NH_3 gases in two similar discharge tubes, connected either in series or in parallel. Their results were hardly those to be expected from kinetic activation nor from thermodynamics, but appear to be capable through the following analysis of affording strong support of the ion-cluster hypothesis. They find under parallel conditions that about 4.8 to 7.6 times as many molecules of N_2O are decomposed as of NH_3. The electrode material made little difference, and the rates were first order with respect to pressure, both of which indicate reaction in the gas phase.

While we have rather meager information about the relative chances for different molecules to be ionized in a stream of electrons under potential fall much greater than the ionization potential, it seems probable that the relative ionization of two gases might be about the same as for ionization by α particles. Therefore we may expect at the same pressure in equal electron streams (approximately the same current) that N_2O would be ionized $1.53/0.81 = 1.9$ times more than NH_3.

Furthermore, if the ions produced are of the same character as those from α particles, we may assume that the chemical yield per ion pair will be equal for each reaction to the ion yield in α radiation, which from Wourtzel's[12] results at 18° is 0.8 for NH_3 and 1.74 for N_2O or a ratio $1.74/0.8 = 2.2$. Both of these factors operate in the same direction, to make the decomposition of N_2O $1.9 \times 2.2 = 4.2$ times that of NH_3, which approximates the factor found experimentally by Hutchinson and Hinshelwood.

It should be emphasized that the relative ionization of two gases is not directly related to their ionization potentials, but is as shown by Glasson, proportional to $Z^{2/3}$ (Z = atomic number), or to the cross-sectional density of orbital electrons in the molecules through which a stream of α particles (presumably also a stream of electrons) is passing. For example, the ionization potential of NH_3 is 11.1 volts, while that of N_2O (hitherto not determined) should according to Eve's rule be about the same as that of CO_2, or about 14 volts, which in itself would give no grounds to expect that N_2O would be more readily decomposed than NH_3. Nor could we expect that N_2O on account of a higher ionization potential would be less frequently ionized than NH_3, because the electrons in Hutchinson and Hinshelwood's experiments are produced by an induction coil, and hence move under voltages far above the ionization potentials.

Claims that reaction in electrical discharge may be attributed to excitation rather than ionization have also been made. On a reexamination of the yield of O_3 per ion-pair, Krüger and Utesch[13] estimate from new experiments a yield of 30 to 40 O_3 molecules per ion-pair which they attribute to excitation. Owing, however, to later confirmation[14] of the ion yield in ozone formation under α radiation as $M_{O_3}/N = 1 \text{ to } 2$ and to the uncertainty of the measurement or calculation of ionization in electrical discharge, we are not prepared to accept the high yield as definite.

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[8] Geo. Glockler, W. P. Baxter, and R. H. Dalton, *J. Am. Chem. Soc.*, 49, 58 (1927).

[9] H. H. Storch and A. R. Olson, *J. Am. Chem. Soc.*, 45, 1605 (1923).

[10] E. B. Andersen, *Z. Phys.*, 10, 54 (1922).

[11] W. K. Hutchinson and C. N. Hinshelwood, Proc. Roy. Soc., 117A, 131–6 (1927).

[12] E. Wourtzel, *Jour. de Phys. Rad.*, 11, 341, 345 (1919).

[13] F. Krüger and O. Utesch, *Ann. d. Physik.* (4), 78, 113–56 (1925).

[14] J. D'Olieslager, *Acad. Roy. Belg.*, 1925, 711; Mund and D'Olieslager, *ibid.*, 1926, 309; *Bull. Soc. Chim. Belg.*, 36, 399 (1927); Lind and Bardwell, "Chemical Effect of Alpha Particles," 2d Ed., p. 92. Chem. Catalog Co., N. Y., 1928.

Finally, I should like to discuss briefly the mechanism of condensing lighter to heavier (condensed or polymerized) molecules either thermally, catalytically, photochemically or electrically. It appears that all of these methods have something in common, though the mechanisms that have been proposed may be differentiated into two quite distinct classes. (1) Primary reaction consisting of clustering followed by splitting (when it takes place) or (2) Primary reaction consisting in first splitting followed by a reassembling of the elements or radicals.

Of these two processes the former has appeared more plausible in conceiving mechanisms for the ionic reactions, and it has recently been suggested[15] that it may also be plausible in some photochemical processes. The hydrocarbon gases, for example, which were formerly thought to be quite difficult to change one into another, have only recently been shown to have great facility, for such changes. H. A. Wilson[16] has proposed, and thermodynamically supported, thermal equilibria of the type

$$2C_nH_{2n+2} \leftrightarrows C_{n+1} + H_{(n+1)2+2} + C_{n-1}\ H_{(n-1)2+2}$$

according to which, ascension in the hydrocarbon scale can be accomplished only by production of an equal number of molecules of lower molecular weight.

It is possible that this type of condensation may occur also in electrical discharge, but apparently more pronounced types predominate, which consist in doubling or multiplying through the elimination of one product of very low molecular weight (H_2 or CH_4) which evidently allows the other product to be correspondingly higher. To illustrate: thermally, according to Wilson, $2C_4H_{10} \leftrightarrows C_3H_8 + C_5H_{12}$; while ionically, according to Lind and Bardwell,[17] $C_4H_{10}^+ + C_4H_{10} = C_8H_{18} + H_2$
or also

$$C_4H_{10}^+ + C_4H_{10} = :C_8H_{16} + 2H_2$$

and

$$x :C_8H_{16} = (C_8H_{16})_x \text{ (liquid).}$$

Evidently the ionic processes arrive more directly at the product of higher molecular weight, but with a much higher energy expense.

A mechanism by which building up of large molecules is effected by clustering, followed by partial splitting, seems more plausible than to assume that the splitting occurs first and building up subsequently. This may apply to some photochemical as well as to ionic syntheses.

Referring to the statement of Elliott, Joshi and Lunt (*loc. cit.*) that, "Despite the numerous investigations that have been made on chemical changes produced by an electric discharge through a gas, no satisfactory general hypothesis has yet been suggested to describe the mechanisms of such changes," I should say that the fault lies rather with the inadequacy of the theory of electrical discharge in gases than with the hypothesis of the nature of the chemical changes produced. As long as we can neither measure nor calculate the ionization, any theory based on ionization must lack quantitative support and depend on indirect evidence, although it may later prove to be a correct theory. Proof that the velocity of reaction (K) is related to the pressure (p) at constant current by a linear relation of p to log K/p would be equally true for the static-ion theory, since p must have a double function in determining the energy received from the electron stream (by any mode whatsoever—ionization, excitation or critical activation) and again in determining collisions between energized and ordinary molecules in the completion of the chemical reaction.

To review the two theories more generally, it would appear that if enough energy has already been expended to produce ions, a very large amount of latent energy is possessed by the ions, so that they need no additional kinetic energy to make them reactive toward other molecules. The only way to disprove this by energy considerations would seem to be by showing that a larger amount of action is accomplished than can be accounted for on the cluster theory. This involves evaluation of the proportionality factor which for electrical discharge has not yet been done and, as we have seen, can not be accomplished until the ionization can be determined. But if we may reason by analogy from the α ray results, static ions without any kinetic energy (resulting from a field) are quite sufficient, and the yields found do not exceed the possibilities of clustering. That the α ray results for the hydrocarbon gases may be applied by analogy to the chemical action of *electrical discharge* in the same gases has already been discussed.

Continuation of the work reported at the last meeting of the Society has yielded further confirmation of the ion cluster theory. By controlling the conditions of condensation[18] the average molecular weight of the liquid product from ethane has been lowered from 467 to 120.

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[15] Lind, *J. Phys. Chem.*, 32, 575 (1928).

[16] H. A. Wilson, Proc. Roy. Soc., 116A, 501–15 (1927).

[17] *J. Am. Chem. Soc.*, 48, 2346 (1926).

[18] Lind and Glockler, *J. Am. Chem. Soc.*, 50, June (1928).