

SCIENCE

VOL. LXIV

JUYL 2, 1926

No. 1644

CONTENTS

<i>The Ionization of Gases as a Type of Chemical Activation:</i> DR. S. C. LIND	1
<i>Sigma Xi in Research:</i> DR. BIRD T. BALDWIN	6
<i>Ezra Townsend Cresson:</i> PROFESSOR PHILIP P. CALVERT	8
<i>Scientific Events:</i>	
<i>The Scientific Jubilee of Charles Richet; Field Excursion of Ohio Geologists; Legislation against the Teaching of Evolution in Louisiana; The Golden Jubilee of the American Chemical Society; The Fifth Philadelphia Meeting of the American Association and Associated Societies</i>	9
<i>Scientific Notes and News</i>	11
<i>University and Educational Notes</i>	15
<i>Discussion:</i>	
<i>The Term Psychozoic:</i> PROFESSOR E. W. BERRY.	
<i>The West Fork of the Gila River:</i> FRED WINN.	
<i>Size Inheritance:</i> R. J. GARBER. <i>Fundamentalism in North Carolina:</i> B. W. WELLS	16
<i>Quotation:</i>	
<i>Leaders in Medicine</i>	18
<i>Scientific Books:</i>	
<i>Holmes on Life and Evolution, Newman on Evolution, Genetics and Eugenics, Shull on Heredity, and Hurst on Experiments in Genetics:</i> PROFESSOR W. E. CASTLE	18
<i>Scientific Apparatus and Laboratory Methods:</i>	
<i>The Measurement of Surface Tension by Means of a Chainomatic Balance:</i> L. W. DURRELL, FRED G. PERSON, CHARLES F. ROGERS	20
<i>Special Articles:</i>	
<i>On the Elimination of Heat from Normal and Pathologic Subjects:</i> DR. CHARLES SHEARD.	
<i>Chromosome VIII in Maize:</i> DR. WILLIAM H. EYSTER	21
<i>Science News</i>	x

SCIENCE: A Weekly Journal devoted to the Advancement of Science, edited by J. McKeen Cattell and published every Friday by

THE SCIENCE PRESS

Lancaster, Pa.

Garrison, N. Y.

New York City: Grand Central Terminal.

Annual Subscription, \$6.00. Single Copies, 15 Cts.

SCIENCE is the official organ of the American Association for the Advancement of Science. Information regarding membership in the Association may be secured from the office of the permanent secretary, in the Smithsonian Institution Building, Washington, D. C.

Entered as second-class matter July 18, 1923, at the Post Office at Lancaster, Pa., under the Act of March 8, 1879.

THE IONIZATION OF GASES AS A TYPE OF CHEMICAL ACTIVATION¹

"CHEMICAL activation" is a generic term embracing the various processes by which substances are brought into a state of chemical activity. The use of this term is by no means new, but the intense investigation of the subject during the past ten years may be regarded as a recognition of the incompleteness of our knowledge of one of the fundamentals of chemistry.

We are by now fully aware of what earlier was not so apparent that the commonest and most useful type of activation, that of temperature influence, is the most complex of all in point of theory. The numerous attempts to relate temperature coefficient of velocity of reaction through the internal radiation theory, or to explain it in other ways have at best left the subject in an unsatisfactory condition. However, it is not my purpose to discuss these attempts but to take up one of the simpler types of activation.

Of the non-thermal modes of activation, besides contact catalysis we have the various radiant forms, including photochemical rays and the different kinds of corpuscular streams which may be made to act on gaseous systems. The primary activated products of these various radiative agencies may be classified as free atoms, excited atoms or molecules, and ionized atoms or molecules. In ionization an electron is entirely removed from an atom or molecule, thus producing negative and positive charges which are capable of quantitative measurement by electrical discharge methods. Uncharged atoms do not have any properties by which their concentrations can be so definitely determined. For this reason, if we apply a source of energy so as to produce a known quantity of ions in a given system, in which the chemical reaction produced can also be measured, we are in a position to establish more accurate and definite relations between primary activation and resulting chemical action than has been done in any other type of activation.

In electrolysis, the ratio of discharge of ions at the electrode to chemical action produced is expressed in Faraday's law. In an ionized gaseous system where no field is imposed and hence no current flow-

¹ Address at the presentation of the W. H. Nichols Medal by the New York Section of the American Chemical Society, March 5, 1926.

ing, the ions are discharged, not at an electrode, but throughout the bosom of the gas by a process of recombination of the positive and negative ions. This process is not extremely rapid because of the low momentary concentration of the ions. A given ion, positive or negative, exists long enough to make a large number of kinetic collisions with the electrically neutral molecules. Owing to the electrostatic field about the ions they exert an attraction toward molecules which they encounter and thus are not only chemically active themselves but also become activating centers by drawing neutral molecules into ionic clusters. When a positive ion cluster thus formed encounters a negative ion cluster or a free electron, electrical neutrality is reestablished. The neutral cluster is then subject to the forces of ordinary chemical valency, and may become stabilized as such, or may break down into simpler compounds or elements, or may even polymerize to form higher molecular compounds. We find these various types of behavior represented by different chemical systems or even occurring simultaneously in the same system. The important point is that gaseous ions are chemically active and cause reactions to take place equally well at ordinary or low temperature as at the higher temperatures usually required. Thus we eliminate the complicating influence of temperature. In the second place, the ion acts only once, the clusters are not catalyzing centers capable of causing, by a process of repetition, a large amount of reaction without being themselves changed, as in contact catalysis. The ion clusters formed are stable only as long as they are charged, and on neutralization then take their final chemical states and become again inert without setting up a reaction chain. Thus the number of molecules entering into reaction per one ion-pair is a small and definite one. If the number of molecules reacting in unit time is M and the number of ion pairs formed in the same time is N , the ratio M/N expresses the relation of the chemical activity of the ions, and has been found to vary for different reactions between narrow limits, about 0.5 up to about 20, with a marked peak in the region of 2 to 6.

Since the gaseous ions, unlike electrolytic ones, continually destroy themselves by recombination, it is necessary in studying their chemical effects to have a source of energy that will continue to generate them in known quantity. Electrical discharge is the most ready source of gaseous ions, but has for our purpose the fatal disadvantage that the ionization produced by it can neither be measured nor accurately estimated. Quite a different source has been found suitable; namely, the ionization produced by alpha particles from radioactive material, the most convenient form of which has proved to be radon

(radium emanation) in equilibrium with its decay products.

Radon has the advantage of very small gaseous volume for very large radiation; hence it can be distributed evenly in any system and does not appreciably absorb its own alpha rays. It may be employed in two ways: (1) by mixing it directly with the gases to be acted on; (2) by confining it over mercury in a small thin glass bulb of 1 to 2 mm diameter and a few thousandths of a mm thick, which transmits the alpha particle with but a small loss of its energy.

By examining such an alpha ray bulb containing radon, one perceives in its immediate vicinity a distinct odor of ozone, due to the action of the alpha rays on the oxygen molecules of the air.

An alpha ray is the doubly charged nucleus of a helium atom ejected from the nucleus of a radioactive atom with a velocity of one fifteenth to one twentieth that of sunlight, or nine to twelve thousand miles per second. When a particle of atomic dimensions is moved with so high a velocity, a tremendous amount of kinetic energy is available. The particles travel in all directions in straight lines through a large number of gaseous molecules, expending their energy by tearing off electrons, each particle producing in its path about two hundred thousand ion-pairs in the form of singly charged and probably molecular ions. The negative electrons thus liberated later recombine with the positive ions, to reestablish electrical neutrality as has already been described. If the gaseous medium be a mixture of gases, each one will be ionized in proportion to its partial pressure and its own specific ionization. The ion clusters then formed will contain more than one molecular species which may be thus brought into chemical interaction.

If a gas is present with affinity for free electrons, union will result in the formation of negative ions. Both positive and negative ions have the property of clustering neutral molecules about them. We do not know definitely the size of these clusters, but we shall have occasion to examine the chemical evidence for certain minimum values.

Returning to the case of ozone, if we mount one of the thin bulbs at the center of a sphere six cms in diameter and surround it with pure oxygen, we can fully utilize the ozoning power of the alpha rays, which will then spend themselves in oxygen in all directions. If the ionized oxygen is passed through a KI absorbing system we can measure chemically the number of ozone molecules formed (M_{O_3}). If the quantity of radon in the small bulb is measured by comparison with the gamma radiation from a known quantity of radium, we will know the number of alpha particles being emitted. Thirty-seven billion

are emitted per second from one curie of radon and an equal number from each of the decay products, RaA and RaC. Then by making allowance for the small loss of path in the thin glass wall, the length of path in oxygen and consequently the number of ion-pairs formed in oxygen can be calculated from a knowledge of the ionization per length of path.

Such an experiment² gave a value of $\frac{M_{O_3}}{N_{O_2}}$ in the neighborhood of unity. This surprising agreement of ionization and ozonization not only strongly suggested an ionic mechanism of ozone formation but raised the question whether a similar relation might not apply in other gas reactions.

Previous to the ozone experiments, Sir William Ramsay and A. T. Cameron³ in London had made a systematic examination of a number of gas reactions employing radon directly mixed with the reactant gases. They used the manometric method of determining the rate of reaction. In order to magnify the pressure change they employed rather small reaction vessels of only a few cc in volume, in which the alpha particles do not complete their paths in the gas but expend most of their energy in the glass wall of the container, where it contributes nothing to the chemical action. This principle is still found very useful, in spite of its inefficiency of utilization of the alpha rays.

The law which Cameron and Ramsay formulated did not deal with ions nor even with alpha particles. They contented themselves in establishing the relation that the rate of reaction in a given volume is proportional to the quantity of radon (E) present at any time t , which rate may be expressed in terms of pressure change by the simple formula:

$$\frac{dP}{dt} = cE_t,$$

where c is a velocity constant. When it is recognized that it is the alpha particles emitted, not the radon atoms themselves which cause reaction, we realize at once that while the law of Cameron and Ramsay is valid for liquid systems, where the concentration of the reactant remains unchanged as in the decomposition of water by radon, the case is different in a gas where the pressure is changing. As the gaseous pressure of the reactants is diminished by the progress of the reaction, the alpha particles encounter fewer molecules along their paths, hence the rate of reaction is proportional also to the changing pressure P_t . This gives a more complete form of law:

$$\frac{dP}{dt} = cE_t \cdot P_t \quad (1)$$

² Lind, *Amer. Chem. Journ.*, 47, 397-415 (1912); *Monatsh. f. Chem.*, 32, 295-310 (1912).

³ Cameron and Ramsay, *J. Chem. Soc.*, 93, 966-92 (1908).

The rate of the production of ions is also proportional to the same two factors:

$$\frac{dN}{dt} = kE_t \cdot P_t \quad (2)$$

$$\text{or } \frac{dN}{dt} = 3 \times 3.7 \times 10^{10} \cdot E_t \cdot 2.5 \times 10^4 \text{ p.i.P/760} \quad (2a)$$

The identity of the two expressions (1) and (2), except for the proportionality factors, would indicate a causal dependence of chemical action on ionization, the same conclusion as was first reached from the ozone work.

$$\text{Therefore, } \frac{dP}{dt} = \mu \frac{dN}{dt} \quad (3)$$

and since $E_t = E_0 e^{-\lambda t}$, by combining (2) and (3) and integrating, we have a general velocity equation:

$$\frac{k\mu}{\lambda} = \frac{\log \frac{P}{P_0}}{E_0(e^{-\lambda t} - 1)} \quad (4)$$

Or in calculating from one interval to the next:

$$\left(\frac{k\mu}{\lambda}\right)' = \frac{\log \frac{P_1}{P_2}}{E_0(e^{-\lambda t_1} - e^{-\lambda t_2})} \quad (5)$$

in which λ is the decay constant of radon. In simplest terms, $\frac{k\mu}{\lambda}$ is a velocity constant, composed of three other constants; k embodies all the constant factors of (2a) with reference to ionization; μ and λ have been defined. In actual numerical value $\frac{k\mu}{\lambda}$ is

the number of times that a given volume of gas would be "cleaned up" by the decay of 1 curie of emanation, while the pressure is held constant in that volume by feeding in fresh gas continuously. The equation is applicable to vessels of any shape or size in which no dimension exceeds the range of the shortest alpha particles, but the constant k will change with the shape and volume of the container; therefore, for convenience in calculating the average path of alpha rays, we have used spherical vessels only. Both k and μ are also dependent on the nature of the gas or gaseous mixture. The function of volume is to increase the effective paths linearly with the diameter, but since the pressure effect will diminish with the volume, i.e., with the cube of the diameter, velocity constants expressed in terms of pressure change will diminish in value with the inverse square of the diameter.⁴

The apparatus used in my earlier work⁵ had two or three disadvantages. The large mercury surface exposed in some cases caused a secondary reaction of mercury with one of the components. The apparatus could not be conveniently placed in a thermostat.

⁴ Lind and Bardwell, *J. Am. Chem. Soc.*, 46, 2005 (1924).

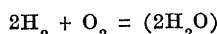
⁵ *J. Amer. Chem. Soc.*, 41, 535 (1919).

In that connection it should be mentioned that ionization by alpha rays is independent of temperature; correspondingly we find most of the ionic-chemical reaction rates independent of temperature, but occasionally some influence of a secondary character is observed, so that all of our recent work is done at 25° C. In the later type⁶ the earlier disadvantages are corrected and in addition a vacuum manometer is provided for the lower ranges of pressure measurement.

It would be impossible to consider in detail all the forty or fifty reactions that have been studied. The kinetics of water synthesis may be considered as a typical case, prior to reviewing briefly the principal features of some of the other reactions we have studied.

The data for water synthesis (Table I) show that the velocity equation (5) applies over a wide range of pressure. Since the constant $\frac{k\mu}{\lambda}$ is calculated from interval to interval, the test is a severe one. A distinct rise in constants is observable toward the end of the reaction. This is due to the relative predominance of the chemical effect of the recoil atoms at low pressures. Correction for this effect has been made in the M/N column where a more satisfactory constant results.

TABLE I
SYNTHESIS OF WATER BY α -RAYS OF RADON



Temp. 25° C.

Reaction Sphere { Vol. = 3.772 cc. $E_0 = 0.1062$ curie
Diam. = 1.932 cm.

Time		P (2H ₂ + O ₂) mm.	$\frac{k\mu}{\lambda}$	$\frac{+M(\text{H}_2\text{O})}{N(\text{H}_2 + \text{O}_2)}$
Days	Hours			
0	0	1115.1		
0	4	1039.1	22.4	3.48
0	22.13	740.1	25.9	3.93
1	2.0	687.9	28.4	4.27
1	23.13	505.3	24.10	3.60
2	22.63	365.6	26.8	3.94
3	22.88	278.5	26.1	3.74
5	0.08	217.7	27.5	3.74
6	23.75	143.1	32.7	4.10
8	23.17	101.1	38.02	4.26

Weighted Ave. = 3.85

The condition that the specific ionization of the mixture remain constant is satisfied by electrolytic gas (2H₂ + O₂), because water is continually removed from the system by condensation, and the proportion

⁶ *Ibid.*, 47, 2679 (1925).

of H₂ to O₂ remains 2:1. If we start, however, with excess of either component,⁷ this is no longer true, and the departure is greater the farther the reaction progresses. If we start with excess of H₂ the constants are lower and fall as the reaction proceeds because the proportion of hydrogen is increasing, and since hydrogen has a specific ionization of only about 1/5 that of oxygen, the ionization of the mixture per unit path of alpha particle diminishes rapidly with increasing proportion of hydrogen. If we begin with excess of oxygen the opposite is true; the constants start high and tend to rise.

The last column of Table I shows the number of water molecules synthesized per ion-pair produced in

the mixture, $\frac{+M(\text{H}_2\text{O})}{N(\text{H}_2 + \text{O}_2)}$. This value, unlike the

velocity constant, has been found to be independent of the variation of the ratio H₂/O₂, which demonstrates a very important principle: the ions of either component are equally efficient in producing chemical action and the reaction mechanism and ionic efficiency are independent of the reaction mixture. As a corollary from this it is evident that only one component need be activated, though both are activated by α -radiation. This principle has been demonstrated for a number of other reactions.

From the M/N ratio we may at least speculate about reaction mechanism. Around a positive ion, either O₂⁺ or H₂⁺, a stoichiometric cluster is formed (H₂·O₂·H₂).⁺ Perhaps the cluster while charged is much larger, but the stoichiometric portion alone reacts chemically; if other H₂ and O₂ molecules are attached to the charged ion, they slough off unchanged when it is neutralized. A similar cluster (H₂·O₂⁻·H₂) is formed about a negative O₂⁻ ion. Since H₂ has no affinity for free electrons no H₂⁻ ions are formed, but all the electrons formed by ionization of hydrogen will be seized by the O₂ molecules, so that full utilization of both positive and negative ions results. Finally the positive and negative clusters recombine in the ordinary way: (H₂·O₂·H₂)⁺ + (H₂·O₂⁻·H₂) = 4H₂O, in agreement with experiment. Slight deficiency below 4 may be accounted for by cross reactions before the clusters are complete, such as (H₂·O₂·H₂)⁺ + (-) = 2H₂O; or (H₂O₂)⁺ + (-) = H₂O₂, etc. The actual formation of H₂O₂ by alpha rays up to considerable percentages was observed by Scheuer.⁸ Taylor⁹ has recently produced H₂O₂ quantitatively in 100 per cent. purity by the action of mercury vapor activated by resonance of the 2537 Hg line on an H₂-O₂ mixture.

⁷ *J. Am. Chem. Soc.*, 41, 542 (1919); "Chemical Effects of Alpha Particles," New York, 1921, pp. 107-110.

⁸ O. Scheuer, *Comp. rend.*, 159, 423 (1914).

⁹ H. S. Taylor, unpublished results by private communication.

The conclusions as to the ionic mechanism of water synthesis have not been drawn from that reaction alone but also by analogy from a large number of other reactions. We may consider briefly, two of them, closely related to water synthesis—the oxidation of carbon monoxide and of methane. If we radiate pure carbon monoxide with alpha rays, two molecules of CO decompose per ion pair and neglecting the formation of sub-oxide we formulate the main reaction: $\text{CO}^+ + \text{CO} = (\text{CO})_2^+$ followed by $(\text{CO})_2^+ + (-) = \text{CO}_2 + (\text{C})$. In the presence of oxygen, however, no free carbon is found, and four instead of two CO molecules and in addition two O_2 molecules all unite to form four molecules of CO_2 per one ion pair (just as in water synthesis) which we formulate similarly $(\text{CO.O}_2.\text{CO})^+ + (\text{CO.O}_2.\text{CO}) = 4\text{CO}_2$ and also for methane oxidation $(\text{O}_2.\text{CH}_4.\text{O}_2)^+ + (\text{O}_2.\text{CH}_4.\text{O}_2)^- = 2\text{CO}_2 + 4\text{H}_2\text{O}$.

From the reactions of oxidation we deduce the principle of the *exclusivity of oxidation*. For example, when alone, CO decomposes to form carbon dioxide, sub-oxide and free carbon, but in the presence of oxygen it is oxidized exclusively to CO_2 . Methane alone condenses to form higher hydrocarbons with the elimination of free hydrogen as: $\text{CH}_4^+ + \text{CH}_4 + (-) \rightarrow \text{C}_2\text{H}_6 + \text{H}_2$ (also $\text{C}_2\text{H}_4 + 2\text{H}_2$), but in the presence of oxygen, methane is completely oxidized to H_2O and CO_2 . One might think this is simply the result of secondary reaction by which C, H_2 or C_2H_6 could not remain in the system in the

presence of oxygen. The kinetics for this reaction leads to the conclusion, however, that the reaction is the direct one formulated, not a series of successive reactions. Moreover, in the case of carbon monoxide twice as many molecules of CO react in the presence of oxygen as in its absence, owing to the effectiveness of the O_2^- in clustering, whereas, when only CO is present there are no negative ions because CO has no affinity for free electrons, which come back "empty handed," so to speak, in completing the reaction by reestablishing electrical neutrality. In other words, in the presence of oxygen, the negative charge which recombines to fix the reaction will always bring with it O_2 , thus making oxidation exclusive, because the positive cluster can find no electrons unaccompanied by oxygen.

The exclusivity of oxidation has held without exception in all the reactions examined. Cyanogen when alone polymerizes to a black solid, probably paracyanogen; with oxygen it forms only oxidation products, including a light yellow addition product $(\text{CNO})_x$. Acetylene alone forms the yellow powdery polymer cuprene; with oxygen it gives a colorless liquid and other oxidation products, but no cuprene. Ethane, propane and butane in the absence of oxygen give liquid and solid condensation products with elimination of free hydrogen, but with oxygen they are either oxidized directly to CO_2 and H_2O as are CH_4 and C_2H_6 or to partially oxidized products as C_3H_8 and C_4H_{10} are. Also in agreement with this

TABLE II
CHEMICAL EFFECTS OF α -RAYS. VARIOUS TYPES OF REACTIONS

Reaction	Assumed Clusters	Theory	Found
$2(2\text{H}_2 + \text{O}_2) \rightarrow$	$(\text{H}_2.\text{O}_2.\text{H}_2)^+ + (\text{H}_2.\text{O}_2.\text{H}_2)^-$	$= 4\text{H}_2\text{O}$	3.85 H_2O
$2(2\text{CO} + \text{O}_2) \rightarrow$	$(\text{CO.O}_2.\text{CO})^+ + (\text{CO.O}_2.\text{CO})^-$	$= 4\text{CO}_2$	4.1 CO_2
$2(\text{CH}_4 + 2\text{O}_2) \rightarrow$	$(\text{O}_2.\text{CH}_4.\text{O}_2)^+ + (\text{O}_2.\text{CH}_4.\text{O}_2)^-$	$= 2\text{CO}_2 + 4\text{H}_2\text{O}$	1.6 $\text{CO}_2 + 3.2\text{H}_2\text{O}$
$2(\text{C}_2\text{H}_6 + 3\frac{1}{2}\text{O}_2) \rightarrow$	$(\text{CO}_2.\text{O}_2.\text{C}_2\text{H}_6.\text{O}_2.\text{O}_2)^+ + (\text{O}_2.\text{C}_2\text{H}_6.\text{O}_2.\text{O}_2)^-$	$= 4\text{CO}_2 + 6\text{H}_2\text{O}$	3.3 $\text{CO}_2 + 5.0\text{H}_2\text{O}$
$2\text{CO} \rightarrow$	$(\text{CO})_2^+ + (-) \rightarrow$	$\text{CO}_2 + (\text{C}) + (\text{C}_3\text{O}_2)$	- 2 CO
$2\text{CH}_4 \rightarrow$	$(\text{CH}_4)_2^+ + (-) \rightarrow$	$\begin{cases} \text{C}_2\text{H}_6 + \text{H}_2 \\ \text{C}_2\text{H}_4 + 2\text{H}_2 \end{cases}$	- 2.2 CH_4
$2\text{C}_2\text{H}_6 \rightarrow$	$(\text{C}_2\text{H}_6)_2^+ + (-) \rightarrow$	$\begin{cases} \text{C}_4\text{H}_{10} + \text{H}_2 \\ \text{C}_4\text{H}_8 + 2\text{H}_2 \end{cases}$	- 1.7 C_2H_6
$2\text{C}_3\text{H}_8 \rightarrow$	$(\text{C}_3\text{H}_8)_2^+ + (-) \rightarrow$	$\begin{cases} \text{C}_6\text{H}_{14} + \text{H}_2 \\ \text{C}_6\text{H}_{12} + 2\text{H}_2 \end{cases}$	- 1.7 C_3H_8
$2\text{C}_4\text{H}_{10} \rightarrow$	$(\text{C}_4\text{H}_{10})_2^+ + (-) \rightarrow$	$\begin{cases} \text{C}_8\text{H}_{18} + \text{H}_2 \\ \text{C}_8\text{H}_{16} + 2\text{H}_2 \end{cases}$	- 1.8 C_4H_{10}
$x\text{C}_2\text{H}_4 \rightarrow$	$(\text{C}_2\text{H}_4)_x^+ + (-) =$	$(\text{C}_2\text{H}_4)_x$	$x = 5.1$
$x\text{C}_2\text{N}_2 \rightarrow$	$(\text{C}_2\text{N}_2)_x^+ + (-) =$	$(\text{C}_2\text{N}_2)_x$	$x = 7.4$
$x\text{HCN} \rightarrow$	$(\text{HCN})_x^+ + (-) =$	$(\text{HCN})_x$	$x = 11.1$
$x\text{C}_2\text{H}_2 \rightarrow$	$(\text{C}_2\text{H}_2)_x^+ + (-) =$	$(\text{C}_2\text{H}_2)_x$	$x = 19.8$

general theory is the fact that hydrogenation of unsaturated compounds is not exclusive; polymerization takes place simultaneously, because H_2 can not form H_2^- ions by trapping low velocity electrons, therefore, the positive polymeric clusters can be neutralized by free electrons.

The following list (Table II) of reactions will illustrate these and other points. In the group of oxidation reactions, it will be observed that the stoichiometric principle for both positive and negative ions is quite well confirmed by the M/N values found.

In the group of five decompositions, where no gas is present with electron affinity, it will be observed that the positive cluster is limited to the value of 2, one neutral molecule and one positive ion entering into reaction. Perhaps this rule may be generalized for the clustering of saturated molecules with themselves.

On passing, however, to unsaturated compounds of carbon, the clusters are larger. Ethylene shows a value above 5, and the triple bond compounds cyanogen, acetylene and hydrogen cyanide show values yet higher, from 8 up to about 20.

As already stated, we do not know the actual size of these clusters, nor has the physical evidence from migration of ions proved unambiguous, even in the simplest cases. If the theories here advanced are correct, we may say that the chemical evidence definitely sets lower limits. Perhaps the clusters are in reality larger. If in general they all initially contain about the same large number of molecules, then evidently the clusters of unsaturated compounds have the greater stability after neutralization. This stability of the clusters of triple bond compounds is further illustrated by the fact that when acetylene polymerizes only 2 per cent. of its H_2 is liberated, cyanogen liberates 5 per cent. of its N_2 , HCN 2.5 per cent. of its H_2 and 8 per cent. of its N_2 , while ethylene splits out 19.5 per cent. of its H_2 , giving a mixture of hydrogen and methane containing 91 per cent. H_2 and 9 per cent. CH_4 by volume, while methane splits out 37.5 per cent. of its H_2 in the free state, during complete reaction.

The studies which I have attempted to describe briefly should be regarded as exploratory. While they set up a general preliminary theory and have put the kinetics in quite a satisfactory state, they have hardly more than scratched the surface of the possible ionic gas reactions, which may prove to have significance in the preparation of new and unusual compounds. Since the reactions take place at low temperatures, they will give many addition-products which would be decomposed at higher temperatures. A number of such compounds not described in the literature have already been observed, but have not yet been prepared in sufficient quantity for thorough

examination. The preparative phase of this subject is an attractive field for future investigation, where perhaps more abundant sources of ionization may profitably be employed, since quantitative knowledge of the ionization itself would not be necessary for preparation alone.

S. C. LIND

FIXED NITROGEN RESEARCH LAB.,
WASHINGTON, D. C.,
MARCH, 1926

SIGMA XI IN RESEARCH¹

SIGMA XI has gained the confidence of all who know its ideals. To-night's initiates are to be congratulated, for the Iowa chapter has had an honorable history. Since it was organized twenty-six years ago, the policy of this chapter has always been conservative, and at the end of the tenth year we find only 161 members, of whom fifty-one were active members. For the year 1911 to 1912, I find the president was Raymond; vice-president, Seashore; recording secretary Pearce; corresponding secretary, Hauser; treasurer, Wylie; and counsellor, Macbride. It was about this time that Iowa began to lay the foundation for the present rapid growth in research.

Sigma Xi stands not only for cooperative research, but also promotes scholarship through selecting the unusual men and women who have that promise of power in research which enables them to go beyond the set limits of knowledge. I fear that sometimes we fail to recognize different types of research workers. Some scientists prefer to discover new material; some to work over the material discovered by others with a view to testing, verifying, or elaborating the principles set forth; some to interpret and to coordinate and correlate the data discovered by others; some prefer to criticize and if possible destroy the principles or theories formulated by others; others, like the professor in the small college, to inspire or train younger students who later catch the spirit of research and carry their training into larger institutions with marked success. All these types are needed; all have their places in furthering the bounds of human knowledge, providing they are in their final endeavors creative.

My own interest in science was comparatively late in maturing. Having lived on a farm in my childhood and youth, I assembled numerous natural history collections, but it was not until I went to college that I became fascinated, under the direction of Dr. Spencer Trotter, with scientific inquiries. While a

¹ President's address at the annual initiation of the Iowa chapter of the Society of the Sigma Xi, State University of Iowa, Iowa City, Iowa, February 17, 1926.