

acetylene). The colorless liquid phase, of vapor pressure less than 1 mm., therefore, has the empirical formula $(C_2H_3)_x$, indicating that the H:C ratio has been increased by the removal of C (from the cluster) in the form of carbon dioxide and monoxide. The preliminary ratio of $-M_{(C_2H_3 + O_2)}/N_{(C_2H_3 + O_2)}$ is indicated as about 27, considerably higher than for pure acetylene.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE CHEMICAL ACTION OF GASEOUS IONS PRODUCED BY ALPHA PARTICLES

VIII. THE CATALYTIC INFLUENCE OF IONS OF INERT GASES

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In the first comparisons between ionization and chemical action in the decomposition of ammonia by alpha particles,¹ the calculation was based on total ionization including that of the decomposition products, nitrogen and hydrogen. The kinetics became more satisfactory, however, on assuming the ionization of ammonia alone, as calculated from its partial pressure, to be effective in producing decomposition. Wourtzell² also later pointed out that the ratio $-M_{NH_3}/N_{NH_3}$ was nearer unity and apparently had greater probability than that of $-N_{NH_3}/N_{total}$. Recent work of the authors on the oxidation of carbon monoxide to carbon dioxide (Part VI) and of methane to carbon dioxide and water (Part IX to follow) seemed to confirm the general assumption that when a gas, present or generated in a mixture of gases, itself takes no part in the further reaction, the portion of ionization produced by alpha particles acting on such an inert gas contributes nothing to the reaction.

It was, therefore, with great surprise that we have encountered the evidence to be presented in this paper, that the ions of inert gases not only *may* contribute as much to a reaction as do the ions of the reactant, but that this seems to be the more general case for a large number of inert substances and for very different types of reaction. In fact, the cases where the inert substances are without effect, which were formerly thought to be the general ones, now stand out as the unexplained exceptions.

In attempting to carry out the reaction $C_2H_2 + N_2 = 2HCN$ under the ionizing influence of α -rays, we found³ that nitrogen did not react (or only very slightly) but nevertheless exerted a large accelerating influence on the rate of polymerization of acetylene to form solid cuprene

¹ *J. Phys. Chem.*, **16**, 580 (1912).

² E. E. Wourtzell, *J. phys. radium*, **1**, 90 (1920).

³ *Science*, **62**, 422 (1925). (Preliminary account.)

(preceding paper, Part VII). The detailed data of this reaction are presented later in this paper as well as the results of a large number of other reactions and catalysts.

The experimental methods are the same as those previously employed. The methods of preparation and analysis of gases if not already described in Parts VI and VII are given in the following section.

Preparation of Gases.—The noble gases, neon, argon, krypton and xenon, were purified by removal of hydrogen by the palladium thimble, and of nitrogen and oxygen by metallic calcium at 475°. Helium was purified by removal of all other gases by activated charcoal at liquid-air temperatures.

Ammonia was purified by treating the liquid with metallic sodium and removal of hydrogen by pumping at liquid-air temperatures.

Analysis.—The methods of analysis used were those previously described in Parts VI and VII, supplemented by the following.

Nitrogen was removed from the noble gases by introducing the mixture into a Pyrex glass thimble containing metallic calcium at 475°. After absorption was complete, the residual gas was pumped out and the nitrogen content obtained by the difference between the initial and final volumes.

The Polymerization of Acetylene Catalyzed by Nitrogen Ions.—In Table I are the data for the polymerization of acetylene mixed with nitrogen. By comparing with Table I of Part VII (preceding paper) it will be seen that the rate at which the pressure of acetylene diminishes is much faster in the presence of nitrogen. This can be made yet clearer by inspecting the present values of $(k\mu/\lambda)'$ when calculated on the partial pressure of acetylene. Instead of constant values which would normally be about 225 in a bulb of this size, they begin at 292.7 and rise to 2634, showing that the reaction is accelerated and becomes very much more so as the proportion of nitrogen increases. Calculation by the *total* pressure (Col. 1) is also unsatisfactory as the values begin too low and show a steady downward trend.

Col. III gives the pressure of acetylene plus 240.6 mm. which is the acetylene equivalent of 358.6 mm. of nitrogen in terms of ionization by α -rays,⁴ ($P_{N_2} \times (i_{N_2}/i_{C_2H_2})$, in which i is the specific ionization). On applying the general kinetic equation to the combined pressures in Col. III, one obtains the $(k\mu/\lambda)'$ values so designated. The values thus obtained are about normal and remain constant until the partial pressure of acetylene drops below 240 mm., at which point more than 50% of the ionization begins to fall on the catalyst (nitrogen). As a still greater portion of the ionization falls on the catalyst the $(k\mu/\lambda)'$ values drop, probably due to "depletion," an effect that will be more fully discussed in a later section. This rule has been found to be quite general, that a full catalytic effect is observed until more than 50% of the ionization falls on the catalyst.

⁴ The mathematical basis of this treatment is given in the following section.

What is meant by a full catalytic effect will be more apparent by inspection of the last column, in which it is seen that the ratio of the number of acetylene molecules disappearing ($-M_{C_2H_2}$) to the total number of ions on both acetylene and nitrogen ($N_{(C_2H_2 + N_2)}$) is constant and has approximately the same value in the first part of the reaction as in pure acetylene (Part VII, Table I). This can only mean that the ionization of nitrogen is just as effective in causing polymerization and precipitation of acetylene as acetylene ions themselves are.⁵

TABLE I
POLYMERIZATION OF ACETYLENE CATALYZED BY NITROGEN

Reaction: $x C_2H_2g + (N_2)g \rightarrow (C_2H_2)_x s + (N_2)g$. Temp., 25°C.
 Reaction sphere: vol. = 3.812 cc.; diam. = 1.938 cm. $E_0 = 0.01907$ curie.
 $P_{N_2} \times (i_{N_2}/i_{C_2H_2}) = 358.3 \times (0.94/1.40) = 240.6$

% Radon $\times 10^{-3}$ $e^{-\lambda t}$	Pressure, mm.				$(k\mu/\lambda)'$			$\frac{-M_{C_2H_2}}{N_{(C_2H_2 + N_2)}}$
	Total (I)	C_2H_2 (II)	$N_2 + (H_2)$	$C_2H_2 +$ 240.6 (III)	Calcd. by (I)	Calcd. by (II)	Calcd. by (III)	
100.000	1064.0	705.7	358.3	946.3
98.511	1008.0	649.5	...	890.1	192.2	292.7	215.7	18.75
97.045	955.2	596.6	...	837.2	191.1	303.9	219.1	19.04
95.600	906.7	547.9	358.3	788.5	189.7	388.2	217.3	18.88
94.176	863.6	504.7	...	745.3	178.9	301.8	206.9	17.98
92.427	811.6	452.5	...	692.1	186.5	327.3	222.4	19.32
91.051	773.4	414.2	...	654.8	183.4	337.0	211.4	18.36
84.156	615.1	255.5	...	496.1	174.1	367.5	211.0	18.34
82.283	579.7	219.8	359.9	460.4	166.3	421.7	208.8	18.15
80.775	555.6	195.6	...	436.2	147.3	406.1	188.2	16.38
75.768	482.5	122.5	...	363.1	149.9	489.9	192.3	15.73
70.293	424.3	64.3	...	304.9	122.7	616.9	167.0	14.55
66.706	403.8	43.8	358.8	284.4	72.3	561.0	102.0	8.91
58.167	360.6	0.6	360.0	241.2	69.5	2634	101.1	8.84
Anal.	354.5	0.0	$\left\{ \begin{array}{l} N_2 \ 329.0 \\ H_2 \ 25.5 \text{ Condensable} \end{array} \right.$				Weighted av. 18.5	
On heating	18.0		$\left\{ \begin{array}{l} 2.0 \\ 16.0 \text{ HCN (?)} \end{array} \right.$					

Although treated as constant, the nitrogen pressure did not, in fact, remain quite constant. Analysis of the final gases shows a deficiency of about 29 mm. of nitrogen, which in total permanent gas pressure was compensated by the addition of 25.5 mm. of hydrogen liberated from acetylene. The error introduced by calculating the ionic catalytic effect of nitrogen as if nitrogen remained constant at its initial pressure is negligible except in the last two values of $(k\mu/\lambda)'$ and of M/N , which would be raised about 10% by the rigid calculation.

⁵ Since $(k\mu/\lambda)'$ has the same value with and without catalyst, one might think at first sight that the amount of reaction per curie will be the same, but it is to be remembered that the total number of times that the given volume is caused to react (definition of $(k\mu/\lambda)'$) now refers to a higher pressure, namely, the pressure of reactant plus the ionic equivalent pressure of the catalyst. Therefore, the total reaction per curie will be the normal $225 \times$ volume multiplied by $i_{(C_2H_2 + N_2)}/i_{(C_2H_2)}$.

After the residual gases had been pumped off at the end of the reaction, and the solid polymer was heated to 350°, 18 mm. of gas was removed, only 2 mm. of which was not condensable in liquid air (N₂ + H₂); the rest had the properties of gaseous hydrogen cyanide. This would still leave more than half of the nitrogen loss unaccounted for, but it is to be remembered that one should expect to find most of the hydrogen cyanide not in the form of gas but as the solid black polymer described in the preceding paper; and, in fact, the yellow acetylene polymer in this case did have a darker hue than that from pure acetylene or from acetylene catalyzed by noble gases.

Evaluation of the Velocity Constant for Ionic Catalysis.—Assuming that the catalytic effect of an inert gas is proportional to its partial pressure and to the number of alpha particles emitted per unit time, the differential equation for rate of pressure drop takes the form⁶

$$-dP/dt = (k_c \mu_c P_c + k \mu P) E_0 e^{-\lambda t} \quad (1)$$

where the subscripts *c* refer to the inert gas as catalyst. If the number of molecules reacting per pair of ions of catalyst is the same as for each ion pair of reactant, we may write $k_c \mu_c / k \mu = i_c / i$, where *i_c* and *i* are the specific ionizations of catalyst and reactant, respectively. Substituting in (1) the differential equation is

$$\frac{dP}{dt} = k \mu \left(\frac{i_c}{i} P_c + P \right) E_0 e^{-\lambda t}$$

and the integrated equation is:

$$\left(\frac{k \mu}{\lambda} \right)' = \ln \frac{\left(\frac{i_c}{i} P_c + P_{t_1} \right)}{\left(\frac{i_c}{i} P_c + P_{t_2} \right)} \div E_0 (e^{-\lambda t_1} - e^{-\lambda t_2}) \quad (2)$$

If the pressure of the catalyst changes during the reaction or, as is more commonly the case, gases are generated during the reaction which are themselves catalysts, *P_c* becomes a variable, and the ionic equivalents of the catalyst (namely, $(i_c/i)P_c$) at the times *t₁* and *t₂* are used in the calculation of $(k\mu/\lambda)'$ for the corresponding interval. Since we wish to calculate $-M_{\text{reactant}}/N_{(\text{re.} + \text{cat.})}$, the $(k\mu/\lambda)'$ values from Equation 2 must be multiplied by the ratio $\Delta P_{\text{reactant}}/\Delta P_{\text{ionic equiv.}}$ ⁷ for each interval of the reaction. The $(k\mu/\lambda)'$ values reported in the tables have been corrected in this way and give the *M/N* ratios by direct substitution in the equation on p. 2682 of Part VI.

The Polymerization of Acetylene in the Presence of Helium.—Although the polymerization of acetylene has been studied in detail for a number

⁶ "Chemical Effects of Alpha Particles and Electrons," Am. Chem. Soc. Monograph, Chemical Catalog Co., New York, 1921, p. 96.

⁷ *P_{ionic equiv.}* is the sum of the pressure of reactant plus the ionic equivalent pressures of the catalysts. The entire correction is usually negligible in autocatalysis except near the end of the reaction.

of other catalysts besides nitrogen, the kinetic results for only one more case, that of helium, will be given. Table II shows that helium acts just as nitrogen in catalyzing the polymerization, except that none of it is carried out of the gas phase by the precipitation of acetylene.

The ionization equivalent of 568 mm. of helium is only 85.6 mm. of acetylene. It will be observed that the velocity constants are sustained until the partial pressure of acetylene has fallen to about this value, or until 50% of the ionization is on the catalyst, thus illustrating the general rule already mentioned.

The evolution of hydrogen during this reaction is less than found for pure acetylene (Part VII), probably because less radon was present and hence the solid polymer received less alpha radiation. The slight discrepancy between rise of pressure of hydrogen and the hydrogen found by analysis, probably means that initial helium was about 575 mm. rather than the 568 mm. assumed for a 1:1 mixture. The first actual measurement at liquid-air temperature was 572.

TABLE II
POLYMERIZATION OF ACETYLENE CATALYZED BY HELIUM

Reaction: $x\text{C}_2\text{H}_2(\text{g}) + (\text{He g}) \longrightarrow (\text{C}_2\text{H}_2)_x(\text{s}) + (\text{He g})$. Temp. 25°C.
Reaction sphere: vol. = 3.443 cc.; diam. = 1.874 cm. $E_0 = 0.00925$

% Radon $e^{-\lambda t}$	Pressure, mm.			$\left(\frac{k\mu}{\lambda}\right)'$	$\frac{-M_{\text{C}_2\text{H}_2}}{N_{(\text{total})}}$
	Total	C_2H_2	He + (H ₂)		
100.000	1134.2	566.2	568.0
98.511	1112.0	543.6	568.4	254	20.5
97.045	1091.0	522.1	568.9	256	20.6
91.737	1024.0	453.7	570.3	243	19.4
85.268	950.6	378.5	572.1	250	20.0
83.527	933.0	361.2	572.5	235	18.8
81.058	909.0	336.1	572.9	253	20.2
77.202	874.4	301.0	573.4	242	19.3
71.355	826.4	252.4	574.0	248	19.8
67.580	799.3	224.5	574.8	246	19.4
56.345	730.5	154.0	576.5	246	19.4
49.783	698.2	120.3	577.9	247	19.2
41.582	667.4	88.9	578.5	216	16.5
32.956	640.4	61.4	579.0	212	16.1
23.783	618.9	39.6	579.3	187	13.8
11.599	599.4	19.4	580.0	153	11.0
1.072	588.4	7.8	580.6	117	8.0
<i>Anal.</i>		8.9	575.0	Weighted av. 19.7	
		Hydrogen	5.0		

Polymerization of Cyanogen in Presence of Xenon.—In Table III are given the detailed results for one other polymerization, that of cyanogen catalyzed by xenon, which should be compared with those for pure cyanogen (Part VII, Table II). Like nitrogen in the polymerization of

acetylene, some xenon was found to have gone out at the end of the reaction but, unlike nitrogen, the xenon was quantitatively recoverable by heating the solid polymer of cyanogen to 350°. Nitrogen was also liberated, just as in the polymerization of pure cyanogen. Both the xenon loss and the nitrogen gain have been treated as if distributed evenly throughout the reaction in proportion to the $-\Delta C_2N_2$ of each interval. Since in a separate experiment it is shown that nitrogen catalyzes the polymerization of cyanogen, it is so treated here. The values of $(k\mu/\lambda)'$ and M/N show fair constancy down to the point where 50% of the ionization falls on the catalysts, but both have values slightly lower than for cyanogen alone.⁸

Various Catalysts and Reactions.—Data similar to those given in Tables I, II and III have been obtained for several other reactions and for a number of catalysts. Our effort has been directed toward finding the limitations of this form of catalysis. It is not necessary to present the detailed kinetics of each case; therefore the results are summarized in

TABLE III
POLYMERIZATION OF CYANOGEN CATALYZED BY XENON

Reaction: $x C_2N_2 (g) + (Xe g) \longrightarrow (C_2N_2)_x (s) + (Xe g)^a$. Temp., 25°
Reaction sphere: vol. = 3.653 cc.; diam. = 1.911 cm. $E_0 = 0.0422$ curie.

% Radon $e^{-\lambda t}$	Pressure, mm.				$P_{C_2N_2 + equiv. (Xe + N_2)}$	$(\frac{k\mu}{\lambda})'$ corr. ^b	$\frac{-M_{C_2N_2}}{N_{total}}$
	Total	C_2N_2	Xe	N_2			
100.000	920.6	785.6	135.0	0	950.0
97.653	811.8	675.7	133.8	2.3	839.8	124.3	7.4
94.885	708.1	570.8	132.6	4.7	734.7	114.1	6.8
93.824	672.4	534.5	132.2	5.7	698.3	113.2	6.8
92.484	629.3	480.7	131.7	6.9	654.6	115.1	6.9
86.071	465.8	323.2	129.8	12.8	487.7	110.1	6.7
83.999	424.4	280.3	129.3	14.8	445.1	105.0	6.4
81.516	381.8	236.0	128.8	17.0	401.2	100.2	6.1
77.589	323.8	175.0	128.1	20.7	341.1	99.3	6.1
71.624	256.6	103.1	127.3	26.2	271.0	93.8	5.7
68.046	230.0	73.6	126.9	29.5	242.6	76.2	4.6
64.971	212.0	53.1	126.7	32.2	223.3	67.9	4.1
59.901	188.9	25.5	126.4	37.0	197.6	61.0	3.7
0.523	166.7	0.0	126.1	40.6	173.6	55.3	3.3
<i>Anal.</i>	168.3	0.0	125.0	43.4		Weighted av. 6.8	
On heating	51.7	36.8	9.0	5.9			

^a The values used for specific ionization are: for Xe 2.34; for C_2N_2 1.92; for N_2 0.94.

^b Corrected for Xe taken out by occlusion.

⁸ This may be due to use of an incorrect value for the specific ionization of xenon. Since no value existed, we estimated 2.34 by multiplying the scintillation value of its stopping power by 1.3, which is the value for most heavy gases of the total ionization of 1 α -particle relative to air = 1.

Table IV, which shows that all of the inert substances used as catalysts behave like nitrogen, helium and xenon. The reactions need not be confined to the unsaturated compounds, but extend to synthesis, decomposition and oxidation of various types of reactants.

TABLE IV
CATALYSIS BY IONS OF INERT GASES

Reaction	Catalyst	% Ionization on catalyst	$(k\mu/\lambda)'$ for 2-cm. sphere	$\frac{-M_{\text{reactant}}}{N_{(\text{react.} + \text{cat.})}}$
Polymerization of C_2H_2	none	0	216	19.8
	He	13-42	215	19.7
	Ne	35-50	209	19.2
	A	31-41	198	18.2
	N_2	25-52	201	18.5
	(CO_2)	52	(179)	(16.4)
	Xe	25-30	196	18.0
	Kr	27-50	213	19.6
Polymerization of C_2N_2	none	0	111	7.4
	N_2	33-62	109	7.3
	Xe	17-34	102	6.8
	Kr	25	114	7.6
Polymerization of HCN	none	0	96	11.3
	N_2	60	(85)	(10.1)
	Xe	38	(85)	(10.0)
$2H_2 + O_2 = 2H_2O$	none	0	20.5	5.13
	Ne	61	18.4	4.6
	A	71	(14.4)	(3.6)
	N_2	60-80	21.5	5.4
$2CO + O_2 = 2CO_2$	none	0	52.0	6.54
	A	56	(30.9)	(3.90)
Decompn. of CO	none	0	14.5	1.86
	Ne	43-49	18.1	2.34
Decompn. of NH_3 at 25°	none	0	6.3	1.0
	Ne	48-52	6.3	1.0

The fact that xenon and krypton exert a full catalytic effect although they have ionization potentials lower than those of the reactants, has already been fully discussed in two preliminary papers,⁹ from which it is quite certain that the ionization potential does not control the catalytic effect, but whether an exchange of electrons does take place within the cluster cannot be decided by the chemical experiments, if at all.

The data in the column for percentage of ionization on the catalyst show the range over which the velocity constant was found to hold. In the cases where only one value of % ionization on the catalyst is given, this corresponds to a single value of $(k\mu/\lambda)'$ and of M/N , the others having been

⁹ *Science*, **62**, 593 (1925); **63**, 310 (1926).

disregarded as less accurate; this does not apply to the case of no catalyst, where always a series of concordant values was obtained.

Effect of Depleting the Reactants.—In the catalyzed reactions just presented, it has been pointed out that the velocity constant $(k_{\mu}/\lambda)'$ and the ratio $-M_{\text{react.}}/N_{(\text{react.} + \text{cat.})}$ usually show good constancy until $N_{\text{cat.}}$ exceeds N_{reactant} and that beyond that point as the percentage of ionization on the catalyst progresses from 50% toward 100%, the ratio $-M/N_{\text{total}}$ diminishes steadily. This may probably be interpreted as the effect of depleting the reactant, while the number of positive ions of the catalyst and free electrons are remaining practically constant owing to the constant pressure of catalyst. Both of these factors work in the same direction; a large number of positive ions are seeking to collect a reduced number of reactant molecules into clusters in competition with a large number of free electrons ready to neutralize the partially formed clusters, thus stopping the process before the clustering is complete.

This arrest of the clustering process, as indicated by $-M/N$ ratios below the normal value is of special interest, since it raises directly the question as to what happens to a cluster thus prematurely neutralized. Does it form a stable polymer, for example $(C_2H_2)_y$, in which $y < x$, x being the normal value 20, or does it break down again to gaseous C_2H_2 ? In other words, if the apparent value of $-M_{C_2H_2}/N_{\text{total}}$ is 10 instead of the normal 20, an efficiency of 50% is shown, which may mean half as many polymers as initial ions, all having the normal polymerizing factor of 20, or it may mean as many polymers as ions, but nearly all smaller with a mean polymerizing factor of only 10. One way of solving this problem lies through a study of the depletion factors.

The synthesis of water in presence of argon offers a good demonstration of depletion. Owing to the low specific ionization of hydrogen, electrolytic gas has a specific ionization of only one-third that of argon. Therefore, in a mixture of 1A:1(2H₂ + O₂) about 70% of the ionization by alpha radiation falls on the argon initially, and as the (2H₂ + O₂) mixture is consumed by reaction, this fraction rapidly approaches 100%. The data are shown in Table V. The calculated catalytic factor is obtained by dividing the values in the column for the pressure of (2H₂ + O₂) plus its argon equivalent by the column for (2H₂ + O₂) alone, which is then evidently the ratio, total ionization:ionization of reactants. The percentage of catalytic efficiency is got by dividing each value of $(k_{\mu}/\lambda)'$ by 20, the normal value for a bulb of that size. The actual or "found" catalytic factor is obtained by multiplying the theoretical (calcd.) by the per cent. efficiency; it expresses how many times faster the reaction is going in the presence of argon than if it were absent. Any of the other catalytic reactions can be treated in the same way. The final column, giving the product, per cent. efficiency \times per cent. ionization on catalyst, has a fairly

constant value of 5000 up to about 95% ionization on the catalyst. From this, one would conclude by backward extrapolation that below 50% ionization on the catalyst, the catalytic efficiency would always be 100%, which corresponds with general experience in the various reactions.

While water synthesis catalyzed by argon demonstrates well the depletion effect and the empirical law governing it, it does not lend itself best to a theoretical consideration of the effect on account of there being three components in the system. Such a study as just outlined is therefore deferred until a theory has been reduced to exact formulation and until more suitable data are available from a one-component reaction.

TABLE V

WATER SYNTHESIS CATALYZED BY ARGON

Reaction: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) + (\text{A})(\text{g}) = 2\text{H}_2\text{O}(\text{l}) + (\text{A})(\text{g})$ Reaction sphere: vol. = 3.821 cc.; diam. = 1.939 cm. $E_0 = 0.0463$ curie.

$$P_A \times \frac{i_A}{i_{(2\text{H}_2 + \text{O}_2)}} = 559.5 \times \frac{1.24}{.51} = 1360.4 \text{ mm. } (2\text{H}_2 + \text{O}_2)$$

% Radon $e^{-\lambda t}$	Pressure, mm.			$\left(\frac{k\mu}{\lambda}\right)$, Re+cat.	% Ion- ization on cat.	Catalytic factor		% Ion- ization × % Eff.
	Total	2H ₂ +O ₂	2H ₂ +O ₂ + A equiv.			Calcd.	Found	
100.000	1117.0	557.5	1917.9
97.045	1077.0	517.5	1877.9	15.32	70	3.3	2.5	75 5200
91.737	1012.0	452.5	1812.9	14.34	72	3.6	2.5	70 5000
84.472	933.5	374.0	1734.4	13.28	75	4.0	2.6	65 4900
80.303	892.3	332.8	1693.3	12.28	78	4.6	2.8	61 4800
76.625	856.9	297.4	1657.8	12.57	80	5.1	3.1	61 4900
70.690	803.2	243.7	1604.1	11.90	82	5.6	3.4	61 5000
64.004	745.4	185.9	1546.3	11.82	85	6.6	3.9	59 5000
59.046	706.5	147.0	1507.4	11.24	88	8.3	4.6	55 4800
47.863	626.1	66.6	1427.0	10.54	95	21.4	10.5	49 4600
41.582	594.4	34.9	1395.0	7.76	97	40.0	15.3	38 3700
28.365	561.1	1.6	1362.0	...	100	852.0	255	30 3000

Discussion

The catalytic effect of the ions of inert gases is so quantitatively explained by considering the total ionization instead of the partial ionization of the reactants that but little remains to be said about the main part of the reactions.

The outstanding exceptions appear to be certain reactions in which the nitrogen or carbon dioxide generated do not appear to have an autocatalytic effect. In the decompositions of ammonia and of carbon monoxide it should be recalled that the reactions not only were not positively catalyzed, but actually showed a diminishing rate as they proceeded. In the case of carbon monoxide, at least, this appeared due to reverse reaction. In both cases the diminishing rate may mask a positive autocatalysis. In the case of the oxidations of carbon monoxide and of methane, however, not even a qualitative explanation of this kind is in sight, and the failure

of the carbon dioxide generated to autocatalyze the reaction is very puzzling.

The use of the term "ionic *catalysis*" appears appropriate in so far as a substance inert to the reaction causes its acceleration; but it should be remembered that the catalyst must itself be energized by being ionized by alpha radiation each time that it acts as catalyst. In this respect the effect is more like photochemical sensitization, but differs in one respect, namely, that both the reactants and "sensitizers" take up energy from the radiant source. This difference is due to the non-specific character of the α -ray effects.

We are much indebted to Dr. R. B. Moore for the loan of krypton and xenon used in these experiments.

Summary

1. Seven different reactions have been shown to be "catalyzed" by the ions of inert gases mixed with the reactants. The ionization is produced by radon directly introduced into the reaction mixture. The reactions studied are the polymerization (1) of acetylene, (2) of cyanogen and (3) of hydrogen cyanide; the oxidation (4) of carbon monoxide and (5) of hydrogen; and the decomposition (6) of carbon monoxide and (7) of ammonia.

2. Inert gases, N_2 , He, Ne, Ar, Kr, Xe, CO_2 and H_2 were found to catalyze the reactions very generally according to the law that the ions of the inerts are quantitatively equal to those of the reactants in producing chemical reaction.

3. A kinetic equation applicable to the catalyzed reactions is developed, which involves adding to the pressure of reactant at each interval, the pressure of reactant that is equivalent in specific ionization to that of the inert; the combined pressures thus obtained are inserted in the usual kinetic equation which is found to be best verified in that way.

4. Certain exceptions are met where nitrogen and carbon dioxide fail to autocatalyze reactions in which they are generated.

5. It is shown that the catalyst may have an ionization potential either higher or lower than that of the reactants without affecting the general addition law; this precludes the primary step consisting of an exchange of charge between ionized catalyst and neutral reactant.

6. An empirical law is given for the "depletion" effect, when water synthesis is catalyzed by argon; namely, per cent. ionization on catalyst \times per cent. efficiency of catalyst = 5000. One deduction is that for any per cent. ionization on the catalyst up to 50%, the catalytic efficiency is 100%; this has been generally confirmed in the reactions studied.

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