[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

THE INTERACTION OF HYDROGEN AND CHLORINE UNDER THE INFLUENCE OF ALPHA PARTICLES.

BY HUGH STOTT TAYLOR.

Received October 26, 1914.

Recent researches upon the photochemical combination of hydrogen and chlorine have advanced considerably our knowledge of and insight into the reaction itself and to a certain extent the general theory of photochemical reaction. The work of Chapman and his co-workers has, to a great degree, elucidated the abnormalities previously observed and due, in many cases, to the presence of impurities. In the later investigations of the series,[1] by variations from equimolecular mixtures of the two gases, the study of the kinetics of the reaction was commenced. Towards the solution of the latter problem the researches of Bodenstein and Dux[2] have materially contributed. By the employment of a very ingenious method of measurement, eliminating the necessity of employing water as absorbent for the hydrochloric acid formed, the following points were established:

1. The combination of hydrogen and chlorine in light is a reaction of the second order, the velocity being proportional to the square of the chlorine concentration. Hydrogen is without influence so long as it is present to the extent of at least $^1/_4$ of the amount of chlorine. At smaller hydrogen concentrations the velocity decreases slightly.
2. The hydrochloric acid formed is without influence on the velocity.
3. Water vapor within certain limits (0.004–2.3 mm.) is also without influence.
4. Oxygen retards the reaction, such that the velocity at all stages of the decomposition is inversely proportional to the oxygen concentration.

For the interpretation of the equation of reaction thus obtained:

$$+\frac{d(2\mathrm{HCl})}{dt} = k\frac{J_0[\mathrm{Cl_2}]^2}{[\mathrm{O_2}]}$$

Bodenstein[3] has developed a theory of photochemical reaction velocities and applied it to practically all the measurements in this branch to be found in the literature. According to this theory the initial absorption process in any photochemical change is to be regarded as a photoelectric effect, as a rupture of the molecule at the expense of the absorbed light energy into a positive radical—an atom or with more complex substances a molecule with a free valence—and a free electron. Both portions may lead to chemical reaction, the positive radicals in that they are, chem-

---

[1] Chapman and Underhill, *J. Chem. Soc.*, 103, 496 (1913).

[2] *Z. physik. Chem.*, 85, 297 (1913).

[3] *Ibid.*, 85, 330 (1913).

ically, exceedingly active, the electrons in that they may attach themselves to molecules and so activate them as to take part in chemical change. A distinction is drawn between primary light reactions, in which the positive radicals enter into combination, and secondary reactions in which the molecules activated by the electrons take part in the reaction, the electrons, after reaction has occurred, being again free to attach themselves to and activate other molecules.

A further development of the theory, as regards the relation of light energy absorbed to chemical reaction produced, reveals a marked point of difference in regard to the two classes of reaction. In the primary reactions, for every molecule brought into combination a quantum of absorbed energy or a small number of quanta is regarded as necessary. In the secondary reactions, owing to the function of the free electron as catalyst, an energy quantum should be in a position to bring about the combination of a large number of the reacting molecules.

If it be true that the first stage of a photochemical reaction, as assumed in the theory of Bodenstein, consists of a photoelectric effect, the rupture of a molecule into a positive radical and an electron, then the theory and the method of development should find rigid application in all such chemical reactions as are effected under the influence of other forms of energy, provided that under such influence the rupture of the molecule with the formation of free electrons may be postulated. It is obvious, therefore, that such processes as are effected by means of electrical energy in gases (*e. g.*, under the influence of the silent electric discharge or of Röntgen rays) or, on the other hand, processes determined by radioactive forms of energy should show a parallelism to those in which light is employed as the source of energy.

As regards reactions brought about by means of the silent discharge or by Röntgen rays, the literature does not reveal a large number of examples. The formation of ozone as studied by Krüger,[1] and the decomposition of ammonia investigated by Davies,[2] show points of resemblance to the primary light reactions. Quite recently an investigation by Le Blanc and Volmer[3] on the combination of hydrogen and chlorine under the influence of Röntgen rays shows, as regards the ratio of energy supplied to chemical reaction produced, a parallelism to the secondary light reactions. Concerning this particular research a more detailed discussion will be given later.

The literature of reactions assisted by radioactive forms of energy has been admirably collected and discussed in detail by Lind.[4] The author

[1] Nernst, *Festschrift*, Halle, p. 240 (1912).

[2] *Z. physik. Chem.*, 64, 657 (1908).

[3] *Z. Elektrochem.*, 20, 494 (1914).

[4] *J. Phys. Chem.*, 16, 564 (1912).

came to the conclusion that in reactions caused by alpha particles, as many molecules are brought into reaction as ions are formed in the same period of time. From a careful study of the ozonization of oxygen under the influence of alpha particles, Lind formulated an "Ionic theory of ozonization," comparable in every way with the theory of primary light reactions as developed by Bodenstein. The theory was shown to be applicable, with one exception, to the reactions caused by radioactive energy then studied. The exception to the above formulation of Lind was the combination of hydrogen and chlorine. Jorissen and Ringer[1] studied this reaction, using a radium salt as the source of energy, the measurements being made in an actinometer over water. According to the calculations of Lind, for every ion produced by the radiant energy 100 to 1000 molecules of hydrogen chloride result. It was further shown that, in this case also, as regards a period of induction and irregularity of sensitivity of the gaseous mixture, due doubtless to variation of its oxygen content, the reaction ran parallel to the photochemical change.

It appeared, therefore, probable that the combination of hydrogen and chlorine under the influence of energy from radioactive sources would prove an interesting and valuable subject for closer investigation. Owing to the development of experimental technique in late years it should be possible not only to evaluate the energy relationships of the reaction but to elucidate the kinetics of the combination.

Experimental.

The method employed in the present work is, with suitable modifications, that employed by Lind[2] in the study of the ozonization of oxygen.

The reaction vessel consisted of a large bulb 12 cm. in diameter into the base of which was sealed the vessel designed to hold the emanation. This consisted of a tube drawn out to a fine thin-walled capillary on the end of which was blown a small bulb approximately 1 cu. mm. vol., uniform as regards thickness of wall. The preparation of such bulbs has been very fully described by Lind[3] and the same procedure was adopted in the present instance with one modification. To create the requisite pressure inside the tube during the drawing of the capillary and the blowing of the bulb, a bomb of compressed nitrogen was employed instead of the foot bellows. In this way a more uniform and more easily regulated pressure was obtained. Each bulb was tested as to strength, uniformity and range. They were tested to withstand a vacuum and an excess pressure of one atmosphere. The uniformity and range were determined by filling the bulb with radium emanation followed by measurement of the diameter of the luminescent circle produced on a zinc sulfide screen placed

---

[1] *Ber.*, **39**, 2095 (1906).

[2] Wiener, *Monatshefte*, **32**, 295 (1912).

[3] *Loc. cit.*

at measured distances from the bulb and on all sides of it. An interval of from two to three hours intervened between the filling of the bulb and the making of the measurements, during which time the emanation comes into equilibrium with its disintegration products, in particular with Radium C, with alpha particle range 7.06 cm. in air. Finally a bulb was chosen of uniform range, averaging 5.6 cm. The determination was not effected without difficulty, as the quantity of radium available (10 mg.) was very small for securing sufficient illumination of the zinc sulfide screen.

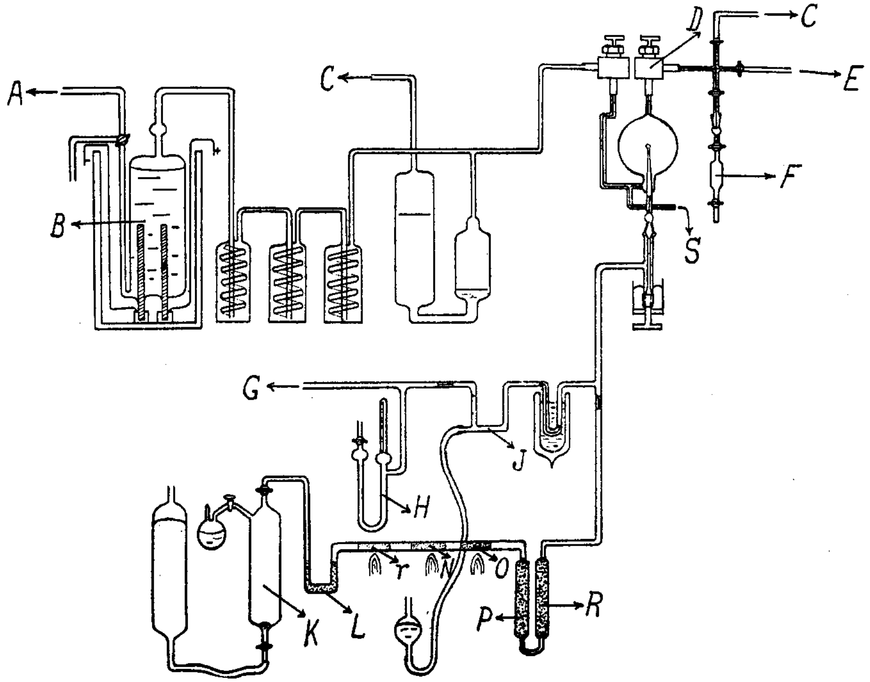

Fig. 1.

A. HCl inlet.
B. Gas generator.
C. Outlet to absorber.
D. Platinum tap.
E. To water and Töpler pumps.
F. Sampling vessel.
G. To Gaede pump.
H. Macleod gage.
J. Mercury trap.
K. Vessel for collecting emanation.
L. Anhydrous calcium chloride.
r. Lead dichromate.
N. Copper.
O. Copper oxide.
P. Solid caustic potash.
R. Phosphorus pentoxide.
S. To manometer.

The hydrogen and chlorine were generated in stoichiometric proportions by the electrolysis of concentrated hydrochloric acid. A vessel of 6 l. capacity was employed, the electrodes consisting of Acheson graphite rods 1 cm. in diameter, soaked in hot paraffin wax in a vacuum. These electrodes were sealed into the glass vessel with marine glue over which a thick layer of paraffin wax was poured. Through a side tube, hydrogen chloride could be led in from time to time, whereby the exhausted hydrochloric acid could be again concentrated. The gases passed from the generator through three spiral wash-bottles, one filled with water followed by two containing concentrated sulfuric acid. They were then conducted to a gasometer in which they could be stored over concentrated sulfuric acid and from which they could be directed either to the reaction vessel or to an absorber.

The entrance to, and exit of the gases from, the reaction vessel were controlled by two platinum taps such as were employed by Bodenstein and Dux[1] in their photochemical investigations. By this means the use of tap-grease and consequent contamination of the gases with organic matter was avoided. The pressure in the reaction vessel was measured by means of the Bodenstein quartz-glass manometer attached by a quartz-in-glass ground joint to a capillary side-tube sealed into the capillary entrance tube of the vessel. The gases were led in from below and conducted out from above to the second platinum tap by means of capillary glass tubing. In this way the volume of dead space, outside the reaction-bulb itself, was reduced to a minimum.

During the reaction the gases were kept mixed by a small circular electric heater placed about 5 cm. from the base of the bulb, and against it. This ensured a slight local heating, causing an upward motion of the gases. Around the top of the bulb was placed a brass collar into which ice could be put in order to cool the gases, to bring about the downward motion. The device worked quite efficiently and caused no difficulties due to temperature variations, as was demonstrated by the perfect constancy of the pressure in the bulb over the extended periods of time intervening between successive measurements of the reaction velocity.

After leaving the reaction vessel the gases could pass by means of a four-way capillary tube in either of two directions. During the process of cleaning the apparatus by washing out with the electrolytic gases, they could be directed to an absorber. During the experiment samples could be taken in an evacuated receiver, which could be evacuated first by means of a water-pump and finally by means of a Töpler pump. The receiver was attached to the four-way capillary tube with the aid of a ground glass joint and by a suitable arrangement of glass taps the various operations could be performed. During purification the taps to the pump and the receiver were closed. During evacuation of the receiver the platinum tap and that to the absorber were closed, while as the sample was being taken the taps to the absorber and pump were closed. By momentarily opening the platinum tap to the evacuated receivers, which were about 25 cc. capacity, a sample of gas sufficient for analysis could be obtained. After each successive withdrawal of gas the pressure in the reaction vessel

---

[1] *Loc. cit.*

was noted. The gases were analyzed after absorption in potassium iodide solution by titration of the liberated iodine with standard thiosulfate solution and estimation of the hydrochloric acid—after expulsion of dissolved carbon dioxide by boiling—with standard baryta solution.

The emanation was obtained from 10 mg. of radium bromide. It was collected from the slightly acidified aqueous solution of the salt in an apparatus similar in every way to that described by Lind, which calls, therefore, for no further description here.

The method of purification employed was a modified form of the procedure adopted in the laboratory of Mme. Curie and described by Lind. The emanation passed from the cylinder in which it was collected, first over heated lead dichromate, copper and copper oxide, to decompose any organic impurities and to remove hydrogen and oxygen. Thence it passed over caustic potash and phosphorus pentoxide through a T-piece into a tube connecting a U-tube with the capillary and bulb sealed into the reaction vessel. The U-tube contained a length of copper wire upon which the emanation could be condensed when the tube was cooled in liquid air. Beyond the U-tube came a mercury trap followed by a MacLeod gage and Gaede mercury pump.

After evacuation of the purification apparatus, capillary and bulb to 0.0001 mm., the mercury trap was closed and the emanation allowed to pass into the purification tubes and to circulate over the heated portions and absorbents into the remaining tubes. After one to two hours the residual gas was collected in the U-tube by cooling this in liquid air, the mercury trap opened and the uncondensed gases remaining were pumped away. The glass was then sealed at the T-piece and still further evacuated to 0.0001 mm. This completed, the mercury trap was again closed and the tube between it and the MacLeod gage was sealed. By withdrawal of the liquid air and by slight warming of the U-tube, the emanation was vaporized. It was then pumped, by means of the mercury in the mercury trap, into the small emanation bulb.

Special attention is directed to Fig. 2, illustrating the arrangement of the emanation bulb. In the study of the ozonization of oxygen it was found by Lind that an uncontrollable variation of the ozone formation, for unknown reasons, could not be avoided. Such variations in the present series of measurements would render a study of the kinetics of the reaction impossible, as a reaction constant must be derived to distinguish the order of reaction. A careful examination of the experimental technique employed by Lind suggested one possible source of error, the variation of the level of mercury, at the neck of the emanation bulb due to variations in the temperature of the apparatus or of the barometric pressure. These could quite possibly be considerable, as the period of experiment varied from 12 to 24 hours. They could operate in two directions. Either the mercury could rise into the bulb, in which case some of the alpha particles would be absorbed by the mercury and the lower portion of the apparatus being shielded by the mercury, ozonization would not occur there; or, on the other hand, the mercury level might fall in the capillary, withdrawing the emanation partially from the bulb into the tube through the wall of which the alpha particles could not penetrate. It is difficult to imagine that these variations could alone be responsible for the considerable variations of the experimental results, but in the present series of measurements a device was employed whereby this possible source of error was eliminated.

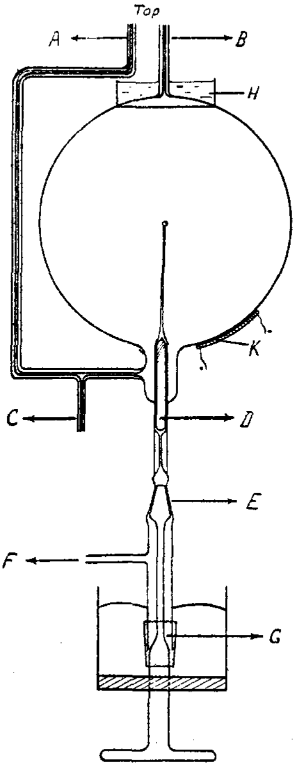

Fig. 2.

A. Capillary inlet from platinum tap.
B. Capillary outlet to platinum tap.
C. Capillary connection to manometer.
D. Silica compensator rod.
E. Ground glass joint.
F. Inlet for emanation.
G. Rubber connection.
H. Ice reservoir.
K. Electric heater.

Immediately below the seal of the capillary in the reaction vessel a ground glass joint was attached, fitted with a tight fitting plunger which operated through a rubber band in the base of the wider tube to which the joint was sealed. The rubber band was sealed both to the wider tube and the plunger by means of marine glue and was rendered vacuum-tight by surrounding it with an outer vessel containing mercury. The emanation entered the wider tube from the purification apparatus through a tube sealed into the side. By pushing the plunger home and suitably supporting it, a mercury-tight seal could be made at the ground glass joint, while by stretching the rubber connection the joint could be opened. In actual work the mercury was brought to such a level in the capillary emanation tube that on pushing the plunger home the mercury rose just to the neck of the bulb.

In this manner influences of barometric pressure were eliminated. It is obvious, however, that with the tube closed at the ground glass joint the bulb and the mercury above the seal would functionate as a thermometer and that changes in temperature would affect the level of mercury in the capillary. To obviate this difficulty an interesting device was employed. By inserting a piece of fused silica (whose coefficient of expansion is very low) in the open space above the ground glass joint, the greater expansibility of the mercury over that of the glass was corrected for. A knowledge of the rates of expansion of the three substances and of the volume occupied by the mercury in the absence of the silica enabled one to calculate the volume of silica required. In this way variations in the level of the mercury due to temperature changes were obviated and a constant level obtained. The device functioned admirably. On one occasion where for experimental reasons (see p. 20) the mercury was cooled twenty to thirty degrees, the level in the tube showed only minute variation.

Theoretical.

The processes occurring may be set forth as follows:[1]

1. In the passage of an alpha particle through the gaseous mixture, ionization is produced and the chlorine molecules decompose into positively charged radicals and electrons.

2. The electrons disappear in two ways:

(*a*) They add on to oxygen molecules, activate these, yielding probably ozone which again forms oxygen (the function of oxygen in the photochemical reaction has been elaborately set forth by Bodenstein and in the present deductions the assumptions then made have been followed).

(*b*) They attach themselves to chlorine molecules, yielding the negatively charged chlorine molecules which are the material for the formation of hydrogen chloride.

3. The negatively charged chlorine molecules disappear in two ways:

(*a*) They regenerate neutral chlorine molecules in that their electrons neutralize themselves with the positively charged rests formed in (1), or in some other way lose their charge.

(*b*) They react with hydrogen to form hydrogen chloride with regeneration of the electron, which then enters upon the cyclic process again and continues thus until eliminated as postulated by (2*a*).

The equations representing these processes may be represented thus:

(1) $Cl_2 + \text{Radiant Energy} = Cl_2 + \ominus$
(2) (*a*) $\ominus + O_2 = O_2^-$ Reaction constant k_4
(*b*) $\ominus + Cl_2 = Cl_2^-$ Reaction constant k_5
(3) (*a*) $Cl_2^- = Cl_2$ Reaction constant k_7
(*b*) $Cl_2^- + H_2 = 2HCl + \ominus$ Reaction constant k_8

The corresponding reaction velocity equations are:

$$(1) \qquad + \frac{d\ominus}{dt} = k_1\ J \text{ absorbed.}$$

In the experimental conditions chosen, all the alpha particles are absorbed and so

$$+ \frac{d\ominus}{dt} = k_2\ J \tag{A}$$

---

[1] Cf. Bodenstein, *Loc. cit.*, p. 346, *et seq.*

where J is the radiant energy employed.

$$(2a \text{ and } b) \quad -\frac{d\ominus}{dt} = k_4[\ominus][O_2] + k_5[\ominus][Cl_2].$$

On attainment of equilibrium conditions,

$$+\frac{d\ominus}{dt} = -\frac{d\ominus}{dt}$$

$+\frac{d\ominus}{dt}$ is composite, being determined by reaction Equation A and the process of regeneration of electrons detailed in (3b). This latter is identical with, and is, therefore, equal to,

$$k_8\ [Cl_2^-]\ [H_2].$$

Assuming that each Cl_2^- formed combined instantaneously with H_2 we have

$$+\frac{d[2HCl]}{dt} = +\frac{d[Cl_2^-]}{dt} = k_5[\ominus]\ [Cl_2] \qquad \text{(B)}$$

Therefore

$$+\frac{d\ominus}{dt} = k_2 J + k_5[\ominus]\ [Cl_2]$$

and so

$$k_2 J + k_5[\ominus]\ [Cl_2] = k_4[\ominus]\ [O_2] + k_5[\ominus]\ [Cl_2]$$

Whence

$$[\ominus] = \frac{k_2 J}{k_4[O_2]}.$$

From (B), therefore, we get

$$+\frac{d[Cl_2^-]}{dt} = \frac{d[2HCl]}{dt} = k_2\frac{k_5}{k_4}\cdot\frac{J[Cl_2]}{[O_2]}$$

a reaction velocity equation of the first order, derived with the assumption that the formation of hydrogen chloride results from the combination of negatively charged molecules of chlorine with hydrogen molecules and that this combination is instantaneous. Were this not the case, a consideration of the reaction equations will show that, if both hydrogen and chlorine were involved in the electronic processes, the formation of hydrogen chloride would yield a velocity equation of the second order.

The experimental results presented below offer a justification for the viewpoint adopted. Column 1 gives the times, in hours, at which measurements were made. In the second column are recorded the pressures. Columns 3 and 4 give the titers of chlorine and hydrochloric acid, respectively. To ensure greater accuracy, the acid titer was made with a more dilute solution (normality of baryta solution, one-third the normality of the thiosulfate solution) than was employed for the titration of the iodine, but in the tables they are presented in equivalent units. Column 5 gives the total volume of hydrogen, chlorine and hydrogen chloride in the same units, whence the actual volumes in millimeters of mercury presented in Columns 6 and 7 could be calculated. Columns 8 and 9 give $d[2\mathrm{HCl}]$ and dt, respectively, while Column 10 gives the reaction constant k_a calculated from point to point for the simple differential equation

$$+\frac{d[2\mathrm{HCl}]}{dt} = k_a[\mathrm{Cl}_2].$$

Column 11 gives the correction-factor E for the decay of emanation calculated from the equation

$$\mathrm{Log\ E} = \frac{\mathrm{Log\ E\ at\ time\ } t + \mathrm{Log\ E\ at\ time\ } t + dt}{2}$$

assuming the initial factor for E to be 100. Column 12 gives the values (k_b) after the introduction of this correction in (k_a). Hence the differential equation employed in this column may be written thus:

$$+\frac{d[2\mathrm{HCl}]}{dt} = k_b\mathrm{E}[\mathrm{Cl}_2]$$

Column 13 gives the value (k_c) of (k_b) multiplied by the pressure during the given time interval. The reason for this is obvious. Since samples are constantly withdrawn for analysis it is obvious that the oxygen concentration also undergoes constant diminution in amount proportional to the volume of gas withdrawn. The equation is, therefore:

$$+\frac{d[2\mathrm{HCl}]}{dt} = k_c\,\mathrm{E}\,\frac{[\mathrm{Cl}_2]}{\mathrm{Total\ Pressure,}\ P}$$

whence it follows that:

$$\frac{k_c}{P} = k_2\frac{k_5}{k_4}\cdot\frac{1}{[\mathrm{O}_2]}$$

as derived in the theoretical portion of this paper.

The hydrogen and chlorine were passed into the evacuated reaction vessel from the gasometer two to three hours after the bulb was filled with emanation. The gases were analyzed immediately in all except the first experiment, Table I, in which case the first analysis ($t = 0$) was made one hour after filling. The experiments were carried out, naturally, in a dark room illuminated by the light of a single carbon filament lamp enclosed in a yellow covering. The reaction vessel was further protected against illumination by a covering of thick black paper.

The results of the four experiments are given in Tables I to IV.

It is evident that in the initial stages of the reaction a period of induction was present. This was doubtless due to impurities in the reaction vessel caused by a modification of the apparatus a day or two previous to the commencement of the experiments. The time available for the completion of the work did not permit of an elimination of this by extended cleansing of the apparatus with the electrolytic gases. Consequently, the induction period was also found in the two following series. In the fourth series this influence seems to have disappeared.

TABLE I.

t.	P.	Titer.		H_2+ Cl_2+ 2HCl.	Mean value		dHCl.	dt.	k_a.	Emanation correction.	k_b.	k_c.
		Cl_2.	HCl.		Mm. HCl.	H_2 or Cl_2. Mm.						
0	676.5	18.35	0.50	37.20	9.15 13.45	332.6	4.30	1	12.93	99.0	13.06	8.83
1	657.5	16.27	0.66	33.20	13.07 26.02	319.0	12.95	1.75	23.20	98.0	23.68	15.56
2.75	638.7	16.50	1.36	34.36	25.28 47.15	301.2	21.87	3.91	18.57	96.0	19.34	12.36
6.66	620.7	13.80	2.20	29.80	45.82 72.65	280.7	26.83	5.0	19.12	92.8	20.60	12.79
11.66	602.8	12.45	3.30	28.20	70.55 140.6	248.6	70.05	13.14	21.44	86.6	24.76	14.92
24.8	585.2	9.30	5.66	24.26	136.6 163.7	217.5	27.10	6.7	18.60	80.3	23.17	13.56
31.5	569.7	8.85	6.87	24.57	159.3 211.9	192.0	52.60	16.4	16.71	73.6	22.70	12.93
47.9	551.8	6.90	8.17	21.97	.....	....	....	....	....	....	...	....

A rough test of the reactivity of the gases towards light showed that, although reactive, they were by no means comparable in activity with the gases employed by Bodenstein and Dux. The cause for this lay doubtlessly in the exhaustion of the hydrochloric acid from which the gases were produced.

TABLE II.

t.	P.	Titer.		H_2+ Cl_2+ 2HCl.	Mean value		dHCl.	dt.	k_a.	Emanation correction.	k_b.	k_c.
		Cl_2.	HCl.		Mm. HCl.	H_2 or Cl_2. Mm.						
0	698.5	16.65	0.566	33.87	11.68 13.43	343.0	1.75	1	5.10	99.7	5.12	3.58
1	678.7	18.00	0.706	36.71	13.05 21.24	330.3	8.19	1	24.08	99.0	24.32	16.51
2	660.0	15.63	1.01	32.37	20.65 39.01	315.1	18.36	2	29.14	98.0	29.73	19.62
4	640.7	15.70	1.973	33.37	37.84 56.50	296.7	18.66	2	31.45	96.4	32.62	20.90
6	622.7	13.10	2.533	28.73	54.90 66.59	281.0	11.69	2	(20.80)	95.0	(21.90)	(13.64)
8	577.2	12.80	3.066	28.67	61.73 127.5	241.3	65.77	9.2	28.97	91.0	31.84	18.38
17.2	526.1	9.00	5.10	23.10	116.2 138.1	199.5	21.90	3.55	30.91	86.7	35.66	18.76
20.75	435.9	8.13 5.70	5.783 4.866	22.04 16.27	114.4 130.4	156.7	16.00	3.25	31.42	84.5	37.20	16.20

The last value in Table III is of interest in view of the remarks made previously as to the importance of maintaining the mercury at a constant level in the emanation bulb tube. The sudden fall in the constant k_c

of the last measurement could not be accounted for until an observation of the reaction vessel showed that from some unknown cause (probably a release at the ground glass joint) the mercury level had fallen a centimeter or so in the capillary withdrawing, therefore, some of the emanation from the bulb, and so decreasing the energy factor E in the equation.

TABLE III.

t.	*P*.	Titer.		H_2+ Cl_2+ 2HCl.	Mm. HCl.	Mean value H_2 or Cl_2. Mm.	*d*HCl.	*dt*.	k_a.	Emanation correction.	k_b.	k_c.
		Cl_2.	HCl.									
0	697.5	19.15	0.466	38.77	8.38 15.94	342.7	7.56	2.1	10.50	99.3	10.57	7.37
2.1	678.8	17.10	0.80	35.00	15.51 27.74	328.6	12.23	1.9	19.59	98.0	19.98	13.57
4	658.6	17.20	1.466	35.87	26.92 36.94	313.3	10.02	2	16.00	96.4	16.60	10.93
6	640.2	13.60	1.617	28.82	35.91 91.94	288.1	56.03	10.1	19.26	92.2	20.89	13.37
16.1	620.2	13.12	4.40	30.64	89.06 105.8	261.4	16.74	3.9	16.42	87.4	18.79	11.65
20	602.8	12.20	5.017	29.42	102.8 122.3	245.1	19.50	4.1	19.40	84.5	22.95	13.83
25.1	303.2	11.10	5.65	27.85	61.5 112.7	108.0	51.20	18.4	25.77	77.3	33.34	10.11
43.5 67.75	294.4	3.80 2.80	4.50 5.266	12.10 10.87	109.5 142.6	84.0	(33.1)	24.25	(16.25)	65.9	(24.65)	(7.36)

TABLE IV.

t.	*P*.	Titer.		H_2+ Cl_2+ 2HCl.	Mm. HCl.	Mean value H_2 or Cl_2. Mm.	*d*HCl.	*dt*.	k_a.	Emanation correction.	k_b.	k_c.
		Cl_2.	HCl.									
0	858.0	15.76	7.66	39.18	167.7 181.1	341.8	13.4	1	39.2	99.7	39.32	33.7
1	835.2	13.12	7.02	33.26	176.3 183.6	327.6	7.3	1	22.3	99.0	22.53	18.8
2	807.2	14.18	7.99	36.35	177.4 185.1	313.0	7.7	1	24.6	98.3	25.04	20.2
3	756.0	10.98	6.533	28.49	173.4 189.0	287.4	15.6	2	27.1	97.2	27.92	21.1
5	733.2	12.00	8.00	32.00	183.3 196.1	271.7	12.8	2	23.56	95.7	24.62	18.0
7	671.3	10.30	7.523	28.12	179.6 240.6	230.6	61.0	10	26.45	91.5	28.90	19.4
17	652.7	7.20	8.04	22.44	233.9 243.5	207.0	9.6	2	23.19	87.3	26.56	17.3
19	601.5	7.27	8.656	23.20	224.0 235.5	185.9	11.5	2.6	23.79	85.7	27.75	16.7
21.6	585.4	5.96	7.693	19.61	229.6 246.7	173.6	17.1	3.1	31.77	84.0	37.83	22.1
24.7	544.3	5.72	8.333	19.77	229.4 291.6	141.9	62.2	16.8	26.10	78.0	33.40	18.2
41.5 46.2	528.0 510.0	4.33 3.86	9.99 10.07	18.65 17.79	282.8 298.8	118.6	16.0	4.7	28.70	71.9	39.92	21.1

At such low pressures as are reached in the later measurements of Expt. 3 (pressures 303 and 294 mm.) it is obvious that the absorption of the alpha particles cannot be regarded as complete, and the value found for k_c is low. To avoid a correction for incomplete absorption and yet at the same time obtain an extended range of pressure variation, Expt. 4 was performed. The residual gases from Expt. 3 were left in the reaction vessel, which was then cooled in a mixture of solid carbon dioxide and acetone. Fresh hydrogen and chlorine were led into the vessel from the gasometer until it was full at the prevailing temperature. The taps were then closed and the cooling mixture removed. On the attainment of room temperature it is clear that the reaction vessel was filled with a hydrogen, chlorine, hydrochloric acid mixture at more than atmospheric pressure. It was during this operation that the contrivance for maintaining a constant mercury level in the capillary emanation tube was shown to functionate so well; for at the low temperature attained (about —20°, as calculated from the pressure measurement) the contraction in volume of the mercury was quite small.

Discussion of the Results.

The constancy of the values tabulated in the last column, k_c, of the several tables permits of the following conclusions being drawn:

1. The combination of hydrogen and chlorine under the influence of alpha particles is a reaction of the first order. As the hydrogen and chlorine are present in equivalent amounts it is not possible to state definitely from the results that the reaction is proportional to the chlorine concentration, though this is probably the case. This point could only be established by variation of the ratios of hydrogen to chlorine employed.

2. The hydrochloric acid formed is without influence on the velocity.

3. Oxygen retards the reaction, such that the velocity at all stages of the decomposition is inversely proportional to the oxygen concentration.

4. The experimental facts may be interpreted by means of a reaction velocity equation:

$$+\frac{d[2\mathrm{HCl}]}{dt} = k\,J\,\frac{[\mathrm{Cl_2}]}{[\mathrm{O_2}]}$$

It will, therefore, be seen that, as regards the kinetics of the combination, the reaction shows complete parallelism to the photochemical reaction. The point of divergence in the two velocity equations, *viz.*, the power of the chlorine concentration, is readily explainable by the fact that in the one case absorption of the available energy is complete and in the other quite small.

As regards parallelism between the ratios of energy absorbed to reaction produced, unfortunately, little can be said from the present work. The condition of affairs prevailing in Central Europe prevented a continuance of the work in the direction of more reactive gases and determination of the amount of radioactive energy employed. In this connection, however, the calculations of Lind from the results of Jorissen and Ringer tend to show that for each ion produced by the radiant energy 100 to 1000 molecules of hydrogen chloride are formed. Also, it must be remembered that the amount of oxygen present in the gaseous mixture exercises a profound influence on the energy ratio, as the present results and those of Chapman and Bodenstein show. For, it follows as a natural consequence of the reaction velocity equation developed, that in gases of absolute purity the reaction would be infinitely rapid; that is, a small quantity of energy would suffice to bring about an infinitely large combination of the gases. This conclusion is confirmed in the observation that extremely pure gases tend so easily to explode.

The point should be especially borne in mind when drawing conclusions such as were recently drawn by Le Blanc and Volmer.[1] The energy ratio required in the light reaction according to the calculations of these authors, *viz.*, that one electron must catalyze at least 10^{12} molecules, would easily be realized in an explosive mixture of the gases. Also, with regard to the further suggested proof which the authors bring forward—namely, that Röntgen rays bring about combination, but that in their gas mixture, at the most 10^4 molecules combine as a result of the liberation of one electron or ion—it must be recognized that such proof cannot be regarded as sound if, as seems very probable from analogy with the present communication, oxygen retards the rate of reaction. The authors mention further that their experimental conclusions do not exclude the possibility of the hydrogen-chlorinecombination taking place through a loosening (Lockerung) of the electrons such as was postulated by Stark. This observation overlooks one consequence of the theory of Stark, already emphasized by Bodenstein,[2] "der Fall, dass mehr als eine Molekel durch ein Quantum umgesetzt werden kann, ist bei Starks Darlegungen überhaupt nicht vorgesehen." As their results show, 10^4 molecules combine due to one ion.

It is evident, therefore, that an extension of this field of work with a view to determining the kinetics of the hydrogen–chlorine combination under the influence of Röntgen rays would not fail to be of interest. Also, an exact evaluation of the energy employed to chemical reaction produced, with a gas of *constant* composition, under the three influences, light, radioactive energy, and Röntgen rays, should be invaluable for the gaining of a closer insight into the reaction mechanism.

Summary.

The kinetics of the combination of hydrogen and chlorine under the influence of the alpha particles from radium emanation has been studied.

---

[1] *Loc. cit.*

[2] *Ibid.*, p. 394.

The technique of such radioactive investigations has been improved with a view to giving greater constancy of experimental conditions.

The reaction has been shown to be one of the first order, in agreement with a theory developed, whereby the velocity of formation of hydrochloric acid should be proportional to the energy employed and to the chlorine concentration, inversely proportional to the oxygen concentration.

The analogy between the photochemical reaction and the reaction studied has been emphasized and the bearing of the experimental results on the problem of the photochemical and Röntgen ray reactions has been discussed.

The experimental work of the preceding paper was carried out in the Koenigliche Technische Hochschule zu Hannover. To Professor Max Bodenstein, at whose suggestion the research was undertaken, the author wishes to express his deep indebtedness, as well for the generous advice and kindly interest as for the many details of experimental technique which made the work possible.

PRINCETON, N. J.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY, No. 242.]

THE DENSITIES AND DEGREES OF DISSOCIATION OF THE SATURATED VAPORS OF THE AMMONIUM HALIDES, AND THE RELATED THERMAL DATA.

BY ALEXANDER SMITH AND ROBERT H. LOMBARD.

Received November 13, 1914.

In the case of solids undergoing thermal dissociation the data which possess the greatest chemical significance are those relating to the *saturated* vapors, in which the components of the vapor are in equilibrium with each other and with the solid. Yet, in regard to the great majority of even the most familiar of such substances, as, for example, phosphorus pentachloride and the ammonium halides, definite, quantitative information in this direction has been absolutely lacking. The vapor (dissociation) pressures have been determined, sometimes repeatedly, but for the most part the densities of the unsaturated vapors (namely, at atmospheric pressure) have alone been measured. Of the very few systems involving saturated vapors which have been subjected to exact study, those of the sulfides of ammonium (Isambert and others) and calomel (Smith and Menzies[1]) may be mentioned.

As regards the ammonium halides, their dissociation pressures had not been determined with the requisite degree of accuracy. To secure consistent values for use in the present investigation, these pressures have

---

[1] THIS JOURNAL, 32, 1541 (1910); *Z. physik. Chem.*, 76, 251.