a difference of 1.8% which is far beyond the experimental error. The simple Stokes' law, therefore, is not applicable; an equation for α of the type mentioned above would have the form

$$\alpha = \frac{\lambda}{\lambda_0} (\eta)^{0.88}$$

if we assume for the present that the relationship between the conductivity and the viscosity, when the latter is changed by change in temperature, is the same as the (possible) relationship between conductivity and viscosity when the latter is changed by change in the concentration of the solutions. If α is calculated from this equation and substituted in the equation for the equilibrium law, no agreement is found with the demands of the latter.[1] Hence we believe that the conclusion of Schlesinger and Martin that in these solutions the true degree of dissociation is to be found from the conductivities without application of viscosity corrections has been corroborated, for we do not believe it possible that agreement as close as we have found between the equilibrium law and these conductivities could result from accidental cancelations of errors in the case of seven different substances, for some of them at two different temperatures.

The work on the behavior of formates and other salts in anhydrous formic acid as solvent is being continued along the lines already mentioned in previous papers. In addition, transference experiments are under way and the effect of the addition of non-ionized substances to the solvent is being investigated.

Chicago, Ill.

[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 December 2, 1915.

In a recent communication to This Journal,[2] the author recorded the results of certain investigations into the combination of hydrogen and chlorine under the influence of the energy obtained from radium emanation. By a study of the velocity with which the reaction proceeded the possible mechanism of the reaction was deduced and the conclusion was reached that the process was parallel in several important respects to that occurring in the photochemical combination of the two substances. The work which had been carried out in the laboratories of the Technische Hochschule, Hanover, Germany, was interrupted by the abnormal situa-

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[1] See footnote 2, p. 279.

[2] This Journal, 37, 24 (1915).

tion which arose in Central Europe last year, and as a consequence the results obtained did not represent the final conclusions from the work in hand. Since publication, the additional material obtained has been worked through and has led to several modifications of the original communication which it is desired here briefly to record.

In a personal communication, Professor Max Bodenstein, under whose direction the work was carried out, has called the attention of the writer to an error which was made in the original calculations from the velocity data which, when considered alone, modified considerably the actual results obtained. Further, to the then available results there is now to be added one further series, confirmatory of the preceding experimental work and supplying a basis for the consideration of several other factors of interest in the investigation. Also, consideration has been given to another factor, the correction factor for the alpha particles not absorbed by the gas but reaching the walls of the containing vessel there to lose the charge. Finally, from the available data, a computation has been made as to the amount of reaction between the constituents which the energy of the alpha particles could effect. It is the purpose of the following to summarize these several points.

As to the error in the calculation of the results from the experimental data. Reference to the original communication (pages 29 and 32) shows that the gases were analyzed after absorption in potassium iodide by titration with standard thiosulfate solution and estimation of the hydrochloric acid with standard baryta solution. To ensure greater accuracy, the acid titer was made with a baryta solution exactly one-third the strength of the thiosulfate solution. In the tables, the titers were presented in equivalent units. The solutions used were actually $N/20$ and $N/60$, respectively. From these tables of titers the actual volumes of hydrogen, chlorine and hydrogen chloride, as well as their respective partial pressures, could be calculated. In the calculations previously made the sum of the three gases in the sample analyzed was set equal to (2 × Thio titer + Baryta titer), on the assumption that Cl_2 was equal to H_2, and that, therefore, for the hydrogen there must be reckoned the same amount as for the chlorine. Obviously this is an error, since it overlooks the fact that the thiosulfate solution is $N/20$ with regard to Cl_1 and not for Cl_2, and that, therefore, the thio titration represents Cl_2 only when divided by two; then, to get the total for hydrogen and chlorine this has again to be multiplied by two. In other words, the thiosulfate titration as communicated in the original paper represents as it stands $H_2 + Cl_2$. The data previously obtained had, therefore, all to be subjected to the recalculation which the discovery of this error necessitated. Naturally in the earlier measurements of a series, in which the thiosulfate titration is large compared with the baryta, the divergence from the former values was considerable. The more hydrochloric acid produced, however, the less the divergence became.

Series 1.

		Titer.		2HCl.		Cl_2.		Emanation correction.			
t.	P.	Cl_2.	HCl.	*a*.	*b*.	*a*.	*b*.		G.	k_1. P/Em. G.	
0	676.5	18.35	0.50	9.4	11.8	328.9	326.5	0.997	0.99	5.2	11.8
1	657.5	16.27	0.66	11.5	26.1	317.3	303.2	0.984	0.98	18.4	
2.75	638.7	16.50	1.36	25.4	45.7	294.0	273.7	0.965	0.98	12.1	
6.67	620.7	13.80	2.20	44.4	67.9	266.0	242.5	0.932	0.97	13.0	
11.67	602.8	12.45	3.30	65.9	117.3	235.5	184.1	0.873	0.96	13.5	
24.80	585.2	9.30	5.66	113.8	131.1	178.8	171.1	0.809	0.95	11.6	
31.50	569.7	8.85	6.87	127.7	157.7	157.2	127.2	0.743	0.95	9.8	
47.9	551.8	6.90	8.17	...	...	...	...	...	..	..	
									General mean,	12.0	

Series 2.

0	698.5	16.65	0.566	12.0	13.8	337.3	336.5	0.997	0.99	3.7
1	678.7	18.00	0.706	13.4	21.5	326.0	317.9	0.989	0.99	17.5
2	660.0	15.63	1.01	20.8	39.2	309.2	290.8	0.978	0.98	18.9
4	640.7.	15.70	1.973	38.1	53.3	281.5	266.3	0.963	0.98	18.8
6	622.7	13.10	2.533	52.4	62.4	259.0	249.0	0.949	0.97	13.3
8	577.2	12.80	3.066	57.9	107.4	230.7	181.2	0.910	0.95	17.5
17.2	526.1	9.00	5.10	98.0	112.2	165.1	150.9	0.867	0.93	16.6
20.75	435.9	8.13	5.783	93.0	...	125.0	...	0.846	..	..
									General mean,	17.1

Series 3.

0	697.5	19.15	0.466	8.3	15.6	340.5	333.4	0.993	0.99	7.4	10.3
2.1	678.8	17.10	0.80	15.2	26.5	324.2	312.9	0.978	0.99	13.2	
4	658.6	17.20	1.466	25.7	35.0	303.6	294.3	0.963	0.98	10.7	
6	640.2	13.60	1.617	34.0	80.4	286.1	239.7	0.921	0.98	12.6	
16.1	620.2	13.12	4.40	77.8	90.3	232.3	219.8	0.874	0.97	10.3	
20	602.8	12.20	5.017	87.8	101.6	213.6	199.4	0.845	0.96	10.0	
25.1	303.2	11.10	5.65	52.3	82.8	99.3	68.9	0.773	0.73	10.1	
43.5	294.4	3.80	4.50	...	...	...	...	...	..	..	
									General mean,	10.6	

Series 4.

0	858.0	15.76	7.66	144.6	154.0	284.4	275.0	0.997	1.00	(28.2)
1	835.2	13.12	7.02	149.8	154.9	267.8	262.7	0.989	1.00	16.2
2	807.2	14.18	7.99	149.6	154.8	254.0	248.8	0.978	1.00	17.0
3	756.0	10.98	6.533	145.0	155.3	233.0	222.7	0.971	1.00	17.6
5	733.2	12.00	8.00	150.6	158.9	216.0	207.7	0.956	1.00	15.0
7	671.3	10.30	7.523	145.4	180.8	190.3	154.9	0.915	0.99	15.2
17	652.7	7.20	8.04	175.8	181.1	150.4	145.3	0.874	0.98	13.7
19	601.5	7.27	8.656	166.9	172.8	133.9	128.0	0.859	0.96	12.3
21.6	585.4	5.96	7.693	168.2	176.3	124.5	118.4	0.841	0.95	15.9
24.7	544.3	5.72	8.333	164.4	192.5	107.8	79.7	0.787	0.94	13.9
41.5	528.0	4.33	9.99	186.6	193.2	77.4	70.8	0.720	0.93	15.0
46.2	510.0	3.86	10.07	...	...	...	...	...	..	..
									General mean,	15.2

Series 5.

		2HCl.		Cl_2.				
t.	P.	a.	b.	a.	b.	Emanation correction.	G.	k_1. P/Em. G.
0	873.1	126.8	216.9	325.4	235.3	0.946	1.00	19.7
15.0	800.0	198.7	214.1	217.7	200.3	0.883	1.00	21.5
18.1	778.0	208.3	220.5	194.7	182.5	0.863	1.00	18.3
21.3	725.0	205.4	213.7	170.1	161.7	0.844	1.00	14.7
24.0	706.3	208.2	250.5	157.7	115.4	0.789	0.99	18.1
39.7	685.0	243.0	256.0	112.8	99.8	0.725	0.99	17.8
46.2	...	...	...	...	...	...	..	..
							General mean,	18.2

To the original material of the previous communication, recalculated in accordance with the above, there is now added a series (5) performed with the same emanation as that employed in Series 4 of the original work, with gas, however, which was obtained after regeneration of the hydrochloric acid solution from which the gases were prepared by electrolysis. The run of the figures obtained is in every way similar to those previously recorded. It will be shown, however, that the gases employed were considerably more reactive, due to replenishment of the hydrochloric acid used.

The correction for incomplete absorption of the alpha particles by the gas may now be considered. The range of the bulb employed was approximately 5.6 cm. in air. According to Rutherford[1] the range in hydrogen-chlorine-hydrochloric acid is greater than this. From the ionization curves there given, it is possible to effect a correction for the alpha particles which reach the outer glass walls. In this regard it must be observed that the range 5.6 cm. of the small bulb refers to the rays from Radium C alone and in this particular calculation for those radiations only which travel normally through the walls of the emanation bulb. The radiations from the emanation and from Radium A will all be absorbed in the gas. Also the alpha particles from Radium C passing transversely through the walls of the emanation bulb have a longer path in the glass and naturally, therefore, a shorter in the gas. It is possible, as was done by Lind,[2] to make an exact calculation of the alpha particles which so behave and to correct for them, but since the alpha particles whose activity is lost in the walls of the containing vessel forms but a small fraction of the total number emitted into the vessel, the correction employed has been taken as one-half of that correction which would be required were all the alpha particles from the Radium C to leave the emanation bulb normal to the bulb surface. In the preceding tables under G there is recorded the fraction of the alpha particles which are absorbed in the gas. The velocity

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[1] "Radioactive Substances and their Transformations," p. 161, *et seq.*

[2] *Sitz. der k. Akad. Wiss. Wien.*, 70 (1911); Wiener, *Monatsh.*, 32, 295 (1912).

constant must be corrected, therefore, for this factor by dividing the constant obtained $\frac{(k_1 \times P)}{\text{Emanation correction}}$ by the corresponding amount tabulated under G.

Certain conclusions may be drawn from the data yielded by the calculations tabulated above with regard to the reactivity of the gases used in the several series of measurements. In the earlier paper it was observed that a rough test of the gases towards light showed that they were by no means comparable in reactivity with the gases employed by Bodenstein and Dux. It was suggested that the cause lay in the exhaustion of the hydrochloric acid from which the gases were generated. This conclusion is confirmed by the following reasoning: Series 2 and 3 were carried out with the same filling of emanation. Likewise also were Series 4 and 5 effected with one sample of the emanation. Expt. 3 was started 24.75 hours later than Expt. 2. The emanation should, therefore, be 0.831 times less active in the later experiment. Were the gases of equal reactivity in the two series the velocity constant in the third series should be equal to $17.1 \times 0.831 = 14.2$. Actually, however, the value obtained was 10.6. The gases were, therefore, considerably less reactive. On the other hand, the time elapsing between the beginning of Expts. 4 and 5 was such that the emanation possessed only 0.686 of its value at the outset of Expt. 4, when the later series was started. In the intervening time, however, the hydrochloric acid had been replenished and so a more reactive gas mixture would be expected. That this is so is evident from the fact that $(0.686 \times k_4) = (0.686 \times 15.2) = 10.4$. Actually a reaction constant 18.2 was found. The gases were therefore considerably better.

It is of interest also to make a computation of the amount of reaction which is brought about by the energy supplied to the gaseous system. The emanation for an experiment was collected for four days from 10 mg. of radium bromide or in other units 6 mg. of radium. This quantity of material would yield approximately 3 millicuries of emanation in the given time. Assuming that of this quantity, the half ultimately arrived in the emanation bulb (which practical experience led one to believe) and that of this amount two-thirds was radiated into the gas and the remaining third was absorbed in the mercury, it may be computed that 4×10^{18} ions were radiated per second into the gas. In the most favorable case, the beginning of Series 2, the data obtained from the titers reveal that 7×10^{16} molecules of chlorine are converted per second into hydrogen chloride. That is, approximately 4000 molecules undergo reaction for each pair of ions radiated into a gas, which as regards light sensitivity was considerably inferior to that employed by Bodenstein and Dux and from which was calculated a reactivity of 10^6 molecules per quantum of light energy. The comparability of the two reactions in this regard is, therefore, in good measure established.

Between the researches here presented in their modified form and the photochemical investigations of the same chemical reaction by Bodenstein and Dux, a considerable degree of parallelism is quite evident. Any theory that aims to represent the facts of the one must evidently suggest, also, explanation of the other. The hypothesis originally put forward by Bodenstein to account for the kinetics of the photochemical reaction covers equally well the facts obtained from this radioactive study. It has, however, excited from many quarters a considerable amount of criticism, which has called for a reconsideration of the original theory. The conclusions to which such reconsideration has led will form the subject of another communication elsewhere by Professor Bodenstein, to whom is due in large part whatever material gain in knowledge the investigations herein recorded have yielded.

PRINCETON, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

THE OXIDATION OF HYDRAZINE. VII.

THE ALLEGED ROLE OF NITROUS ACID IN THE FORMATION OF HYDRONITRIC ACID.[1]

BY A. W. BROWNE AND O. R. OVERMAN.

Received August 26, 1915.

In a series of investigations[2] conducted in this laboratory, the behavior of a number of oxidizing agents toward hydrazine in aqueous solution, and usually in the presence of sulfuric acid, has been studied. On the basis of the results obtained it was found possible to classify the oxidizing agents provisionally into three groups comprising those substances that oxidize hydrazine at the boiling temperature in the presence of sulfuric acid:

(*a*) with formation of fairly large amounts of hydronitric acid and ammonia;

(*b*) with formation of little or no hydronitric acid, but large amounts of ammonia;

(*c*) with formation of little or no hydronitric acid and ammonia. Hy-

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by O. R. Overman in partial fulfilment of the requirements for the Degree of Doctor of Philosophy. The experimental work was completed in June, 1915.

A typewritten copy of the original thesis will be found in the files of the Cornell University Library.

[2] Browne, THIS JOURNAL, **27**, 551–5 (1905); Browne and Shetterly, *Ibid.*, **29**, 1305–12 (1907); **30**, 53–63 (1908); **31**, 221–37, 783–99 (1909); Hale and Redfield, **33**, 1353–62 (1911); Hale and Nunez, **33**, 1555–63 (1911).