

SUMMARY.

Substance.	Temperature.	Specific gravity.	Cub. coeff. of expansion.
As ₂ O ₃	50°	3.851	(50-25°)
	25°	3.865	0.00012 (25-0°)
	0°	3.874	0.00011
PbCl ₂	50°	5.872	(50-25°)
	25°	5.885	0.00009 (25-0°)
	0°	5.899	0.00009
PbBr ₂	50°	6.644	(50-25°)
	25°	5.669	0.00009 (25-0°)
	0°	6.676	0.00010
PrCl ₃	25°	4.020	

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, THE UNIVERSITY OF CHICAGO.]

STUDIES IN CONDUCTIVITY. III. FURTHER STUDIES ON THE BEHAVIOR OF THE ALKALI METAL FORMATES IN (ANHYDROUS) FORMIC ACID.

BY H. I. SCHLESINGER AND CLYDE COLEMAN.¹

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The work herein reported is a continuation of that of Schlesinger and Martin² on the conductivity of formic acid solutions of formates. It was shown by them that the formates of sodium, potassium, ammonium and phenyl ammonium obey *the law of chemical equilibrium* over a fairly large range of concentration *even though these salts are highly ionized*, provided that the degree of ionization is calculated without reference to the viscosity of the solutions. When a viscosity correction was made it was found that the agreement between the law and the experimental data disappeared. It was pointed out, however, that the viscosity data might have been somewhat inaccurate because a small viscometer of the Ostwald type was used. Hence it seemed necessary to repeat the viscosity determinations under more favorable experimental conditions. Furthermore, since the simple inverse proportionality between viscosity and conductivity, as predicted by Stokes' law does not usually fit experimental data on conductivity, information on the possible relation was sought by

¹ The work presented in this article constitutes the basis of a dissertation submitted by Clyde Coleman to the faculty of the University of Chicago in part fulfillment of the requirements for the degree of Doctor of Philosophy.

² THIS JOURNAL, 36, 1589 (1914). We shall use the abbreviation S. and M. hereafter in referring to this paper.

obtaining conductivity and viscosity data at two temperatures. Investigation of these points fully confirmed the work of S. and M. Strong electrolytes, however, do not in general obey the law of chemical equilibrium. Hence it was desired to extend the measurements to as many uni-univalent salts as possible and we, therefore, chose the as yet uninvestigated formates of the alkali metals. In this way we have obtained the ionization constants of a series of salts within the same chemical group and the values of these constants show some interesting relationships. We shall, however, present first the new experimental data in their entirety and leave the discussion of the results to a brief summary.

In most of the details the methods of S. and M. were followed without change. The formic acid was prepared according to their method and was of the same quality as reported by them.¹ The solutions were made up and the conductivities and densities measured as described by them. In place of the small Ostwald viscometer which they used, and which gave too short a period of transpiration to assure agreement with Poiseuille's law and accurate time measurement, we employed a quartz viscometer, made according to the directions of Washburn and Williams.² The formates were prepared from the carbonates by treatment with formic acid. The sodium formate was part of the same sample as that used in the previous work. Lithium formate was recrystallized from the anhydrous acid, the resulting product heated for about a day at 125° to drive off most of the acid and then recrystallized from alcohol. The rubidium carbonate from which the formate was made contained a small amount of potassium as revealed by the spectroscope. The formate on recrystallization from the acid retained the latter so tenaciously that it was necessary to neutralize the residual acid with the carbonate before recrystallization from alcohol. The final sample did not show the potassium lines; as the rubidium and potassium red lines are so close together it is possible that a trace of potassium remained in the salt, but it must have been very small. The procedure for the preparation of caesium formate is like that for the rubidium salt except that ether must be added to reprecipitate the salt from the alcohol solution. The original caesium carbonate contained sodium. Here likewise there appeared to be only a trace, if any, of the impurity left after the recrystallizations. All of the salts were analyzed by conversion into the sulfate and found pure within the limits of the analytical method. Rubidium and caesium formates are exceedingly hygroscopic. They were, therefore, always kept in a glass stoppered weighing tube, one end of which was drawn out so as to fit the neck of the volumetric flask. This permitted the transfer and weighing of the material, prelim-

¹ The conductivity of the acid at 25° averaged about 6.4×10^{-5} and at 18° about 5.6×10^{-5} reciprocal ohms.

² THIS JOURNAL, 35, 737 (1913).

inary to making the solutions, with a minimum exposure to moisture.

Table I gives the data for the conductivity of sodium formate at 18°. In Col. 1 is given the concentration c in gram mols per liter of solution; in Col. 2 the specific conductivity (χ) in reciprocal ohms; in Col. 3, the specific conductivity (χ_a) corrected for the conductivity of the solvent; in Col. 4 the equivalent conductivity (λ_a) calculated from the corrected specific conductivity; in Col. 5 the degree of ionization (α), the necessary λ_0 being found by plotting $C\lambda_a/1000$ against $100/\lambda_a$;¹ in Col. 6 the ionization constant K as given by the equation $\alpha^2c/1 - \alpha = K$; and in Col. 7 the percentage error in the measured conductivity which would account for the deviations of the individual values of K from the average value. This percentage error is given because relatively large deviations in the constant may be due to very small errors in the conductivity, which is the measured quantity most liable to error. It will be seen that this error does not exceed in any case 0.20%.

TABLE I.—THE CONDUCTIVITY OF SODIUM FORMATE SOLUTION AT 18°
In Anhydrous Formic Acid.

C.	χ .	χ_a .	λ_a .	α .	K.	% error.
0	57.57
0.05869	0.003206	0.003152	53.71	0.933	0.760	0.16
0.06438	0.003495	0.003441	53.31	0.926	0.746	0.00
0.07724	0.004115	0.004059	52.55	0.913	0.738	0.10
0.08320	0.004418	0.004364	52.33	0.909	0.759	0.15
0.09323	0.004886	0.004832	51.83	0.900	0.757	0.10
0.09739	0.005074	0.005018	51.52	0.895	0.741	0.05
0.1111	0.005696	0.005642	50.78	0.882	0.732	0.19
0.1158	0.005909	0.005855	50.55	0.878	0.732	0.20
0.1310	0.006611	0.006555	50.02	0.869	0.755	0.15
0.1365	0.006828	0.006774	49.63	0.862	0.734	0.17
0.1569	0.007711	0.007656	48.78	0.847	0.738	0.15
0.1660	0.008108	0.008054	48.52	0.843	0.750	0.06
0.1808	0.008722	0.008666	47.93	0.832	0.748	0.05
0.1878	0.009014	0.008960	47.71	0.829	0.752	0.14
0.2238	0.01043	0.01037	46.35	0.805	0.744	0.04
0.2794	0.01253	0.01248	44.66	0.776	0.750	0.10
0.2832	0.01267	0.01261	44.55	0.774	0.749	0.13
0.2997	0.01330	0.01324	43.99	0.764	0.741	0.16
0.3258	0.01417	0.01412	43.34	0.753	0.746	0.00
0.3453	0.01480	0.01474	42.70	0.742	[0.735]	..

Av., 0.746

Table II gives the viscosity data obtained with the quartz viscometer.² In Col. 1 are presented the concentrations (c) in gram mols per liter of solution; in Col. 2 the relative viscosity, $\text{rel } \eta_{25^\circ}$, of the solution at 25°;

¹ See Kraus and Bray, *THIS JOURNAL*, 35, 1324 (1913); also S. and M., p. 1596.

² The simple formula, $n_2 = n_1 t_2 d_2 / t_1 d_1$, can be used with this instrument and the viscosities were calculated by its means from the time of transpiration and the densities.

in Col. 4 and 6 the densities (d_{18°) and the relative viscosities, $\text{rel } \eta_{18^\circ}$, respectively of the solutions at 18° . The viscosity data obtained with the quartz viscometer and those obtained with the small Ostwald instrument have been compared with one another by means of the interpolation formula which was found by S. and M. to reproduce their values.¹ These calculated values are found in Col. 3 and are seen to be in excellent agreement with those obtained in the more reliable Washburn viscometer. Hence we may conclude that all of the viscosity data of S. and M. have the same degree of reliability as those for the sodium formate solutions because for all of them the same instrument was used and about the same range of time of transpiration obtained. It is to be noted that the relative viscosities at 25° are based on the viscosity of the pure acid at this temperature, while those at 18° are based on the viscosity of the acid at 18° .² Finally it is possible to reproduce accurately the relative viscosity of the solutions at 18° by the method of interpolation used for the 25° data. This consists of choosing values for A corresponding to the concentration c and substituting them in the formula

$$\eta_{18^\circ} = 1 + Ac.$$

The values, A, for the different concentrations are given in Col. 5.

TABLE II.—RELATIVE VISCOSITY OF SODIUM FORMATE SOLUTIONS IN ANHYDROUS FORMIC ACID AT 25 AND 18° , AND DENSITIES AT 18° .

C.	rel η_{25° .	rel η_{25° calc.	d_{18° .	A_{18° .	rel η_{18° .
0	1.0000	1.0000	1.0000
0.05741	1.0408	1.041
0.06191	1.2254	0.756	1.0468
0.08267	1.2262	0.747	1.0618
0.1263	1.0876	1.086
0.1283	1.2275	0.735	1.0943
0.1962	1.1359	1.136
0.2107	1.2304	0.732	1.1543
0.2629	1.1834	1.181
0.3027	1.2331	0.732	1.2216
0.3708	1.2649	1.264
0.4925	1.2400	0.764	1.3763
0.5617	1.4103	1.409
0.5642	1.2421	0.771	1.4352

The densities at 18° can be reproduced very accurately by the formula

$$d = 1.2233^3 + 0.0335c.$$

¹ *Loc. cit.*

² The values of the viscosity of the pure acid at the two temperatures are given on p. 279.

³ It is to be noted, however, that the density of formic at 18° was found to be 1.2224 in several actual determinations. This figure was used in calculating the viscosities, as the difference is not within the error of the viscosity measurements. The analogous formula for rubidium formate solutions also contains the value 1.2233.

In Tables III and IV are given the conductivity data, together with the calculations for the equilibrium constants for lithium formate solutions at 25° and 18°, respectively. The various columns correspond entirely to those in Table I. It will be seen that the agreement with the equilibrium

TABLE III.—THE CONDUCTIVITY OF LITHIUM FORMATE SOLUTIONS AT 25°
In Anhydrous Formic Acid.

C.	κ .	κ_a .	λ_a .	α .	K.	% error.
0.00000	64.62
0.05748	0.003446	0.003379	58.79	0.9101	0.530	0.00
0.06920	0.004062	0.003995	57.74	0.8938	0.521	0.12
0.07777	0.004517	0.004450	57.22	0.8856	0.533	0.06
0.08100	0.004693	0.004626	56.98	0.8821	0.535	0.09
0.08619	0.004932	0.004865	56.43	0.8736	0.520	0.20
0.1102	0.006113	0.006047	54.85	0.8491	0.527	0.12
0.1218	0.006658	0.006591	54.11	0.8377	0.527	0.13
0.1365	0.007338	0.007270	53.30	0.8252	0.532	0.05
0.1550	0.008172	0.008105	52.30	0.8096	0.534	0.10
0.1785	0.009178	0.009111	51.07	0.7906	0.533	0.09
0.1955	0.009901	0.009834	50.31	0.7791	0.537	0.25
0.2078	0.01039	0.010326	49.70	0.7694	0.533	0.10
0.2331	0.01139	0.01132	48.57	0.7518	0.531	0.04
0.2622	0.01249	0.01242	47.37	0.7333	0.529	0.05
0.2833	0.01327	0.01321	46.62	0.7217	0.530	0.00
0.3056	0.01408	0.01401	45.85	0.7098	0.530	0.03
0.3081	0.01412	0.01405	45.62	0.7062	0.523	
0.3374	0.01513	0.01507	44.66	0.6914	0.522	
0.3605	0.01588	0.01581	43.86	0.6789	0.517	
0.3869	0.01671	0.01664	43.01	0.6658	0.513	
0.4272	0.01792	0.01786	41.81	0.6472	0.507	
0.4545	0.01874	0.01868	41.10	0.6363	0.506	
0.4938	0.01978	0.01972	39.93	0.6182	0.494	

TABLE IV.—THE CONDUCTIVITY OF LITHIUM FORMATE SOLUTIONS AT 18°
In Anhydrous Formic Acid.

C.	κ .	κ_a .	λ_a .	α .	K.	% error.
0	56.79
0.07305	0.003748	0.003691	50.53	0.8898	0.525	0.16
0.08728	0.004377	0.004320	49.51	0.8718	0.517	0.05
0.1257	0.005983	0.005925	47.15	0.8303	0.511	0.14
0.1678	0.007621	0.007567	45.09	0.7940	0.513	0.06
0.1690	0.007665	0.007608	45.02	0.7929	0.513	0.12
0.2018	0.008855	0.008799	43.60	0.7678	0.512	0.12
0.2054	0.008997	0.008939	43.50	0.7660	0.515	0.01
0.2216	0.009569	0.009510	42.92	0.7558	0.518	0.10
0.2531	0.01063	0.01057	41.75	0.7353	0.517	0.05
0.2642	0.01098	0.01092	41.36	0.7283	0.516	0.01
0.3045	0.01225	0.01219	40.05	0.7052	0.514	0.08
0.3598	0.01383	0.01377	38.27	0.6739	0.500	
0.4178	0.01540	0.01535	36.74	0.6470	0.495	
0.4501	0.01623	0.01617	36.04	0.6347	0.496	
0.4834	0.01698	0.01630	35.01	0.6130	0.469	

law at both temperatures is excellent; in only one experiment does the maximum experimental error corresponding to the deviation from the average value amount to more than 0.20%, and in most of them the error is only about one-half of this. Systematic deviation from the equilibrium law seems to begin at a concentration of about 0.3 molar, from which point, as the concentration increases, the value of the "constant" falls steadily.¹

In Table V are given the relative viscosity and the density data for lithium formate solutions at 25° and 18°. The meaning of the data in the various columns will need no further description. The terms relative viscosity are used in this table as in all others in the sense described in the discussion of Table II.

TABLE V.—RELATIVE VISCOSITY AND DENSITY OF LITHIUM FORMATE SOLUTIONS IN FORMIC ACID AT 18° AND 25°.

C.	d_{25}° .	d_{18}° .	rel η_{25}° .	rel η_{18}° .
0	1.2142	1.2224	1.0000	1.0000
0.08513	..	1.2242	..	1.0595
0.08583	1.2174	..	1.0566 ¹	..
0.08729	1.2164
0.1292	..	1.2255	..	1.0884
0.1347	1.2170	..	1.0885	..
0.1810	..	1.2264	..	1.1202
0.2039	1.2181	..	1.1330	..
0.2605	1.2190	..	1.1711	..
0.2703	..	1.2284	..	1.1861
0.3441	..	1.2301	..	1.2343
0.3446	1.2275 ²	..
0.4064	1.2223	..	1.2690	..
0.4335	..	1.2319	..	1.2914
0.4669	1.2240	..	1.3117	..

The densities of the solutions at 25° are accurately reproduced by the formula $d = 1.2142 + 0.021c$; at 18°, by the formula $d = 1.2224 + 0.0222c$.

As was pointed out by S. and M. the viscosities are not a linear function of the concentration, the constant A in the formula $\eta = 1 + Ac$ usually showing a minimum. The variation in A for the data at 25° is very small, however, in the case of lithium formate solutions, so that they can be reproduced fairly well by the formula $\text{rel } \eta_{25}^{\circ} = 1 + 0.66c$ while at 18° the formula $\text{rel } \eta_{18}^{\circ} = 1 + 0.695c$ gives merely a rough interpolation. The minimum, which is reached at a concentration about 0.18 molar, in the A value for the last equation is 0.68, which is sufficient to introduce an error greater than the experimental one.

¹ See S. and M., *Loc. cit.*, p. 1599.

² The viscosity of this solution was calculated from the density obtained by the formula.

In Table VI and VII are given the conductivity data for rubidium formate solutions at 25° and 18°, respectively. It will be seen that agreement with the equilibrium law is again excellent; in only one of the determinations is there an error greater than 0.2%. Systematic deviation from the law begins apparently at a concentration somewhat greater than 0.3 molar.

TABLE VI.—CONDUCTIVITY OF RUBIDIUM FORMATE SOLUTIONS IN FORMIC ACID AT 25°.

C.	κ .	κ_a .	λ_a .	α .	K.	% error.
0	69.88
0.04964	0.003390	0.003322	66.92	0.9579	1.082	0.00
0.06852	0.004581	0.004517	66.86	0.9434	1.078	0.03
0.08026	0.005302	0.005238	65.27	0.9341	1.063	0.12
0.1088	0.007025	0.006961	64.05	0.9167	1.096	0.08
0.1489	0.009334	0.009272	62.29	0.8910	1.084	0.01
0.1742	0.01075	0.01069	61.33	0.8776	1.096	0.08
0.1990	0.01200	0.01194	60.30	0.8626	1.072	0.09
0.2438	0.01437	0.01431	58.70	0.8400	1.075	0.08
0.2779	0.01610	0.01603	57.70	0.8257	1.087	0.03
0.3096	0.01762	0.01755	56.69	0.8112	1.079	0.02
0.3477	0.01943	0.01937	55.69	0.7970	1.088	0.04
0.3877	0.02117	0.02110	54.44	0.7790	1.065	..
0.3924	0.02131	0.02125	54.23	0.7760	1.055	..
0.4237	0.02274	0.02268	53.53	0.7661	1.063	..

TABLE VII.—THE CONDUCTIVITY OF RUBIDIUM FORMATE SOLUTIONS IN FORMIC ACID AT 18°.

C.	κ .	κ_a .	λ_a .	α .	K.	% error.
0	61.35
0.07128	0.004146	0.004094	57.37	0.935	0.964	0.17
0.1066	0.005994	0.005942	55.74	0.908	0.961	0.22
0.1583	0.008580	0.008524	53.82	0.877	0.995	0.05
0.1685	0.009071	0.009015	53.51	0.872	1.000	0.16
0.2200	0.01143	0.01138	51.73	0.843	0.999	0.10
0.2685	0.01358	0.01352	50.35	0.821	1.008	0.30
0.3210	0.01572	0.01566	48.80	0.796	0.994	0.05

In order to be able to make the calculation discussed in the footnote on p. 280, the densities of the rubidium formate solutions were determined to an accuracy of about 0.2% by the method already mentioned. The data for the individual experiments need not be given as the following formulas reproduce them sufficiently closely. At 25°

$$d = 1.2142 + 0.085c$$

and at 18°

$$d = 1.2233 + 0.080c.$$

In Table VIII are given the conductivity data for caesium formate solutions at 25°. Here again deviation from the equilibrium law is very small—in most cases far below 0.2%. Systematic deviation seems to begin at about 0.38 molar.

TABLE VIII.—CONDUCTIVITY OF CAESIUM FORMATE SOLUTIONS IN ANHYDROUS FORMIC ACID AT 25°.

C.	α .	α_a .	λ_a .	α .	K.	% error.
0	64.96
0.03057	0.002001	0.001938	63.39	0.9756	1.193	0.03
0.05543	0.003515	0.003454	62.29	0.9586	1.230	0.16
0.07919	0.004899	0.004836	61.07	0.9399	1.164	0.05
0.1019	0.006185	0.006121	60.09	0.9249	1.160	0.10
0.1419	0.008374	0.008311	58.57	0.9013	1.169	0.04
0.2008	0.01142	0.01136	56.55	0.8704	1.174	0.01
0.2577	0.01421	0.01415	54.90	0.8449	1.186	0.01
0.2961	0.01601	0.01595	53.84	0.8286	1.186	0.01
0.3449	0.01816	0.01810	52.47	0.8076	1.169	0.15
0.3893	0.01996	0.01989	51.10	0.7864	1.159	..

Summary.

1. The solutions of the highly ionized formates of lithium, rubidium and caesium in (anhydrous) formic acid are found to obey the law of chemical equilibrium over a fairly large range of concentration when the degree of dissociation is calculated from the conductivity data without correction for the changing viscosity of the solutions. For the formates of sodium, lithium and rubidium this has been established at the two temperatures, 25° and 18°. Table IX gives a list of the formates thus far investigated from this point of view, and summarizes briefly the numerical values of a number of the important constants. In the table, K means the equilibrium constants; the other headings need no further explanation.

TABLE IX.—TABLE OF CONSTANTS.¹

Substance.	K _{25°} .	K _{18°} .	$\lambda_{25°}$.	$\lambda_{18°}$.	$\lambda_{25°}/\lambda_{18°}$.
Lithium formate.....	0.530	0.515	64.6	56.8	1.138
Phenyl ammonium formate.....	0.798*	...	64.7*
Sodium formate.....	0.815*	0.746	65.4*	57.6	1.135
Potassium formate.....	1.019*	...	68.9*
Rubidium formate.....	1.082	0.989	69.9	61.3	1.139
Caesium formate.....	1.181	...	65.0
Ammonium formate.....	1.230*	...	69.9*

Av., 1.137

There are a number of regularities which may be pointed out very briefly.

(1) The value of the constant increases with the atomic weight of the alkali metal ion² and consequently also with the electrolytic solution tension of the metal. In the same way, the value of the conductivity at infinite dilution increases with the atomic weight, but in this series there is a striking exception in the case of caesium. Furthermore it will be seen

¹ Data marked * are taken from the work of S. and M.

² Leaving out of consideration, of course, the ammonium and the phenyl ammonium ions.

that the constant at 18° is, in each case where the data are at hand, less than that at 25° indicating that the process of ionization in these solutions is accompanied by absorption of heat.¹ If we use these data for a rough calculation of the heat of dissociation by means of the formula

$$\frac{d \ln K}{dt} = \frac{Q}{RT^2},$$

integrated on the assumption that the heat of reaction is constant over this small range of temperature we obtain about 700, 2180 and 2200 cal. for the heat of dissociation of lithium, sodium and rubidium formates, respectively. In aqueous solutions it is believed that the degree of electrolytic dissociation of the strong electrolytes usually decreases with rise of temperature, whereas in the cases here described the reverse is true.

(2) We have repeated the work of S. and M. on the viscosity of sodium formate at 25°, using a Washburn quartz viscometer, and have found that the new data correspond practically exactly with the older ones. Hence we may have the same degree of confidence in all of the older data on the viscosity of formate solutions as has already been explained. Furthermore, while all of the conductivity data thus far at hand agree with the demands of the equilibrium law if the degree of dissociation is calculated from the equation $\alpha = \lambda/\lambda_0$, none of them show this agreement if the equation $\alpha = \eta \lambda/\lambda_0$ is used,² where η is the relative viscosity of the solutions. Since it has been frequently suggested that a more suitable equation for calculating the degree of dissociation is $\alpha = (\eta)^p \lambda/\lambda_0$ we have compared the viscosities of the solvent and the conductivities at infinite dilution at two temperatures (18° and 25°) for three of the formates in order to get some indication of the value of "*p*." It will be seen from Col. 5 of Table IX that the ratio of the conductivities at infinite dilution (λ_0) at the two temperatures is practically the same for the three substances for which we have the necessary data; the difference between them, about 0.35%, is probably within the range of experimental error when it is considered that each λ_0 value is obtained by extrapolation. The viscosity of formic acid was found by us to be 0.01865 at 18°, while at 25° it was 0.01605. The ratio of viscosities at the two temperatures is, therefore, 1.16, while the average of the inverse of the corresponding ratio of λ_0 values is 1.14,

¹ By means of the density data given in this paper and in that of S. and M., it is possible to calculate the concentrations of the solutions in terms of gram molecules per 1000 cc. of solvent instead of 1000 cc. of solution as herein given. From these new values for the concentrations new values for the equivalent conductivities and for the constants can be obtained. While these new constants differ somewhat from the others, their *relative* value is the same and the agreement with the equilibrium law is as good as when calculated the other way. Also of course the calculated values for *Q* are the same as those given herein.

² The data resulting from these calculations have not been presented in this paper because they are just like those given by Schlesinger and Martin.

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.

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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-

¹ See footnote 2, p. 279.

² *THIS JOURNAL*, 37, 24 (1915).