

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE VELOCITY OF THE REACTION BETWEEN FERROUS CHLORIDE, POTASSIUM CHLORATE AND HYDROCHLORIC ACID.

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I. PURPOSE OF THE INVESTIGATION.

THE velocity of the reaction between ferrous sulphate, potassium chlorate, and sulphuric acid was investigated many years ago by J. J. Hood.¹ The results of his experiments are briefly as follows: In the presence of an undetermined excess of sulphuric acid, the velocity of the reaction at any moment was found to be directly proportional, throughout each separate series of experiments, to the product of the concentrations of the ferrous sulphate and potassium chlorate. This was proved to be true not only in the series where these two substances were originally present in equivalent amounts, but also in those where one or the other of the two substances was present in excess. The author states, without presenting experimental results, that the same law was found to govern the reaction between ferrous chloride, potassium chlorate, and hydrochloric acid. He also studied the effect of acid on the former reaction, and showed that its velocity increased more rapidly than the increase in the concentration of the acid. He determined, furthermore, the relative influence of sulphuric and hydrochloric acids on the rate of the reaction, and also the effect of varying the temperature between the limits of 10° and 32°.

We have undertaken the investigation of the very similar reaction referred to in the title of this article with several objects in view: First, in order to confirm Hood's conclusion that the reaction is one of the second order with respect to the ferrous salt and the chlorate, by the far more reliable method² of varying the initial concentration and comparing the velocity constants of the different series. Second, in order to determine more definitely the influence of acid, especially hydrochloric acid, on the speed of the reaction: if found proportional to the concentration of the acid, the result would be of interest as furnishing a new

¹ *Phil. Mag.* (5), 6, 371; 8, 121; 20, 323.

² See Noyes: *Ztschr. phys. Chem.*, 18, 118.

example of a third order reaction; if not proportional, the velocity might prove, like that of the reaction between hydriodic and bromic acids,¹ to be proportional to the square or some other simple power of the concentration of the hydrogen ions. Third, in order to investigate within wider limits the effect of temperature on the velocity of the reaction, with a view of further confirming the remarkable laws which have lately been discovered in regard to the relation between temperature and reaction-velocity.

It seemed desirable, moreover, to undertake this investigation in spite of the extended experiments of Hood on the analogous sulphate reaction, by reason of the fact that, according to the Electrolytic Dissociation Theory, the molecular composition of the dissolved substances is much simpler in the case of the chlorides than in that of the sulphates; namely, at the concentration used in these experiments, hydrochloric acid is nearly completely dissociated, while sulphuric acid is dissociated only to a moderate extent, so that its degree of dissociation varies considerably with its concentration, which is therefore not proportional to the concentration of the hydrogen ions. Furthermore, ferrous sulphate is less dissociated than ferrous chloride; and ferric sulphate, which is a product of the reaction, is hydrolyzed to a greater extent than the corresponding chloride. A closer correspondence of the experimental results with simple empirical and theoretical formulas is therefore to be expected in the case of the chloride.

2. THE EXPERIMENTAL METHOD OF PROCEDURE.

The standard stock solutions employed in our investigation were a half-normal solution of ferrous chloride and one of potassium chlorate, a normal solution of hydrochloric acid, and an approximately tenth-normal solution of potassium permanganate.¹ The ferrous chloride solution was prepared by boiling strong hydrochloric acid with a large excess of pure iron wire, with a return cooler, as long as any action took place; the solution was then diluted until it became exactly half-normal, a standard potassium bichromate solution being used for this purpose. The

¹ Noyes: *Ztschr. phys. chem.*, 19, 599.

² The word normal is used throughout this article with reference to the oxidizing power of the substance.

ferrous chloride solution was kept under a pressure of carbon dioxide, in order to prevent its oxidation. A chlorine determination made in it showed that it was almost perfectly neutral. The half-normal potassium chlorate solution was made by dissolving 10.21 grams of the recrystallized commercial salt in one liter of water. The hydrochloric acid solution was prepared by diluting the chemically pure acid, pure calcium carbonate being used for its standardization. The permanganate solution used was standardized against the ferrous chloride solution, and was found to be 0.1011 normal; 25.00 cc. of the ferrous solution, measured after it was diluted to a tenth-normal concentration, therefore required 24.72 cc. of this permanganate solution.

In carrying out the velocity experiments, a mixture of the reacting substances consisting of 250 or 500 cc. was made up by means of pipettes from the stock solutions and from freshly boiled distilled water in glass-stoppered bottles from which the air had been displaced by carbon dioxide. The appropriate amounts of water, ferrous chloride solution, and hydrochloric acid, were first placed in the bottles, which were then put into a large water thermostat provided with an efficient stirrer. After the mixture had attained the temperature of the bath, the proper amount (50 or 100 cc.) of the chlorate solution previously brought to the same temperature, was added from a rapidly delivering pipette, the time noted, and the mixture instantly shaken. After suitable intervals, portions of twenty-five or fifty cc. were removed, and run into 200-300 cc. of cold, boiled water containing about one gram of manganous sulphate and small quantities of sulphuric acid and sodium phosphate; this solution was then immediately titrated with the permanganate. It is known¹ that under these conditions the permanganate process furnishes accurate results, even though chlorides are present; and in our own experiments no difficulty was found in getting a sharp endpoint.

The temperature of the thermostat was kept constant in all cases within 0.1° C., and was 20° unless otherwise mentioned.

3. EXPERIMENTAL RESULTS ON THE EFFECT OF THE CONCENTRATION OF THE REACTING SUBSTANCES.

The three reacting substances were brought together in nine

¹ Zimmermann: *Ber. d. chem. Ges.*, 14, 779; Reinhardt: *Chem. Ztg.*, 13, 323; Mixer and DuBois: *This Journal*, 17, 406.

different proportions, in order to establish with certainty the order of the reaction, and to show the effect of each substance separately on its velocity. In the first five series the concentrations of the ferrous chloride and potassium chlorate were kept constant, and that of the hydrochloric was varied. In five of the series, on the other hand, the amount of acid present was constant, and the concentrations of the other two substances were variable.

Check determinations were made in every case. The results of all these experiments are presented in the table below. The values in the column headed t are the times in minutes counted from the moment of mixing. Those in the columns headed x_1 and x_2 are the number of cubic centimeters of the permanganate solution corresponding to the amount of ferrous salt already oxidized at the time t in the two duplicate experiments. The values of x are the means of these two quantities. The values of $A - x$ represent the number of cubic centimeters corresponding to the unoxidized ferrous salt present at the time t . The initial value of ferrous salt in terms of the permanganate—that is, the value of A —is 24.72 in all the series except Nos. 7 and 9, and 49.44 in the case of these two series.¹ The columns headed $10^6 C_2$ and $10^7 C_3$ contain the calculated values of the velocity-constants of the second and third orders respectively. The values of C_2 are those of the constant in the differential equation :

$$\frac{dx}{dt} = C_2(A - x)(B - x),$$

where A and B represent the initial quantities of ferrous chloride and potassium chlorate, and x the amount changed over at the time t , and where the variation in the concentration of the hydrochloric acid is disregarded. The values of C_2 are those of the constant in the equation :

$$\frac{dx}{dt} = C_3(A - x)(B - x)(C - x),$$

which states that the velocity of the reaction is directly proportional to the concentration of each of the three reacting substances. For the integrated forms of this equation by which the numerical calculations were made in the different cases, we refer

¹ For twenty-five cc. of the reaction-mixture were titrated in series Nos. 1 to 5, and in No. 9, and fifty cc. in the other series (Nos. 6 to 8).

to the article of Fuhrmann.¹ All of these constants are expressed in the same arbitrary units, those corresponding to the number of cubic centimeters of permanganate required for the titration. If the values of A , B , C , and x were expressed in gram-equivalents per liter, the values of C_2 would be 247.2 times, and the values of C_3 61120 times as great as those here given. We mention this fact, for we think it unfortunate that authors in presenting the results of investigations on the velocity of reactions so often neglect to determine, or at any rate to state, the factor by which their arbitrary reaction-constants can be reduced to an absolute standard.

TABLE I.

Series No.	Normal concentration of			t .	x_1 .	x_2 .	x .	$A - x$.	$10^6 C_2$.	$10^7 C_3$.
	FeCl ₂ .	KClO ₃ .	HCl.							
1	0.1	0.1	0.0	15	0.00	0.00	0.00	24.72
				45	0.03	0.01	0.02	24.70
				100	0.08	0.05	0.06	24.66
				250	0.55	0.48	0.51	24.21
2	0.1	0.1	0.1	5	1.22	1.14	1.19	23.53	408	171
				15	3.04	3.00	3.02	21.70	375	162
				35	5.79	5.97	5.88	18.85	360	168
				60	8.24	7.97	8.12	16.60	331	166
				110	11.26	11.07	11.17	13.55	303	173
				170	13.05	12.96	12.98	11.74	264	165
3	0.1	0.1	0.2	5	2.50	2.42	2.46	22.28	886	189
				15	5.42	5.40	5.41	19.31	756	162
				35	9.60	9.82	9.70	15.08	746	171
				60	12.25	12.35	12.30	12.40	670	160
				107	15.27	15.40	15.32	9.40	616	158
				167	17.54	17.67	17.62	7.10	600	136
4	0.1	0.1	0.3	5	3.37	3.22	3.32	21.40	1250	174
				12	6.57	6.42	6.49	18.23	1200	170
				22	9.56	9.47	9.52	15.20	1150	168
				35	12.27	12.22	12.25	12.47	1130	174
				55	14.47	14.60	14.54	10.18	1050	177
				85	16.97	16.97	16.97	7.75	1030	166
5	0.1	0.1	0.5	1	1.20	1.12	1.16	23.56	2000	163
				3	3.44	3.52	3.48	21.24	2210	181
				7	7.00	6.92	6.96	17.76	2240	189
				12	9.72	9.72	9.72	15.00	2180	185
				22	13.28	13.22	13.24	11.48	2120	185
				37	16.10	16.14	16.12	8.60	2050	182

¹ *Ztschr. phys. Chem.*, 4, 89.

Series No.	Normal concentration of			<i>t</i> .	x_1 .	x_2 .	x .	$A-x$.	$10^6 C_0$.	$10^7 C_3$.
	FeCl ₂ .	KClO ₃ .	HCl.							
6	0.05	0.05	0.2	5	1.12	1.08	1.10	23.62	708	153
				15	3.22	3.14	3.18	21.54	796	164
				50	7.97	8.10	8.02	16.70	776	165
				100	11.84	11.89	11.86	12.86	768	162
				160	14.62	14.67	14.65	10.07	738	165
				250	16.82	16.97	16.90	7.82	700	160
7	0.1	0.05	0.2	5	2.14	2.49	2.30	47.14	788	157
				12	4.72	4.87	4.30	44.64	790	160
				40	11.81	11.64	11.74	37.70	744	164
				70	15.54	15.51	15.53	33.91	708	161
				110	18.44	18.52	18.49	30.95	668	154
				170	21.10	20.94	21.04	28.40	642	149
8	0.05	0.1	0.2	5	2.02	2.27	2.17	22.55	762	161
				12	4.92	5.07	5.00	19.72	804	166
				22	8.02	8.10	8.07	16.65	798	169
				40	11.92	11.92	11.92	12.80	762	168
				70	15.92	15.86	15.89	8.83	740	160
				110	18.82	18.87	18.82	5.90	700	162
9	0.2	0.2	0.2	1	1.94	1.94	1.94	47.50	830	170
				2	3.72	3.76	3.74	45.70	830	175
				4	6.71	6.77	6.74	42.70	800	174
				7	10.29	10.24	10.26	39.20	749	170
				15	16.49	16.71	16.61	32.83	682	173
				25	21.32	21.26	21.29	28.15	612	170

4. DISCUSSION OF THE RESULTS ON THE EFFECT OF THE CONCENTRATION OF THE REACTING SUBSTANCES.

The first series of experiments presented above clearly shows that in neutral solution the reaction does not take place to an appreciable extent. The very slight decrease in the concentration of the ferrous salt, amounting only to a quarter of a per cent. in 100 minutes and to two per cent. in 250 minutes, may well be due to oxidation by the air or to the presence of a small quantity of acid in the ferrous chloride solution.

Attention may next be directed to the fact that, in the experiments in which the acid was present in large excess, especially in Series No. 5, the values of C_0 are nearly constant, thus confirming Hood's conclusion that the velocity of the reaction under such circumstances is directly proportional to the product of the concentrations of the ferrous salt and of the chlorate.

The order of the reaction and the effect of each substance on

its velocity, is, however, best determined by applying to the results as a whole the two distinct methods available for this purpose.

The first of these methods is the one most commonly employed. It consists in determining which order of constants shows the smallest variations throughout each *separate* series of experiments. Now, a brief inspection of the foregoing table suffices to show that, in all the series except those where a large excess of the acid was present, the values of C_2 show a continuous decrease as the reaction progresses; that the value of C_3 , on the other hand, in every case remains practically constant, or exhibits only irregular variations plainly arising from experimental errors. Judged by this method, the reaction is therefore one of the third order.

The second method of determining the order of reactions was first employed by van't Hoff,¹ and its importance was later emphasized by the experiments of Noyes and Scott.² In the form used by the latter investigators it consists in determining which order of constants has most nearly the same value in independent series of experiments in which the initial concentrations are made widely different from one another. This method is much more reliable than the first one by reason of the fact that the influence of disturbing causes, such as the effect of the products of the reaction on its velocity, becomes insignificant in comparison with the much greater effect of the large changes in the initial concentrations. In order to show more clearly the result of the application of this second method to the reaction here considered, we have prepared the following table, in which are brought together the comparable values of the two orders of constants derived from the eight series of experiments; namely, the mean values of C_2 and the values of C_3 corresponding to that stage of the reaction at which one-half of the iron is oxidized.

TABLE II.

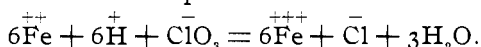
Series No.	Normal concentration of			$10^6 C_2$	$10^7 C_3$
	FeCl ₂	KClO ₃	HCl		
2	0.1	0.1	0.1	243	168
3	0.1	0.1	0.2	670	163
4	0.1	0.1	0.3	1130	172
5	0.1	0.1	0.5	2130	184
6	0.05	0.05	0.2	763	163
7	0.1	0.05	0.2	739	157
8	0.05	0.1	0.2	760	164
9	0.2	0.2	0.2	727	172

¹ Etudes de dynamique chimique.² Ztschr. phys. Chem., 18, 118.

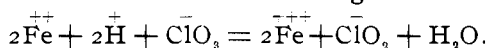
It is seen that the values of C_3 are approximately the same in all eight series of experiments, conclusively proving that the reaction is one of the third order, and that its velocity is proportional to the concentration of each of the reacting substances. The values of C_2 increase as the concentration of the acid increases, but are, like those of C_3 , approximately constant in the last four series of experiments, in all of which the same excess of acid was present, showing that the reaction is one of the second order in the presence of an excess of acid.

These experiments furnish the first satisfactory example of a reaction of the third order in which three distinct substances are involved.

It is worth while to consider briefly the question of the theoretical significance of the fact that this reaction is one of the third order. The following equation expresses the change which, according to the Electrolytic Dissociation Theory, takes place in the molecular composition of the substances in solution :



It is seen that no less than thirteen molecules are involved in this reaction. It is, however, highly probable that the reduction of the chlorate takes place in three separate stages, and that it is only the first one of these which requires an appreciable time for its completion ;¹ in which case the reaction whose velocity is measured would be the following one :



But even in this reaction five molecules participate ; and it would, therefore, be expected, in accordance with kinetic and thermo-dynamical considerations, that the reaction would be one of the fifth order, or one of the third order in presence of the excess of acid.

The only kinetic explanation of the actual order of the reaction that we are able to suggest is that the ferrous ions are diatomic (namely of the formula $[\overset{++++}{\text{Fe}_2}]$, and that the hydrogen ions in the first instance act catalytically. The reaction whose velocity is measured would then be : $[\overset{++++}{\text{Fe}_2}] + \overset{-}{\text{ClO}_3} = [\overset{++++}{\text{Fe}_2\text{O}}] + \overset{-}{\text{ClO}_2}$, or $[\overset{++++}{\text{Fe}_2}] + \overset{-}{\text{ClO}_3} + \text{H}_2\text{O} = 2\overset{+}{\text{FeOH}} + \overset{-}{\text{ClO}_3}$, the basic ferric ion

¹ Compare Noyes : *Ztschr. phys. Chem.*, 19, 599.

($[\text{Fe}_2\text{O}]^{++++}$ or FeOH^{++}) being subsequently instantaneously neutralized by the acid. But, in the absence of confirmatory evidence, very little weight can be attached to such a hypothesis, and it must be admitted that, apparently at least, the reaction forms an exception to van't Hoff's principle, which states that the order of a reaction is determined by the number of molecules taking part in it.

5. EXPERIMENTAL RESULTS ON THE EFFECT OF TEMPERATURE.

It is very desirable that the interesting conclusions which have been drawn from recent investigations on the effect of temperature on the velocity of reactions should be confirmed within wider limits of temperature and by the study of new reactions. Since no experiments had been made in this direction on the reaction between ferrous chloride, potassium chlorate, and hydrochloric acid, and since the experiments of Hood on the analogous sulphate reaction were confined to the range of temperature between 10° and 32° , we have measured the velocity of the former reaction at six different temperatures varying uniformly (by differences of 10°) between 0° and 50° . Owing to small variations in the temperature of the thermostat, the series at 30° and 50° are unfortunately less accurate than those of Table I.

The results are contained in the following table. The headings have the same significance as before. The concentration of the solution was in all six cases the same; namely, one-tenth normal with reference to each of three reacting substances.

TABLE III.

Series No.	Temperature.	<i>t</i> .	x_1 .	x_2 .	x .	$A - x$.	$10^8 C_2$.	$10^7 C_3$.
IO	0°	5	0.20	0.15	0.18	24.73	56.0	21.0
		20	0.70	0.62	0.65	24.25	54.0	21.5
		40	1.38	1.32	1.35	23.55	57.4	23.4
		100	2.95	2.98	2.96	21.94	53.9	22.9
		195	4.81	4.97	4.90	20.00	50.9	22.7
II	10°	5	0.58	0.55	0.57	24.33	188	76.2
		20	1.70	1.72	1.70	23.20	148	61.0
		50	3.60	3.70	3.65	21.25	138	60.0
		100	6.34	6.17	6.25	18.65	134	63.0
		160	8.37	8.40	8.38	16.52	126	64.0
		250	10.52	10.47	10.50	14.40	117	64.0

12 20°

See Series 2, Table I.

Series No.	Temperature.	t .	x_1 .	x_2 .	x .	$A-x$.	$10^6 C_2$.	$10^7 C_3$.
12	30°	5	2.45	2.35	2.40	22.50	856	357
		10	4.50	4.55	4.52	20.38	891	387
		18	6.70	6.72	6.70	18.20	821	390
		32	9.52	9.50	9.50	15.40	774	406
		55	12.07	12.05	12.06	12.84	703	404
		95	14.65	14.70	14.68	10.22	606	418
13	40°	5	5.30	5.15	5.22	19.68	2130	971
		9	7.57	7.61	7.59	17.31	1950	954
		16	10.50	10.42	10.46	14.44	1810	992
		30	13.40	13.59	13.50	11.40	1580	1010
		50	15.65	15.60	15.62	9.28	1350	990
		80	17.48	17.50	17.49	7.41	1180	1030
14	50°	1	2.55	2.40	2.48	22.42	4440	1970
		3	6.18	6.25	6.22	18.68	4480	2050
		6	9.55	9.38	9.46	15.44	4100	2140
		11	12.62	12.65	12.64	12.26	3760	2290
		20	15.38	15.42	15.40	9.50	3250	2370
		30	17.00	16.97	16.98	7.92	2150	2390

6. DISCUSSION OF THE RESULTS ON THE EFFECT OF TEMPERATURE.

As was first shown by van't Hoff,¹ it follows from the laws of thermodynamics that the following relation must exist between the absolute temperature T , the heat effect q accompanying the reaction, and the velocity-constants, k' and k'' , of the two opposing reactions which are considered to be in equilibrium with one another:

$$\frac{d \log_{\cdot e} k'}{dT} - \frac{d \log_{\cdot e} k''}{dT} = \frac{q}{2T^2}.$$

Van't Hoff adds that, although this equation does not give the desired relation between temperature and the velocity constants of the *separate* reactions, it shows nevertheless that the relation has the following form:

$$\frac{d \log_{\cdot e} k}{dT} = \frac{A}{T^2} + B.$$

It is to be noted, moreover, that in this equation A is a quantity which, like q in the preceding one, will, in general, probably vary but little with the temperature, and that B is a quantity which must have the same numerical value for the two opposed

¹ Etudes de dynamique chimique, p. 115.

reactions at any temperature at which they may be compared, for only in that case would this term disappear in the preceding equilibrium equation. This fact in regard to the quantity B makes it seem probable that its value is zero. At any rate, this is the simplest assumption that can be made in regard to it, and the one whose validity it is first natural to test by a comparison with the facts. Integrating then the differential equation between the limits T_1 and T_2 (to which correspond the velocity constants k_1 and k_2), under the assumptions that $B = 0$, and that A does not vary with the temperature, we get :

$$\log_e \frac{k_1}{k_2} = \frac{T_1 - T_2}{T_1 T_2}.$$

Now, it has been shown by Arrhenius¹ that this equation does in fact satisfactorily represent the relation between temperature and velocity-constants in the case of five different reactions. In the case of two other reactions considerable deviations from the formula were found to exist, but these were attributed to experimental errors arising from the high temperatures employed.

In order to determine whether our results are in accord with this formula, we have calculated the ratios ($k_1 : k_2$) of the mean values of C_3 for each successive pair of temperatures, and from these ratios we have calculated the constant A in the above equation, and have brought the results together in the following table :

TABLE IV.				
Series No.	Temperature.	$10^7 C_3$ or k .	$k_1 : k_2$.	A .
10	0	22.7	2.75	7820
11	10	62.4	2.68	8180
12	20	167.0	2.36	7620
13	30	394.0	2.52	8760
14	40	992.0	2.22	8070
15	50	2200.0

It will be seen that the values of A show only irregular variations, not a progressive one, and therefore the equation is correct within the experimental error. It is to be noted that the simpler equation :

$$\log_e \frac{k_1}{k_2} = B(T_1 - T_2)$$

(where B is a constant) corresponding to the relation ($k = ab^t$)

¹ *Ztschr. phys. Chem.*, 4, 226.

employed by Berthelot in connection with his esterification experiments, would be a less satisfactory expression of the results; for this equation would require that the values of the ratios $k_1 : k_2$ should be constant at all temperatures, instead of slowly decreasing with rising temperature, as the previous equation required, as is in fact the case.

Another remarkable conclusion to which the study of the effect of temperature on the velocity of reactions has led, is that temperature apparently accelerates all chemical changes in approximately the same ratio. In other words, the values of the ratios $k_1 : k_2$ for equal differences of temperature are of the same order of magnitude for all the various reactions investigated, although these reactions differ from one another in character as widely as possible. For a ten-degree interval the average value of $k_1 : k_2$ is about 2.8, the separate values varying from 2.0 to 3.6.¹ We wish now only to call attention to the fact that the reaction here considered is another example of this principle, the value of the ratio $k_1 : k_2$ being about 2.7 for the two lower temperature-intervals.

7. SUMMARY.

This investigation has proved that the reaction between ferrous chloride, potassium chlorate, and hydrochloric acid is a reaction of the third order, its velocity being directly proportional to the concentration of each of the three substances. This conclusion is based not only on a consideration of the variations of the constants of the individual series, but also on the far more reliable comparison of the constants of different series of experiments made with varied initial concentrations.

It has also been proved that the effect of temperature on its velocity is expressed by van't Hoff's theoretical equation :

$$\frac{T_1 T_2}{T_1 - T_2} \log_e \frac{k_1}{k_2} = A \text{ (a constant),}$$

a formula whose applicability to several reactions had already been demonstrated by Arrhenius.

Finally, our experiments have shown that this reaction furnishes another confirmation of the empirical principle that the influence of temperature on the velocity of all reactions is of the same order of magnitude.

¹ For a summary of the results, see van't Hoff-Cohen: Studien zur chemischen Dynamik, p. 129.

DISCUSSION.

Mr. Hazen: There is a question, different, although somewhat similar, to that presented in the paper, which has been interesting me of late; that is, the speed with which ferrous iron in waters is oxidized to the ferric state. Ferrous iron in solution in public water supplies is a very troublesome substance. In order to get rid of it, it has to be first converted into ferric iron which can be readily removed by filtration. I have made some experiments with this removal during the past year in connection with a plant for removing iron from municipal supply, installed under our advice.

After the water was aerated and had been standing in a basin for several hours, apparently every bit of the iron was in the ferrous condition, no oxidation whatever having taken place, although the water was thoroughly aerated. The effluent from the filtration of this water was entirely free from iron, and the iron removed from the water was deposited on top of the filtering sand. It was not in the upper layers of the sand but actually on top of it.

It seems to me from this that the oxidation of the iron took place practically instantaneously and at the time when the water came in contact with the surface layer of the filter. There was no oxidation up to that time, and the oxidation then must have been complete, as no iron was deposited below or came through in the effluent. I have noticed in other cases that when the oxidation takes place gradually, the removal of iron is never complete, a small quantity remaining unoxidized in solution; but if the oxidation can be brought about at once, the action is complete and every trace of the iron is removed. In the above mentioned case, the oxidation of the iron must have been due to the water coming in contact with the ferric hydroxide already oxidized and precipitated, or to the friction and agitation of the water in getting into the filter; which, of course, introduces an entirely different condition of affairs from that of quiet standing water.

Dr. Loeb: In the equation, as written by Dr. Noyes, there seems to me to be one little matter left out of account, and that is as to the chlorine ions from the hydrochloric acid. Of course the hydrogen is being taken away with a part of the chlorine, the

hydrogen being oxidized, but at the same time fresh chlorine is being generated by the reduction of potassium chlorate to potassium chloride, and it seems to me, therefore, that that ought to be taken into account. I want to ask whether some neutral salt had been added in this reaction, say potassium chloride in definite quantities to see whether the influence of chlorine not in the shape of acid should be taken into account. It seems to me, if it is proved that potassium chloride is of absolutely no effect, that a question would arise, whether the influence of chloric acid, or, say, ClO_3 as an ion as compared with Cl as an ion will produce the difference or not. The other question I want to ask is this: I see an equation, the actual ratio between zero and ten. In some experiments I have made, with the same reaction I found that at zero and at three or four degrees I was unable to produce action at all; that is, if I took the proportion given here at zero degrees I had no reaction whatever. It would be interesting to know whether Dr. Noyes obtained a reaction at zero or whether the value is obtained by extrapolation.

Dr. Noyes: Replying to the first question I would say that no experiments were made on the effect of potassium chloride on the velocity of the reaction; nor, as far as the reliability of the conclusions are concerned, are they necessary. For the effect of the reaction products is eliminated by the comparison of the constants of the independent series.

In regard to the experiments at zero degree, I would say that the temperature was kept at that point as nearly as possible by adding to the water in the thermostat a very considerable quantity of ice. It is probable, as is usual in such cases, that radiation raised the temperature a little above zero; I suppose it may have been one or two-tenths of a degree above zero, perhaps. But as the column of ratios shows, there was nothing at all abnormal in the results at zero degree.

President Dudley: It has seemed to me that the field opened here by Dr. Noyes has a very remarkable and wide extended application in the commercial process for making steel, which we hope to see this afternoon. Some years ago I had somewhat of a contest with the manufacturers over the question of the quality of the metal used for making rails. To make a

very long story short, the point I was trying to reach was to get a softer, tougher steel for rails than the steel maker wanted to make. The final answer to me was, "We cannot make a soft, tough steel as fast as we can make a hard or more brittle steel." Part of this result was due to mechanical characteristics, that is to say, the rolling of a harder, higher carbon steel is easier, since its melting-point is lower, and it softens more under heat. But, and the point I want to bring out is, the amount of the final additions, as they are called in the steel trade, that is of the spiegel and ferromanganese added at the end of the blow to remove the oxides that are formed, is considerably greater when you make a hard steel than when you make a soft steel. Now, I think it is perfectly clear that if you add to a bath of metal, after the blow is finished—which is in reality a substance containing a good deal of metallic iron and a good deal of oxide of iron—if you add say, in one case, 500 pounds of melted spiegel, and in another case 1000 pounds, the reaction will take place more rapidly in the second case. In reality therefore, the question of the speed of the reaction, which results in freeing the bath of metal from the oxide, is a very live and important question commercially, and I am only sorry to have to tell you that the steel people were a little stronger than I was, and consequently they are making steel about as they have a mind to, and getting out the oxide, we hope, but fear that they do not.

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THE OXIDES OF TUNGSTEN.¹

BY EN. D. DESI.

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WHILE engaged in re-determining the atomic mass of tungsten, by reduction of its trioxide in a current of hydrogen, the writer carefully observed the color changes taking place in the oxide as the temperature varied.

When studying the literature of this metal, no precise information was found about the bodies formed during the reduction, as was expected. Although a great many compounds of tungsten have been investigated, those of the metal with oxygen have

¹ From author's thesis presented to the University of Geneva, Switzerland, for the degree of Doctor in Science.