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STUDIES ON SOLUTIONS OF STANNOUS SALTS.

II. THE OXIDATION OF SOLUTIONS OF STANNOUS CHLORIDE BY MEANS OF FREE OXYGEN.

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PART. I.   THE RATE OF OXIDATION.

THE following paper gives some of the results thus far obtained from a study of the rate of oxidation of stannous chloride solutions by means of free oxygen. Although the investigation is only in the beginning stage it seems that, on account of the rather unusual results obtained, and on account of the fact that this particular work is, for a few months, necessarily interrupted, it may be well to publish the results already at hand.

The method used consisted in thoroughly shaking a solution of stannous chloride in an atmosphere of pure oxygen and measuring the decrease in volume, for definite periods of time, by means of a gas-burette. Thus far all measurements have been made at atmospheric pressure. The shaking apparatus is described here somewhat fully as it is thought that it may possibly be of service to others. It consists of a flask (Fig. 1) with two outlets, a and b. When the apparatus is in use, a is used for filling and b is
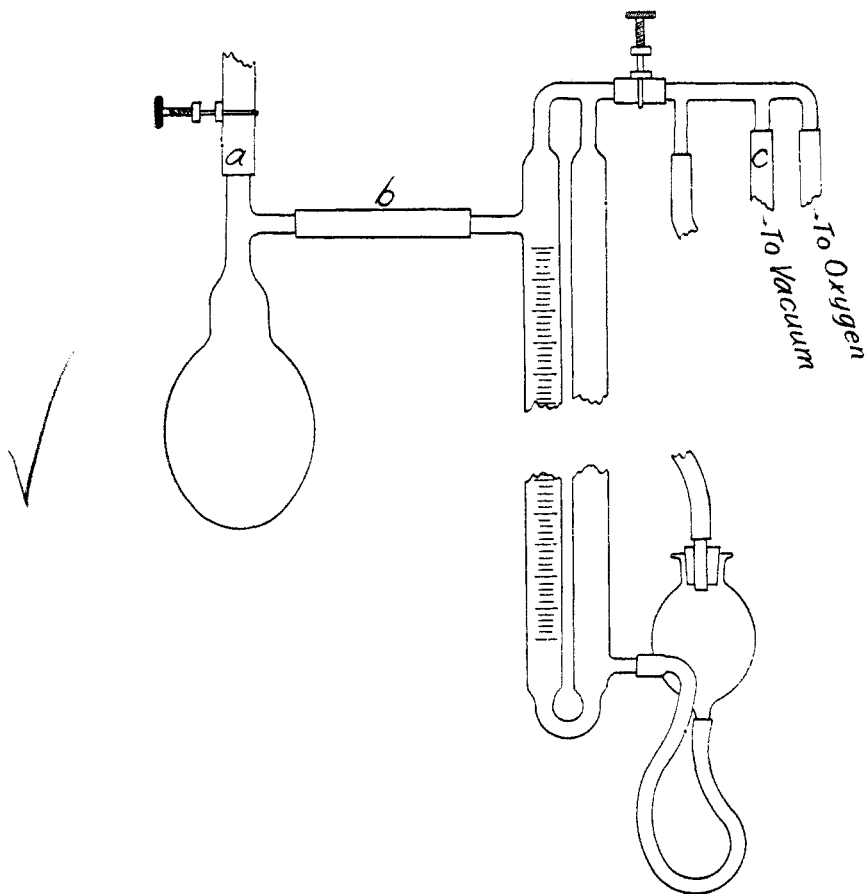
Fig. 1.

connected with the gas-burette. The flask is carried in a holder
(Fig. 2). The rods of the holder, *a a'* (Fig. 2), pass through
holes, *a a'* (Fig. 3). in a brass plate which is soldered to a brass
rod which may be held in the clamp of an ordinary ring stand.
The manner of setting up the whole apparatus is indicated in
Fig. 4, in which the whole device is shown in the thermostat.
The string, *s*, is connected with the crank of a motor, by whose
first half-revolution the carrier and flask are pulled from the posi-
tion of rest (indicated by solid lines) to that indicated by the
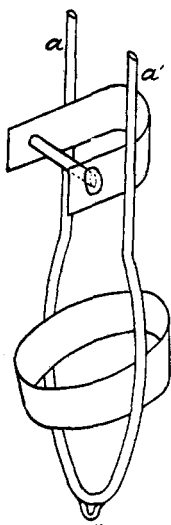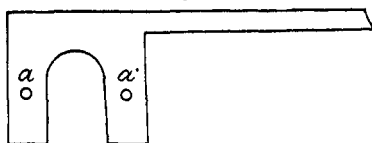dotted lines. During the second half-revolution of the motor-
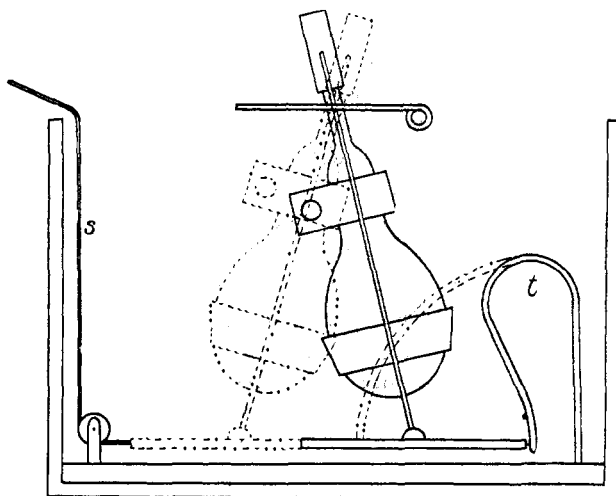
Fig. 2.

Fig. 3.

Fig. 4.

crank the strain on the string is relaxed and the flask and carrier are brought back into the original position by the U-shaped spring, *t*. Each revolution of the motor corresponds to one backward and forward journey of the flask. It was found that the apparatus responded readily to a rate of 400 revolutions per minute, whereas, so far as could be determined, the rate of reaction was independent of the velocity of shaking above 250 per minute, when 20 cc. of solution absorbing at the rate of not more than 2 cc. per minute were used. As will be seen from what follows, no very thorough test of the efficiency of the device is as yet possible because other accidental factors which have not as yet become avoidable have a much greater influence upon the velocity of reaction than does the rate of shaking.

In a thermostat of ordinary size the apparatus works better at high shaking rate than at slow because the waves in the thermostat are automatically broken. In using the apparatus for low shaking rates it was found necessary to provide a collar to fit around the carrier and to float upon the surface of the water in the thermostat. The collar used was about 7 inches in diameter.

The oxygen used was prepared electrolytically, using nickel electrodes and potassium hydroxide solution as electrolyte. Potassium hydroxide has the advantage over sulphuric acid, that by its electrolysis no ozone nor hydrogen peroxide is formed.[1]

The general method of procedure (with a few exceptions to be related later) was as follows :

1. The flask, after having been thoroughly cleaned and steamed out, was placed in the thermostat in the carrier. The upper outlet of the tube was provided with a piece of thick-walled rubber tubing, which could be closed with a screw-clamp. The side-tube was connected with a gas-burette (Fig. 1) and the whole apparatus thoroughly evacuated. Oxygen from the electrolytic generator was admitted until the apparatus was filled. The evacuation was then repeated and fresh oxygen allowed to enter. This whole operation was repeated a third time to insure the apparatus being filled with pure oxygen.

2. The apparatus being thus prepared, 20 cc. of the solution to be investigated were filled in through the upper opening by

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[1] Bodenstein : *Ztschr. phys. Chem.*, **29**, 667.

means of a special device, and the corresponding volume of air allowed to escape at c (Fig. 1).

3. All openings were now quickly closed (except c which was left open to the air) and the motor started. The reading of the gas-burette usually became slightly larger for the first few seconds and then began to steadily grow smaller, owing to the absorption of oxygen by the solution. The first increase of volume is undoubtedly due to the slight evaporation of water from the solution until the vapor-pressure is reached throughout the flask.

4. After the volume has been decreasing for about ten seconds the reading of the gas-burette is taken and at the same time a stop-watch is started, and further readings are taken at convenient intervals.

5. The residual stannous chloride, after the reaction had become very slow, was titrated with standard bichromate solution, with starch and potassium iodide as indicator. In some cases where the reaction went very rapidly it was considered better to continue the experiment until no more oxygen was absorbed; $i.\ e.$, until all stannous chloride had been oxidized.

The beginning concentration of stannous chloride was determined by the whole volume of oxygen absorbed and the volume of bichromate used, while the amounts of stannous chloride converted at the end of different periods were calculated from the readings on the gas-burette. Since the rate of decrease in the volume of oxygen was independent of the velocity of shaking ($i.\ e.$, the velocity of shaking was made so great that it had no further influence), we can place the concentration of the oxygen as constant for any series of experiments with solutions of the same compositions (if the slight correction be made for variation of the atmospheric pressure).

That with solutions of different concentrations this is probably not strictly allowable, seems to be shown by the experiments of Setschenow,[1] who found that the solubility of carbon dioxide in salt solutions decreased very considerably with increasing concentration of the salt. However, since the investigation has not yet reached a point where exact determinations are possible, this need not be taken into further consideration at present.

[1] *Ztschr. phys. Chem.*, **4,** 117.

The concentration of the hydrochloric acid in the solutions was determined by taking standardized solutions of the acid in making up the solutions for investigation. All measurements were made at 25° C.

Before relating the results of the above-described method of investigation it will be well to take into consideration a few preliminary results which were obtained by a slightly different method. This method consisted in placing an approximately weighed quantity (0.5 gram) of stannous chloride crystals into the flask of the apparatus, then filling with oxygen, adding solvent (either water or hydrochloric acid of known strength), starting the motor and making measurements from the start. Other experiments in comparison were made by allowing the so-prepared solutions to stand for considerable periods, in order that any reaction between solvent and stannous chloride might become complete. The object of these experiments was to see if the slow hydrolysis of the salt which appears to take place,[1] would have any influence upon the rate of oxidation. In this connection the following series of measurements are given : A. Measurements with 0.25 normal stannous chloride without hydrochloric acid. Experiment started immediately upon mixing of the solution. B. Measurements with some of the same solution which had stood for one hour. C. Measurements with similar solution which had stood forty-eight hours. D. Parallel with C.

In Columns T are given elapsed time in minutes, and in V the absorbed volumes of oxygen, in cubic centimeters. Columns D give volume of oxygen for each time interval.

EXPERIMENT A.

Conc. $SnCl_2$, $\frac{1}{4}$ normal.   HCl $= 0$.

T.	V.	D.
0	0.00	...
4	0.40	0.40
8	0.88	0.48
12	1.38	0.50
16	2.02	0.64
20	2.80	0.78
24	3.62	0.82
28	4.50	0.88
32	5.52	1.02
36	6.50	0.98

(Experiment interrupted.)

[1] This Journal, **23**, 21.

EXPERIMENT B.

Conc. $SnCl_2$, $\frac{1}{4}$ normal. HCl = 0. Solution 1 hour old.

T.	V.	D.	T.	V.	D.
0	0.00	...	40	10.95	1.25
4	0.80	0.80	44	12.12	1.17
8	1.75	0.95	48	13.25	1.13
12	2.72	0.97	52	14.34	1.09
16	3.80	1.08	56	15.44	1.10
20	4.90	1.10	60	16.35	0.91
24	6.05	1.15	64	17.22	0.87
28	7.25	1.20	68	17.94	0.72
32	8.45	1.20	72	18.62	0.68
36	9.70	1.25			

EXPERIMENT C.

Same solution. 48 hours old.

T.	V.	D.	T.	V.	D.
0	0.00	...	45	13.11	1.38
5	1.43	1.43	50	14.51	1.40
10	2.83	1.40	55	15.68	1.17
15	4.28	1.45	60	16.70	1.02
20	5.68	1.40	65	17.58	0.88
25	7.18	1.50	70	18.28	0.70
30	8.73	1.55	80	19.23	0.95
35	10.28	1.55	90	19.91	0.68
40	11.73	1.45	100	20.26	0.35

EXPERIMENT D.

Parallel with C, but with new solution. Also 48 hours old.

T.	V.	D.	T.	V.	D.
0	0.00	...	40	12.14	1.54
5	1.35	1.35	45	13.63	1.49
10	2.80	1.45	50	14.94	1.31
15	4.28	1.48	55	16.13	1.19
20	5.84	1.50	60	17.14	1.01
25	7.45	1.61	65	17.94	0.80
30	9.03	1.58	75	19.04	1.10
35	10.60	1.54	85	19.74	0.74

In the above experiments the solutions were prepared before placing them in the flask. In the following ones (E–H) the solutions were prepared as described above, by first placing the crystallized salt in the flask, then filling the apparatus with oxygen, adding solvent (water or dilute hydrochloric acid), and starting the motor. One-half gram stannous chloride was used which made the solution approximately $\frac{1}{5}$ normal.

EXPERIMENT E.

0.5 gram SnCl$_2$ — 20 cc. pure water.

T.	V.	D.	T.	V.	D.
0	0.00	...	50	13.98	1.50
5	0.70	0.70	55	15.33	1.35
10	1.61	0.91	60	16.65	1.32
15	2.95	1.34	65	17.83	1.18
20	4.51	1.56	70	18.83	1.00
25	6.03	1.52	75	19.62	0.79
30	7.66	1.63	80	20.20	0.58
35	9.24	1.58	85	20.70	0.50
40	10.88	1.64	90	21.12	0.42
45	12.48	1.60			

EXPERIMENT F.

Parallel with E.

T.	V.	D.	T.	V.	D.
0	0.00	...	50	14.60	1.50
5	0.82	0.82	55	15.98	1.38
10	1.94	1.12	60	17.22	1.24
15	3.40	1.46	65	18.32	1.10
20	4.98	1.58	70	19.22	0.90
25	6.52	1.54	75	19.95	0.73
30	8.12	1.60	80	20.54	0.59
35	9.80	1.68	85	21.00	0.46
40	11.48	1.68	90	21.35	0.35
45	13.10	1.62			

The agreement between E and F is fairly good, especially as the two portions of 0.5 gram each of stannous chloride were not weighed very exactly. Further, two or three minutes' time was accidentally lost at the beginning of F, so that all of the early readings are somewhat too large. However, the general course of the absorption corresponds very closely in both cases, and as preliminary experiments they are satisfactory.

Experiments G and H, following, were made in exactly the same way except that $\frac{1}{2}$ normal hydrochloric acid was used instead of pure water in making up the solutions.

EXPERIMENT G.

0.5 gram SnCl$_2$ + 20 cc. $\frac{1}{2}$ normal HCl.   End strength = 0.80[1] cc.

T.	V.	D.	T.	V.	D.
0	0.00	...	20	7.10	1.55
5	2.13	2.13	25	8.63	1.53
10	3.95	1.82	30	10.10	1.47
15	5.55	1.60	35	11.45	1.35

[1] All titrations are expressed in terms of the number of cubic centimeters of 0.10 normal K$_2$Cr$_2$O$_7$.

T.	V.	D.	T.	V.	V.
40	12.70	1.25	80	20.55	0.75
45	13.87	1.17	85	21.27	0.72
50	14.99	1.12	90	21.95	0.68
55	16.07	1.08	95	22.57	0.62
60	17.06	1.02	100	23.16	0.59
65	18.07	0.98	105	23.72	0.56
70	18.95	0.88	110	24.22	0.50
75	19.80	0.85	115	24.65	0.43

EXPERIMENT H.

0.5 gram $SnCl_2$ + 20 cc. $\frac{1}{2}$ normal HCl.   End strength = 2.2 cc.

T.	V.	D.	T.	V.	D.
0	0.00	. . .	55	15.75	1.09
5	1.87	1.87	60	16.77	1.02
10	3.52	1.65	65	17.72	0.95
15	4.96	1.44	70	18.62	0.90
20	6.63	1.67	75	19.44	0.82
25	8.18	1.55	80	20.18	0.74
30	9.62	1.44	85	20.90	0.72
35	11.00	1.38	90	21.58	0.68
40	12.28	1.28	95	22.26	0.68
45	13.50	1.22	100	22.87	0.61
50	14.66	1.16			

Here, again, is fair agreement, although the absorption was noticeably faster in G than in H. The most noticeable feature is that in these experiments, with $\frac{1}{2}$ normal hydrochloric acid, the increase of the rate of absorption for the first thirty or forty minutes, so noticeable in the previous experiments, has disappeared. The absorption per five minutes falls off from the start to the finish of the reaction.

The approximate agreement of the results of parallel experiments by the above method permits of the hope of determining the true reaction velocity between oxygen and stannous chloride solutions, by some refinement of the above method. From this point on, a modification of the above method was introduced. By this method a considerable quantity of a solution $\frac{1}{2}$ normal as to hydrochloric acid and $\frac{1}{8}$ normal as to stannous chloride, was prepared. This was filled into carefully cleaned tubes of about 80 cc. capacity, sealed up after thorough evacuation, and allowed to stand until wanted. In making a series of measure-

ments a tube was opened, a portion taken out, the tube then
closed with a piece of thick-walled rubber tubing, and evacuated
again, and thus kept until another portion was wanted.   Contrary
to expectations, this method gave extraordinarily irregular
results, the variation between the rates of oxidation of two por-
tions taken from the same tube being sometimes as great as several
hundred per cent.   The results of a number of measurements
made by this method are given below.   There are also given in
some cases the velocity constants of the reaction calculated upon
the basis that the concentration of the stannous chloride is the
only one that changes during the reaction (*i. e.*, assuming that
the oxygen concentration is constant and that the products of the
reaction exert no catalytic action).   In many cases only the read-
ings for the first few minutes are given because it was not con-
sidered necessary to complete each experiment when varying
results were obtained.   Experiments I_α, I_β, and I_γ were made
with one and the same solution. I_α and I_β were about two hours
apart, while I_β and I_γ were about twenty-four hours apart.   All
following experiments were made with $\frac{1}{2}$ normal HCl and $\frac{1}{5}$ nor-
mal $SnCl_2$ solutions.

EXPERIMENT I_α.

End strength = 0.90 cc.   A = 0.2008.

T.	V.	D.	X.	$\dfrac{\log \dfrac{A}{A-X}}{T} = K.$
0	0.00	...	0.00000	....
5	3.60	3.60	0.02925	0.01370
10	6.65	3.05	0.05405	0.01362
15	9.30	2.65	0.07558	0.01367
20	11.45	2.15	0.09296	0.01350
25	13.30	1.85	0.10810	0.01346
30	14.95	1.65	0.12150	0.01348
35	16.42	1.47	0.13350	0.01359
40	17.80	1.38	0.14460	0.01382
45	19.00	1.20	0.15460	0.01418
50	19.98	0.98	0.16240	0.01439
55	20.80	0.82	0.16900	0.01455
60	21.65	0.85	0.17600	0.01530
65	22.40	0.75	0.18200	0.01582
70	23.05	0.65	0.18730	0.01675
75	23.60	0.55	0.19180	0.01798

EXPERIMENT Iβ.

A $=$ 0.2008.

T.	V.	D.	X.	$\dfrac{\log \dfrac{A}{A-X}}{T} = K.$
0	0.00	..	....	....
5	4.80	4.80	0.03900	0.01876
10	9.05	4.25	0.07353	0.01979
15	12.50	3.55	0.10160	0.02041
20	15.25	2.75	0.12390	0.02084

EXPERIMENT Iγ.

End strength $=$ 1.10.   A $=$ 0.1998.

T.	V.	D.	X.	$\dfrac{\log \dfrac{A}{A-X}}{T} = K.$
0	0.00	...	....	....
5	4.70	4.70	0.03735	0.01802
10	8.70	4.00	....	....
15	11.98	3.28	....	....
20	14.52	2.54	0.11530	0.01870
27	17.40	1.98	....	....
30	18.40	1.00	....	....
35	19.88	1.48	....	....
40	21.15	1.27	0.16810	0.02000
45	22.25	1.10	...	....
50	23.12	0.87	....	....
55	23.80	0.68	....	....
60	24.40	0.60	0.1938	0.02540

It will be noticed that in each of these last three series of measurements the rate of oxidation is very considerably greater than with solutions of the same concentration, but which were prepared in the flask of the shaking apparatus (Experiments G and H). In fact the rate is more than doubled. It would thus seem that the rate of oxidation of the solution increases with its age to a certain extent. The same may be noticed by comparison of Experiments A, B, C, and D.

Another very marked regularity among the irregularities was noticed. The phenomenon may be briefly described, as follows : If a tube of the fresh solution were opened and allowed to stand for about twenty minutes in the air, different portions of the solution gave results in approximate agreement. But if care were taken not to open the tube until immediately before an experiment, and then to transfer the first portion immediately into the appa-

ratus, this first portion invariably gave results much higher than succeeding portions, and the succeeding portions again gave results agreeing fairly well. The following two experiments illustrate the falling off in the rate of oxidation after the tube with solution had stood for a few moments exposed to the air. Measurements α are with first portions, taken as soon as possible after opening the tube. Measurements β are taken about one-half to one and one-fourth hours later. The influence of oxidation by the air on standing thus long was not significant, as the solutions gave practically the same concentrations of stannous chloride for β-measurements as for α-measurements.

EXPERIMENT Jα.

T.	V.	D.	T.	V.	D.
0	0.00	. . .	20	13.80	2.40
5	4.50	4.50	25	15.80	2.00
10	8.24	3.74	30	17.75	1.95
15	11.40	3.16	35	19.45	1.70

EXPERIMENT Jβ.

T.	V.	D.	T.	V.	D.
0	0.00	. . .	50	21.00	1.10
5	3.32	3.32	55	22.20	1.20
10	6.40	3.08	60	23.22	1.02
15	9.20	2.80	65	24.18	0.96
20	11.65	2.45	70	25.00	0.82
25	13.80	2.15	75	25.70	0.70
30	15.80	2.00	80	26.10	0.40
35	17.40	1.60	85	26.30	0.20
40	18.75	1.35	90	26.45	0.15
45	19.90	1.15			

EXPERIMENT K (α AND β).

Kα.			Kβ.		
T.	V.	D.	T.	V.	D.
0	0.00	. . .	0	0.00	. . .
5	6.52	6.52	5	2.56	2.56
10	11.70	5.18	10	4.80	2.24
15	15.50	3.80	15	6.90	2.10
20	18.40	2.90	20	8.80	1.90
25	20.52	2.12	25	10.50	1.70
30	22.20	1.78	30	12.00	1.50
35	23.50	1.30	35	13.50	1.50

It was thought possible that the reaction in question might be sensitive to the influence of light and a very considerable number

of experiments were carried out to determine whether or not this was the case. The results of the investigation showed clearly that if light had any influence upon the rate of reaction, it was so small as to be insignificant in comparison to other disturbing factors. It will scarcely be necessary to relate these experiments in detail here, as the results are purely negative.

On account of the fact that a solution that had been preserved *in vacuo* for some time experienced a considerable fall in oxidation rate on exposure to the air for a few moments, it was thought possible that the re-evacuation of the tube might remove at least partially the agent which brought about the depression in the oxidation rate. Several experiments were carried out to determine this. The re-evacuation had no apparent influence. as the following measurements show. Only the volumes absorbed in the first five minutes are given. Under "α" are the values for the first portions, taken immediately upon opening the tube : under "β" the values taken after the solution had stood for some little time exposed to the air (usually with one or two shakings) ; under "γ" are the results after the solutions had been re-evacuated, and had remained sealed up from four to eighteen hours.

No.	α.	β.	γ.
1	6.00	3.70	3.43
2	7.50	4.20	3.25
3	6.85	4.20	4.10
4	9.00	5.00	5.30

In No. 4 a small increase in γ over β is observed. Otherwise the γ-values are regularly smaller than the β-ones. This is probably due to the effect that after β-portions were taken out it was necessary to allow the tube to stand open for a few moments longer before re-evacuation.

As a result of the above measurements, we may draw the conclusion that the reaction between stannous chloride solutions and oxygen is extremely sensitive to minute quantities of substances with which the reagents may come in contact in the ordinary, careful methods of laboratory manipulation.

The investigation was at this point turned toward the determination of these disturbing actions, and considerable headway has already been made in this direction. Before relating the results of this part of the investigation, however, it may be well

to consider the results of the measurements already given from a
somewhat critical standpoint. In the following table a summary
is given of the values of $\dfrac{\log \dfrac{A}{A-X}}{T}$ for several series of meas-
urements. The values are determined from the data of solu-
tions of practically equal concentrations; viz., 0.2 normal.
Constants calculated for five minute differences.

					Experiments not given in the foregoing.		
Expt. E.	Expt. H.	Expt. Ia.	Expt. Iγ.	Expt. Ka.			
1.	2.	3.	4.	5.	6.	7.	8.
0.00244	0.00666	0.01370	0.01802	0.02432	0.01120	0.01150	0.0230
0.00284	0.00633	0.01362	....	0.02506	0.01158	0.01175	....
0.00356	0.00625	0.01367	....	0.02516	0.01200	0.01217	....
0.00424	0.00652	0.01350	0.01870	0.02539	0.01239	0.01219	0.0222
0.00466	0.00670	0.01346	....	0.02550	0.01217	0.01244	....
0.00516	0.00683	0.01348	....	0.02757	0.01233	0.01270	0.0252
0.00555	0.00698	0.01359	....	0.02591	0.01242	0.01287	....
0.00603	0.00711	0.01382	0.02000	0.02588	0.01266	0.01335	0.0268
0.00645	0.00724	0.01418	....	0.02940	0.01282	0.01385	....
0.00688	0.00739	0.01439	....	0.03252	0.01317	0.01381	0.0310
0.00724	0.00756	0.01455	....	0.03040	0.01356	0.01451	0.0306
0.00764	0.00771	0.01530	0.02540	0.03040	0.01403	0.01536	0.0310
0.00802	0.00788	0.01582			0.01464		
0.00830	0.00808	0.01675					
0.00846	0.00827	0.01798					
0.00850	0.00845						
0.00850	0.00868						
0.00846	0.00897						
	0.00935						
	0.00975						

Column 1 is for an experiment made without hydrochloric acid
and by mixing the solution in the apparatus and starting the
experiment immediately. On the assumption that the reaction is
simply proportional to the analytically determined concentration
of stannous chloride these numbers should be constant. They
increase, however, to a value at the end of the experiment which
is nearly four times its original value. The values in Column 2

are for an exactly similar experiment, made, however, with 0.5 normal hydrochloric acid instead of pure water. The values here show the same sort of an increase except that it is much less marked. The remaining values are all for experiments made with solutions containing 0.5 normal hydrochloric acid and kept sealed up in vacuum tubes for from twenty-four hours to one week before using. It will be noticed that all columns show marked increase from the beginning to the end values, and, with the exception of a few scattered values (presumably experimental errors), this increase is fairly regular. A further regularity will be noticed also in that the ratio between the first and last values of a column is approximately the same for all columns (excepting Column 4, which may be due to an experimental error ; in my note-book I find that the determination of the end reaction in this case was doubtful). In other words, although the actual values of the velocity constants vary greatly in different series, the increase in a given series is approximately proportional to the change in concentration for solutions of the same concentration in hydrochloric acid. In solutions made without hydrochloric acid the ratio of increase is very much larger, and may be so large that it causes an actual increase in the volume of oxygen absorbed with decreasing (analytical) concentration of stannous chloride (Experiments A, B, C, D, E, and F). The simplest explanation of this would be that some product of the reaction acts as an accelerator of the reaction. The products we should naturally look for are hydrochloric acid, stannic hydroxide, and stannic chloride, one or more of which might be formed. The reaction may take place as follows :

$$SnCl_2 + 3H_2O + O = Sn(OH)_4 + 2HCl. \qquad (1)$$
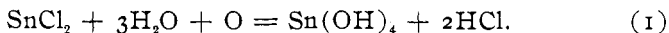
It is well known that in moderately dilute solutions stannic chloride is almost completely hydrolyzed, and this might lead one to expect that the hydrolyzed system would be formed under the conditions of these experiments. However, according to the Ostwald rule[1] it happens very generally that, as the product of a reaction, not the most stable, but rather some intermediately stable product, is formed. If the rule held in this case, we should get stannic chloride formed as first product according to the equation :

$$SnCl_2 + 2HCl + O = SnCl_4 + H_2O. \qquad (2)$$
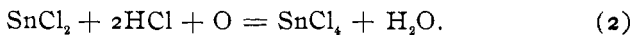
[1] *Ztschr. phys. Chem.*, **22**. 306.

and the stannic chloride would then slowly hydrolyze :

$$SnCl_4 + 2H_2O = Sn(OH)_4 + 4HCl. \qquad (3)$$
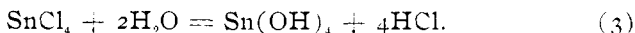
The only experimental evidence bearing upon this point that I have found is the following :

Thomsen[1] found that when stannous chloride solutions were oxidized with free chlorine, they showed a strong yellow color. This yellow color is also shown when an old solution of stannic chloride is mixed with stannous chloride. The solution must be some days old to give a distinct color. This color reaction is taken by Thomsen[2] as a test for the "metastannic" condition. At any rate, the color is evidence of a condition in the stannic solution which appears only after long standing of its solution. In the foregoing work it was noticed that after an experiment the oxidized solution was invariably yellow and the yellow color was deeper in solutions which contained less free hydrochloric acid. This would indicate that the stannic chloride stage in this reaction was passed by and the reaction took place according to equation (1). The point cannot, however, be looked upon as definitely settled as yet. The matter is open to direct determination by electrolytic methods, and this will be done in the near future.

The course of the reaction has an important bearing on the theoretical considerations concerning the reaction velocity. If the reaction takes place according to equation (1) we can place the increase in concentration of hydrochloric acid directly proportional to the decrease in concentration of stannous chloride. If the reaction takes place according to equations (2) and (3) we should have to set the increase in hydrochloric acid as a function of the velocity of oxidation of stannous chloride and of the velocity of hydrolysis of the stannic chloride formed. That hydrochloric acid acts as an accelerator in some way cannot be doubted since the solutions made with $\frac{1}{2}$ normal hydrochloric acid give constants from three to ten times as large as those made with water. If the reaction takes place according to equation (1), the fact that hydrochloric acid acts as an accelerator allows of a ready explanation of all the peculiarities noticed in the different series

of values of $\dfrac{\log \dfrac{A}{A-X}}{T}$ except the lack of agreement among the

1 " Thermochemische Untersuchungen." Vol. II. p. 445.
2 Thomsen : *Loc. cit.*

different series, which matter will be discussed later. Assuming that the reaction takes place according to equation (1), an increase in the concentration of the hydrochloric acid must occur. The first effect of this hydrochloric acid will be to drive back hydrolysis, if notable hydrolysis exist in the solution. If we consider that the hydrolyzed portion of the stannous chloride has a lower oxidation rate than unhydrolyzed stannous chloride (or that it is not directly oxidizable at all),[1] it would necessarily follow that the activity of a stannous chloride solution made with water would increase as the oxidation proceeded, since more and more of the hydrolyzed product would be converted into unhydrolyzed. This would take place at all concentrations of hydrochloric acid at which noticeable hydrolysis occurred. The fact that the velocity constants for solutions in 0.5 normal hydrochloric acid still show a marked increase, might be taken as evidence that hydrolysis is still noticeable at that concentration, or it may be that the hydrochloric acid has other accelerating influences aside from the mere pushing back of the hydrolysis. It is also possible that the molecular complexes of stannous chloride and hydrochloric acid have a greater rate of oxidation than the simple substances.

If the reaction takes place according to equations (2) and (3), the explanation of the facts is not so simple. The first effect of the oxidation will then be to form stannic chloride at the expense of stannous chloride and hydrochloric acid ; and secondly, this stannic chloride will begin to slowly hydrolyze.[2] Thus, during the first part of the reaction we shall have two increasing concentrations ; viz., stannic chloride and stannic hydroxide, while the concentration of hydrochloric acid will decrease, if the hydrolysis of stannic chloride is very slow compared to its rate of formation. Somewhere during the reaction stannic chloride will, on account of its being more and more slowly produced, cease to increase in concentration, and will, on account of continuous hydrolysis, begin to decrease. If the rate of oxidation of stannous chloride is much faster than the rate of hydrolysis of

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[1] An experiment with colloidally suspended stannous hydroxide nearly free from hydrochloric acid showed an extraordinarily slow rate of oxidation, which became very fast upon addition of a few drops of potassium hydroxide solution. This cannot be taken as a wholly satisfactory determination of the above point, since it does not necessarily follow that all hydrolyzed stannous salt is held in the solution in colloidal form.

[2] Kohlrausch : *Ztschr. phys. Chem.*, **33**, 257.

14-23

stannic chloride, the latter reaction must go on after the former is practically complete. This hydrolysis is measurable by elec‑ trolytic methods[1] and thus we have a possible means of determining whether or not the reaction takes place in this second way or not. These measurements will be made in the near future. Of course it is by no means excluded that stannic chloride and stannic hydroxide may act as accelerators.

Another wholly different explanation of the whole matter is possible. It may be that it is an error to assume that the reac‑ tion rate is directly proportional to the concentration of the stan‑ nous chloride. It might be proportional to some other power of the concentration than the first (*i. e.*, to C^2 or to $C^{\frac{1}{2}}$, etc.). Such cases are not unknown, apparently. In this case the values of the exponent v may be calculated from the changes in concentration during the reaction, by the well-known equation of van 't Hoff :[2]

$$ n = \frac{\log \left(\dfrac{dc_1}{dT_1} : \dfrac{dc_2}{dT_2} \right)}{\log \left(c_1 : c_2 \right)}. $$

If the reaction took place in a perfectly uniform manner, *i. e.*, in such a manner that no accelerating or retarding influences were developed during the reaction, these values of n should be con‑ stant. I have calculated n for some few cases, and the results obtained are as follows :

A.	B.
0.464	0.435
0.433	0.412
0.401	0.355
0.372	0.320
0.337	0.270
0.293	
0.242	

The values are by no means constant, but show a marked and invariable (several sets were calculated) tendency to decrease. Thus it seems necessary to conclude that during the course of the reaction accelerating influences are developed. These influences can not be named catalytic nor autocatalytic, because they may be

[1] Kohlrausch : *Loc. cit.*

[2] See van 't Hoff : "Vorlesungen." Vol. I. p. 194 ; also Ostwald : "Lehrbuch." II, 2, p. 232.

apparently of such a nature as to change the whole equilibrium existing in the solution.

It is perfectly evident from the foregoing that before any thoroughly satisfactory explanation of the phenomena above described can be obtained, it will first be necessary to be able to control the reaction so that constant results may be obtained under a given set of conditions. It has already been suggested that the reaction seemed to be extraordinarily sensitive to the influence of small quantities of substances which it was apparently able to take up from the air on a few minutes' exposure. In Part II is given the results of an (almost purely qualitative) investigation into the cause of the great variations which were found to occur in different series of measurements under apparently like conditions. As will be seen, the phenomena of variation are readily explained, although at present the method of wholly avoiding such disturbances or even of studying them with any considerable degree of quantitative accuracy, has not been found.

PART II. CATALYTIC PHENOMENA IN THE OXIDATION OF STANNOUS CHLORIDE BY OXYGEN.

As has been stated in the previous portion of this paper, the influence of light and of re-evacuation of tubes upon the rate of oxidation of stannous chloride solutions seems to be nothing. It was now further attempted to determine the influence of other substances which could possibly come in contact with the solution. The first substance investigated was rubber. Since portions of the apparatus were made of rubber tubing, it was thought that the fact that the solution came (or might come) in contact with the rubber, could possibly exert some influence. The method of procedure was as follows : The rubber tubing was rubbed to a fine powder by means of a clean file. From 0.25 to 0.5 gram of this powder was placed in the tube containing the solution to be investigated, and the tube sealed off and rotated in the thermostat for about eighteen hours. The solution was tested as to its oxidation rate before and after the addition of the rubber. The results of two such experiments are given in the following table. Under α are the values for T, V, and D before addition of rubber, and under β the same values after the addition :

TABLE I.

Experiment 1.

α.			β.		
T.	V.	D.	T.	V.	D.
0	0.00	. . .	0	0.00	. . .
5	4.35	4.35	5	11.20	11.20
10	8.32	3.97	10	22.20	11.00
15	11.90	3.58	13	26.20	4.00

Experiment 2.

α.			β.		
T.	V.	D.	T.	V.	D.
0	0.00	. . .	0	0.00	. . . .
5	4.70	4.70	5	18.20	18.20
10	9.05	4.35	10	25.60	7.40
15	12.85	3.80			

As will readily be seen, the influence of the rubber is that of a wonderfully active accelerator, the acceleration in the first case being over 150 per cent. and in the second nearly 300 per cent. Thinking that possibly the sulphur in the rubber might be the active agent in bringing about this acceleration, experiments were carried out in the same way as those with rubber, using sulphur instead of the rubber. The sulphur used was the ordinary crystallized sulphur ground up to a fine powder. The tube with solution and sulphur was rotated in the thermostat as in the case of rubber, for about eighteen hours.

In Table II are given the results of one of these experiments, the results in all being of the same nature. Under α results before and under β results after addition of sulphur :

TABLE II.

α.			β.		
T.	V.	D.	T.	V.	D.
0	0.00	. . .	0	0.00	. . .
5	3.30	3.30	5	9.95	9.95
10	7.40	3.10	10	18.10	8.15
15	9.20	2.80	15	24.90	6.80

Here there is noticed a similar acceleration to that brought about by rubber, and the value of it is about 200 per cent. The influence of sulphur and rubber is evidently one which gradually develops in the solution, since experiments which were started with simple solution were not noticeably influenced by dropping in bits

of rubber or of sulphur during the experiment. The effect appears first after the solution and the accelerator have stood together for some time. Thus it is evident that the phenomenon is due either to slow solution of the accelerator or to a slow chemical reaction between the substance and the solution.

Solutions of iron, copper, manganese, and chromium salts were next qualitatively investigated. The method was to take a portion of a solution, measure its initial velocity, then add a few drops of the dilute solution of the salt in question, and continue the experiment. By noting the rate of absorption before and after the addition of the salt solution it was possible to determine whether the addition had any considerable influence. There was no attempt made to determine the quantity of salt added. Three or four drops of the ordinary laboratory solutions were used. Following, in Table III, are the results. The values in parentheses indicate the points at which the addition of the salt solution was made :

TABLE III.

$FeSO_4$.			$CuSO_4$.		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
5	2.80	2.80	1	0.90	0.90
(5)	(2.80)	...	2	1.85	0.95
10	10.90	8.10	3	2.80	0.95
			(3)	(2.80)	...
			4	5.30	2.50
			5	7.30	2.00
			6	9.20	1.90
			7	10.90	1.70
			8	12.40	1.50

$MnSO_4$.			$Cr_2(SO_4)_3$.		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
1	1.00	1.00	1	0.72	0.72
2	2.00	1.00	2	1.40	0.68
3	2.90	0.90	3	2.20	0.80
(3)	(2.90)	...	4	3.10	0.90
4	3.65	0.75	5	4.05	0.95
5	4.35	0.70	(5)	(4.55)	...
6	5.05	0.70	6	5.33	0.78
7	5.75	0.70	7	6.20	0.87
			8	7.05	0.85
			9	7.95	0.90

Thus iron and copper both cause very notable accelerations, manganese a slight retardation, while the results for chromium are somewhat irregular and leave us in doubt.   The influence of chromium would appear at best to be very slight.

Up to this point it will be observed that all catalysors[1] studied are positive (*i. e.*, accelerating), or very weakly negative, in their action, while in the experiments related in Part I it is evident that one or more negative catalysors were at work (see Experiments J and K.

It was thought likely, as the rate of oxidation of the solution kept in evacuated tubes became considerably reduced upon the opening of the tube, that some constituent of the air might cause the variations.   It was my custom to smoke freely in the room in which the work was being done, and it occurred to me that this might possibly be the cause of the trouble.   In the following table (IV) are contained the results of an experiment to determine this point.   Under α are the values for a clean, fresh solution, taken directly from the tube, and under β corresponding values for the same solution through which tobacco smoke had been blown.

<div align="center">TABLE IV.</div>

a.				β.		
T.	V.	D.		T.	V.	D.
0	0.00	...		0	0.00	...
1	1.00	1.00		1	0.30	0.30
2	1.90	0.90		2	0.60	0.30
3	2.85	0.95		3	0.95	0.35
4	3.80	0.95		4	1.28	0.33
				5	1.60	0.32
				10	3.13	1.53
				15	4.55	1.42

In Table V are the results of a series of readings taken upon a solution by the same method as was used in investigating the metallic salts (above Table III), except that instead of solution of metallic salts a few drops of an extract of tobacco were added.

[1] I use the word 'catalysor' as equivalent to the German word 'Katalysator.' It is much less cumbersome than the usual terms "catalytic agent" and "contact agent."

TABLE V.

T.	V.	D.	
0	0.00	...	
1	1.45	1.45	
2	2.90	1.45	
3	4.38	1.48	
(3)	(4.38)	...	(extract added)
4	4.80	0 42	
5	5.20	0.40	
6	5.60	0.40	
7	6.03	0.43	

These results leave not a shadow of doubt but that both tobacco smoke and tobacco extract retard the oxidation rate of stannous chloride to a high degree. The next experiments were carried out with a number of common alkaloids and with a variety of other substances, including aniline and alcohol. The results are given in Table VI.

TABLE VI.

$1/1000$ Normal brucine.				$1/200$ Normal brucine.		
T.	V.	D.		T.	V.	D.
0	0.00	...		0	0.00	...
1	1.25	1.25		1	2.38	2.38
2	2.50	1.25		(1)	(2.38)	...
3	3.75	1.25		2	3.00	0.62
(3)	(3.75)	...		3	3.56	0.56
4	4.75	1.00		4	4.06	0.50
5	5.75	1.00		5	4.55	0.50
6	6.75	1.00		6	5.04	0.48

$1/150$ Normal morphine.				$1/200$ Normal morphine.		
T.	V.	D.		T.	V.	D.
0	0.00	...		0	0.00	...
1	3.55	3.55		1	1.40	1.40
(1)	(3.55)	...		(1)	(1.40)	...
2	4.35	0.80		2	2.10	0.70
3	5.10	0.75		3	2.85	0.75
4	5.83	0.73		4	3.55	0.70
5	6.55	0.72		5	4.20	0.65
6	7.15	0.60				

$1/350$ Normal nicotine.				$1/35$ Normal nicotine.		
T.	V.	D.		T.	V.	D.
0	0.00	...		0	0.00	...
1	1.82	1.82		1	1.50	1.50
2	3.65	1.83		2	2.80	1.30
(2)	(3.65)	...		(2)	(2.80)	...
3	5.15	1.50		3	3.60	0.80
4	6.45	1.30		4	4.40	0.80
				5	5.20	0.80

$1/_{250}$ Normal phenol.

T.	V.	D.
0	0.00	. . .
1	1.25	1.25
2	2.40	1.15
(2)	(2.40)	. . .
3	3.75	1.35
4	5.05	1.30

$1/_{25}$ Normal phenol.

T.	V.	D.
0	0.00	. .
1	1.35	1.35
2	2.65	1.30
(2)	(2.65)	. . .
3	3.90	1.25
4	5.05	1.15
5	6.15	1.10

$1/_{200}$ Normal aniline.

T.	V.	D.
0	0.00	. . .
1	1.55	1.55
2	3.10	1.55
(2)	(3.10)	. . .
3	4.05	0.95
4	5.00	0.95

$1/_{40}$ Normal aniline.

T.	V.	D.
0	0.00	. . .
1	0.95	0.95
2	1.90	0.95
(2)	(1.90)	. . .
3	2.25	0.35
4	2.60	0.35
5	2.90	0.30

$1/_{200}$ Normal aniline.

T.	V.	D.
0	0.00	. . .
1	1.30	1.30
2	2.55	1.25
3	3.90	1.30
(3)	(3.90)	. . .
4	4.70	0.80
5	5.50	0.80

$1/_{40}$ Normal aniline.

T.	V.	D.
0	0 00	. . .
1	0.80	0.80
2	1.60	0.80
(2)	(1.60)	. . .
3	1.90	c.30
4	2.20	0.30
5	2.50	0.30

$1/_{200}$ Normal pyridine.

T.	V.	D.
0	0.00	. . .
1	1.40	1.40
2	2.80	1.40
(2)	(2.80)	. . .
3	4.40	1.60
4	5.90	1.50

$1/_{40}$ Normal pyridine.

T.	V.	D.
0	0.00	. . .
1	1.60	1.60
2	3.10	1.50
(2)	(3.10)	. . .
3	4.30	1.20
4	5.30	1.00
5	6.35	1.05

$1/_{100}$ Normal KCN.

T.	V.	D.
0	0.00	. . .
1	1.07	1.07
2	2.15	1.08
3	3.23	1.08
(3)	(3.23)	. . .
4	4.03	0.80
5	4.83	0.80
6	5.65	0.82

$1/_{20}$ Normal KCN.

T.	V.	D.
0	0.00	. . .
1	0.80	0.80
2	1.60	0.80
3	2.42	0.82
(3)	(2.42)	. . .
4	2.74	0.32
5	3.15	0.41
6	3.52	0.37

| $\frac{1}{100}$ Normal ethyl alcohol. | | | | $\frac{1}{10}$ Normal ethyl alcohol. | | |
T.	V.	D.		T.	V.	D.
o	0.00	...		o	0.00	...
1	2.30	2.30		1	0.45	0.45
(1)	(2.30)	...		2	0.90	0 45
2	5.80	3.50		3	1.35	0.45
3	8.70	2.90		4	1.80	0.45
4	11.45	2.75		(4)	(1.80)	...
5	13.80	2.35		5	2.80	1.00
6	15.50	1.70		6	3.55	0.75
				7	4.25	0.70
				8	5.00	0.75

A single test was also made with mannite which retards the reaction to a considerable extent, but as the concentration of the mannite used was not known, figures are not given. The experiments were carried out in the same way as those with metallic salts, and the numbers in parentheses indicate the point at which the foreign substance was added. In most cases where experiments with two concentrations were made they were both made in the same solution, the effect of the foreign substance in the more dilute form being first observed, after which a second portion of the foreign substance was added sufficient to give the solution the greater concentration. Thus the figures for greater concentrations do not give a really fair idea of the total influence of the foreign substance, because the oxidation rate in such cases had already been considerably influenced by the previous small addition. Further no attempt was made to determine accurately the concentration of the foreign substances added, although the values are probably correct to within 5 per cent. There was no object in attempting greater accuracy, because the initial rates could not be controlled to within less than from 50 to 100 per cent.

Finally there remains to be related the results of a series of experiments made with hydrogen sulphide. A solution of hydrogen sulphide was prepared in the usual way and diluted with thoroughly boiled water to the concentration desired. One cc. of such solution was added to stannous chloride solutions during the progress of their oxidation. Since always 20 cc. portions of stannous chloride solution were used, the concentration of the stannous sulphide formed in the whole solution could be calculated readily, on the assumption that the reaction

$$SnCl_2 + H_2S = SnS + 2HCl$$
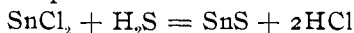
is a complete one. In Table VII are given the results of such determinations. The first column gives the concentration of the stannous sulphide in the solution. The second column gives the rate of oxidation in cubic centimeters of oxygen per minute *before* the addition of the hydrogen sulphide. The third column gives the value of the same *after* addition. The fourth column gives the ratios between the third and the second columns : *i. e.*, the number of times faster the reaction goes after than before the addition.

The concentrations in the first column are given in terms of normality of hydrogen sulphide, considering this substance to be a monobasic acid.

TABLE VII.

1. C_{H_2S}.	2. Rate before.	3. Rate after.	4. $\dfrac{\text{Rate after}}{\text{Rate before}}$.
	cc.	cc.	
$\frac{1}{1000}$ N	1.30	11.50	8.80
$\frac{1}{50000}$ N	0.73	7.40	10.00
$\frac{1}{100000}$ N	1.35	5.70	4.20
$\frac{1}{250000}$ N	1.00	3.50	3.50
$\left\{ \frac{1}{500000} \text{ N} \right.$	1.00	1.30	$\left. 1.30 \right\}$
$\left. \frac{1}{500000} \text{ N} \right\}$	1.20	1.45	$\left. 1.20 \right\}$

It will be seen that we have here a case of enormous acceleration of the rate of reaction due to exceedingly minute concentra·tions of the accelerating agent. For the greatest concentration given ($\frac{1}{1000}$ normal) the rate is lower than for a fifty-times more dilute solution. This is possibly due to the fact that in this case the stannous sulphide precipitated out in fine particles of the black form, while in the others (where visible at all) it was in the form of the colloidal, brownish sulphide, which separated only very slowly from the solution.

DISCUSSION OF THE RESULTS.

It is evident from the results in Part II of this paper that we have in the reaction between stannous chloride solutions and oxygen, a reaction that is exceedingly sensitive to the influence of catalytic agencies. It is not my purpose to enter into any considerable discussion of these results here. Such discussion would be practically useless at this time, and a further investigation of the whole matter is what is most necessary. I merely wish to

call attention to what few relationships may be found between these results and the results of previous investigators. As has been seen, a very considerable number of the reagents examined decrease the rate of the reaction ; *i. e.*, act as negative catalysors, while others accelerate. As negative catalysors we find : Salts of manganese and chromium (not very active), some constituents of tobacco smoke and extract, brucine, morphine, nicotine, mannite, aniline, and potassium cyanide. As positive catalysors were found : Rubber, sulphur, hydrogen sulphide (stannous sulphide), salts of iron and copper, and alcohol. Pyridine and phenol do not exert a sufficiently strong influence to allow any decided conclusion to be drawn as to their action at present. Mannite acts negatively, but how strong its action may be is not yet determined.

Taking up the negative catalysors first, it is to be remarked that Bigelow[1] found considerable variations in the rate of oxidation of sodium sulphite by air, some of which (impurities in the air, etc.) could be at least partially controlled. His results as to the action of mannite, which was the most carefully studied agent, seem to be comparable to the results stated above. It will be noticed that most of the negative catalysors which I have found are poisons. This may very likely be due to the fact that nothing much but poisons were studied. The action of the alkaloids was investigated because of the accidental discovery that tobacco smoke was a very active agent. It is quite likely that this negative catalytic action upon the reaction is in no way characteristic of poisons. It is, however, to be remarked that Bredig and Müller von Berneck[2] found that poisons were often very active agents in destroying the catalytic action of colloidal platinum solutions.

Among the positive catalysors are found salts of copper and iron. These are already known as strong agents in this respect. The appearance of alcohol among these accelerators is quite anomalous. One would naturally expect that its influence in pushing back the dissociation of the solution would cause it to retard the reaction. But if it pushes back the dissociation it will also push back the hydrolysis and might thus hasten the reaction. The value for its influence, however, is so large

[1] *Ztschr. phys. Chem.*, **26**, 493.
[2] *Ibid.*, **31**, 258.

that it seems to me likely that its action is due to wholly other causes. Bigelow[1] found alcohol to retard the oxidation of sodium sulphite in a high degree.

The three remaining accelerators—rubber, sulphur. and hydrogen sulphide—all contain sulphur. The first two exert their influence upon the solution only after long standing, while hydrogen sulphide acts immediately.

These facts allow of a formulation of a working hypothesis, by means of which the action of all three may be ascribed to a common agent, *viz.*, stannous sulphide. Stannous sulphide is formed when hydrogen sulphide is introduced into a solution of stannous chloride. If we consider that the reaction between water and sulphur is an appreciable one, *viz.*.

$$2H_2O + 2S \overset{\longrightarrow}{\longleftarrow} 2H_2S + O_2,$$
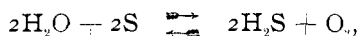
we can account readily for the formation of stannous sulphide through the action of either rubber or sulphur. This should be susceptible of experimental determination.

It remains to be noted that Mohr, in his "Titrirmethode" (6th Ed., 1886),[2] mentions the fact that, unless great care is taken to free arsenious acid from sulphur compounds, solutions of it oxidize with great rapidity in the air. The phenomenon appears analogous to the one observed with stannous chloride.

From the results above given it would seem that a method might possibly be devised by means of which the oxidation rate of stannous chloride would be so reduced that it could be used directly as a solution for titration. If this were possible it would be of very considerable convenience for some purposes. The investigation of this point has been undertaken in the quantitative laboratory of this university.

<div align="center">CONCLUSION.</div>

In Part I of this paper it is shown that the suggestion made in a previous paper[3] as to the necessity of a strict definition of the reagents in a reaction before the velocity constant or the order of the reaction can be satisfactorily determined, is not without ground. The reaction between stannous chloride solutions and oxygen is shown to undergo an acceleration during the course of the reac-

[1] *Loc. cit.*
[2] *Loc. cit.*, p. 364.
[3] This Journal, **23**. 21.

tion which finds its simplest and readiest explanation in the pushing back of the hydrolysis[1] by means of hydrochloric acid produced by the reaction, and in possible catalytic action of reaction products. In solutions free (or as free as possible) from acid this acceleration is so great that an actual increase in the rate of oxygen absorption occurs during the first part of the reaction. It soon appears, however, that although the results of any one series of measurements are consistent within themselves and in certain ways also the results of different series are consistent with one another (*i. e.*, the ratios of initial value to end value of velocity constants are very approximately constant), nevertheless the velocity constants for different series vary within very wide limits. This suggests the action of catalytic influences, and Part II is devoted to the detection and qualitative investigation of some of these catalytic agents. The way for further investigation is perfectly apparent. The first task will be to protect the stannous solutions from possible catalytic influences and to determine, if possible, the normal values for the velocity constants of the reaction with varying concentrations of hydrochloric acid, after which the influence of the various catalytic agents will be open to quantitative investigation.

The chief result of the work at present is, however, the development of an apparatus and a method by means of which reactions between liquids and gases may be readily and quantitatively studied.

The main portion of this work was carried out in the laboratory of the Physical-Chemical Institute, at Leipzig.

STANFORD UNIVERSITY.
December 11, 1900.

DETERMINATION OF SULPHUR IN WROUGHT IRON AND STEEL.

By GEORGE AUCHY.

SEVEN or eight years ago in four samples of high carbon steels sent to two firms of commercial chemists (same drillings to each) for analysis, the sulphur was reported as follows :

	Sample No. 1.	Sample. No. 2.	Sample No. 3.	Sample No. 4.
Chemists A	0.013	0.015	0.012	0.015
" B	0.002	0.001	0.003	0.002

[1] Kortright (*Am. Chem. J.*, **17**, 116) has called attention to the probable influence of hydrolysis in the reaction between $SnCl_2$ and $FeCl_3$.