$$\frac{d^{1/2}[\text{HCl}]}{dt} = k_\text{A}\frac{[\text{H}_2]^2[\text{Cl}_2]}{{}^{1/2}[\text{HCl}]}$$

which fits the results in Pyrex 2 fairly well. Failure to find the inhibition by hydrogen chloride predicted from this equation for experiments in which some hydrogen chloride was formed in the system previous to the addition of the reactants may be attributed to the interference and counter-influence of an initial accelerated period in the temporarily hydrogen chloride-coated bulb, similar to that found with the potassium chloride-coated vessel. The wide variation in the constants calculated in the last column of Table III is partly caused by the great sensitivity of this equation to small experimental variations.

Further discussion appears in the following paper.

Summary

The thermal reaction between hydrogen and chlorine in clean Pyrex and in Pyrex coated with potassium chloride has been investigated. The rate of reaction has been shown to depend upon the type of vessel used, and to decrease as the reaction proceeds, in a manner suggestive of inhibition by product, but not attributable to it. A possible explanation for the inhibition in clean Pyrex has been suggested.

Different kinetic equations were found necessary for the reaction in clean glass and in glass coated with potassium chloride. In the coated bulb the results could be best interpreted by means of the equation:

$$\frac{d^{1/2}[\text{HCl}]}{dt} = k_\text{B}[\text{H}_2][\text{Cl}_2]^{1/2}$$

whereas for clean Pyrex the expression

$$\frac{d^{1/2}[\text{HCl}]}{dt} = k_\text{A}\frac{[\text{H}_2]^2[\text{Cl}_2]}{{}^{1/2}[\text{HCl}]}$$

was developed in an attempt to correlate the data. These equations differ somewhat from those of previous authors.

The Thermal Hydrogen–Chlorine Reaction. II. Relation to the Theory of Chain Reactions[1]

By J. C. Morris[2] and R. N. Pease

In a previous paper[3] experimental data on the thermal reaction between hydrogen and chlorine were presented. In this paper an attempt will be made to correlate the data with those of other workers and to explore resulting theoretical implications.

The chain character of this reaction may be considered definitely established. The inhibition by oxygen, the lack of acceleration with packing, the calculations of Eyring[4] have all shown a chain mechanism to be the most probable. Along with this, experiments and calculations have tended to show that the chains start and end on the walls of the reaction vessel. Further evidence to support this will be considered later. It will be assumed also that the chain which is operating is the Nernst chain.

Some general principles of chain processes which are applicable to the hydrogen–chlorine reaction are worthy of consideration. For example there are very definite limits to the absolute rate of such reactions. Suppose that, as in the case of $\text{H}_2 + \text{Br}_2$, the chains in the present case are started by a thermal gas phase dissociation of chlorine molecules and ended by a recombination of the atoms. Then, whatever the reactions in the body of the chain may be, the steady-state concentration of chlorine atoms will be equal to the thermal equilibrium concentration in a similar system where no reaction is occurring, and the rate of formation of hydrogen chloride will be equal to the rate at which this concentration of atomic chlorine interacts with hydrogen, multiplied in this case by two. Since the dissociation equilibrium of chlorine and the activation energy of the reaction are known, one can calculate the rate of formation of hydrogen chloride if these chain-starting and -ending processes prevail.

Now if another chain-ending reaction is to be

(1) Submitted in partial fulfillment of the degree of Doctor of Philosophy.

(2) Present address: Mallinckrodt Laboratory, Harvard University, Cambridge, Mass.

(3) Morris and Pease, This Journal, 61, 391 (1939).

(4) Eyring, ibid., 53, 2537 (1931).

the predominant one, it must take place more rapidly than the recombination process. This results in a decrease in the steady state concentration of chlorine atoms, and consequently a slower over-all reaction rate. It follows that the rate given by the equilibrium concentration of chlorine atoms is the maximum absolute rate possible if the dissociation of chlorine molecules is to be the chain-starting process. On the other hand, the rate can go higher with a different chain-starting process which does not involve the previous equilibrium.

The above deductions are for a gas phase formation of chains, but exactly the same considerations hold if the chains start on the walls. For if the beginning and end of the chains be such reactions as

$$Cl + W \longrightarrow 2Cl + W \text{ (or ClW + Cl)}$$
$$2Cl + W \text{(or Cl + ClW)} \longrightarrow Cl_2 + W$$
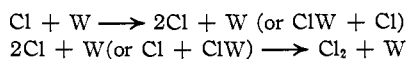
where W is the wall of the vessel, then the surface is effectively functioning as a catalyst, and, since a catalyst cannot change the equilibrium in the gas phase, the concentration of chlorine atoms will be the same as in the gas phase dissociation and recombination, and consequently the rate of reaction will be the same. The substitution of any other chain-ending reaction will again make the over-all rate less, and the substitution of a different starting reaction will make the formation of hydrogen chloride more rapid. The "equilibrium rate" thus constitutes a base line from which to consider mechanism.

These deductions may be applied to the mechanisms for this reaction set up by various authors to test their practicability. All the recent authors agree that the chain starting reaction is some sort of dissociative formation of chlorine atoms on the wall. Thus Christiansen[5] writes for the beginning and end of his Nernst chains

$$Cl_2 \overset{W}{\longrightarrow} 2Cl \qquad (1)$$
$$H \longrightarrow Z \qquad (6)$$

Pease[6] has a different chain-ending process to fit his quite different equation. He writes

$$Cl_2 + \text{wall} \longrightarrow 2Cl$$
$$Cl + \text{wall} \longrightarrow ?$$
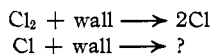
Those of Kornfeld and Khodschaian[7] are a combination of the above two. They give

$$W_{Cl_2} \longrightarrow 2Cl$$

$$W + Cl \longrightarrow WCl$$
$$\text{and } W + H \longrightarrow WH$$

with the latter of the chain-breaking reactions predominating. By any of these proposed starting mechanisms the maximum possible rate of reaction will be the "equilibrium rate." Actually, since each of them includes a chain-ending process which is not the reverse of the initiation, the observed rate of reaction should be less than the maximum.

Calculation of the maximum rate for comparison with the observed rates of these authors can be made by means of the equation

$$\frac{dn_{HCl}}{dt} = 2k_1 n_{Cl} n_{H_2}$$

where n_{Cl} is the equilibrium number of chlorine atoms for the system under the experimental conditions, and k_1 is the rate constant for the reaction $Cl + H_2 \longrightarrow HCl + H$. Since the equilibrium constant, $K_{eq.} = n_{Cl}^2/n_{Cl_2}$, this equation may be written

$$\frac{dn_{HCl}}{dt} = 2k_1 \sqrt{K_{eq.}} \cdot \sqrt{n_{Cl_2}} \, n_{H_2}$$

The values for n_{H_2} and n_{Cl_2} are from the data. Values for $K_{eq.}$ may be derived from the paper of Lewis and von Elbe,[8] and k_1 may be calculated either from collision theory or by the statistical method.[9] Both methods have been used here and give practically identical results.

According to collision theory the rate constant is given by

$$k_c = 2 \left[2\pi R \frac{M_1 + M_2}{M_1 M_2} \right]^{1/2} \sigma^2_{12} T^{1/2} e^{-E/RT}$$

Viscosity data[10] give 1.09 Å. for the radius of hydrogen and 1.43 Å. for that of argon, which was taken equal to the chlorine atom. E is obtained from the results of Rodebush and Klingelhoeffer.[11] Its value is 6000 cal. Constants found by this calculation are listed in the fifth column of Table I.

The rate constant by the statistical method is

$$ks = \frac{\dfrac{K(2\pi m_{ClH_2}kT)^{3/2}}{h^3} \dfrac{8\pi^2 I_{ClH_2}kT}{h^2} \overset{3}{\underset{i=1}{\Pi}} \dfrac{1}{1 - e^{-h\nu_i/kT}} \dfrac{kT}{h} e^{-E_0/kT}}{\dfrac{(2\pi m_{Cl}kT)^{3/2}}{h^3} \dfrac{(2\pi m_{H_2}kT)^{3/2}}{h^3} \dfrac{8\pi^2 I_{H_2}kT}{2h^2} \dfrac{1}{1 - e^{-h\nu_{H_2}/kT}}}$$

The values for the terms here can be obtained from the paper of Wheeler, Topley and Eyring.[12]

(5) Christiansen, Z. physik. Chem., **B2**, 405 (1929).

(6) Pease, THIS JOURNAL, **56**, 2368 (1934).

(7) Kornfeld and Khodschaian, Z. physik. Chem., **B35**, 403 (1937).

(8) Lewis and von Elbe, THIS JOURNAL, **57**, 612 (1935).

(9) Eyring, J. Chem. Phys., **3**, 107 (1935).

(10) Landolt–Börnstein, "Tabellen," Eg. I, 1927, p. 69.

(11) Rodebush and Klingelhoefer, THIS JOURNAL, **55**, 130 (1933).

(12) Wheeler, Topley and Eyring, J. Chem. Phys., **4**, 178 (1936).

TABLE I

COMPARISON OF OBSERVED RATES WITH THOSE CALCULATED ASSUMING EQUILIBRIUM $Cl_2 \rightleftharpoons 2Cl$

Temp., °A.	Mm. H_2 av.	Mm. Cl_2 av.	$K_{eq.} \times 10^{20}$ atm.	$K_c \times 10^{12}$	$K_s \times 10^{13}$	$\frac{Mm. HCl}{Min.}$ Coll.	$\frac{Mm. HCl}{Min.}$ Stat.	$\frac{Mm. HCl}{Min.}$ Found	$\frac{Ratio Found}{Stat.}$	Author
516	360	383	15.2	1.42	5.4	122	46	1.7	0.037	Sirk
531	350	350	71	1.70	6.4	284	107	2.0	.019	Sirk
512	341	367	11	1.36	5.2	93	35	1.9	.054	Melander
473	242	193	0.103	0.804	3.2	2.9	1.2	1.32	1.1	Christiansen
503	361	360	3.55	1.20	4.6	49	19	42	2.2	Pease
513	354	353	12	1.36	5.3	98	38	69	1.8	Pease
523	336	346	36	1.54	5.8	178	67	91	1.4	Pease
493	293	293	1.3	1.06	4.1	20	7.6	0.47	0.062	Kornfeld and Khodschaian
457	350	332	0.013	0.63	2.7	3.2	1.4	17.3	12	Pyrex 2
457	346	377	.013	.63	2.7	3.4	1.5	4.8	3.2	Pyrex 3
457	412	322	.013	.63	2.7	3.8	1.6	6.8	4.3	KCl

Constants found by this method are listed in the sixth column of Table I.

Comparison of the theoretical maximum rates with the actual results of the different investigators shows clearly the wide variation in the rate of reaction, from one hundredth of the calculated rate to ten times that amount. The early results of Sirk and of Melander, which are so low, need not be considered further, but examination of the others leads to interesting conclusions. The results of Pease and of Christiansen check the calculated "equilibrium rate" remarkably well. This indicates a dissociation and recombination as the chain-starting and -ending reactions, such as

$$Cl_2 + W \longrightarrow 2Cl + W$$
$$2Cl + W \longrightarrow Cl_2 + W$$
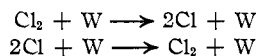
which modifies the mechanisms of both authors to a certain extent. The kinetic equation calculated by means of these reactions gives satisfactory constants with the results of both authors.

On the other hand, the results of Kornfeld and Khodschaian are considerably below the "equilibrium rate." Since the presence of an impurity as an inhibitor seems unlikely in their careful experiments, this must be caused by the predominance of some faster chain-ending reaction at the walls. Such a reaction might well be

$$H + wall \longrightarrow H \ ads.$$
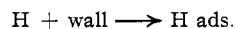
which they postulate. This attributes the difference in rate entirely to a change in the chain-stopping process.

Whether or not this is plausible can be tested by an examination of the absolute rates in the presence of oxygen. Then the various chain-ending mechanisms are replaced by a common one involving the reaction of the chain carrier with oxygen. This should make the rates in all three cases equal, except for differences in specific surface activity, which have given no indication of being large. Data on the absolute rates in the presence of oxygen are given in Table II. The measured rates, listed in the fifth column, have been corrected to 200° by assuming a temperature factor of 2 per 10°, and by dividing the observed rate by the surface–volume ratio. The corrected rates are shown in the seventh column. Whereas results with pure gases differed by a factor of 20 between Kornfeld and Khodschaian, and Christiansen, in the mixtures containing oxygen this is reduced to a 50% difference, and

TABLE II

COMPARISON OF ABSOLUTE RATES IN PRESENCE OF OXYGEN

Temp., °C.	Mm. H_2 av.	Mm. Cl_2 av.	Mm. O_2	Rate mm./min.	Rate $\times O_2$	Corr. rate	Author
200	253	388	0.65	1.64	1.06	1.28	Christiansen
220	298	298	10.00	0.113	1.13	0.85	Kornfeld and Khodschaian
184	386	381	1.1	2.8	3.08	9.24	Pyrex[a] 2
184	377	390	1.1	0.70	0.77	2.31	Pyrex[a] 4 (extrapolated)
184	320	335	2.0	1.0	2.0	6.00	KCl[a] (extrapolated)
184	373	349	1.1	0.30	0.33	0.99	Pyrex[b] 2
184	360	375	1.1	.10	.11	.33	Pyrex[b] 4
184	336	300	2.0	.28	.56	1.68	KCl[b]

[a] These represent initial rates.   [b] These represent "steady state" rates.

definitely checks with the previous assumptions as to mechanisms.

However, the results of the preceding paper,[3] all of which represent higher rates than the maximum possible under the proposed series of reactions, must also be correlated with this scheme. This is fairly easy with the Pyrex 4 and potassium chloride-coated bulbs. In the discussion there of the variation of the rate of reaction with time it was stated that for these bulbs there seemed to be an initial accelerated rate, which soon slowed to a "steady rate" that maintained itself. If one compares this "steady rate," rather than that for the initial period which was listed in Table I, with the calculated "equilibrium rate," he finds as good numerical agreement as was noted for the results of Christiansen and Pease. Thus, for both Pyrex 4 and the potassium chloride-coated bulbs the measured steady rate is approximately 2 mm. per minute hydrogen chloride formed for 0.5 atmosphere each of hydrogen and chlorine at 184°. The calculated rates, by collision and statistical methods, respectively, give 3.4 and 1.5 mm. The same distinction is maintained in oxygen-containing mixtures, where again, as shown in Table II, the initial rates are higher but the "steady rates" are approximately the same as those of other authors.

The results in Pyrex 1 and 2 cannot be explained in the same way. For these, and to be sure for the initial periods with Pyrex 4 and the potassium chloride coating, since the results are faster than the "equilibrium rate," a different type of chain-starting mechanism must predominate. Because any reaction of chlorine alone with the wall will provide the "equilibrium rate" maximum, it must be some process involving both hydrogen and chlorine, as well as the wall. A simultaneous collision seems improbable, and therefore one of the reactants undoubtedly is adsorbed by the surface. A possible chain-starting reaction would then be $WH_2 + Cl_2 \longrightarrow WHCl + H + Cl$. However, this type of mechanism seems to be thus far confined to a particular Pyrex bulb, and to the initial periods in other bulbs. The "equilibrium rate" is therefore of greater significance.

Now further proof can be given that the chains actually do start on the walls. Since an equilibrium concentration of chlorine atoms is required to attain the observed rates of formation of hydrogen chloride, the length of time necessary to

achieve this concentration by gas phase dissociation may be estimated and examined for reasonableness.

At 200° the rate of dissociation of chlorine molecules is

$$\frac{dCl}{dt} = Z_{11}n^2_{Cl_2}e^{-57,000/RT} + Z_{12}n_{Cl_2}n_{H_2}e^{-57,000/RT}$$

in a mixture of chlorine and hydrogen. Using molecular radii from viscosity data,[10] and with concentrations of 0.5 atmosphere each of hydrogen and chlorine, this expression becomes $dCl/dt = 700$ molecules per cc. per second. At equilibrium there are 1.86×10^8 chlorine atoms per cc. at 200°. So it requires $1.86 \times 10^8/700$ or 2.7×10^5 seconds, about three days, to attain the required number of chlorine atoms by gas phase dissociation. On the other hand, Kornfeld and Khodschaian present calculations to show that the rate of dissociation on the wall can be quite adequate. Therefore the chains must start on the walls, and because of the packing experiments[6] end there as well.

Chain Length.—With such a chain process operating, namely, starting by a reaction of molecules with the wall releasing atoms into the gas phase, and ending by a reversal of that process, the chain length should be calculable by mathematical means. However, it is best to begin the discussion of chain length from the standpoint of an apparent anomaly in this reaction, namely, the *comparatively slight* inhibition by oxygen. The similarity between the retardation of both the photochemical and thermal reactions by oxygen has been stressed, without bringing out how peculiar it is that they should be of entirely different orders of magnitude. Kornfeld and Khodschaian consider it somewhat, but do not show the full significance of this difference. In the photochemical reaction 1% of oxygen in the chlorine will reduce the rate of reaction to about one-thousandth of its value for pure gases. This inhibition is more pronounced for higher temperatures, since the coefficient of the reaction in pure gases is 1.37, whereas in oxygen-containing mixtures it is 1.12. Actually the retardation should be ten times as great at 200°. Yet in the thermal reaction at 184° 1% of oxygen only reduces the rate by a single power of ten from its value in pure gases.

The explanation lies in the difference in chain length for the two processes. In the photochemical reaction the chains are started in the gas

phase and probably end on the walls.[13] Suppose that the chains are started on the average about 2 cm. from the wall of the vessel. To reach the wall the chain carrier will suffer, according to Smoluchowski's equation

$$n = 3\pi d^2/4\lambda^2$$

collisions, where d is the distance to the wall, and λ is the mean free path, approximately 10^{-5} cm. under normal conditions. This gives 10^{11} as the number of collisions a chlorine atom will undergo before reaching the wall. Since 10^5 collisions are necessary for one reaction of a chlorine atom with hydrogen,[11] an effective chain length of $10^{11}/10^5$ or 10^6 results, which checks that observed in practice.

With oxygen present in the chlorine the chain ends by the reaction $H + O_2 + M \longrightarrow HO_2 + M$ which takes place at every 10^3 bimolecular collision.[14] At room temperature the competing reaction $H + Cl_2 \longrightarrow HCl + Cl$, occurs at every 10^2 collisions, and hence the chain length in the presence of oxygen will be $10Cl_2/O_2$. With 1% of oxygen this is 10^3, and thus the chain length has been reduced a thousandfold (*i. e.*, from 10^6).

When the chains both start and end on the walls the chain length is much shorter. A uniform concentration of chlorine atoms is maintained in the gas phase, and thus the number of collisions the average chlorine atom makes between contacts with the wall is the ratio of total gas phase collisions to the total number of collisions with the surface in a given time. The number of gas phase collisions per second is $\sqrt{2}\pi\sigma^2\bar{u}nNV$, where σ is the reduced diameter of the collision complex, n is the total number of chlorine atoms, $\bar{u}$ is the average velocity of a chlorine atom, N is the number of hydrogen molecules per cc., and V is the volume of the vessel. The corresponding number of collisions with the wall is $^3/_{13}\bar{u}nA$, where A is the surface area of the bulb. The ratio of these in the present experiments, in which the surface–volume ratio is approximately one, is $13\sqrt{2}/3\cdot\pi\sigma^2N$. With 0.5 atmosphere of hydrogen this is about 10^5. Thus at room temperature, where only one collision in 10^5 between $Cl + H_2$ is fruitful, an *average chain length* of only *1* would be recorded for the thermally initiated reaction. At 200° this average chain length will only be increased to 10^2–10^3,

because of the increased efficiency of reaction of a chlorine atom with hydrogen at this temperature. All this is with an accommodation coefficient of 1 at the surface.

The effect of oxygen may be estimated as before. At 200° the reaction $H + O_2 + M \longrightarrow HO_2 + M$ may be assumed to retain its frequency of 10^{-3}, but at this temperature $H + Cl_2 \longrightarrow HCl + Cl$ occurs at every tenth collision. The chain length in the presence of oxygen will be 100 Cl_2/O_2, or with 1% of oxygen, 10^4. This is greater than the chain length estimated above. Thus, according to this calculation 1% of oxygen should not inhibit the thermal reaction at 200° at all. The calculations, because of their approximate nature, may be off by a power of ten, but even if these figures are correct, there are two good reasons why the actual inhibition by oxygen might be expected.

First the average chain length of 10^2–10^3 for pure gases does not represent a good statistical distribution, but is made up of a great many short chains and a few very long ones. By breaking the very long chains a large inhibition may be achieved without the great majority of short chains having been touched in any way. Second, the accommodation coefficient for chlorine atoms may not be one. If it were 10^{-2}, then the average chain length in pure gases would be longer than that expected with 1% of oxygen present.[15] Numerous workers have already suggested that the accommodation coefficient might be small on other grounds.

A best figure for the chain length of the thermal hydrogen–chlorine reaction at 200° in pure gases is probably 10^4, which gives about equal weight to the two reasons given for the excess of actual inhibition over that calculated. In any case, all evidence points to the chains being notably shorter for the thermal reaction than for the photochemical one.

Summary

Some principles of chain reaction theory have been developed and applied to the thermal hydrogen–chlorine reaction. By means of them some degree of correlation has been achieved

(13) Semenoff, "Chemical Kinetics and Chain Reactions," Oxford University Press, 1935, pp. 95–98.

(14) Morris and Pease, *J. Chem. Phys.*, **3**, 796 (1935).

(15) It should be noted in passing that an accommodation coefficient at the walls for chain breaking smaller than 10^{-6} would be necessary to produce any large effect on the chain length of the photochemical reaction. The average number of collisions before striking the wall the first time is 10^{11}, whereas each additional rebound adds only 10^5 links to the chain. Hence 10^6 rebounds will but double the chain length.

among the widely varying results of different authors. It has been shown that treatment of the reaction as a Nernst chain, starting on the walls by a dissociation of chlorine molecules and ending by a reversal of that process will explain most of the experimental data.

The chain length in the thermal reaction at 200° has been calculated to be about 10^4 as contrasted with 10^6 in the photochemical reaction at room temperature. This explains the comparatively slight inhibition of the thermal reaction by oxygen as compared with the retardation in the photochemical reaction.

Nature of Aluminum Oxyiodide Hydrosols as Revealed by their Action on Hydrogen Peroxide

BY ARTHUR W. THOMAS AND BENJAMIN COHEN

In a previous paper[1] evidence was submitted showing that iodide which is bound to basic aluminum micelles in "aluminum oxide" hydrosols is several times more reactive in catalyzing the decomposition of hydrogen peroxide than free iodide ion. Thus there is available a technique which can be used to investigate qualitatively the iodo group $\rightleftarrows$ iodide ion equilibrium of these colloidal systems. Utilizing the technique and hydrosols previously described[1] some information has been obtained concerning this equilibrium and thus of the nature of the micelles under certain conditions.

Effect of Dilution of Sols upon Decomposition of Hydrogen Peroxide.—Since addition of water should shift the reaction iodo group $\rightleftarrows$ iodide ion to the right, one would expect a diminution of the velocity constant (calculated to original concentration) upon dilution of the hydrosol.

Sols were diluted with water and were permitted to stand in a thermostat at 25° overnight. In Table I are given the results obtained with two sols.[2] K (calcd.) was obtained by multiplying the velocity constant of the original sol by the concentration of sol used for the particular experiment. It is seen that as the sol is diluted the

TABLE I

EFFECT OF DILUTION UPON VELOCITY CONSTANTS OF SOLS

Concn. of sol	Sol 1 K (obsd.) $\times 10^4$	Sol 1 K (calcd.) $\times 10^4$	Sol 2 K (obsd.) $\times 10^4$	Sol 2 K (calcd.) $\times 10^4$
1.0	7.84	...	4.29	...
0.75	5.79	5.88	2.93	3.22
.50	3.86	3.92	1.78	2.15
.33	2.18	2.61	...	...
.25	...	...	0.73	1.07

(1) A. W. Thomas and B. Cohen, THIS JOURNAL, 59, 268 (1937).
(2) The sols are described in Table I of ref. 1.

difference between K(calcd.) and K(obsd.) becomes greater. Correction for the effect of water on the decomposition of hydrogen peroxide would tend to make this difference still larger.

Effect of Addition of Potassium Iodide to Sols. —Five cc. of the appropriate potassium iodide solution was added to 95 cc. of sol 3, and the mixture was kept in the thermostat overnight; 5 cc. of hydrogen peroxide was added to start the reaction. The results are recorded in Table II. K(calcd.) was obtained by assuming the catalytic effect of the added potassium iodide was purely additive.

TABLE II

EFFECT OF ADDED POTASSIUM IODIDE ON THE CATALYTIC ACTIVITY OF SOL 3

Final normality $\times 10^4$ of KI	K (obsd.) $\times 10^4$	K (calcd.) $\times 10^4$
0	8.11	...
0.95	9.54	9.43
2.85	12.8	12.1
4.75	15.7	14.7

A similar result was obtained with Sol 8 where the velocity constant ($\times 10^3$) in the presence of 0.009 N potassium iodide was 4.81 as compared to the additively calculated value of 4.65.

These results indicate that for the concentration of potassium iodide used, a relatively small part of the added iodide becomes bound to the micelles. This small difference between K(obsd.) and K(calcd.) suggested the following experiment. Sol 5 was made at room temperature by permitting a dilute solution of hydriodic acid to react with an excess of hydrous alumina for a week, at the end of which time the resulting sol was centrifuged and dialyzed. Its velocity constant was found to be 5.7 $\times 10^{-5}$ min.$^{-1}$ as compared to 5.6 $\times 10^{-5}$