This indicates the presence of positive chlorine ions in such a solution and the amphoteric ionization of the acid.

4. If the Lewis-Langmuir hypothesis is accepted, it requires an interpretation consistent with these facts.

URBANA, ILLINOIS

THE CATALYTIC FORMATION OF WATER VAPOR FROM HYDROGEN AND OXYGEN IN THE PRESENCE OF COPPER AND COPPER OXIDE

BY ROBERT N. PEASE AND HUGH S. TAYLOR

In an earlier paper,[1] dealing with the reduction of copper oxide by hydrogen, it was shown that the presence of small concentrations of oxygen in the hydrogen markedly diminished the rate of reduction of copper oxide. It was demonstrated, moreover, that this reduction *occurred only at an interface between copper metal and copper oxide*, when moderate reduction temperatures (100–200°) were employed. The free oxygen in the hydrogen manifestly affects, therefore, the reactivity of oxygen attached to copper at a copper-copper oxide interface. These observations are of undoubted importance in the problem of hydrogen-oxygen catalysis in the presence of copper or copper oxide or both. It is natural to infer that a catalytic action of this type, conducted in presence of a metal which is readily oxidized and whose oxide is easily reduced, should occur by a series of alternate oxidations and reductions. Bone and Wheeler,[2] however, contend that this is not true in the case of copper oxide. They suggest that the explanation of the catalytic process,........"in the case of copper oxide, would appear to involve the condensation of a film of 'active' oxygen on the surface and that this film actually protects the catalyzing oxide from the attacks of the hydrogen, which would otherwise energetically reduce it. At low pressure (that is after the reaction has proceeded for some time), the film becomes too attenuated to ensure complete protection and, in consequence, the formation of steam is accelerated by reason of hydrogen penetrating through on to the oxide and reducing it. In conformity with this idea,[3] the rate of steam formation when the gases are not present in combining ratios was found to be proportional to the partial pressure of the oxygen." In regard to the combination of hydrogen and oxygen in the presence of

[1] Pease and Taylor, THIS JOURNAL, **43**, 2179 (1921).

[2] Bone and Wheeler, *Phil. Trans.*, **206A**, 1 (1906).

[3] Presumably the idea of reaction being between hydrogen and a surface film of "active" oxygen. (Pease and Taylor.)

copper, Bone and Wheeler state that, using their flow method, "all attempts to obtain reliable velocity measurements in the case of the metal were frustrated by the fact that at even the lowest temperature where there was any marked action on the gases, the formation of steam was always accompanied by an *independent* oxidation of the surface, at least during the initial stages of an experiment."

For several reasons, the experiments of Bone and Wheeler appear indecisive and their conclusions incomplete. Adsorption measurements made in this laboratory by Dr. A. F. Benton on ignited copper oxide show no such strong adsorption of oxygen as would be expected on the basis of Bone and Wheeler's suggested mechanism. The adsorption of oxygen is markedly less than that of carbon monoxide at the same temperature, so that, if the latter form a complete molecular layer on the copper oxide, oxygen must leave the copper oxide relatively bare. Such results do not support a theory of a protecting oxygen film which prevents hydrogen reaching the copper oxide.

The observations made by us in the earlier study, that reduction occurs readily only at an interface, that oxygen inhibits reduction at an interface, and that in case the interfaces are small in dimensions as, for example, at the outset of a reduction experiment oxygen may even suppress the formation of water entirely, are all consistent with the results of Bone and Wheeler with electrolytic gas and with a hydrogen-nitrogen mixture. They suggest, too, that the claim that the experiments of Bone and Wheeler at once disprove the alternate reduction and oxidation theory may be somewhat premature. The simultaneous oxidation of a copper surface during catalysis of hydrogen and oxygen and the permanent reduction of a copper oxide surface under the same conditions, both being recorded observations of Bone and Wheeler, appear to us to be of fundamental importance. For, it is evident that, whatever the real nature of the catalysis, these reactions occur simultaneously with it. Whatever the original nature of the surface, whether metal or oxide, the equilibrium state of the surface will be intermediate in nature between metal and oxide and the equilibrium, it cannot be doubted, will be mobile. Oxide will be continually reduced, metal will be continually oxidized and at equal rates under equilibrium conditions.

The object of our catalytic study, therefore, was to compare the catalytic reaction with the oxidation and reduction reactions. We have used the same apparatus as employed by us in the previously recorded reduction reaction and have extended our study over the same temperature range (100–200°) and the same oxygen concentrations (0–5%) as were employed in the reduction study. The method consists in passing hydrogen at the rate of 50 cc. per minute through the catalyst held at constant temperature. Oxygen was added to the gas by mixing with it electrolytic gas, which was

generated at constant rate in a suitable cell. The extent of catalysis was determined by passing the effluent hydrogen through a weighed calcium chloride tube for a definite length of time, noting the gain in weight due to absorption of the water formed and comparing this with the theoretical amount of water corresponding to the electrolytic gas added. Since the water formed was expressed in terms of milligrams of water absorbed by the calcium chloride tube in 5 minutes, it was convenient to express the oxygen contents of the hydrogen in terms of the theoretically possible yield of water. This is usually abbreviated in the following way: such a concentration of oxygen as would give, for example, 10 mg. of water in a 5-minute passage of the gas mixture if all the oxygen were converted to water, is expressed as a concentration of "oxygen equivalent to 10 mg. water per 5-minute interval;" or, "10 mg. oxygen."

The following table gives the currents used and the concentrations of oxygen in volume percentage corresponding.

Oxygen concentration			
Equiv. mg. of H_2O 5 min.	Volume % 25°, 760 mm.	Cell current Amp.	Total volume Cc./min.
2.5	0.76	0.090	51.0
5.0	1.30	0.180	52.0
10.0	2.55	0.360	54.1
15.0	3.66	0.540	56.2
20.0	4.71	0.720	58.2

Since the rate of hydrogen flow, and not the combined rates of hydrogen and electrolytic gas, was kept constant, the total volume of gas passed increased with the oxygen content. This is shown in the last column of the table above. Also, the volume percentages of oxygen are not quite proportional to the water equivalents for the same reason. They increase somewhat more slowly. An imported copper oxide in granules intended for organic analysis (10–20 mesh) was used. Samples of 5 cc. apparent volume of copper oxide, weighing within a few tenths of 10 g. and giving about 8 g. of reduced copper, were always employed. The catalyst was prepared by slow reduction in electrolytic hydrogen at 150–200°.

Catalytic Activity of Copper Oxide.—If reduction of copper oxide be prevented, the catalytic activity of the copper oxide granules is very slight in comparison with that of the copper. As was shown in our earlier paper, when hydrogen containing oxygen equivalent to 10 mg. of water per 5-min. interval was passed over fresh copper oxide at 150°, the rate of formation of water by catalysis and reduction together was too slight to be detected by the method used. At 200°, water was formed at an initially low, slowly accelerating rate. How much of this was due to combination of hydrogen and oxygen, it is impossible to say. The combined effects are much smaller in magnitude than with an initial copper surface.

Results with Metallic Copper as Catalyst.—The combination of hydrogen and oxygen in presence of metallic copper was studied at 100°, 130°, 150° and 200°, as this proved to be the temperature range within which combination varied from measurable to complete under the conditions chosen. Oxygen concentrations equivalent to 2.5, 5.0, 10.0 and (at 150°) 15.0 and 20.0 mg. of water vapor per 5-min. interval were used. Higher concentrations were excluded partly because of the complications introduced by condensation of the water formed. The concentration of 10 mg. was chosen as the standard.

In many of the experiments, it was found that after the oxygen supply was cut off and pure hydrogen alone run over the catalyst, the rate of water formation was increased markedly for a short time before finally falling to zero. Evidently any water adsorbed by the catalyst would be given off to the hydrogen stream, after the oxygen was shut off, at a steadily diminishing rate never exceeding that when the oxygen was passing over the catalyst. This water vapor obtained under these conditions was, therefore, not due to adsorbed water. Now, in our experiments on the reduction of copper oxide it was found that the presence of oxygen markedly inhibited the rate of reduction of the oxide. Evidently the same thing is occurring in this case. Oxide is formed simultaneously with water when hydrogen containing small percentages of oxygen is passed over heated catalytically-active copper and this oxide is reducible by hydrogen at the same temperature. The presence of excess oxygen, however, tends to inhibit this reduction reaction so that while oxygen is present the rate of reduction is kept down and, when the oxygen is shut off, the rate of water formation rapidly rises to a value several times the previous rate, only to drop to zero as the oxide is exhausted. These observations are clearly of considerable importance in considering the mechanism of the catalytic action, for they prove that under the conditions of many experiments copper oxide is actually formed and that this oxide may be reduced by hydrogen at the same temperature, but they also prove that while oxygen is present the reduction is inhibited. Now, if this inhibition is complete under all conditions, the mechanism of the reaction *cannot be* alternate oxidation and reduction. If, on the other hand, the inhibition is only partial, the mechanism *must be*, in part at least oxidation and reduction. Our experiments on the reduction reaction showed that at 200° the oxide granules were progressively reduced in presence of 10 mg. water equivalent of oxygen. It is further known that the oxide formed during a catalytic experiment—at low temperatures —is very much more reactive than the original oxide from which the copper catalyst was prepared. These facts prove then that at 200°, the mechanism must be, in part at least, alternate oxidation and reduction, and point very strongly to the conclusion that the same is true at lower temperatures.

There are further considerations which indicate that the mechanism is largely oxidation and reduction, or something which approximates closely to this. Further discussion is postponed, however, until the experimental results have been given.

The results of experiments with hydrogen containing oxygen equivalent to 10 mg. of water per 5-minute interval are given in Fig. 1.

At 200° (Curve I), the rate of water formation rose rapidly to that corresponding with complete conversion and remained constant. After the oxygen was cut off, the rate dropped abruptly to zero. Clearly, little oxide is formed under these conditions.
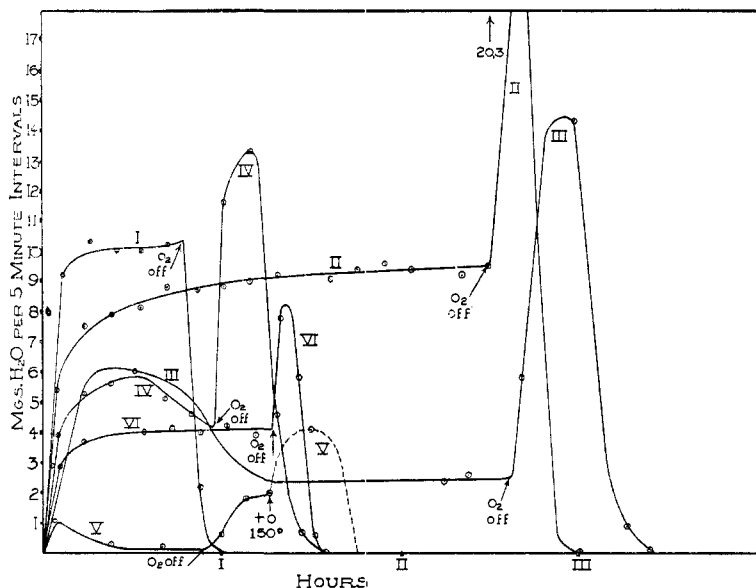

Fig. 1.—Concentration of oxygen equivalent to 10 mg. of water vapor per 5-min. interval. Curve I, 200°; II, 150°; III, 130°; IV, 130°; V, 100°; VI, oxygen concentration of 5 mg. at 130°.

At 150° (Curve II), the rate rose more gradually to a constant maximum corresponding with 94% conversion. When the oxygen was cut off, the rate rose rapidly to more than double its previous value for a short time before falling to zero.

At 130° (Curve III), the rate of water formation first rose to a maximum and then fell off rather rapidly to a fairly constant value. At the maximum, the rate was 6.0 mg.; the constant value was 2.5 mg. of water in 5 minutes. Upon shutting off the oxygen, the rate of water formation rose as before to a value nearly 6 times the previous value and eventually dropped to zero. In another run at 130° (Curve IV), the oxygen was cut off when the rate was a maximum in order that the amount of oxide

present at this time might be estimated. In order to find out whether any unchanged oxygen was passing through the catalyst, effluent gas samples were taken at the beginning and at the end of the first experiment and analyzed. The first sample contained less than 0.03% of oxygen and the second contained 1.25%. The original oxygen content was 2.55%. It may, therefore, be concluded that at the beginning all the oxygen was reacting, while at the end 125/255 or about 50% was escaping unchanged. Of the 50% reacting, the curve shows that 25/100 or 25% was converted to water, so that the remaining 25% must have been permanently fixed as oxide.

The catalytic activity at 100° (Curve V) was very slight. The rate of water formation was highest at the start—about 10% conversion—
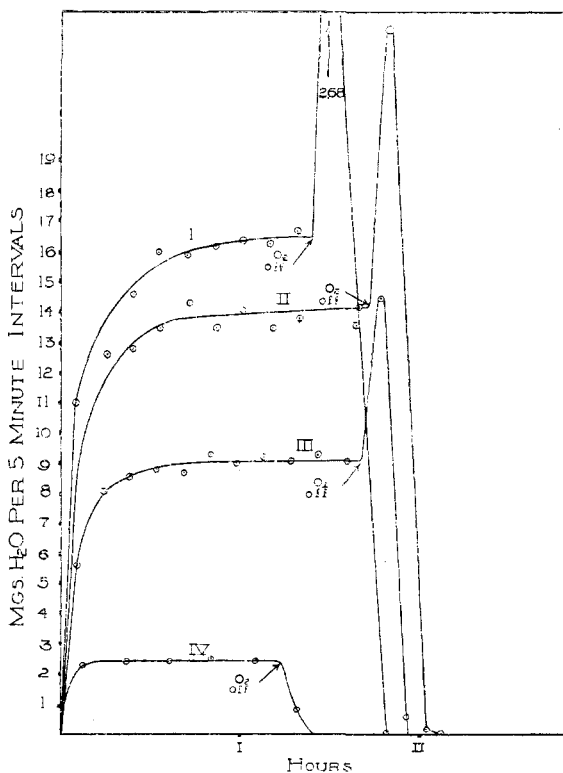

Fig. 2.—Experiments at 150°. Curve I, oxygen equiv-
alent to 20 mg. of water vapor per 5-min. interval; II, 15
mg.; III, 10 mg.; and IV, 2.5 mg.

but fell off rapidly to between 1 and 2%. When the oxygen was cut off, the rate rose as before but was very much less than at 130°. Moreover, the total amount of oxide formed was considerably less than at 130°, although the amount of oxygen not converted to water was very

much greater. In view of these facts, it appears quite certain that there must have been unchanged oxygen passing through the tube almost from the beginning. No analyses were made.

In Fig. 1 (Curve VI) is also given the result of a run at 130° with oxygen equivalent to 5.0 mg. of water. With this concentration there is no maximum such as was observed with 10 mg. and the final rate of water formation *is actually greater than with ro mg.*, due, undoubtedly, to the absence of much free oxygen in this case.

In Fig. 2 are given the results of experiments at 150° with hydrogen containing oxygen equivalent to 2.5, 10.0, 15.0 and 20.0 mg. of water per 5-minute interval. Up to a concentration of 15.0 mg., the conversion is between 90 and 95% complete while with 20.0 mg., it falls to 80%. It was hoped that with the higher concentrations at 150° the behavior would be analogous to that at 130° with 10 mg. Such a result was not obtained, however, even by doubling the concentration. Because of the heavy condensation of water, higher concentrations could not be tried.

The results of these experiments are summarized in Table II, in which are given the temperature of the experiment, the oxygen concentration (expressed in terms of mg. of water obtainable per 5-minute interval), the final yield of water, the percentage conversion, the amount of oxide formed (in terms of mg. of water obtained on reduction) and the length of the run in minutes. It is not believed that the amounts of oxide formed correspond strictly to equilibrium conditions.

Temp. °C.	Conc. O_2 Mg. of H_2O	Yield H_2O Mg.	Conversion %	Oxide formed Mg. of H_2O	Length of run Min.
200	10.0	10.0	100	3.1	45
150	10.0	9.5	95	41.6	180
130	10.0	4.2[a]	42	49.2	55
130	10.0	2.5	25	68.5	180
100	10.0	0.1	1	21.3	60
150	2.5	2.4	95	2	75
150	10.0	9.3	93	27.6	105
150	15.0	14.0	93	55.2	105
150	20.0	16.5	83	80	85
130	5.0	4.0	80	24.0	115

[a] 6.0 maximum in 30 minutes.

If the predominant action were a purely contact action at a copper surface, it would be expected that the amount of conversion would depend in some way upon the amount of free copper surface and would fall off in the proportion in which the copper is covered over with oxide. The results of the experiments at 130° and 150° show that there is no such simple relation and to this extent serve as evidence against this view. Thus, at 150° with 10 mg. of oxygen, conversion is 93% complete when there is a 28 mg. equivalent of oxide (that is, oxide equivalent to 28 mg. of water) present. With 20 mg. of oxygen, conversion is 80% when there is an

80 mg. equivalent of oxide present. Since with nearly triple the amount of oxide the relative conversion efficiency has only been changed from 93% to 80% (the absolute conversion being increased from 9.3 to 16 g. water) it is evident that the quantities of oxide here represented (28–80 mg.) can cover only a small fraction of the surface, provided the action is a purely contact action at a copper surface. At 130° on the other hand, with 10 mg. of oxygen, the conversion is 42% complete with 49.2 mg. of oxide present; but with 68.5 mg. of oxide, it is only 25% complete. On the basis of the contact-action hypothesis, this would require that the increase from 49.2 mg. to 68.5 mg. of oxide represent a change in the amount of free copper surface in the ratio 42:25 or 8 + :5. But these quantities of oxide are within the range (28 to 80 mg.) which the results at 150° indicated to represent only a small fraction of the catalyst surface. This contradiction argues against the contact action hypothesis.

In view of the known inhibitory influence of free oxygen on the reduction reaction, one is strongly tempted to correlate the rate decreases noted at 100° and 130° with the appearance of free oxygen in the effluent gas. Such a result would certainly be in harmony with the alternate oxidation and reduction mechanism.

Our results appear to indicate clearly that the factors which control the catalytic combination of hydrogen and oxygen in presence of metallic copper are identical with those which are active in the oxidation of the catalyst and the reduction of the resulting oxide. There is no question but that under the conditions of the majority of the experiments copper oxide is formed and that hydrogen is capable of reducing the oxide at the same temperature. It is equally true that in the temperature interval within which the catalytic activity drops sharply, namely, between 130° and 100°, the reducibility of the oxide formed during a run also abruptly falls off, and the rate of oxidation of the copper undergoes a considerable decrease. Thus, with 10 mg. of water equivalent of oxygen, a minimum of 2.5 mg. of water is formed at 130°, and only about 0.1–0.2 mg. at 100°; the initial rate of reduction of oxide is 5.8 (mg. of water) at 130° and 0.6 at 100°; and the amount of oxide formed in an hour at 130° is about 50 mg. (water equivalent) while it amounts to about 20 mg. at 100°, although during this period about 50% of the oxygen is passing through as water vapor at 130° and only 1% at 100°.

In view of these results, it appears that whatever the conditions may be that control the oxidation and reduction reactions, they also control the catalytic activity. This is in sharp contrast to the action of metallic nickel reduced from the oxide at 150–200°, as preliminary experiments of ours have shown. Nickel so prepared will catalyze the combination of small quantities of oxygen in hydrogen with the hydrogen at room temperature. The catalyst will slowly oxidize in the air at this temperature

but the oxide so formed is not reducible below 100–150° and the oxidized material is inactive as a catalyst.   Clearly, with nickel it is a case of purely contact action.   The chemical properties of the catalytic material are in no way related to its activity as a catalyst.   With metallic copper, on the other hand, it is quite clear that a close connection between the two does exist.

Were it not for the inhibitory action of oxygen on the reduction reaction the mechanism could be at once set down as an alternate oxidation and reduction process; and only to the extent that this inhibition is complete is this mechanism ruled out.   Now it has been found that at 200° the original oxide granules are progressively though slowly reduced by hydrogen containing 10 mg. of oxygen and that the oxide formed during a catalytic experiment is very much more reactive than the original granules.   It is, therefore, quite certain that there is some oxidation and reduction at 200° and probably also at the lower temperatures.

While all of our results are consistent with the alternate oxidation and reduction mechanism, there is another closely related mechanism which cannot be ruled out and merits consideration.   This may be called the incipient oxidation mechanism.   The reaction between an oxygen molecule and the copper atoms of the catalyst involves a disruption of the molecule and the subsequent formation of two oxide ions.   It would appear that at the moment of this transformation, the oxygen would be in a particularly reactive state, since the stable electron structure of the molecule has been destroyed and that of the ion has not yet had opportunity to be built up.   If, at this moment, the oxygen is struck by a hydrogen molecule, water would be formed, for this process represents the greatest decrease in free energy.   The catalyst may, therefore, be able to activate the oxygen because of its ability to combine with it and in the process of combination to open it to attack by hydrogen.   This power of the catalyst would evidently parallel closely its oxide-forming power and would decrease with the latter as the catalytic activity actually does.   If this action can only take place at a copper-copper oxide interface it cannot be distinguished from that resulting from alternate oxidation and reduction, in which the oxygen actually reaches the ion stage.   There is a little evidence, however, that if this can take place at *any* copper surface—and from the results of Wright and Mencke,[4] it does not appear that oxidation is an interface phenomenon—this action does not predominate.   For, as has been already demonstrated, a purely contact action appears to be excluded and the reasons adduced against such contact action are equally cogent in the present instance.

It appears to us that our results are most simply explained by assuming that the combination of hydrogen and oxygen in presence of copper

[4] Wright and Mencke, *J. Chem. Soc.*, **37**, 785 (1880).

takes place mainly in two steps; the first, oxidation of the copper catalyst; and the second, reduction of the oxide so formed, the latter reaction being complicated by the inhibitory action of free oxygen. The extent to which free oxygen interferes will depend upon the amount present. This in turn will depend upon the extent to which it is fixed by the copper, and this, finally, will depend not only upon the temperature but also upon the efficiency of the hydrogen in keeping the copper surface clear of oxide, for the more oxide there is already present on the surface, the less efficient the copper will be in fixing further oxygen. The efficiency of the catalyst depends upon a favorable balance being maintained among these separate actions. If the oxygen is all fixed in the top layers of catalyst and the oxide reduced as fast as formed, the reaction will proceed smoothly to complete conversion. This is evidently the situation at 200°. At 150° the inhibitory influence of oxygen is noticeable but the rates of oxidation and reduction are so nearly balanced from the start that this never becomes serious. At 130°, however, the rate of reduction at the start lags markedly behind the rate of oxidation and as this tends to interfere with the ability of the catalyst to fix oxygen, the influence of free oxygen soon begins to make itself felt. Eventually a further increase in free oxygen evidently can inhibit the rate of reduction no further and a steady state results. The behavior at 100° is the same except that free oxygen is probably present from the start.

It will be seen that our observations are, therefore, consistent with the simple alternate oxidation and reduction theory and appear to exclude the possibility of any purely contact action predominating, at any rate. Of the contact actions, that made possible by the oxide-forming ability of the copper should perhaps have greatest weight. In fact, it would appear probable that at 200° and higher temperatures this action may become more and more important. The incipient oxide mechanism differs in general from the alternate oxidation-reduction mechanism only in the length of time the oxygen is fixed to the copper surface. If this is infinitesimal, the action is of the incipient oxide type; if the time is measurable, it is of the alternate oxidation and reduction type.

These results throw no further light on the cause of the inhibiting influence of oxygen. An attempt was made to obtain evidence of adsorption of oxygen on partially reduced oxide but the results were negative. We are still of the opinion that adsorption of oxygen at the copper-copper oxide interface is the explanation. The difficulty appears to arise in obtaining sufficient quantities of surface interface to make the adsorption measurable.

Summary

A study has been made by a flow method of the catalytic combination of hydrogen and oxygen in the presence of metallic copper, (produced

by reduction of the oxide in hydrogen at 150–200°), in the temperature range 100–200°, using gaseous mixtures containing up to 5% oxygen.

1. Combination is practically complete at 200° and is just measurable at 100°.

2. In nearly all cases copper oxide is formed simultaneously with water. After the oxygen is shut off and pure hydrogen alone passed over the catalyst, the oxide so formed is reduced at a greater rate than that of the formation of water while the oxygen is on.

3. Between 130° and 100°, the rate of oxidation of the copper and the rate of reduction of the oxide so formed, as well as the catalytic activity, suffer a marked reduction.

4. At 130° with oxygen equivalent to 10 mg. of water in 5 minutes, the rate of water formation passes through a maximum to a steady minimum value.

These results are believed to be satisfactorily explained by assuming that the combination takes place mainly as a result of the alternate oxidation and reduction of the catalyst, the reduction reaction being complicated by the known inhibitory influence of free oxygen on that reaction.

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STUDIES IN ELECTRIC-ENDOSMOSE[1]

BY ALVIN STRICKLER AND J. HOWARD MATHEWS

Practically all of the previous work on electric-endosmose has been with water and aqueous solutions. The work to be described was extended to 9 typical organic solvents, and it will be shown that some of the general conclusions based on a study of aqueous solutions are quite erroneous.

Since the publication of Briggs'[2] bibliography in 1917 and his experimental results in 1918 but little has been reported. Loeb[3] has carried out experiments to determine the influence of electrolytes on the electrification and the rate of flow of water through colloidal membranes, and the cause of this influence. Articles by Girard and Morax,[4] and by Frank and Withrow[5] have appeared but have no bearing on our work.

[1] Submitted by Alvin Strickler in partial fulfilment of the requirements for the Degree of Doctor of Philosophy at the University of Wisconsin.

[2] Briggs, J. Phys. Chem., 21, 198 (1917); 22, 256 (1918).

[3] Loeb, J. Gen. Physiol., 1, 717 (1919); 2, 577 (1920).

[4] Girard and Morax, Compt. rend., 170, 821 (1920).

[5] Frank and Withrow, THIS JOURNAL, 42, 671 (1920).