

decomposition, but it also catalyzes the oxidation of the quinoline by the peroxide.

In order to study the relation between the conductivity and the effect of the different concentrations of catalyzer, conductivity measurements were made at 25° with quinoline saturated with conductivity water at 25°, then with manganese acetate dissolved in 26 cc. portions of the solution in the concentrations in which it was used as a catalyzer in the experiments described. The results obtained are tabulated below:

Gram of manganese acetate per 26 cc.....	0.00	0.00125	0.0025	0.005
Specific conductivity....	$2.3 \times 10^{-6}$	$3.4 \times 10^{-6}$	$3.75 \times 10^{-6}$	$5.2 \times 10^{-6}$

From these data it is evident that there is no simple relation between the conductivity of the solutions of manganese acetate in water-saturated quinoline and the velocity with which the peroxide solutions are decomposed in the presence of the corresponding amounts of manganese acetate.

#### Summary.

The results of this investigation may be briefly summarized as follows:

1. A number of compounds that decompose aqueous solutions of hydrogen peroxide catalytically are also active as catalyzers towards solutions of hydrogen peroxide in amyl alcohol, amyl acetate, isobutyl alcohol and quinoline.
2. Hydrogen peroxide in quinoline solution is decomposed quantitatively by manganese acetate. If the manganese acetate is present in so small a concentration that the reaction is slow, a side reaction, *viz.*, the oxidation of the quinoline by the hydrogen peroxide, is also appreciably catalyzed by the manganese acetate.
3. A solution of hydrogen peroxide in quinoline containing about 2% of water, when decomposed catalytically by manganese acetate, follows the second order of reaction. If the quinoline is saturated with water the reaction is monomolecular.
4. In solutions containing the catalyzer in high concentrations the velocity of reaction is approximately doubled by doubling the concentration of the catalyzer.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

## STUDIES IN DIALYSIS. I. THE DIALYSIS OF A COLLOIDAL SOLUTION OF HYDROUS CHROMIC OXIDE IN CHROMIC CHLORIDE.<sup>1</sup>

BY MARKS NEIDLE AND JACOB BARAB.

Received July 14, 1916.

In an effort to prepare the red form of colloidal chromic oxide<sup>2</sup> by pass-

<sup>1</sup> Presented at the Spring Meeting of the American Chemical Society, 1916.

<sup>2</sup> Woudstra, *Z. Chem. Ind. Kolloide*, 5, 33 (1909).

ing steam through a chromic acetate solution and dialyzing with intermittent changing of the diffusate, it was found that the chromium continued to diffuse until none was left in the membrane. Analysis of the diffusate from a solution of hydrous chromic oxide in chromic chloride showed a ratio of chromium to chlorine considerably greater than for pure chromic chloride. Colloidal solutions of hydrous ferric oxide in ferric chloride<sup>1</sup> do not behave in this way. At the end of twenty-four hours the ratio of iron to chlorine is 56 : 137 or less than Fe : 3Cl; it diminishes very rapidly until the amount of iron which diffuses can no longer be detected.

With very few exceptions, the process of dialysis has been employed simply to obtain a colloidal solution as free from electrolytes as possible. The observation that, in the dialysis of colloidal solutions of hydrous chromic oxide, the chromium diffuses more rapidly than the chlorine, suggested that a quantitative study of the dialysis of such solutions might throw some light on the nature of colloidal solutions and also on the process of dialysis.

#### **Preparation of Solution of Hydrous Chromic Oxide in Chromic Chloride.**

—Analysis of a commercial "C. P." preparation<sup>2</sup> of chromic chloride in the form of a gluey mass, gave the following results: chromium, 100 equivalents ( $\frac{1}{3}$  Cr); chlorine, 90 equivalents (1 Cl); sulfate, 3.3 equivalents ( $\frac{1}{2}$  SO<sub>4</sub>). The sulfate was removed by precipitation with the calculated amount of barium chloride added to a boiling solution of the chromic chloride. The filtrate was greatly diluted, heated to boiling and treated with ammonium hydroxide. Boiling was continued until the odor of ammonia became very faint. The hydrous chromic oxide was allowed to settle, washed three times by decantation, and finally filtered on a Büchner funnel. The desired amount of this hydrous chromic oxide, which now gave no tests for sulfate, was dissolved in small portions in the calculated amount of boiling 6 *N* hydrochloric acid. To bring the last portions into solution it was necessary to evaporate the solution to a small bulk. The resulting colloidal solution was filtered, diluted to a convenient volume, and kept as a stock solution. Its composition was: chromium, 0.1610 gram-equivalents ( $\frac{1}{3}$  Cr); chlorine, 0.0786 gram-equivalents (1 Cl) per 100 cc.

**Continuous Dialysis.**—One hundred cubic centimeters of the colloidal solution were placed in a parchment paper membrane, set up as shown in the diagram, and adjusted so that the levels of liquid, inside and outside,

<sup>1</sup> Picton and Linder, *J. Chem. Soc.*, 87, 1908 (1905).

<sup>2</sup> As an instance of the reliability of the analysis on the labels of C. P. chemicals, the label on this preparation reads: CrCl<sub>3</sub> + ?H<sub>2</sub>O. H<sub>2</sub>S metals, . . . . "nil." Fe, . . . . 0.0023%. S, . . . . present. K, . . . . present.

were the same. By means of stopcock C the flow of distilled water was regulated to a rate of about 800 cc. per hour. At intervals the vessel F was removed and replaced by another. The volumes of the diffusates were measured and convenient portions taken for analysis. The results expressed in terms of milliequivalents are given in Columns 4 and 5, Table I.

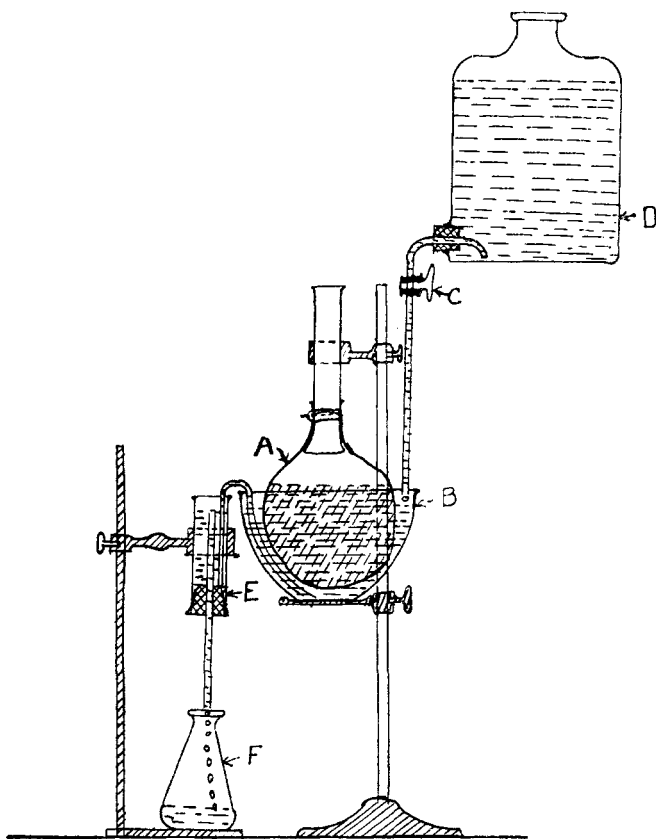


Fig. 1.

**Intermittent Dialysis.**—One hundred cubic centimeters of the stock solution were introduced into a parchment paper dialyser and suspended in a two-liter beaker containing 400 cc. of distilled water. The levels of the liquids on both sides of the membrane were practically the same initially. At the intervals given in Col. 3, Table II, the outer vessel was removed and another beaker containing 400 cc. of distilled water was placed in its stead.

**Dialysis without Changing Diffusate.**—Fifty cubic centimeters of the stock solution were placed in a parchment paper membrane and suspended in a liter beaker containing 400 cc. of distilled water. The dialysis was not disturbed except for the removal of samples from inside the membrane and from the diffusate for analysis. As no precaution was taken to prevent evaporation from the diffusate, its concentration is higher than it would have been if this precaution had been taken.

Each membrane was tested for leaks, at the conclusion as well as at the beginning of the experiment, by introducing colloidal hydrous ferric oxide and immersing in water. In no case did the colloidal hydrous ferric oxide pass through the membrane.

Unless specifically stated otherwise, the term "ratio" will mean the ratio in gram equivalents of chromium ( $1/3$  Cr) to chlorine (1 Cl).

TABLE I.—CONTINUOUS DIALYSIS.

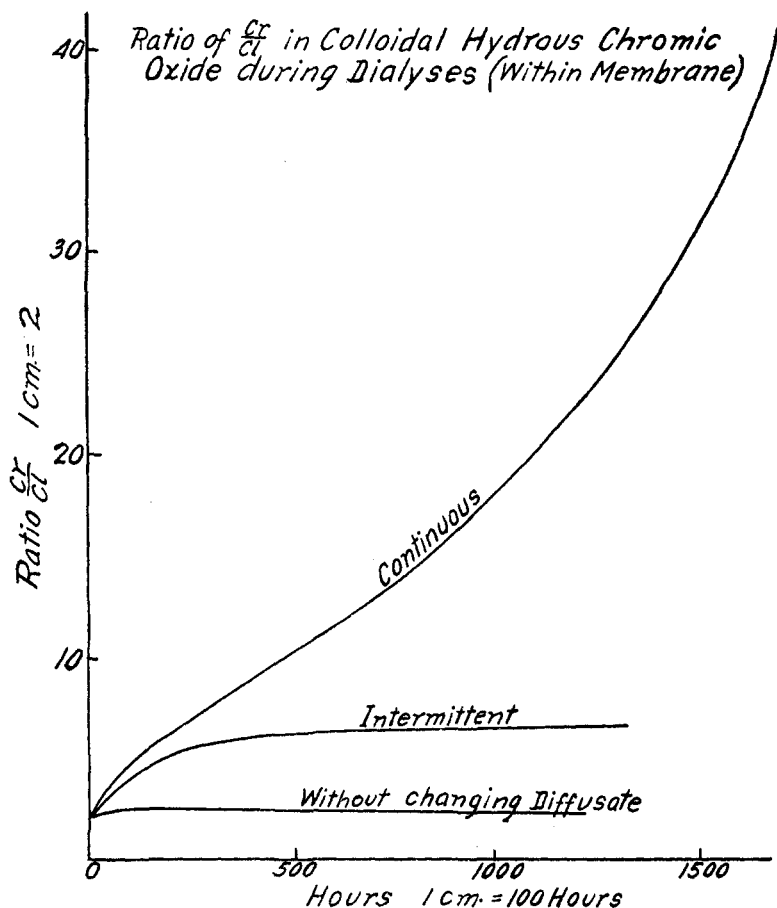
Interval number.	Total time. Hours.	Time interval. Hours.	Amounts diffused through membrane. Milliequivalents.		Rates of diffusion. Milliequivalents per hour.		Ratio Cr/Cl in diffusate.	Amounts remaining in membrane. Milliequivalents.		Ratio Cr/Cl within membrane.
			Chlorine.	Chromium.	Chlorine.	Chromium.		Chlorine.	Chromium.	
1	1/2	1/2	1.916	1.916	3.832	3.832	1.00	76.73	159.08	2.07
2	1	1/2	3.594	4.017	7.188	8.034	1.16	73.19	155.07	2.12
3	1 1/2	1/2	3.505	4.237	7.010	8.474	1.21	69.69	150.83	2.16
4	2	1/2	3.549	4.522	7.098	9.044	1.28	66.14	146.31	2.21
5	3	1	6.438	8.670	6.438	8.670	1.35	59.70	137.64	2.30
6	4	1	5.264	7.575	5.264	7.575	1.44	54.43	130.06	2.39
7	5	1	4.035	5.749	4.035	5.749	1.42	50.40	124.31	2.47
8	6	1	3.198	4.955	3.198	4.955	1.55	47.20	119.36	2.53
9	8	2	4.800	7.375	2.400	3.688	1.54	42.40	111.98	2.64
10	24	16	15.334	24.170	0.959	1.511	1.57	27.07	87.81	3.24
11	27	3	1.226	1.870	0.404	0.623	1.53	23.84	85.94	3.33
12	48	21	5.021	6.805	0.239	0.324	1.36	20.82	79.14	3.80
13	52	4	0.579	0.832	0.145	0.208	1.44	20.24	78.31	3.88
14	72	20	2.641	3.040	0.132	0.152	1.15	17.60	75.27	4.27
15	96	24	2.136	2.663	0.089	0.103	1.16	15.46	72.80	4.73
16	120	24	1.437	1.323	0.0611	0.0551	0.902	14.00	71.48	5.10
17	144	24	1.124	1.127	0.0468	0.0469	1.00	12.87	70.36	5.47
18	168	24	0.856	0.651	0.0356	0.0271	0.76	12.02	69.71	5.80
19	192	24	0.630	0.463	0.0263	0.0193	0.735	11.39	69.24	6.08
20	244	52	1.162	0.751	0.0223	0.0144	0.646	10.23	68.49	6.70
21	341 1/2	97 1/2	1.789	1.082	0.0183	0.0111	0.605	8.44	67.41	8.00
22	448 1/2	117 1/2	1.481	0.672	0.0127	0.0057	0.454	6.96	66.74	9.57
23	642	194	1.510	0.355	0.078	0.0018	0.235	5.45	66.38	11.98
24	834	192	0.874	0.134	0.0046	0.0007	0.153	4.57	66.25	14.50
25	1003	169	0.925	Trace	0.0055	....	...	3.65	66.25	18.10
26	1358	355	1.108	Trace	0.0031	....	...	2.54	66.25	26.06
27	1752	394	0.950	....	0.0024	....	...	1.59	66.25	41.60

TABLE II.—INTERMITTENT DIALYSIS.

Interval number.	Total time. Hours.	Time. interval. Hours.	Amounts diffused through membrane. Milliequivalents.		Rates of diffusion. Milliequivalents per hour.		Ratio Cr/Cl in diffusate.	Amounts remaining in membrane. Milliequivalents.		Ratio Cr/Cl within membrane.
			Chlo-rine.	Chro-mium.	Chlo-rine.	Chro-mium.		Chlo-rine.	Chro-mium.	
A	1/3	1/3	2.911	1.916	8.733	5.748	0.66	75.69	158.08	2.06
B	5/6	1/2	3.357	2.611	6.714	5.222	0.78	72.33	155.47	2.15
C	1 1/3	1/2	3.416	2.910	6.832	5.820	0.85	68.92	152.56	2.22
D	2 1/3	1	6.003	5.299	6.003	5.299	0.88	62.91	147.26	2.36
E	4 1/3	2	7.437	9.001	3.719	4.500	1.21	55.48	138.06	2.49
F	17 1/2	13 1/4	15.005	26.003	1.131	1.962	1.73	40.47	112.06	2.77
G	20	2 1/2	2.523	3.114	1.001	1.245	1.23	37.95	108.95	2.87
H	4 1 1/2	2 1 1/2	6.280	12.200	0.292	0.567	1.94	31.67	96.75	3.05
I	44 1/2	3	1.497	1.602	0.499	0.534	1.07	30.17	95.14	3.15
J	47 1/2	3	1.343	1.526	0.488	0.509	1.13	28.83	93.62	3.25
K	65 1/2	18	3.532	5.868	0.196	0.326	1.66	25.30	87.75	3.47
L	69 1/2	4	1.123	1.674	0.281	0.419	1.49	24.17	86.08	3.56
M	73 1/2	4	1.191	1.808	0.298	0.452	1.52	22.98	84.27	3.66
N	89 1/2	16	2.637	6.194	0.165	0.387	2.35	20.35	78.17	3.84
O	93 1/2	4	0.958	1.751	0.240	0.438	1.83	19.39	76.42	3.94
P	114	20 1/2	3.443	10.415	0.168	0.507	3.12	15.94	66.01	4.14
Q	116	2	0.468	1.036	0.234	0.518	2.21	15.48	64.97	4.20
R	138	22	3.098	10.425	0.141	0.474	3.36	12.38	54.55	4.41
S	142	4	0.432	0.518	0.108	0.130	1.20	11.94	54.02	4.54
T	146	4	0.366	0.383	0.092	0.096	1.05	11.58	53.75	4.65
U	162	16	0.627	1.044	0.039	0.065	1.66	10.95	52.70	4.81
V	170	8	0.576	1.403	0.073	0.175	2.44	10.38	51.30	4.93
W	186	16	1.275	5.122	0.080	0.321	4.02	9.10	46.18	5.08
X	189	3	0.284	0.765	0.095	0.255	2.70	8.82	45.41	5.15
Y	234	45	2.162	9.509	0.048	0.211	4.39	6.65	35.90	5.40
Z	330	96	2.142	10.800	0.0223	0.1125	5.03	4.21	23.63	5.63
A'	354	24	0.544	2.021	0.0227	0.0842	3.72	3.66	21.60	5.89
B'	667	312	1.620	8.700	0.0052	0.0279	5.68	2.04	12.90	6.31
C'	1339	672	0.943	5.656	0.0014	0.0084	6.00	1.10	7.25	6.58

TABLE III.—DIALYSIS WITHOUT CHANGING DIFFUSATE. COLLOID.

Sample number.	Time. Total.	Interval time.	Cc. sample.	Milli-equivalents. Chlorine.	Milli-equivalents. Chromium.	Ratio Cr/Cl.
1	48	48	..	.....	.....	....
2	96	48	5	0.541	1.343	2.58
3	172	76 1/2	5	0.482	1.229	2.55
4	285	113	10	0.962	2.424	2.52
5	538	253	10	1.075	2.487	2.31
6	1232	694	10	1.409	3.114	2.21
DIFFUSATE.						
1	48	48	10	1.199	1.677	1.40
2	96	48	10	0.800	1.380	1.73
3	172	76 1/2	10	0.809	1.485	1.835
4	285	113	10	0.844	1.612	1.910
5	538	253	10	0.991	1.942	1.960
6	1232	694	10	1.337	2.653	1.985



### Observations on Results.

#### I. Continuous Dialysis.

- a. At the end of the first interval, the ratio in the diffusate was 1, or the same as in chromic chloride.
- b. This ratio increased to 1.57 without abrupt changes, and then decreased continuously to zero.
- c. The ratio within the membrane increased continuously from 2.05 to 41.6. (See curve.)
- d. More than three-quarters of the colloidal hydrated chromic oxide remained in the membrane at the end of the dialysis, when the chromium had ceased to diffuse.

#### II. Intermittent Dialysis.

- a. The ratio in the diffusate at the end of the first interval was 0.66 and was less than 1 for the three following intervals.

- b. After the first four intervals the ratio was always greater than 1.
- c. While there are considerable irregularities, it is evident that, in general, the ratio in the diffusate is greater the longer the interval of dialysis.
- d. The ratio in the membrane, at the start, increased fairly rapidly, but very slowly after the first 400 hours. At the end of 1300 hours, the ratio in the membrane was only 6.58, *i. e.*, only slightly greater than in the diffusate. (See curve.)
- e. At the conclusion of the dialysis less than one-sixteenth of the colloidal hydrous chromic oxide remained in the membrane, and the chromium had not yet ceased to diffuse.

### III. *Dialysis without Changing Diffusate.*

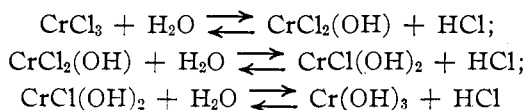
- a. The ratio of Cr to Cl in the diffusate rose rather rapidly during the first 96 hours, and then more slowly, gradually approaching the value within the membrane. (See curve.)

#### Interpretation of Results.

The first point which must be decided is whether the diffusates, with ratios greater than one, contain a basic chloride of chromium, or colloidal hydrous chromic oxide. It is noteworthy that the basic chlorides recorded in Gmelin-Kraut are all noncrystalline, and their compositions suggest either a mixture of simpler compounds or colloidal complexes. The existence of basic chlorides of chromium as true chemical individuals, has not been positively demonstrated. Hence we will assume that all diffusates with ratios greater than one, contain colloidal hydrous chromic oxide. This assumption is supported by the fact that these diffusates give a gel on evaporation, and, when the ratio is appreciably greater than one, yield a precipitate with potassium sulfate.

A striking difference between continuous and intermittent dialysis, as conducted in this work, is that in the former the colloidal particles finally cease to pass through the membrane, while in the latter it is seen that, after dialysis for 56 days, they continue to diffuse. A plausible as well as simple explanation of this strange behavior is that in continuous dialysis, the colloidal particles grow in size until they are too large to pass through the membrane, but in the intermittent dialysis they do not grow to such a size. We will now attempt to account for our observations on the basis of the prevailing theory of colloids, which maintains that the particles in a colloidal solution are polymers of the simplest molecule, with all the constituents in the dispersion medium more or less adsorbed.

Chromic chloride in aqueous solution is hydrolyzed according to the following equations:



The addition of hydrous chromic oxide will change these equilibria somewhat, but all the substances in the above equations and the ions into which they dissociate will be present in our stock solution—in true solution in the dispersion medium and adsorbed in the disperse phase. The charges on the colloidal particles and their stability are due to the adsorption of an excess of positive ions.

**The Ratios of Chromium to Chlorine in the Diffusate.**—The rates of dialysis of the various solutes contained in a membrane immersed in water will, at the start, be proportional to the diffusion constants and to the molar concentrations. For simplicity, the solutes in the original solution will be taken as follows: colloid, chromic chloride, hydrochloric acid, and an excess of chloride ion, whose negative charge is equivalent to the positive charge on the colloidal particles. The excess of chloride ion in the dispersion medium is practically a part of the colloid and therefore will not be considered separately in the following treatment. The order of the diffusion constants is: hydrochloric acid (highest), chromic chloride, colloid (lowest). At the beginning of the dialysis, in view of the difference in their diffusion constants, we will expect in the diffusate a greater ratio of hydrochloric acid to chromic chloride than exists within the membrane in the dispersion medium, and in a short interval very little of the colloid will have diffused. Thus we may explain the low ratios in the diffusates in intermittent dialysis for the first four intervals, which are short.

An increase in the molar concentration of colloid relatively to the solutes in the dispersion medium will result in a greater relative diffusion of the colloid. The initial rapid diffusion of chromic chloride and hydrochloric acid will greatly reduce their effective concentrations in a short time, and again the relative diffusion of colloid will increase. A greater relative diffusion of colloid means a greater ratio in the diffusate. Both of the above effects exert particular influence in intermittent dialysis, the more so the longer the interval. Hence, for intermittent dialysis, the longer the interval, the greater the ratio in the diffusate.

A ratio in the diffusate less than that in the membrane will lead to a greater relative molar concentration of the colloid in the membrane, if the colloidal particles remain of the same size, *i. e.*, if the molecular weight of the colloid does not increase. Growth of the particles will have the opposite effect, not only diminishing the relative molar concentration but also the diffusion constant of the colloid.

In the continuous dialysis, the constant flow of distilled water maintains fairly uniform,\* or uniformly changing conditions in the diffusate, and therefore the results are far more regular than in the intermittent process. As the dialysis progresses, the ratio in the diffusate increases because the molar concentration of the colloid relatively to the solutes



in the dispersion medium increases. Since the relative concentration of the colloid in grams per liter increases throughout, the ratio in the diffusate must continue to increase unless the particles grow larger. From Interval 10, Table I, the ratio in the diffusate begins to decrease, and furthermore, the increase of this ratio from Intervals 1 to 10 is insufficient to account for the increase in the relative concentration of the colloid. Hence the data in Table I indicate that continuous dialysis is accompanied by a continuous growth of the particles.

Little need be said concerning the dialysis without changing the diffusate. It is evident that osmotic equilibrium is established in a relatively short time, while the establishment of complete uniformity between internal and external liquids takes place very slowly.

#### Mechanism of the Growth of the Particles.

Two distinct processes are probably involved in the growth of the particles: first, aggregation of particles to form larger ones; second, a gradual increase of the hydrous chromic oxide in the nuclei of the particles due to hydrolysis of the chromic chloride adsorbed.

Aggregation of the particles may be explained on the basis of Bredig's theory of colloid precipitation, according to which a decrease of the potential between disperse phase and dispersion medium will cause an increase in the surface tension of the latter at its interface with the former. This increase in surface tension is conducive to aggregation. As the concentration of electrolyte in the dispersion medium relatively to the colloid diminishes during dialysis, the excess of positive ions adsorbed by the particles decreases. Thus the potential between disperse phase and dispersion medium is lowered continuously, and aggregation takes place continuously.

The large amount of water adsorbed is in no small measure responsible for the size of colloidal particles of hydrous oxides. It is also likely that adsorbed electrolytes greatly diminish the proportion of adsorbed water. Thus diffusion of adsorbed electrolytes, particularly hydrochloric acid, from disperse phase into dispersion medium, during dialysis, may result in a growth of the particles: first, by increasing the adsorbed water, and second, by progressive hydrolysis of the adsorbed chromic chloride by the adsorbed water. In the latter the chromic hydroxide formed becomes part of the nuclei.

#### Summary.

1. In intermittent or continuous dialysis, in a parchment paper membrane, of a solution of hydrous chromic oxide in chromic chloride, the colloidal particles diffuse through the membrane.

2. In intermittent dialysis the ratio of chromium ( $\frac{1}{3}$  Cr) to chlorine (1 Cl) in the diffusate after a short time is always greater than one. In general, it is greater the longer the interval of dialysis for the same diffusate.

3. In continuous dialysis, the ratio of chromium to chlorine in the diffusate increases from 1 to a maximum of 1.57, then gradually diminishes and approaches zero.

4. In intermittent dialysis, as conducted in this research, about 6% of the original colloid, still associated with considerable electrolyte, remains in the membrane at the end of 56 days, and colloid still diffuses. This dialysis could have been continued until no colloid remained within the membrane.

5. In the continuous dialysis, 75% of the original colloid remains in the membrane. Continuing the process beyond 35 days, increases the purity of the colloid without loss of chromium, *i. e.*, only hydrochloric acid diffuses.

6. If the intervals in intermittent dialysis are made smaller, more satisfactory results are to be expected. In fact, by conducting the entire process in very short intervals, the efficiency may even exceed that of continuous dialysis. The latter procedure, however, is impractical.

7. The variations of the ratios of chromium to chlorine in the diffusates are accounted for. They indicate a gradual growth of the particles. In the intermittent process, the particles did not grow sufficiently to be retained by the membrane, whereas in continuous dialysis they did.

8. The growth of the particles is explained partly by aid of Bredig's theory of colloid precipitation and partly by assuming that the nuclei of the particles grow as the adsorbed chromic chloride is hydrolyzed by the adsorbed water.

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[CONTRIBUTION FROM THE SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE.]

## THE COLLOIDAL ARSENATES AND PHOSPHATES OF IRON.

By HARRY N. HOLMES AND R. E. RINDFUSZ.

Received July 13, 1916.

The usual method of analysis of sulfide ores requires the dissolving of the sample in aqua regia and the addition of potassium chlorate or bromine to oxidize separated sulfur. After evaporation to dryness, addition of hydrochloric acid, filtration and treatment of the filtrate with ammonium hydroxide, any iron present is precipitated as ferric hydroxide.

In attempting to apply this method to arsenopyrite, as directed by Olsen,<sup>1</sup> we failed to get the expected precipitate of ferric hydroxide. Instead a rich red solution resulted.

Assuming that ferric orthoarsenate was formed in the process, we attempted to duplicate the final result by mixing solutions of ferric chloride and disodium arsenate and treating the precipitate thus formed with

<sup>1</sup> Olsen's *Quant. Chem. Anal.*, 4th Ed., p. 172.