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Inhomogeneity in Coprecipitated Copper Hydroxide-Magnesium Hydroxide Catalysts and its Effect upon their Activity

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The method of coprecipitation is frequently used in the preparation of multi-component catalysts, and has been shown, in particular cases, to give more active catalysts than alternative methods such as mixing of the dry components, precipitation of one component on a suspension of the other, etc.¹ The greater activity is presumably associated with the more intimate mixing of the components obtainable by this method. That this method does produce more intimate mixing of the components has been shown by X-ray studies on catalysts of copper and magnesia and of cobalt and magnesia.²

Ordinary coprecipitation, however, has the disadvantage that if the compounds being precipitated have different solubilities, the resulting catalyst may not be homogeneous. This possibility has been pointed out before,³ but has not been investigated in detail. Proof of the existence of such inhomogeneity would be important for two reasons. First, it would be important in its bearing on theories of promotion, for quantitative information about the dependence of activity on promoter concentration cannot be obtained from experiments on catalysts of non-uniform composition. One cannot know the composition of the surface where the reaction is occurring unless one knows that the whole catalyst is of the same composition, for analysis gives only the gross composition. Second, it would be important economically, for the maximum activity could not be achieved in a catalyst that was not uniformly of the optimum composition.

Two types of inhomogeneity may be imagined, either one or both of which may occur in a particular case. First, there may be homogeneity within each catalyst particle, but inhomogeneity between different particles. Second, there may be inhomogeneity within each particle, but homogeneity between particles in the sense that each particle is like every other one. For any catalyst

whose components differ in solubility, there will be (at least momentarily) a difference between the composition of the material precipitated at the beginning and that precipitated at the end. The extent to which this difference will persist in the final catalyst will depend upon the relative solubilities of the components, the concentrations of the solution and the precipitant, the rate of addition of the precipitant, the rate of stirring, the temperature, and the intrinsic rate of rearrangement of the precipitated material.

The work described in this paper was done in order to determine whether this inhomogeneity is present to an appreciable extent in a particular case, and, if present, what effect it has on catalytic activity. The catalysts chosen for the investigation were composed of the hydroxides (hydrated oxides) of copper and magnesium. This combination was chosen because of the relative ease of analysis and because considerable work has already been done on it.^{2,4} The decomposition of dilute hydrogen peroxide was chosen as a reaction for assessing the activity of the catalysts because it may be followed conveniently and because preliminary experiments showed that it was sufficiently sensitive to the changes in activity involved.

Two approaches to the problem were employed. For the first, intended to show the composition and activity of a catalyst at various stages of its precipitation, a series of six catalysts was prepared by adding to equal portions of a stock solution of copper and magnesium nitrates various fractions of the equivalent amount of sodium hydroxide solution. It was thought that the differences, if any, in the compositions and activities of these fractions would be closely parallel to the differences between successive portions of a catalyst completely precipitated from the same solution. For the second approach, intended to show any difference in activity between catalysts prepared by ordinary coprecipitation and catalysts prepared so as to be homogeneous, five pairs of catalysts were prepared from five stock solutions

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(1) Frolich, Fenske and Quiggle, *Ind. Eng. Chem.*, **20**, 694 (1928).

(2) Joris, Verhulst and Taylor, *Bull. soc. chim. Belg.*, **46**, 393 (1937).

(3) Griffith, "The Mechanism of Contact Catalysis," Oxford University Press, Oxford, 1936, p. 5.

(4) Schwab and Schultes, *Z. physik. Chem.*, **B9**, 265 (1930); Lewis, *J. Phys. Chem.*, **37**, 917 (1933); Taylor and Joris, *Bull. soc. chim. Belg.*, **46**, 241 (1937).

containing different ratios of copper to magnesium. One catalyst of each pair was prepared by ordinary coprecipitation and the other by the addition of the mixed nitrates to the sodium hydroxide. This method will be referred to as "reverse coprecipitation," since it is the reverse of the usual method.

Experimental

Preparation of Catalysts.—Each catalyst of the first series (A) was precipitated by adding to the solution of mixed nitrates a known fraction of the equivalent amount of sodium hydroxide solution, the fraction varying from about 0.1 to about 1.0. For the second series (B), two catalysts were precipitated from each of five solutions, the ratio of copper to magnesium varying from about 1:1 to about 1:5. The first catalyst of each pair was prepared by ordinary, and the second by reverse, coprecipitation. All precipitations were made by dropwise addition of the reagent at a rate controlled between 6 and 8 ml./min. The solutions were stirred during precipitation (at as nearly as possible the same rate for all catalysts) and maintained at $25 \pm 1^\circ$. All solutions were made from reagent grade chemicals dissolved in distilled water, and all catalysts of a series were prepared from the same stock solutions of the components. The details for each catalyst are summarized below. Each catalyst was allowed to

TABLE I

SERIES A^a

Catalyst	Fraction of equiv. vol. of NaOH added	Rate of addition, ml./min.
1	0.0986	6.1
2	.197	7.6
3	.395	8.1
4	.585	7.7
5	.794	7.7
6	.993	7.7

^a The solution of mixed nitrates was 0.1506 *M* in magnesium and 0.05002 *M* in copper; 2 l. was used for catalyst 1 and 1 l. for each of the others. The sodium hydroxide solution was 0.2000 *M*.

settle for one day in the supernatant liquid, and then washed four times by decantation, using 0.2 l. of water for each 0.04 mole of precipitate and allowing the precipitate to settle for one to three days between washings. Each was then filtered with suction, dried with the others at about 110° for twenty-five hours and ground in an agate

TABLE II

SERIES B^a

Catalyst	Cu in mixed nitrates, moles/l.	Mg in mixed nitrates, moles/l.	Rate of addition, ml./min.
10, 10-R	0.102	0.0995	7.0 6.9
11, 11-R	.0680	.133	6.9 6.7
12, 12-R	.0510	.149	7.0 6.7
13, 13-R	.0408	.159	7.1 7.2
14, 14-R	.0340	.166	7.1 6.7

^a The sodium hydroxide solution was 0.202 *M*; 400 ml. of it were used for each catalyst, with 180 ml. of the solution of mixed nitrates.

mortar. To make these catalysts comparable with those of Series B, they were later dried with the latter at 150° for forty-two hours and then reground. They were stored in glass-stoppered bottles over calcium chloride. Each catalyst was centrifuged immediately after precipitation, and washed three times with 0.2-l. portions of water, each washing being followed by centrifuging. All were dried simultaneously for thirty hours at $60-80^\circ$, for twenty-eight hours at $100-130^\circ$, and finally for forty-two hours at 150° , after which they were ground and stored like those of series A.

Determination of Activity of Catalysts.—The activity of each catalyst was determined by measuring the amount of dilute hydrogen peroxide decomposed by it under standardized conditions. The hydrogen peroxide was prepared by diluting reagent quality 30% hydrogen peroxide to about 0.06 *M*. The reaction vessel was a 1-liter round-bottomed flask with a hole in the neck for introducing the reactants. The reactants were stirred by a glass propeller turning at a rate just short of that producing marked splashing. Experiments showed that reasonable variations in the rate of stirring had no appreciable effect upon the results. Before each run the reaction vessel was rinsed with dilute hydrogen peroxide acidified with nitric acid (to decompose any traces of permanganate left from a previous analysis), rinsed with water and dried at $160-180^\circ$. Each run was made at $25.00 \pm 0.05^\circ$ as read on an uncalibrated mercury thermometer. All catalyst samples for a series of runs were weighed out at the same time into crucibles and kept in a desiccator until used. Each sample was weighed to 0.1 mg. and was within 2% of 50 mg. Two 25.00-ml. portions of the dilute hydrogen peroxide were measured out for each run of a series and kept in covered test-tubes until used.

About ten minutes before a run, a catalyst sample was rinsed into the reaction flask with 100 ml. of water, the flask placed in the thermostat and the stirrer started. At the same time one of the tubes of hydrogen peroxide was hung in the thermostat. To start the run this hydrogen peroxide was poured quickly through the hole in the flask into the mixture of water and catalyst. The hydrogen peroxide remaining in the tube was determined by titration with standard permanganate. The amount found was subtracted from the original amount (determined at the end of the run by titration of the other 25.00-ml. portion) to give the actual initial concentration of hydrogen peroxide. After 10.00 ± 0.01 minutes, the reaction was stopped by pouring quickly through the hole a measured excess of acidified standard permanganate. A measured excess of standard sodium oxalate was then added and back-titrated with the standard permanganate. From the known ratio of oxalate to permanganate, the final concentration of hydrogen peroxide could be calculated.

The results were expressed as first order rate constants since that order ordinarily fits the heterogeneous decomposition of hydrogen peroxide better than any other integral order, and because a comparison of the ten-minute runs with some three-minute ones showed that such was the case here. The results would, however, be comparable among themselves no matter how expressed, since all variables (weight of sample, initial concentration, etc.) were held within 5%.

After the method had been standardized, from two to six runs were made on each catalyst. For the sixty-five runs the average deviation from the appropriate mean was 4%. In no case for which the average rates for a pair of catalysts were significantly different was there any reversal of the order of activity if the comparison was made, not between the average rates, but between the slowest run on the more active catalyst and the fastest on the less active.

Analysis of Catalysts.—All catalysts were analyzed for copper by the iodide method, using 0.01–0.02 *N* sodium thiosulfate standardized against electrolytic copper. For all but two catalysts duplicate determinations were made and the average for all determinations of the deviations from the appropriate mean was 0.2%. Two of the catalysts (12 and 12-R) were analyzed for magnesium using the bromate modification of the 8-hydroxyquinoline method after removal of copper as sulfide.

For the catalysts of series A (excluding catalyst 1) the composition to be expected could be calculated from the known amount of sodium hydroxide, from the fact that the supernatant liquids after precipitation gave no test for copper with ferrocyanide ion, and from the assumption that the precipitates were the hydroxides. (For catalyst 2 it was necessary to assume that part of the precipitate was a basic nitrate, since not enough sodium hydroxide had been added completely to precipitate the copper as hydroxide.) For these catalysts the calculated and observed percentages of copper agreed, on the average, within 3%. Because of this agreement, the mole fraction of copper hydroxide in all catalysts was calculated from the experimental percentage of copper and the assumption that the catalysts were the hydroxides. These calculations could be checked for catalysts 12 and 12-R by comparing the calculated with the experimental percentages of magnesium. For catalyst 12 the calculated percentage of magnesium was 30.6 and the experimental 32.4. For catalyst 12-R the corresponding figures were 26.3 and 24.7. Since the apparent uncertainties in the mole fractions were of the same order of magnitude as the uncertainties in the rate constants, the results are plotted with the mole fraction, the rational unit, as the unit of composition of the catalysts. There is no significant difference between the shapes of the activity–composition curves plotted on this basis and those plotted with weight per cent. as the unit of composition.

Experimental Results

The results of the rate runs and analyses are presented in the tables.

TABLE III
SERIES A

Catalyst	Fraction pptd.	Wt. % Cu	Mole fraction Cu compd. calcd.	No. of rate runs	Av. dev. from mean, %	Av. $k \times 10^2$ per g. catalyst (sec.) ⁻¹ (g.) ⁻¹
1	0.0986	57.4	1.00	2	1	2.33
2	.197	56.6	1.00	4	2	3.42
3	.395	48.4	0.629	4	6	3.38
4	.585	35.3	.426	4	5	3.28
5	.794	28.2	.314	4	2	3.02
6	.993	21.8	.251	4	2	3.05

TABLE IV
SERIES B

Catalyst	Wt. % Cu	Mole fraction Cu compd. calcd.	No. of rate runs	Av. dev. from mean, %	Av. $k \times 10^2$ per g. catalyst (sec.) ⁻¹ (g.) ⁻¹
10	43.2	0.540	6	9	4.08
10-R	41.8	.515	3	4	6.84
11	29.1	.326	3	5	3.97
11-R	29.2	.327	3	3	4.02
12	17.3	.177	5	3	2.50
12-R	24.0	.258	4	1	3.42
13	16.7	.171	4	2	2.38
13-R	19.3	.201	6	5	4.02
14	11.9	.118	5	6	2.05
14-R	16.5	.168	4	2	3.28

Two special experiments and some observations made during centrifuging are pertinent to the discussion. It has already been pointed out that for each catalyst of series A (except catalyst 1) the supernatant liquid gave no test for copper, showing that the copper had been precipitated completely by that stage. Since these catalysts were allowed to stand a day in the supernatant liquid, it was thought that some of this precipitation of copper might have occurred during that period through exchange with magnesium hydroxide precipitated at first. If this were true, it would mean that in a continuous precipitation appreciable magnesium would accompany the copper during the first part of the precipitation. A small-scale experiment showed this to be true. A portion of the stock sodium hydroxide solution was added to an equivalent portion of the stock solution of mixed nitrates at a rate equivalent to that used in the precipitation of the catalysts. Small samples of the supernatant liquid were removed at intervals during the precipitation and tested for copper. Copper was found in the supernatant liquid up to about the half equivalence point, but not beyond. Since the copper present was equivalent to only about one fourth of the total sodium hydroxide, some magnesium must have accompanied the copper as it was precipitated.

During the centrifuging of catalysts of series B, observations of interest were made. Each catalyst prepared by ordinary coprecipitation appeared after the first or second washing to be in layers in the centrifuge tubes, the layers varying in color and thickness with the catalyst. The effect was particularly pronounced at the end of the washing when all of the catalyst was brought into two tubes by centrifuging successive portions

in the same tubes. Each tube then exhibited a series of bands of alternating light and dark material. The catalysts prepared by reverse coprecipitation did not show this effect except for one or two which, after the final washing, showed very thin lines of white material between the successive portions centrifuged down.

These observations suggested a second special experiment⁵ which constitutes conclusive proof of the existence of inhomogeneity in these catalysts. A catalyst was prepared by ordinary coprecipitation from a solution of the mixed nitrates having a Mg:Cu ratio of about 3:1. After the usual washing and centrifuging, it had the expected banded appearance in the centrifuge tubes. The moist precipitate was made into a suspension with a little water, and centrifuged in one operation in one tube. The resulting material was in two layers, which were removed, dried, and ground separately. The lower, light blue layer contained 9.6% copper and had a first-order rate constant, k , of 3.8×10^{-2} sec.⁻¹ per gram of catalyst, while the upper, dark blue layer contained 24.3% copper and had a k of 5.5×10^{-2} . The inhomogeneity suggested by the bands observed during centrifuging is thus confirmed.

Since the copper-rich upper layer must have been denser than the magnesium-rich lower layer, the separation during centrifuging probably depended upon the particle size rather than upon density. In later work, catalysts prepared by reverse coprecipitation sometimes showed marked banding after centrifuging, but attempts at separation of the layers were unsuccessful, because of the disappearance of the banding when all the material was centrifuged from a small amount of liquid in one tube. It seems probable that this elusive inhomogeneity was in particle size only and not in composition.

Discussion of Results

Physical Evidence for Inhomogeneity.—The separation during centrifuging proves that the catalysts prepared by ordinary coprecipitation were inhomogeneous and that the inhomogeneity was at least partly of the second kind suggested in the introduction, with difference in properties (including composition) between different particles. It does not exclude difference in properties within particles. The failure of an attempted similar separation indicates that the catalysts

prepared by reverse coprecipitation were homogeneous as far as the second type of inhomogeneity is concerned, and it seems reasonable that these would also be homogeneous with regard to the first type. Since the inhomogeneity appeared only after washing, the larger agglomerates present in the unwashed precipitate must have been pretty much alike, the smaller particles which separated after washing out of the coagulating electrolyte being the seat of the non-uniformity.

Effect of Inhomogeneity upon Activity.—The rate runs on the two series of catalysts indicate that the inhomogeneity had a marked effect upon the activity of the catalysts. To facilitate the discussion of this effect, the results are shown in two sets of curves, one representing the activity per mole of catalyst and the other the activity per mole of copper as a function of catalyst composition.

Although these curves are not known in sufficient detail for a complete discussion in connection with theories of promotion, they do show that there is a pronounced difference in the activity-composition relation between the catalysts prepared so as to be homogeneous and those prepared by ordinary coprecipitation. This is most obviously evident in the marked superiority of three of the five catalysts prepared by reverse coprecipitation over those of similar gross composition prepared by the ordinary method. For example, catalyst 10-R is over 60% more active than catalyst 10, although the latter was prepared from the same solution and had practically the same final composition. Such a difference in a technical catalyst might be of economic importance.

The difference between the homogeneous and the inhomogeneous catalysts in the activity-composition relation appears not only in this higher activity of several of the homogeneous catalysts but also in the quite different shapes of the curves. In Fig. 1, the curve for the homogeneous catalysts descends steeply on the left, apparently from a large maximum, and goes through a small local maximum on the right. The curve for the other catalysts, however, is almost horizontal on the left and falls off steeply on the right. The departure of catalysts 12, 13 and 14 from their expected compositions (due probably to differential peptization during washing, and in the case of catalyst 12 to a loss of part of the material) leaves part of this curve indefinite. Catalyst 6 of series

(5) Performed by Mr. John W. Holmes.

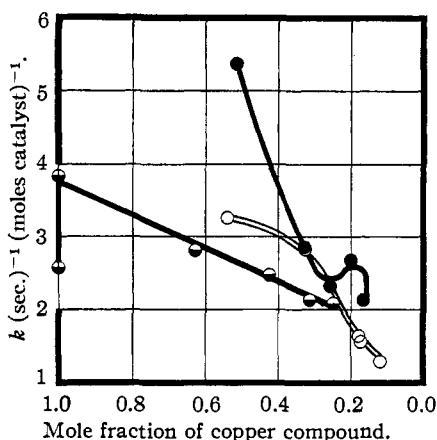


Fig. 1.—Catalyst activity per mole catalyst vs. catalyst composition: ●, series A, left to right: 1 and 2 to 6; ○, series B, ordinary coprecipitation, left to right: 10 to 14; ●, series B, reverse coprecipitation, left to right: 10-R to 14-R.

A, however, falls in the composition range of the uncertainty, and since it was prepared under nearly the same conditions as those of series B, it may be used to indicate the course of the curve in the indefinite region. In Fig. 2, the curves are again markedly different. The curve for the homogeneous catalysts falls on the left to a minimum around 0.3 mole fraction copper hydroxide and rises to a maximum (apparently quite sharp) around 0.2 mole fraction copper hydroxide. The curve for the inhomogeneous catalysts, in contrast, rises rather steadily from left to right.

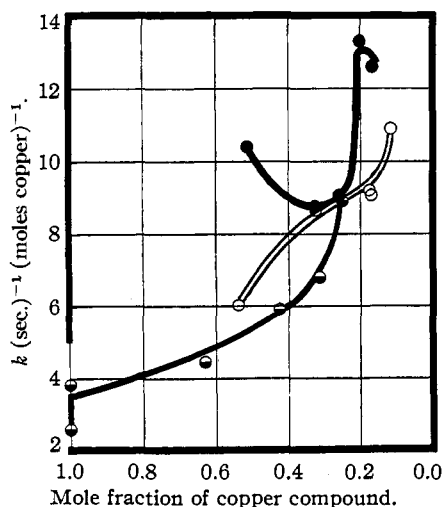


Fig. 2.—Catalyst activity per mole copper vs. catalyst composition: ●, series A, left to right: 1 and 2 to 6; ○, series B, ordinary coprecipitation, left to right: 10 to 14; ●, series B, reverse coprecipitation, left to right: 10-R to 14-R.

It seems reasonable to suppose that such differences in the form of the activity–composition curves between homogeneous catalysts and those prepared by ordinary coprecipitation are not confined to these particular catalysts, but may appear whenever compounds of different solubilities are coprecipitated. This suggests that further studies of the relation between catalyst activity and composition should be made on catalysts known to be homogeneous.

It is interesting, in this connection, to note that Lewis,⁴ in his study of the sodium hypochlorite decomposition, found a maximum at about the same composition as the one in Fig. 2 (0.2 mole fraction copper hydroxide). His catalysts, precipitated in the reaction mixture, were prepared essentially by reverse coprecipitation, and his results were expressed per unit weight of copper, so that the upper curve of Fig. 2 is comparable to his curve. In comparing the activity of similar catalysts for several reactions, one should bear in mind the method of preparation. Thus catalysts prepared by ordinary coprecipitation should be compared with those of the lower curves in Figs. 1 and 2 rather than with the upper curves or with Lewis's curve.⁴

Homogenization of Catalysts during Precipitation.—Evidence that the catalysts tend to change, during precipitation, toward a homogeneous distribution may be obtained from the curves for series A, the fractionally precipitated series. One of the special experiments described showed that in the preparation of these catalysts the copper was completely precipitated when about half the equivalent amount of sodium hydroxide had been added. Hence, barring rearrangement within the precipitates, catalysts 4, 5 and 6 should have consisted of intimately mixed copper hydroxide–magnesium hydroxide of composition about like that of catalyst 3 plus excess magnesium hydroxide. Therefore, compared on the basis of equal amounts of copper (Fig. 2), these catalysts should have shown about the same activity as catalyst 3 if the excess magnesium hydroxide were present as separate particles, or lower activity than catalyst 3 if the excess magnesium hydroxide were deposited on the surface of the particles already formed. Figure 2 shows that the activity per mole of copper increases steadily through the series. It must be, therefore, that rearrangement takes place within the precipitate, incorporating some of the excess

magnesium hydroxide with the copper hydroxide-magnesium hydroxide mixture precipitated at first. If this rearrangement were complete, each catalyst of this series should have the same activity as one of the homogeneous catalysts of the same composition. This is not the case, for all of the catalysts of this series except catalyst 6 fall well below the curve for the homogeneous catalysts.

Applications.—In conclusion, it may be desirable to suggest possible applications of the ideas presented here. As already pointed out, they should be considered in any attempt to prepare highly efficient promoted catalysts, and in any research dealing with the effect of promoter concentration on activity. They may have a bearing on X-ray studies of the degree of dispersion of one component in the other. Finally, they may be important in helping to explain the effect upon activity of alternative methods of preparation.

Summary

1. Successive portions of a copper hydroxide-magnesium hydroxide catalyst have been prepared by fractional coprecipitation.

2. Five pairs of copper hydroxide-magnesium hydroxide catalysts of varying composition have been prepared, each pair consisting of one catalyst prepared by ordinary and one by reverse coprecipitation from solutions of the same composition.

3. Physical and analytical observations prove that catalysts of these components prepared by ordinary coprecipitation are inhomogeneous.

4. Rate experiments on the decomposition of hydrogen peroxide on these catalysts show that the inhomogeneity has a marked effect on the activity.

5. The bearing of these results on research in the field of promoter action has been discussed.

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The Effect of Method of Preparation upon the Activity of Coprecipitated Copper Hydroxide-Magnesium Hydroxide Catalysts

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It was suggested in the previous paper² that part of the effect of preparational variables upon the activity of multi-component catalysts might be explained by the inhomogeneity there shown to exist in such catalysts. A change in the rate of precipitation, for example, could change both the original amount of inhomogeneity in each portion of material, and the time available for homogenization during precipitation. Thus, although the over-all composition was identical with that of a previous preparation, the composition of the active surface might be significantly different.

It is the purpose of this paper to show that, in the case of a particular two-component catalyst, the details of the method of preparation affect importantly the activity, and that the results can be explained with the aid of the ideas previously advanced.² Data are presented which show the effect upon catalyst activity of systematic variations in the rate of precipitation and the number of washings. Two different ratios of components were used, and catalysts were prepared both by

ordinary and by reverse coprecipitation. As in the previous paper,² the catalysts studied were of copper and magnesium hydroxides, and the reaction used to assess the activity was the decomposition of dilute hydrogen peroxide. Table I classifies the catalysts according to the preparational variables.

TABLE I

Series	Molar ratio Cu:Mg	Direction of pptn.	No. catalysts	Variable	Range of variable
A	1:3	Forward	13	Time of pptn.	0-8 hr.
B	1:1	Forward	9	Time of pptn.	0-8 hr.
C	1:1	Reverse	7	Time of pptn.	0-6 hr.
D	1:1	Forward	4	No. of washes	0-3 washes
E	1:1	Reverse	4	No. of washes	0-3 washes
F	1:3	Forward	5	Special ^a
G	...	Reverse	10	Composition	Mg(OH) ₂ - Cu(OH) ₂

^a Rate of precipitation different at different stages of precipitation.

Experimental

Preparation of Catalysts.—The catalysts fall into two classes with respect to the details of preparation. Those of series F and G were prepared by adding 180 ml. of sodium hydroxide from a buret to 140 ml. of the vigorously stirred nitrates (vice versa for series G). The solution of

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(2) E. H. Taylor, *THIS JOURNAL*, **63**, 2906 (1941).