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A NEW METHOD OF PREPARATION AND SOME INTERESTING TRANSFORMATIONS OF COLLOIDAL MANGANESE DIOXIDE.

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Within the last few years several papers on the formation of colloidal manganese dioxide have appeared. Thus far, however, the intermediate formation of colloidal manganese dioxide in the ordinary oxidations of organic compounds with potassium permanganate has not been reported. The following paper is a report of some observations on this subject. In the course of the experiments it was found that the gelatinous form of colloidal manganese dioxide first obtained is slowly and automatically converted into a limpid colloidal solution. This transformation was studied somewhat more in detail and was found to be readily influenced (1) by the temperature at which the gel form was prepared, (2) by the concentration of the reacting solutions, (3) by the temperature to which the gel was subjected during the transformation, and (4) by the variations in the small concentrations of alkali necessary to cause the oxidation to take place rapidly.

The unusual chemical properties of manganese dioxide have for a long time occupied the attention of chemists, so that its existence as a colloid did not escape observation very long. Georgeu[1] boiled pure finely powdered Mn_3O_4 repeatedly with concentrated nitric acid and then washed the residue with water. When the wash waters were no longer acid the hydrated manganese dioxide went into solution, giving a brown liquid. He observed that the manganese dioxide is easily precipitated by the addition of very small amounts of nitric, sulfuric, or hydrochloric acids, ammonia, potassium or barium hydroxides and other compounds. Swiontkowski[2] found that on reducing a solution of potassium permanganate with pure neutral hydrogen peroxide a coffee-colored solution of colloidal manganese dioxide was obtained. This colloid was not obtained if the hydrogen peroxide was not neutral and was readily precipitated by the addition of very small quantities of acids and salts. Spring[3] and Spring

[1] *Ann. chim. phys.*, [3] 66, 154 (1862); *Jahresberichte*, 1862, 155.
[2] *Ann. Chem. Pharm.*, 141, 205 (1867).
[3] *Ber.*, 16, 1142 (1883).

and Boeck[1] prepared colloidal manganese dioxide by the action of hypochlorous acid on manganese hydroxide and of potassium permanganate on sodium thiosulfate. The precipitate formed dissolved in part, on washing thoroughly with water, to give dark brown solutions. The undissolved part corresponded to $Mn_8O_{12}.4H_2O$. The dissolved part, after evaporation of the water, gave $Mn_7O_{12}.4H_2O$. Spring and Boeck determined the concentrations of various electrolytes necessary to precipitate colloidal solutions of manganese dioxide and found the values to be relatively quite small. In fact it is this sensitiveness to the presence of electrolytes, no doubt, that has prevented the observation of this colloid in more instances. Aland likewise reported[2] that the addition of potassium permanganate to sodium thiosulfate gave no precipitate but that on the addition of sodium chloride solution manganese dioxide is precipitated. Deiss[3] prepared stable colloidal manganese dioxide hydrosol direct by reducing potassium permanganate solutions with arsenious acid in the presence of sodium hydroxide. By the use of this solution he was able to observe a number of new and interesting properties of this colloid, some of which will be mentioned in more detail below. Marck[4] reported some new observations on the formation of colloidal manganese dioxide by the reduction of potassium permanganate with hydrogen peroxide. But his results and additional data were published later in a somewhat more accessible form.[5] Some remarkable facts about the catalytic activity of colloidal manganese dioxide are brought out in the above paper.

My own observations on the formation of colloidal manganese dioxide during organic oxidations began several years ago. On one occasion especially,[6] while oxidizing pyruvic acid with potassium permanganate at room temperature in the presence of potassium hydroxide, the reaction mixture remained perfectly liquid after the addition of potassium permanganate, although no unchanged potassium permanganate was present as shown by the red-brown color. Gradually the mixture became more and more viscous until it set into a fairly stiff jelly. This jelly was made filterable by heating for a time.

Later[7] the formation of colloidal manganese dioxide was observed many times in the oxidation of acrolein diethylacetal to glyceric aldehyde diethylacetal in the synthetic preparation of dl-glyceric aldehyde. In this oxidation 540 cc. of water were placed in a three-liter flask and 50 g.

[1] Bull. soc. chim., [2] 48, 170 (1887).

[2] Z. anal. Chem., 40, 574 (1901).

[3] Z. Chem. Ind. Koll., 6, 69 (1910).

[4] Dissertation, Heidelberg (1907).

[5] G. Bredig and A. Marck, "Ueber kolloides MnO_2 sol und sein Verhalten gegen H_2O_2;" J. M. van Bemmelen, Gedenkboek, 1910, 342; for abstracts, cf. Koll. Ztschr., 8, 333; C. A., 5, 2470.

[6] Evans and Witzemann, THIS JOURNAL, 34, 1099 (1912).

[7] Ibid., 36, 1912 (1914).

acrolein acetal were added. To this, 1100 cc. of an aqueous solution containing 60 g. of potassium permanganate (*i. e.*, nearly saturated at room temperature) were added from a dropping funnel at the rate of 100 cc. in five minutes. Throughout the addition the mixture was vigorously agitated in an ice bath. By the time the last of the potassium permanganate is being added the whole reaction mixture has increased in viscosity very markedly. The viscosity continues to increase gradually until in 15 to 30 minutes the entire mass has set into a dark brown jelly with a shiny mirror-like surface. This gel was so stiff that frequently the flask could be inverted for an instant without disturbing the gel. Gradually, if left undisturbed, little globules of colorless liquid appeared on the upper surface. In a short while the sides of the gel broke away from the wall of the flask and fluid filled the crevice. Presently crevices filled with liquid were formed throughout the whole mass of the gel. The quantity of liquid increased as the gel continued to contract and break up until finally the gel was submerged in the syneresis water. At about this point the syneresis water usually began to be more or less brown in color. The mixture was now placed on a steam bath and the coagulation of the very sensitive colloidal gel hastened.

When the same quantities of materials given above were used, but when the potassium permanganate was added at the rate of 100 cc. in 10 minutes, the increase in viscosity appeared some time before the addition was complete and more or less gel formation occurred toward the end of the addition, so that it was frequently difficult to agitate the reaction mixture thoroughly because of its high viscosity. In some instances coagulation took place as soon as the maximum viscosity appeared; gel formation in this case did not interfere with the process of agitation. It may be, when the potassium permanganate oxidation of acrolein acetal is carried out as originally prescribed by Wohl,[1] *i. e.*, where the permanganate is added very slowly, that the intermediate formation of colloidal manganese dioxide is almost entirely concealed. In fact, it may even be that this procedure[2] was originally adopted to avoid the difficulty of stirring the gel. Be that as it may, it is clear from my own experiments, that by carrying out this oxidation as described above (1) a great deal of time is saved, (2) a greater yield of the oxidation product desired is obtained, and (3) the interference offered by manganese dioxide gel to adequate agitation is avoided.

Because of the interesting and rapid transformations of this colloidal manganese dioxide, it was desirable to learn if some cheaper and more accessible organic substance would not reduce the potassium permanganate in such a way as to produce the same colloidal phenomena.

[1] *Ber.*, **31**, 2394 (1898); Wohl and Neuberg, *Ber.*, **33**, 3095 (1900).
[2] Wagner, *Ber.*, **21**, 1230 (1888).

The first experiments were made with formaldehyde. 200 cc. of an aqueous solution containing 5.7 g. potassium permanganate were added to 10 cc. of 40% formaldehyde in 50 cc. of water containing a little sodium carbonate. The mixture warmed up rapidly in spite of constant agitation in the ice bath. Granular manganese dioxide was precipitated at once. The above experiment was repeated with one-half of the materials and the potassium permanganate was added very slowly. Manganese dioxide was precipitated as before. The colloidal manganese dioxide is no doubt precipitated by the potassium carbonate formed by the oxidation of the formaldehyde. The small excess of alkali added in the beginning is necessary to make the reaction take place more rapidly.

With Glucose.

(a) From the above it seemed probable that colloidal manganese dioxide would only be stable in those reaction mixtures in which the salts formed are relatively little ionized. 5 g. glucose were dissolved in 20 cc. of warm water. The mixture was now cooled in an ice bath. A few cubic centimeters of 10% sodium hydroxide were added and 100 cc. of potassium permanganate (60 g. per 1100 cc.) were added through a dropping funnel in five minutes while agitating the mixture in an ice bath. The mixture rapidly became viscous and in 5 to 10 minutes set into a stiff jelly. From this point on, the transformations were entirely similar to those described above in the oxidation of acrolein acetal. Instead, however, of placing the flask containing the brownish solution, in which lumps of gel were suspended, on the hot plate it was kept at room temperature. Twenty-four hours later the brown solution had deepened in color and the lumps of gel had been changed into a thin semi-liquid gel which had separated to the bottom of the flask. In a few days more all signs of gel had disappeared and there was only a small amount of granular (perhaps crystalline) mass on the bottom of the flask. The colloid in this form was stable for months.

The limpid liquid thus obtained was dark brown, almost black, in color. In thick layers it was opaque to diffuse daylight, but in layers about $1/16$ inch thick it was transparent and when held over pencil marks had the effect of making them look darker in color and therefore somewhat more sharply legible. It was found that this colloid could be diluted to any extent with distilled water without causing colloidal manganese dioxide to precipitate out at any point in the dilution. The only observable effect was a gradual weakening of the brown color as the dilution progressed. This brown color persists to a very high dilution. In general the more concentrated solutions are the most stable. In one case 60 cc. of the concentrated colloid was diluted to 1.5 liters with distilled water. The solution which was too dense to be transparent while in the bottle was clear and red-brown in color when observed in a test tube. This solution was

filtered through a close thick filter (S. and S. No. 584) and only a small trace of insoluble matter remained on the filter.

It will not be necessary to enumerate all of the properties of colloidal manganese dioxide previously observed and to relate just how the above solutions showed the same characteristics. Only a few of the most striking properties will be mentioned. Deiss[1] observed that solutions of colloidal manganese dioxide dropped from a capillary tube into still water give beautiful vortex rings. If a fairly dilute solution of the above colloid is used the successive series of rings are developed very beautifully. The first ring increases to a certain size and breaks into 3 to 5 new small rings. These in turn develop until they each also break into 1 to 3 new rings. In favorable instances several more generations of rings are produced. All these rings are connected with each other by thin lines of manganese dioxide, thus giving the whole system a striking clustered or festooned appearance. This apparently little-known phenomenon was described first by Thomson and Newall[2] and is not limited to colloids like milk, blood, ink, etc., but is also shown by many salt solutions. Potassium permanganate of appropriate concentration gives beautiful rings. If the colloidal manganese dioxide is dropped into the solution of a salt the colloid is precipitated in the form of miniature rings. If the proper dilution of the colloid is dropped into a dilute solution of a salt (barium chloride, for example) the coagulation does not take place until the elaborate system of rings described above has been developed. It is interesting to note in this connection that the same rings and coagulated ring systems may be obtained with silver chloride, silver bromide, silver chromate, barium sulfate, etc., by dropping the proper reagents into a suitable concentration of the precipitant.

Bredig and Marck[1] studied the behavior of colloidal manganese dioxide with hydrogen peroxide very exhaustively. No attempt was made to repeat their careful quantitative experiments, but their qualitative experiments were easily duplicated with the colloid as obtained above. It was thus found, on adding hydrogen peroxide to a dilute but distinctly brown solution of the colloid, that the solution was decolorized at once but no oxygen or precipitate was formed. With somewhat stronger solutions a marked fading of the brown color took place, accompanied presently by the slow evolution of oxygen and the formation of a faint flocculent precipitate. Still stronger solutions gave a copious precipitate and oxygen very freely. Bredig and Marck explain these results by assuming that in dilute solutions a salt, $Mn\begin{smallmatrix}O\\ \diagup\\ \diagdown\\ O\end{smallmatrix}$, is formed which has no

[1] *Loc. cit.*
[2] *Proc. Roy. Soc.*, **39**, 417 (1886).

catalytic activity, but in more concentrated solutions the catalytic proper-
ties of the unchanged manganese dioxide become effective. Their ob-
servations on the catalytic activation of the reduction of mercuric chloride
with hydrogen peroxide by the addition of traces of colloidal manganese
dioxide were also verified qualitatively.

Perhaps one of the most interesting properties of this colloid as obtained
in the above and succeeding experiments is the behavior of the drops and
splashings on the inside wall of the flask. These drops and thin films
undergo the same syneresis described above except that here the syneresis
water flows away or evaporates. The consequence is that once the cracks
have begun to appear the various segments contract and curl up exactly
like thin layers of drying liquid mud. If the films of colloidal solution are
very thin they show after drying the metallic colors phenomena of thin
films. In washing such flasks many of these scales become detached and
show up brilliantly against the dark brown background of precipitated
manganese dioxide. Deiss[1] considers the formation of these and other
mirrors (Ag, Au, etc.) as dependent on colloidal phenomena.

(b) The preparation of colloidal manganese dioxide as described in
(a) was repeated a large number of times. In these experiments additional
observations on the transformation were made. It was found that on
diluting the freshly prepared colloid, i. e., before gelling had taken place,
it could similarly be diluted to any extent without causing any precipi-
tation of manganese dioxide. These solutions are less stable than those
described in the preceding paragraphs. If other portions were diluted
at different stages as the gelling progresses it was found that presently
only a part of the material was dissolved. When the gelling was at its
maximum nothing was dissolved and the water in which the gel was placed
remains quite colorless.

Another striking indication that a molecular transformation is here
taking place is shown by the marked change in color. When first prepared
the colloidal solution is a rich cherry-red in color, but the red phase of the
color fades out gradually as the transformation takes place, leaving a rich
brown color.

From all that has gone before it is clear that we have a colloidal solution
with a rather high viscosity automatically, without any marked change
in temperature, being quickly converted into an insoluble gel which in
turn is subsequently slowly changed into a limpid colloidal solution of
the same compound. That is, there is a transformation from one molecular
state in the solution into a markedly different one—a transformation
which outside of colloidal chemistry might easily be spoken of as a trans-
formation of an α-form of colloidal manganese dioxide into a β-form or
vice versa. As a matter of fact it is quite probable that what really takes

[1] Loc. cit.

place is the transformation of an emulsoid form of "colloid" manganese dioxide into a suspensoid.

Examples of spontaneous isothermic transformations of the kind just described (*i. e.*, the transformation of a highly viscous colloid or gel into a colloid of low viscosity) are apparently quite rare among colloids. In some ways the transformations of molten sulfur on further heating are quite similar. But since sulfur is an isocolloid the analogy between it and the above heterogeneous colloid is only relative. Perhaps the transformation of the emulsoids of gum arabic or gelatin in water into suspensoid by the addition of definite small amounts of ethyl alcohol to the cold emulsoids is more strictly analogous.[1] It had previously been known that the addition of ethyl alcohol to these solutions would cause the gum or gelatin to separate as an amorphous or crystalline precipitate,[2] but Scarpa observed, if smaller concentrations of alcohol were added and the mixture kept cold throughout the addition, that a suspensoid was formed from the emulsoid, as was shown by the enormous fall in viscosity, by its electrophoric properties and by the difference in its behavior toward inorganic ions.

Our own transformation differs from that of Scarpa in that no external reagent was added in order to produce the transformation.

The spontaneous increase in the degree of dispersion of colloidal solutions of glycogen, benzopurpurin, hemoglobin, etc.,[3] with increasing age of the solutions are in some respects similar, but not nearly so striking.[4]

The so-called "peptizations" of hydrogels[5] by the addition of alkali are similar in effect to the observations described above. It seemed possible that some reaction between the sugar and the alkali might produce a difference in the chemical nature of the medium such that the gel would be liquified in it. Accordingly the glucose and alkali were allowed to stand in the aqueous solution for one week before adding the permanganate in the customary manner. The glucose solution became markedly yellow as was expected, due to characteristic chemical changes produced by the action of alkali under these conditions. When the glucose solution thus prepared was oxidized with permanganate the transformations of the colloidal manganese dioxide were just the same as those described in (*a*). So that it seemed clear that the changes produced in the glucose

[1] O. Scarpa, *Rend. soc. chim. ital.*, [2] 5, 375–9 (1913); *Koll. Z.*, 15, 8 (1914); *C. A.*, 8, 3522.

[2] P. P. v. Weimarn, *Grundzüge d. Dispersoidchemie*, p. 116; *Koll. Z.*, 2, 78 (1907).

[3] Rachlmann, *Berl. klin. Wochenschr.*, 1904, No. 8; W. Biltz and Z. Gatin-Gruszewska, *Pflüger's Arch. f. d. ges. Physiol.*, 105, 115 (1904); *Compt. rend.*, 139, 507 (1904); Lemanissier, *L 'etude des corps ultramicroscopiques*, Thèse, Paris (1905); R. Zsigmondy, *Z. Erkenntnis der Kolloide*, Jena 1905, p. 160.

[4] Cf. also W. Ostwald, *Grundriss der Kolloid-Chem.*, 1909, 283, 294–7.

[5] Lottermoser, *Z. physik. Chem.*, 60, 456 (1908); 70, 239 (1910).

by the alkali alone are not responsible for the transformations in the colloidal manganese dioxide.

L. Michaelis,[1] A. Mayer, G. Schaeffer and E. Terroine,[2] and v. Henri[3] have observed that the size of colloidal particles varies very markedly in dye suspensions and metal and metallic sulfide sols under minute variations in the concentrations of electrolytes. And Mayer, Schaeffer and Terroine have shown that positively charged colloidal particles tend to increase in size under small concentrations of alkali, while acids cause them to diminish in size.[4] In the case of negatively charged colloids the conditions are reversed. Now Bredig and Marck[5] have shown that colloidal manganese dioxide is negatively charged. Further, as will be seen from the following paragraph, the transformation takes place more rapidly the more alkali there is present. So that the generalizations of Mayer, et al., fit all of the observed facts and furnish a very simple explanation of the transformation of the gel into the sol. It must be stated, however, that if alkali causes this change the concentrations required to bring it about slowly, as it was observed at first, are rarely strong enough to color red litmus paper blue. It may be that the colloid protecting action of the excess glucose serves to assist the alkali effect at these low alkali concentrations, by preventing the precipitation of the manganese dioxide during the first stages of the transformation. The fact noted above, that on diluting the transformed colloidal manganese dioxide the most dilute solutions are least stable, may now be explained as being due to the fact that the alkali concentration is decreased to such an extent that condensation takes place. The rate of condensation is faster the smaller the alkali concentrations, i. e., the greater the dilution.

The explanation of the first phase of the transformation of colloidal manganese dioxide involves phenomena much better known than those discussed in the preceding paragraph. There has been much work done on the changes in the viscosity of emulsoids since 1902.[6] In general it

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[1] Deut. med. Wochschr., 1904, No. 2; Virchow's Arch., 179, 195 (1905).

[2] Compt. rend., 145, 918 (1907); 146, 484 (1908).

[3] Le Caoutchouc et la Guttapercha, 1906, 510; 1908, 2404; Compt. rend., 144, 431 (1907); 146, 62, 1024 (1908).

[4] There is a tendency in discussing general properties of this kind to speak of the OH ion and H ion effect. It may be true that some colloids are not influenced by the other ion but in the case of colloidal manganese dioxide the character of the other ion is important. Colloidal manganese dioxide is precipitated by $Ba(OH)_2$ solutions but not by NaOH or KOH. In this case the precipitating effect of the divalent ion or the molecular $Ba(OH)_2$ supercedes any effect of the OH ion itself. Throughout the remainder of this paper the word alkali will be used meaning KOH or NaOH only.

[5] Loc. cit.

[6] P. von Schroeter, Z. physik. Chem., 45, 75 (1903), gelatin; v. Henri, et. al., Compt. rend. soc. de Biol., 55, 1668 (1903) and H. Garrett, Phil. Mag., [6] 6, 374 (1903)

has been shown that whereas suspensoids undergo condensations slowly so that days are required to complete observations, in emulsoids much more marked increases in viscosity take place in as many seconds or minutes. So that rapid condensation of the fresh colloidal manganese dioxide into a gel is rather to be expected.

All the properties of the colloidal manganese dioxide may therefore be explained by the simultaneous action of two forces: the one tending to condense and precipitate the colloid and the other tending to disperse the colloid. The former is a very rapid-acting process and is hastened by increase in temperature and absence of alkali. The latter is a slow-acting process in any case, but can be accelerated greatly by relatively small increases in the alkali concentration and less markedly by increase in temperature up to a certain rather low maximum. One would expect that with two interacting processes of this character quite a variety of results could be obtained by varying the conditions. This is perhaps most strikingly shown by the variations in the gel, as representing the maximum viscosity, that were observed in the experiments described below.

On the chemical side very little may be said with certainty about the changes involved here. According to Morawski and Stingl[1] the precipitated manganese dioxide has the composition $KH_3Mn_4O_{10}$ (plus or minus small amounts of impurities). The emulsoid is therefore possibly a highly hydrated form of this compound and the transformation consists in a systematic gradual squeezing out of this water until the highly dehydrated suspensoid is obtained.[2] The process is also probably accompanied by a decrease in the size of the molecular aggregates of manganese dioxide. Of course the truth or error of the above can only be determined by extensive further work.

It was found that the transformation of the colloid is readily affected by changes in concentration and in temperature. For instance, when 2.5 g. glucose were dissolved in 20 cc. of water and treated with a little

gelatin, silicic acid and protein; A. Muller, *Ber.*, **37**, 11 (1903 or 4), organic colloids; Du Pré Denning, *Diss.* Heidelberg, **1904**, ferric hydroxide; G. Fano, G. Rossi, *Arch. di Fisiol*, **1**, 492, 609 (1904), gum arabic, starch and serum; G. Rossi, *Idem.*, **2**, 500 (1905) and with O. Scarpa, *Idem.*, **2**, 246 (1905), ferric hydroxide sol; G. Rossi, *Idem.*, **2**, 272, 599 (1905), albumin; E. Cavazzani, *Idem.*, **2**, 513 (1905), milk; G. Rossi, *Idem.*, **3**, 171, 507 (1906), with a bibliography of 127 titles; J. Simon, *Idem.*, **4**, 594 (1907); **5**, 394, 402, 470, 477, 479 (1908), albumine + alcohol, etc.; P. Schidrowitz, Goldsbrough, *J. Soc. Chem. Ind.*, **28** (1909); *Koll. Z.*, **7**, 241 (1910); but especially W. Biltz, *et. al.*, *Z. physik. Chem.*, **73**, 500 (1910); cf. W. Ostwald, *Grundriss d. Kolloid-Chem.*, **1910**, 190, *et seq.*, for many other references.

[1] *J. prakt. Chem.*, [2] **18**, 86 (1878); *Jahresber.*, **1878**, 275; cf. also Smolka, *Sitzungsber. d. Math. Naturwissensch. Classe D. Kais. Akad. Wissensch., Wien.*, **95**, II, 5–30, and Gmelin-Kraut-Friedheim, *Handbuch der Anorg. Chem.*, **3**, II, 254, etc.

[2] Cf. Scarpa, *Loc. cit.*, for a similar effect on gelatin and gum arabic solutions produced by adding ethyl alcohol.

10% sodium hydroxide and 100 cc. of permanganate (30 g. in 1100 cc.) as in (a), the changes were typical, so far as the gel formation was concerned, but the liquefaction of the gel was only observed to a very limited extent. On the other hand, the manganese dioxide was not properly precipitated. That is, the concentration of alkali was not sufficient to disintegrate the gel rapidly.

When the above experiment was repeated by warming the glucose solution to 30°, using a little more alkali and adding the potassium permanganate as before, the temperature of the mixture rose to 45° and the mixture gelled almost instantly after the addition was completed. Coagulation in this case did not take place suddenly as it does when the concentration is double the above (Cf. Experiment 3 below). When this coagulated mass, having the appearance of thick apple butter, was allowed to stand it showed signs of liquefying and in eight days at room temperature liquefaction was complete. The limpid colloidal solution thus obtained, where complete precipitation was expected, was typical in every way.

If the same amount of glucose and water are treated with 15 cc. sodium hydroxide and then with 50 cc. potassium permanganate (60 g. in 1100 cc. water), in an ice bath, gel formation does not take place within 3 hours in the ice bath nor within 3 hours after removing it from the bath. The mixture had a somewhat higher viscosity than the transformed colloid obtained in (a), but after standing over night even this slight difference in viscosity disappeared. By increasing the concentration of the alkali, even when the permanganate concentration was doubled, the intermediate gel stage was avoided and transformation was limited to a slight loss in viscosity. This experiment showed very strikingly that the transformation is clearly dependent on the alkali concentration, whatever explanation may be accepted, and that any effect of the glucose as a colloid protector is of secondary importance in this case.

The effects of temperature were further studied as follows:

(1) The reaction was carried out as in (a) using a little more alkali. When the gel had set the mixture was placed in the refrigerator. The transformation was typical but very slow. In four days the gel had completely liquefied in the usual way.

(2) Repeated (1) but allowed the mixture to stand at room temperature. The gel completely liquefied over night.

(3) Repeated (1) except that cooling during the addition of permanganate was omitted. The temperature of the mixture went up to 45°. In about two minutes after the addition was complete the manganese dioxide set into a gel and then almost instantly coagulated completely. It was not preserved any longer.

Without giving any further details it may be said that in general, no matter what the temperature or concentration are, the viscous or gel stage tends to be formed in all cases. The rate at which this viscous stage is dispersed into the limpid stage depends primarily on the concentration of the alkali used, but also on the temperature at which the colloid is formed and also on the temperautre at which it is maintained subsequently.

With Other Substances.—2.5 g. each of galactose, fructose, lactose, and sucrose were dissolved in 10 cc. of water and treated with 2 cc. 10% sodium hydroxide and with 50 cc. potassium permanganate solution (60 g. per 1100 cc.) in the ice bath. With galactose and fructose the results were practically the same as with glucose. With lactose, gelling took place only after an hour. With sucrose, a skin was formed on top of the solution before gelling took place. The gel underwent syneresis very rapidly. When the same amount of sucrose was similarly treated in the presence of 10 cc. of 10% sodium hydroxide the green color of potassium manganate was more persistent and when the red-brown color of colloidal manganese dioxide appeared, gelling and syneresis were slower. Very little, if any, of the manganese dioxide passed into solution again. Using 2.5 g. tartaric acid as the sodium salt and 2 cc. 10% sodium hydroxide as above, reduction took place with the intermediate formation of potassium manganate, and this was gradually reduced to manganese dioxide which finally set into a stiff gel. The gel did not go into solution again. Similar experiments with 3.5 g. of glycerol showed rapid reduction and coagulation to the gel stage and but little tendency to go into solution again. The above experiments were not extended in order to determine whether conditions could be found in which the results would in all ways resemble those obtained with glucose.

Hypothetical Applications.

Although the above experiments on colloidal manganese dioxide are of much interest in themselves, their interest is considerably heightened when looked at from another point of view. The enormous role of compounds of manganese in catalytic phenomena is well known. More recently, however, the role of manganese compounds in biochemical reactions has been studied rather intensively. Without attempting to review the literature (only a few recent references will be given) a few instances of its effects may be pointed out. It has been observed that small amounts of manganese compounds stimulate alcoholic fermentation as carried out in the fermentation industry.[1] The growth of fungi (*Aspergillus niger*, etc.) is markedly stimulated by the presence of manganese salts.[2] Many plant experiments have been made and manganese in

[1] Kayser, Marchand, *Compt. rend.*, **145**, 343 (1907).

[2] G. Bertrand and Javillier, *Ann. inst. Pasteur*, **26**, 241–9, 515–21 (1912); *Bull. soc. chim.*, **11**, 212–21 (1912); *C. A.*, **6**, 1916, 3444; G. Bertrand, *Compt. rend.*, **154**, 381–3 (1912); *Bull. soc. chim.*, **11**, 494–8 (1912); *C. A.*, **6**, 3443; *Ann. inst. Pasteur*, **26**, 767–77 (1912); *C. A.*, **7**, 496; H. I. Waterman, *Proc. Akad. Wetenschappen*, **15**, 753–64 (1913); *J. Chem. Soc.*, **104**, I, 229 (1913); *C. A.*, **7**, 3985.

general also has a stimulating effect on the growth of plants.[1] It is now known for instance, that the production of wheat per acre may be increased 10%, in certain soils, by sprinkling a manganese salt upon the soil. Pyrolusite (MnO_2) is one of the most effective compounds in this respect. Other experiments appear to have shown that manganese compounds stimulate metabolism in animals and increase the hemogenetic power.[2] And it is proposed that manganese should properly be administered therapeutically with iron in order to make the latter effective. Further, the addition of minute amounts of manganese salts increases the activity of the enzyme laccase.[3] All the foregoing processes are thought to be regulated by enzymes and the manganese must therefore enter into the action of the enzyme in some way. Since enzymes are admitted to be colloidal it may be that the manganese enters into combination with the colloidal particles. These enzymes are very sensitive to slight changes in the temperature and in the chemical character of the medium in which they exist. In most cases there is no adequate chemical explanation of the variations in the activity and least of all is there any known explanation as to how minute traces of certain foreign substances can influence these reactions so markedly. Of course it is quite likely that the manganese in these cases enters into the enzymic activity in the hydrolyzed form.[4] Now if the regulatory effect in colloidal enzymes is dependent on a variation of the total surface of the colloidal particles of the enzyme a relatively small variation would cut down or increase the catalytic activity of the enzyme enormously. If, now, something was added to the enzyme which would increase the tendency of the colloidal enzyme to remain in a greater degree of dispersion, under conditions which normally would be unfavorable to this effect, then this something would have a positive influence on the enzymatic actions under consideration. Since manganese dioxide does so definitely have this tendency to become more dispersed, it is not inconceivable that the effect of manganese compounds in biochemical reactions may be accounted for on this basis.

Summary.

1. It was found that colloidal manganese dioxide is formed not only by the use of inorganic reagents but is normally formed in the oxidation of a series of organic compounds.

[1] G. Masoni, *Stas. sper. agrar. ital.*, **44,** 85–112 (1911); *C. A.,* **6,** 135; Luigi Montemartini, *Staz. sper. agrar. ital.*, **44,** 564–71 (1911); *C. A.,* **6,** 1488; Thomassin, *Engrais,* **27,** 293 (1912); *C. A.,* **6,** 2130; H. Bartmann, *J. Agr. prat.,* [2] **20,** 666 (1911); *C. A.,* **6,** 133; G. Bertrand, *Orig. Com. 8th Intern. Congr. Appl. Chem.,* **15,** 39; *C. A.,* **6,** 3150; J. J. Skinner, M. X. Sullivan, *et. al., U. S. Dept. Agr. Bull.* **42,** *C. A.,* **8,** 2442; Th. Pfeiffer, E. Blanck, *Landw. Vers. Stat.,* **77,** 33–6 (1912); **83,** 257–81 (1914); *C. A.,* **6,** 2481; **8,** 1635.

[2] Guido M. Piccinini, *Biochem. terap. sper.,* **2,** 385–94 (1910–11); *Zentr. Biochem. Biophys.,* **13,** 124; *C. A.,* **7,** 369; cf. also *Arch. farm. sper.,* **10,** 419–36 (1911); *Chem. Zentr.,* 1911, I, 823; *C. A.,* **5,** 3075; and *Orig. Com. 8th Intern. Congr. Appl. Chem.,* **19,** 263; *C. A.,* **6,** 2950.

[3] Bertrand, *Compt. rend.,* **122,** 1132 (1896); **124,** 1032–35 (1897); *Chem. Zentr.,* **96,** II, 93; **97,** II, 47; *Bull. soc. chim.,* [3] **17,** 619–24 (1897); *Compt. rend.,* **124,** 1355 (1897); *Chem. Zentr.,* **97,** II, 177; *Bull. soc. chim.,* [3] **17,** 753–6 (1897); *Ann. chim. phys.,* [7] **12,** 115–40; cf. also A. Bach, *Ber.,* **43,** 364–70 (1910); *C. A.,* **5,** 300; B. Sjollema, *Chem. Weekblad,* **6,** 287–94; *C. A.,* **5,** 2266; O. Dony-Henault, E. Leroy, *Bull. soc. roy. Belgique,* **1909,** 387–404; *C. A.,* **4,** 56.

[4] Cf. on this N. L. Sochngen, *Centr. Bakt. Parasitenk.,* **40,** II, 345–54 (1914); *C. A.,* **8,** 3193.

2. That colloidal manganese dioxide is especially easily obtained by incompletely oxidizing glucose (as well as fructose and galactose) in alkaline solution with potassium permanganate.

3. That the colloidal manganese dioxide is formed under these conditions first passes into a viscous or gel stage which subsequently changes into a limpid colloidal solution.

4. That the properties of the first stage agree well with those of a typical emulsoid, while the later stage seems more characteristically a suspensoid.

5. That the transformations of the emulsoid are typical and would be normal in every way if it were not for a slower but simultaneous transformation of the emulsoid into a suspensoid, owing to the effect of the alkali in accordance with the generalizations of Mayer, et al.

6. That both transformations are readily affected by variations in temperature, concentration of the reacting mixture and concentration of the alkali (KOH or NaOH).

7. That low temperatures are more favorable to the formation of the colloid.

8. That the concentrated colloid described here is readily coagulated by warming.

9. Suggestions are made indicating possible relationships between the remarkable properties of manganese in biochemical reactions and the properties of colloidal manganese dioxide as described above.

CHICAGO, ILL.

A CONDUCTIVITY STUDY OF THE REACTION BETWEEN CALCIUM NITRATE AND DIPOTASSIUM PHOSPHATE IN DILUTE SOLUTION.[1]

By W. A. WITHERS AND ALEX. L. FEILD.

It is generally agreed that a soluble calcium salt reacts with dipotassium phosphate in the presence of an excess of ammonia to form an amorphous precipitate of tricalcium phosphate with no tendency to become crystalline on standing. When, on the other hand, ammonia is not added, there occurs a reaction in regard to which there is a great difference of opinion. The present investigation was made in order to determine the nature of the latter reaction.

Introductory.

It has been known for some time that tricalcium phosphate, when precipitated in neutral solution, has a composition which only approximates to the theoretical, due to the hydrolytic action of the solvent. This

[1] Read at the meeting of the North Carolina Section of the American Chemical Society, Raleigh, N. C., May 2, 1914.