Some Preliminary Observations on the Oxidation of Manganese II by Persulphate

Marshall[1]) and Dittrich and Hassel[2]) found that Mn(II) in aqueous solution is oxidized to MnO_2 by persulphate. Marshall and Stehmann[3]) observed that oxidation to permanganate occurs if the reaction is catalyzed by silver ion. Dekker, Levy and Yost[4]) and Gupta and Ghosh[5]) reported the formation of MnO_2 as the first stage in the silver ion catalyzed reaction. Bekier and Kijowski[6]) also studied the kinetics of the formation of the permanganate in the reaction in acidic medium. In the present note some qualitative observations have been reported in view of contradictory statements of previous workers.

A number of test tubes containing 3 ml of 0·2 M potassium persulphate, 1 ml of 0·2 M manganous sulphate and varying amounts of concentrated sulphuric acid, were arranged. Volume was made up to 9 ml by the distilled water. 1 ml of 0·04 M silver nitrate was added in the end.

It was found that while the concentration of H_2SO_4 was 3·15 M or less, first the reaction mixture turns red and then successively yields a red colloidal solution, brown suspension, brown precipitate and finally black particles of MnO_2 which settle to the bottom. This observation is also made when no acid has been added. After some time, depending on the acidity of the solution, the upper liquid layer gradually turns purple. Finally this colour also fades out leaving the upper liquid layer colourless and MnO_2 still settled at the bottom.

Further, it was found that the more the concentration of the persulphate and silver nitrate and the less the concentration of the acid is, the quicker is the appearance of the turbidity, precipitation of MnO_2 and the development of purple colour. The intensity and stability of the purple colour increases with higher concentrations of the acid, up to a maximum at 2·7 M of H_2SO_4.

When the concentration of the H_2SO_4 is 3·6 M, a stable red colour is obtained which neither gives MnO_2, nor turns purple. Above this concentration of the acid, no red or purple colour or MnO_2 is observable. If, however, of all the reactants, persulphate is added in the last, the red colour is obtainable up to the acid concentration of 5·4 M (exclusive), but the intensity of the colour decreases with the increase in the concentration of the acid above 3·6 M. Very slight blue or green tinge was also visible before the formation of purple colour, when viewed against light, provided the silver ion concentration is 0·008 M or more and the acid concentration is 1·8 M or less.

From these observations it is suggested that the red colour first produced is of trivalent manganese as was checked by the determination of λ_{max} at 510 mμ[7]). Mn(III) soon hydrolyzes to hydrated manganese III oxides and finally black MnO_2 is formed which settles. The oxidation stages seem to include Mn(V) (blue) and Mn(VI) (green). The medium being acidic, they disproportionate into MnO_2 and higher valent manganese, so that finally purple coloured solution is obtained along with MnO_2, but this purple colour is not formed as long as there is any Mn(II) in the system. The purple colour had λ_{max} at 525 mμ characteristic of the permanganate. This colour faded after some time, obviously due to the reduction of the permanganate by some reductant in the system. The liquid layer did not give test for H_2O_2. Moreover, a portion of the purple coloured solution removed from the reaction mixture, without disturbing the settled MnO_2, remained stable and did not decolourize. Hence there appears to be some reducing substance with MnO_2 precipitate which is responsible for the reduction of the permanganate and which is formed at a later stage and not in the beginning.

Further work to elucidate the mechanism is in progress.

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Effect of Presence of Some Carbohydrates on the Precipitation of Aluminum Hydroxide from Sodium Aluminate Solution

The precipitation of aluminum hydroxide from a sodium aluminate solution was investigated in the presence of some carbohydrates. Three kinds of carbohydrate, i.e. glucose, sugar, and starch, were chosen and added to a sodium aluminate solution in various amount of dry state. Then, these solutions were decomposed with seeding of hydrargillite, and these decomposition rates were compared in each case. As a result, it was observed that the addition of glucose or sugar acts to retard the decomposition, and that the increase of the amount of starch added promotes the decomposition. But the retarding action of glucose was larger than that of sugar. Besides, the relation between the amount of seed added and the addition of carbohydrate was investigated. Then it was seen that the presence of seed is stronger than that of glucose or sugar in the action on the decomposition, and that this relation is different upon the presence of starch. Furthermore, the properties of particles precipitated by these decompositions, i.e. sedimentation behavior, sedimentation volume, distribution of particle size, and bulk density were investigated. Moreover, the ignition loss of each particle was examined.

In consequence of these experiments, the following presumption upon the action of glucose or sugar on the decomposition was made. Glucose or sugar combines with Al^{3+} or $Al(OH)_3$ molecules and it must be soluble in solution, and besides it is combined relatively stronger on the surface of seed. Hence, as the activity of the seed is decreased by the binding between seed and glucose or sugar, the addition of glucose or sugar retards the decomposition rate of sodium aluminate solution and disturbs the formation of new crystal nuclei and assists the crystal growth of precipitated particles.

On the other hand, it was supposed that starch is chemisorbed on the surface of seed and the starch causes the aggregation of individual particles by the bridge action towards other particles[1]). Furthermore, the decomposition of the sodium aluminate solution of prescribed concentration was made without seeding in the presence of starch. Then its decomposition rate was compared with that of the autoprecipitation or the seeding decomposition in the absence of starch. As a result, it was observed that the decomposition by the addition of starch without seeding is remarkably promoted, and its effect increases with increase of the amount added. From this result, the author believes that the presence of starch itself has a promoting action on the decomposition. Moreover, when the decomposition of sodium aluminate solution with seeding of hydrargillite and starch gelatinized by boiling was made, its decomposition rate was almost the same as that of the seeding decomposition in the absence of starch. Therefore, the author presumed that two counter phenomena play an important role in the action of starch on the decomposition of sodium aluminate solution. In the first place, starch is retarding in making active surface of seed-crystallites smaller by the chemisorption (negative action). In the second place, starch is promoting in the colloidal effect on the decomposition rate (positive action).

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Papierchromatographische Identifizierung von Emetin. Ein Beitrag zur Emetin-Oxydation

Zum Nachweis des Emetins auf Papierchromatogrammen wurde bisher nur Dragendorff-Reagenz angewandt[1]). Bei kleineren Alkaloidmengen ist dieses Reagenz nicht empfindlich genug. Wir konnten die in mehreren Arzneibüchern[2]) zur Identifizierung von Emetin bzw. Ipecacuanha-Tinktur vorgeschriebene Reaktion mit saurem Chlor-Wasser gut anwenden. Zu einer 10%igen Chlorogen-Lösung wird Eisessig zugesetzt und die deutlich saure, filtrierte Lösung als Sprühreagenz verwendet. Die starke orangegelbe UV-Fluoreszenz der Flecke ermöglicht noch den Nachweis von 2γ Emetin. Die Reaktion ist mit anderen Alkaloiden und Inhaltsstoffen der Ipecacuanha-Wurzel negativ.