

of 0.1 per cent alcoholic methyl red solution with 10 parts of *M*/15 phosphate buffer solution pH 7.0 gave pink spots on a yellow background. The latter fades slowly to a very pale pink or disappears completely, leaving the spots still distinct. A mixture of equal portions of methyl red and bromo phenol blue (0.1 per cent alcoholic solutions) with twice the volume of buffer gave bright pink spots on a pale grey background, fading overnight to a pale violet. Benzoic and mandelic acids showed up better with this indicator mixture than with any of the other mixtures tried.

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Ferric-ion Catalysed Decomposition of Hydrogen Peroxide and the Polymerization of Acrylonitrile

THE question of the mechanism of the iron (III) ion catalysed decomposition of hydrogen peroxide has been discussed in two recent communications¹. The formation of free radicals initiating the polymerization of monomers during reaction between iron (II) ion and hydrogen peroxide has been demonstrated by Baxendale, Evans and Park², and the mechanism of the reaction of iron (II) ion and iron (III) ion with hydrogen peroxide has been discussed by Barb, Baxendale, George and Hargrave³.

To clarify the question of the formation of free radicals in the iron (III) ion catalysed decomposition of hydrogen peroxide, I used water solutions of acrylonitrile (from the American Cyanamid Co., redistilled before use). The amount of hydrogen peroxide decomposed and that of polymer formed were determined during the course of the reaction. All other conditions remaining unchanged, the velocity of the decomposition of hydrogen peroxide in the presence of acrylonitrile is much slower than without it. The velocity of decomposition depends on the concentration of acrylonitrile. As an example, in a reaction mixture at $25.00 \pm 0.05^\circ \text{C}$. which was 8.00 millimolar in iron (III) nitrate, 0.100 molar in hydrogen peroxide, and contained nitric acid so that the pH of the solution was 1.68 and was 0.40 molar in respect of acrylonitrile, the first-order reaction constant of hydrogen peroxide decomposition was $5.5 \times 10^{-4} \text{ min.}^{-1}$, while without acrylonitrile the corresponding constant was $3.1 \times 10^{-2} \text{ min.}^{-1}$. (The reaction constants were calculated analytically using the method of least squares.) The decomposition of the hydrogen peroxide was thus slowed down 56-fold. In the presence of acrylonitrile in the above case, the concentration of hydrogen peroxide was

followed for 450 min., at which time about 22 per cent of the original hydrogen peroxide was used up. At the same time, 86 per cent of the monomer originally present was precipitated as an insoluble polymer. The velocity of formation of the polymer, after an initial induction period of about six minutes, during which time the solution remained clear to the eye, goes through a not very pronounced maximum. The maximum occurred between 30 and 40 mm., from the appearance of the heterogeneity in the solution; the rate of the disappearance of the monomer was then $3.7 \times 10^{-3} \text{ mol. min.}^{-1} \text{ lit.}^{-1}$. The ratio of disappearing monomer to that of hydrogen peroxide at the above maximum (expressed as molar ratio) is about 70.

At practically the same pH of the solution, but with the concentration of the monomer increased to 1.06 mol. lit.⁻¹ and that of hydrogen peroxide decreased to 0.021 mol. lit.⁻¹, the constant for the first-order decomposition of hydrogen peroxide was decreased only 17-fold compared with a monomer-free solution. The maximum velocity of monomer disappearance as measured by polymer formation was $2.1 \times 10^{-2} \text{ mol. min.}^{-1} \text{ lit.}^{-1}$, and the ratio of disappearing monomer to that of hydrogen peroxide was then about 560. The formation of the polymer proceeds with easily determinable velocity even in the presence of hydrogen peroxide having a concentration of 1.8 millimoles lit.⁻¹.

The increasing acidity of the solution decreases the rate of formation of the polymer; it also decreases the rate of decomposition of hydrogen peroxide in the presence of the monomer.

These results extracted from the experimental data can only be interpreted in favour of the chain mechanism of the hydrogen-peroxide decomposition.

Hitherto, the amount of hydrogen peroxide which decomposed in the presence of a monomer with the formation of oxygen has not been determined. The molecular weight of the polyacrylonitrile formed has not been determined. It seems probable that such determination would be possible after polyacrylonitrile is transformed into polyacrylic acid by careful hydrolysis.

A detailed report and analysis of the results will be published in due course.

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Acid Front in Granitization

DURING the course of field mapping a part of the khondalitic region near Salur (lat. $18^\circ 36' \text{N}$., long. $83^\circ 11' \text{E}$.) in the Vishakapatnam hill tracts, an interesting contact has been observed between a lens-like band of quartz-biotite-granulite (a member of the khondalites) and a porphyritic granite considered as intrusive¹ into the members of the khondalites in this region. The lens measures about 50 ft. in length, and 10 ft. in width, and appears at first sight as a caught-up xenolith amid the porphyritic granites.