

crystalline. Upon diluting the crude sulphuric-acid solution with water the smell of valeric acid is in each case distinctly perceptible.

The solution of either of the sulphonic acids when warmed with very dilute nitric acid gives a yellow precipitate, the formation of which may be used as a test for nitric acid.

ART. XLIV.—*Note on Interaction of Citric and Sulphuric Acids.*

By JAMES BEE.

[*Read before the Wellington Philosophical Society, 4th November, 1903.*]

DURING the preparation of aconitic acid by Hentschel's method (in which citric acid is heated with a 66-per-cent. sulphuric acid under a reflux condenser) it was found that the yield varied very considerably according to the length of time during which the acids were heated together. If the reaction were carried on for too short a time unchanged citric acid was left behind; if the heating was continued for twelve hours instead of six very little aconitic acid separated from the mixture on cooling; and in a third experiment, in which the materials were heated on a reflux apparatus for twenty-four hours, no crystallization took place after cooling.

It was found that, on pouring off the black liquid from the vessel in which the reaction had taken place, a small black deposit resembling charcoal was left. This turned out to be undecomposed aconitic acid. Suspended in the dark liquid was a flocculent dark-brown precipitate, which was separated from the liquid by straining through a large Buchner filter. From this a little aconitic acid was isolated.

The filtrate was diluted with water and extracted many times with ether. The united residues were recrystallized from glacial acetic acid, whereby aconitic acid was separated. The mother liquors were freed from acetic acid by evaporation with water, the residue taken to dryness and recrystallized from chloroform and acetone. By this means a small quantity of an acid which melted at 206° C. (uncorrected) was obtained. Upon combustion it gave numbers agreeing accurately with those of diconic acid, $C_9H_{10}O_6$.

Calculated for $C_9H_{10}O_6$.		Found.
C = 50.47 per cent.	...	50.49
H = 4.67 "	...	4.56
O = 44.86 "	...	44.95

Diconic acid was prepared by Hergt by heating citric acid and strong hydrochloric acid in sealed tubes to 190° , and according to him melted at $199-200^{\circ}$ C.

There can be little doubt of the identity of the two substances, more especially as they agree in the following qualitative reactions: (1.) A solution of the ammonium salt of the acid gave, with ferric chloride, an orange precipitate which was not dissolved on boiling. (2.) Barium-chloride gave no precipitate either cold or hot. (3.) Calcium-chloride gave no precipitate either cold or hot.

Notwithstanding that the yield of diconic acid by this method is disappointingly small, the observation that it does result by the action of sulphuric acid at comparatively low temperatures is not only worthy of note, but suggests that by suitable variations of the conditions of the reaction the substance may be prepared in large quantities by some easy method, instead of the exceedingly tedious process described by Hergt.

During the investigation certain hitherto unnoticed peculiarities in the silver and barium salts of aconitic acid were observed: (1.) Silver-aconitate, on being heated, decomposes with explosive violence. (2.) Ammonium-aconitate: On adding a solution of barium-chloride to a solution of ammonium-aconitate no precipitate is formed, but on boiling the solution a crystalline precipitate results. The precipitate does not dissolve on cooling, but becomes gelatinous. It is insoluble in a solution of ammonium-benzoate, but soluble in a solution of ammonium-acetate.

The reaction is very characteristic, taking place even in dilute solution.

ART. XLV.—*An Experiment bearing on the Wave Theory of Light.*

By J. S. S. COOPER, M.A., B.Sc.

[Read before the Otago Institute, 9th June, 1903.]

1. THEORY.

CONSIDER a parallel plate of some transparent medium whose refractive index varies as the distance of the point from an initial plane at right angles to the face of the plate. Let light from a distant source (a plane wave) be incident normally on this plate. The wave theory indicates that there will be a deviation.