

solution, the copper being precipitated as cuprous thiocyanate by standard  $\text{NH}_4\text{CNS}$  solution and the iron estimated by titration with standard  $\text{KMnO}_4$  solution.

This method gives highly accurate results for both elements and requires a minimum of time for its completion.

The method is especially adapted to the rapid estimation of copper and iron in ores.

UNIVERSITY OF VIRGINIA.

---

### NOTES.

**Note on the Blackening of Yellow Phosphorus.**—The sticks of yellow phosphorus in two laboratories in Colombo were found in time to become covered with a dull black coating. In one case the phosphorus had been kept in a stone jar and in the other in a glass bottle in a dark store-room. The experiments recorded below were undertaken with the object of discovering the nature and cause of the blackening.

A quantity of yellow phosphorus was purified by melting under a solution of potassium bichromate and concentrated sulfuric acid and leaving overnight; the still liquid phosphorus was then washed many times with distilled water and was solidified in the form of small globules by violent shaking.

Small quantities of the pure phosphorus were sealed up in glass tubes, two of which (A) contained distilled water and two (B) tap water (any oxygen in the small air space would soon be absorbed by the phosphorus). Small quantities were also placed in glass bottles loosely plugged with cotton wool to exclude dust and two of these bottles (C) contained tap water and two (D) distilled water.

One of each of the vessels A, B, C and D was placed in a dark cupboard and the remaining four were kept in the light. The contents were examined after seven months. The sealed tubes containing distilled and tap water which were kept in the dark, appeared to have undergone no change, while the corresponding tubes which had been kept in the light merely showed reddening due to the formation of red phosphorus. Another tube which contained melted phosphorus and distilled water and which had been kept in the light also, became covered on the surface with red phosphorus but still remained liquid at the end of seven months and only solidified on shaking vigorously; an interesting example of supercooling.

In the case of the vessel whose contents were exposed to air both those containing tap water showed slight blackening, while that containing distilled water and kept in the dark had a white coating, the nature of which is still being investigated; possibly the white coat is the suboxide  $\text{P}_4\text{O}$ , the existence of which has been asserted by Michaelis and Pitsch<sup>1</sup> and

<sup>1</sup> *Ber.*, 32, 337 (1899).

others but was denied by Chapman and Lidbury<sup>1</sup> and by Burgess and Chapman.<sup>2</sup>

The experiments seemed to indicate that the blackening is caused by some impurity in the tap water, the negative results in the case of the sealed tubes containing tap water being due to the much smaller quantity of water used than in the case of the bottles.

A small quantity, 2 or 3 g., of the black coating was obtained by scraping the sticks under water; the black solid was shaken with carbon disulfide, separated and heated in a crucible; by this means all traces of phosphorus must have been removed; the solid was then heated with concentrated nitric acid to dryness several times and the residue was extracted with dilute sulfuric acid and was tested for the metals with a positive result for copper; the remaining solid was again treated with nitric acid and this solution gave the test for phosphoric acid with ammonium molybdate.

Vogel, in 1836,<sup>3</sup> stated that yellow phosphorus acts on copper sulfate solution with the production of copper phosphide. The reaction has been studied by Straub,<sup>4</sup> who found that a dark film of copper phosphide was formed on yellow phosphorus in two months with a solution containing only one gram molecule of copper sulfate in one million liters of water.

A piece of copper wire was cleaned and placed in distilled water with some pure phosphorus and in two days both the wire and the phosphorus were covered with black phosphide. It seems likely, therefore, that the blackening observed was due to small traces of copper salts derived either from the water taps or from the copper tongs used to remove the phosphorus from the water (in another laboratory here, where only iron tongs are used, no blackening was observed). The experiments make it clear that phosphorus should be kept in distilled water, in stoppered jars, in the dark, and that iron tongs should be used to remove the sticks when necessary.

WILLIAM NORMAN RAE.

Ceylon Medical College,  
February 14, 1916.

---

**Saponification of Esters.**—We are repeating the work on the saponification of esters by aqueous solutions of salts, and find values for methyl acetate which are lower than those earlier recorded in *THIS JOURNAL*, **38**, 105 (1916). This is especially true of some of the strongly hydrated salts.

Furthermore, the results that we are now obtaining under apparently the same conditions are not satisfactorily concordant with one another.

<sup>1</sup> *J. Chem. Soc.*, 75, 973 (1899).

<sup>2</sup> *Ibid.*, 79, 1235 (1901).

<sup>3</sup> *J. prakt. Chem.*, 8, 109 (1836).

<sup>4</sup> *Z. anorg. Chem.*, 35, 460 (1903).

We are unable to explain fully the lower values now being found and the lack of concordance of the results. The latter fact would indicate the presence of some unknown catalyzer, possibly the surface of the glass vessels in which the reaction takes place.

The work is being pushed forward as rapidly as possible, and we hope in the near future to throw more light on this phase of the problem.

H. C. JONES.

BALTIMORE, MD.

### CORRECTIONS.

"The Calomel Standard Cell," by G. F. Lipscomb and G. A. Hulett, THIS JOURNAL, 38, 20.

Page 24. Column "July 12," 0.67098 should be 0.67078.

Column "Apr. 24," 0.67044 should be 0.67024.

Page 25, line 9. .0525(T - 25)<sup>2</sup> should be —.000025(T - 25)<sup>2</sup>.

Page 25, line 15. For 0.67159 read 0.67139.

Page 25, line 18. For 0.67159 read 0.67139 and for 30060 read 30047.

Page 25, line 22. For HgCl<sub>2</sub> read Hg<sub>2</sub>Cl<sub>2</sub>.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

### THE ADDITION OF ALIPHATIC NITRO COMPOUNDS TO UNSATURATED COMPOUNDS.

By E. P. KOHLER.

Received January 20, 1916.

The object of this investigation was to find a method for preparing cyclopropane derivatives that have a nitro group in combination with one of the carbon atoms of the ring. Substances of this type are unknown and they cannot be made by any of the means commonly employed for making aliphatic nitro compounds. It was necessary, therefore, to make a suitable aliphatic nitro compound first and then to close the cyclopropane ring. A promising series of reactions for this purpose is represented by the following equations:

