

give the value obtained for the hydrogen triple point pressure. The apparatus, method and accuracy have been described.¹ Since our manometric accuracy is about ± 0.02 mm., the agreement shown is poor.

Pressure, int. mm.	Observed by
50.7	Kamerlingh Onnes and Keesom ²
53.8	Simon and Lange ³
54.86	Henning ⁴
54.	Scott, <i>et al.</i> ⁵
54.1	Henning and Otto ⁶
	Cryogenic Laboratory, State College
53.83	(1) October 23, 1937
54.18	(2) October 23, 1937
54.23	(3) December 17, 1938
53.89	(4) August 15, 1940
53.93	(5) August 15, 1940
54.18	(6) August 15, 1940

The measurements of August, 1940, were made with the purpose of determining the cause of the uncertainty. The calorimeter contained 10 cc. of liquid hydrogen (previous measurements had been made with about this same quantity). After being cooled below the triple point, the cryostat was evacuated and the calorimeter allowed to drift slowly to the triple point temperature. Ten minutes after the temperature drift became zero, as determined by the constantan resistance thermometer on the calorimeter, the result (4) was obtained, in fair agreement with (1) which had previously been determined in the same way. Thirty minutes later point (5) was taken. Enough electrical energy was then supplied to the calorimeter to melt a third of the sample of hydrogen, after which point (6) was taken.

It appears that when an appreciable quantity of liquid was present, a vertical temperature gradient through the liquid layer on top of the solid in the calorimeter prevented the measurement of the true triple point pressure. This true pressure was obtained only when the quantity of liquid present was too small to allow the establishment of any appreciable thermal gradient. It seems likely that disagreement among the results of other workers is due to the same cause. We have accordingly taken 53.85 ± 0.03 int. mm. as the triple point pressure of normal hydrogen.

(1) Aston and Messerly, *THIS JOURNAL*, **58**, 2354 (1936); Messerly and Aston, *ibid.*, **62**, 886 (1940).

(2) *Comm. Phys. Lab. Univ. Leiden*, **137a** (1913).

(3) *Z. Physik*, **15**, 307 (1923).

(4) *Ibid.*, **40**, 775 (1927).

(5) *J. Chem. Phys.*, **2**, 454 (1934).

(6) *Physik. Z.*, **37**, 633 (1936).

In connection with the use of the triple point of hydrogen as a fixed point in thermometry, it is important to note that, depending upon the geometry of the apparatus, the triple point temperature may be measured whether or not the triple point pressure prevails; when the latter condition is fulfilled, however, the true triple point temperature is certainly measured.

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G. H. MESSERLY⁷

RECEIVED APRIL 5, 1941

PROCEDURE FOR THE PREPARATION OF CERTAIN DERIVATIVES OF STARCH

Sir:

Heretofore no solution or paste of starch in an inert organic solvent suitable for use in esterification or etherification reactions has been available. Attempts to gelatinize native starch directly in tertiary nitrogenous bases, such as pyridine, quinoline, etc., have not been successful, since even upon boiling the starch in such solvents the granules remain unburst. We have found that if first the starch granules are burst in various ways, such as by boiling in water, autoclaving, grinding, etc., it is possible to prepare solutions and pastes of starch in such solvents. A suitable procedure is to boil the native starch in water and then add pyridine and continue the boiling with distillation so as to eliminate the water as pyridine-water azeotrope boiling at $92-93^\circ$, thereby producing a solution or paste of starch in pyridine. The products so obtained range from clear solutions, when the pyridine contains a small amount of water (about 4%), to thick jellies, when the water is absent. Instead of treating the native starch, we may separate the alpha and beta amyloses thereof [Pacsu and Mullen, *THIS JOURNAL*, **63**, 1168 (1941)] and gelatinize each separately in the tertiary nitrogenous base. The starch gelatinized in tertiary bases is highly reactive toward esterification and etherification reagents, such as the anhydrides and acyl halides of aliphatic and aromatic acids, benzyl chloride, etc., and is found to be trifunctional giving rise to triesters and ethers in practically quantitative yield. The products so obtained are thermoplastic, yielding clear, glass-like substances, which appear to be of interest in the

preparation of plastics, resins, etc., suitable for molding and coating.

Detailed description of the procedure and of the mostly new starch derivatives so prepared will be published later.

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EUGENE PACSU
JAMES W. MULLEN, 2ND
RECEIVED APRIL 17, 1941

ABSORPTION OF OXYGEN BY GLUTATHIONE IN ALKALINE SOLUTIONS

Sir:

In a recent communication, Xan, Wilson, Roberts and Horton¹ have called attention to the fact that certain mercaptans in alkaline solution absorb more oxygen than should be required to oxidize them to the corresponding disulfides. These authors report that the amount of oxygen absorbed per mole of mercaptan increases with increasing hydroxide ion concentration with the formation of an unknown end-product of oxidation.

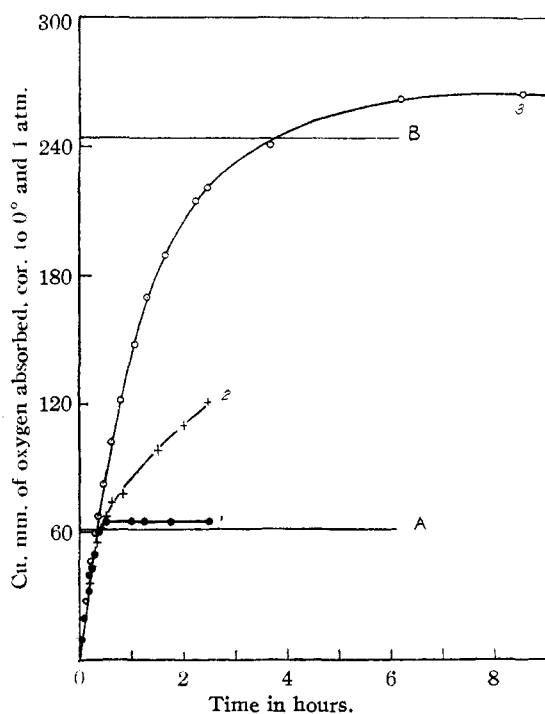


Fig. 1.—Absorption of oxygen at 37° and 1 atm. pressure by glutathione in alkaline solutions.

In an investigation under way in this Laboratory, the oxidation by oxygen of a mercaptan, glutathione, in alkaline solution with small

(1) Xan, Wilson, Roberts and Horton, *THIS JOURNAL*, **63** 1139 (1941).

amounts of copper sulfate as catalyst has been studied over a considerable range of hydroxide ion concentration. In this case also the amount of oxygen absorbed per mole of glutathione increases as the hydroxide ion increases and the end product, as indicated by the volume of oxygen absorbed, is predominantly the salt of the sulfinic acid. Figure 1 shows the results of three experiments in which approximately equal amounts of glutathione, 5 cc. of 0.00220, 0.00217 and 0.00218 molar solution, respectively, were oxidized by oxygen in the well-known Warburg apparatus at 37°. The concentrations of copper ion, assuming no reaction with either glutathione or hydroxide ion, were 4.70×10^{-6} , 4.63×10^{-6} and 3.70×10^{-6} molar, respectively. In Expt. 1, the initial pH of the solution is about 9.0. Although the volume of oxygen absorbed is somewhat higher than the calculated volume (represented by the straight line A) required to change the mercaptan to the disulfide, there is no indication of a further reaction involving the formation of a higher oxidation product. In Expt. 2, the hydroxide ion concentration is 0.0431 and there is definite evidence of a follow reaction after the formation of the disulfide. In Expt. 3, the hydroxide ion is 0.171. The straight line B indicates the calculated volume of oxygen absorbed to change the mercaptan to the sulfinic acid. Again the actual value is somewhat high and yet the type of curve and the apparent completion of the reaction indicate that the principal product formed is the salt of the sulfinic acid.

The rates of the above reactions increase with increase in copper sulfate concentration and oxygen pressure and, in general, the slower (but still complete) the reactions the nearer do the total oxygen absorptions approach the theoretical values for disulfide and sulfinic acid formation. The kinetics involved in the above reactions are now under consideration and further details will be given in a later publication.

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M. B. YOUNG
H. A. YOUNG
MAX KLEIBER

RECEIVED APRIL 19, 1941

A COLOR TEST FOR *p*-AMINOBENZOIC ACID, THE CHROMOTRICHIA FACTOR

Sir:

The following is a very delicate and simple test for the newest member of the vitamin B complex,