accuracy in the determinations of gaseous pressures may be obtained by the simultaneous use, as above, of several good barometers.

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A QUALITATIVE TEST FOR WATER BY THE USE OF THE ACETYLENE-CUPROUS CHLORIDE REACTION.[1]

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CONTENTS.

In the course of the examination of certain carefully purified organic compounds[2] it was found that a simple, quick and very delicate qualitative test for water, showing approximately the amount present, can be made in the following manner: The substance under examination is placed in contact with calcium carbide in the presence of a solvent for acetylene, and any acetylene formed by the action of water is detected by adding the resultant solution to an ammoniacal solution of cuprous chloride. The following paper describes the application of this method simply as a qualitative test for water. A large amount of work has already been done with a view to applying the acetylene-cuprous chloride reaction to the quantitative determination of both water and acetylene, and a colorimetric method for acetylene depending upon the formation of copper carbide in a colloidal form has been devised. The publication of this work is planned for the near future.

Calcium carbide has recently been quite extensively used for the determination of water in substances which, for any reason, do not permit the application of the more usual methods of analysis. It was suggested by Berthelot,[3] that the acetylene evolved in the reaction could be determined by absorption in an ammoniacal solution of a silver salt with subsequent titration of the excess of silver. This method was tried by Rivett[4] for the determination of water in butter, but was not successful on account of the incomplete absorption of the evolved acetylene. With this exception, all the chemists who have used the calcium carbide method seem to have determined the evolved acetylene either volumetrically or by loss in weight. Obviously, neither of these methods is applicable to

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[1] Published by permission of the Director of the Bureau of Standards.

[2] THIS JOURNAL, 35, 1309 (1913).

[3] *Compt. rend.*, 129, 361 (1899).

[4] *Chem. News*, 104, 261 (1911).

the detection of very small amounts of water, especially in the presence of other volatile substances.

Preparation of Reagents.

Preparation of Anhydrous Solvents.—When testing for water in organic liquids it is usually most convenient to allow the liquid under test to serve as the solvent for acetylene, in which case the previous preparation of an anhydrous solvent is not necessary. In applying the tests to solids, however, it is necessary to allow the reaction with carbide to take place in the presence of an anhydrous liquid, preferably a solvent of the substance under test; and the first difficulty met with in the use of the method was that of preparing even approximately dry solvents. Samples of gasoline, benzene, ether, ethyl acetate, amyl alcohol, amyl acetate, ethyl alcohol, methyl alcohol, acetone, chloroform, carbon tetrachloride, carbon disulfide, and pyridine were treated with calcium chloride, lime, metallic sodium, metallic calcium, and phosphorus pentoxide, except in those cases where a given drying agent was known to be inapplicable on account of reaction with the solvent. The five solvents first mentioned were thus prepared so nearly free from water that it was impossible to detect a trace of acetylene dissolved in them after several minutes' contact with calcium carbide. Sodium appeared to be the best drying agent for the hydrocarbons and ether, and calcium for the esters. Drying of the other solvents was not carried to completion by the above treatment, but all except pyridine were dried sufficiently to be used successfully as solvents for substances containing any considerable amount of water. The list could, no doubt, be extended almost indefinitely; and nearly all, if not all, of those mentioned, could be completely dried by the use of proper drying agents and the observance of suitable precautions. All the liquids tested in this investigation were found to dissolve enough acetylene to give the desired test. Since any of these solvents will, if exposed to the air for a very short time, absorb enough water to show a decisive test, they should be kept, after being dried, in bottles containing some of the drying agent and communicating with the air through a tube containing phosphorus pentoxide; since it is difficult to exclude the air sufficiently by the use of ordinary glass, cork, or rubber stoppers unless the pressure differences, due to temperature changes, are eliminated by the use of a drying tube.

The most sensitive tests are obtained when a solvent is employed which is immiscible with water, since the precipitate formed by the subsequent treatment with cuprous chloride solution, if small in amount collects at the surface of separation of the two liquids and is very easily detected. If a fairly large amount of acetylene is present the aqueous layer dissolves enough acetylene to form a precipitate throughout the solution. When the acetylene is dissolved in liquids miscible with water, such as alcohol and acetone, the copper carbide first appears in a colloidal form, giving an intense red color to the liquid, but a visible precipitate quickly separates out. Since the precipitate is distributed through a much larger volume when these solvents are used, the test is not nearly so sensitive as with ether or chloroform with which, as above noted, the precipitate is concentrated in a single layer. Furthermore, with some of the miscible solvents, especially with acetone, the precipitation does not appear to be always complete. In fact, it is sometimes possible to discharge the color of a colloidal solution of copper carbide by adding a large excess of acetone.

Preparation of Cuprous Chloride Solution.—The test for acetylene is most conveniently made by the use of an ammoniacal solution of a copper salt reduced by hydroxylamine. Such solutions were used by Ilosvay[1] for the detection of acetylene in gas, and the methods of preparation which would give the most sensitive reagent were carefully investigated. He recommends the following proportions for solutions made from several salts:

1. 0.75 g. copper chloride ($CuCl_2.3H_2O$), 1.5 g. ammonium chloride, 3 cc. ammonium hydroxide (20–21% NH_3), 3 g. hydroxylamine hydrochloride.

2. 1 g. copper nitrate ($Cu(NO_3)_2.5H_2O$), 4 cc. ammonium hydroxide, 3 g. hydroxylamine hydrochloride.

3. 1 g. copper sulfate ($CuSO_4.5H_2O$), 4 cc. ammonium hydroxide, 3 g. hydroxylamine hydrochloride.

In each case the copper salt is dissolved in a small amount of water, the ammonia and hydroxylamine hydrochloride are added and the solution is diluted to 50 cc. The first of these solutions seems, in general, to give the most satisfactory results. This solution may be used for the detection of acetylene in any of the solvents previously mentioned except carbon bisulfide, which is reduced to hydrogen sulfide by hydroxylamine and precipitates the copper from the solution as a sulfide. When it is necessary to use carbon bisulfide as a solvent the precipitating solution must be made up from cuprous chloride without the use of any reducing agent. It is very difficult to prepare such a solution which is entirely colorless, but a very small precipitate of copper carbide may be readily detected even in a deep blue solution, and tests have shown that the presence of a cupric salt does not interfere with precipitation, provided a sufficient amount of the cuprous salt is present.

On account of the difficulty caused by the oxidation of cuprous to cupric chloride, experiments were made with a view to replacing the copper solution with an ammoniacal solution of a silver salt; but the white or yellowish precipitate of silver carbide was so much less characteristic

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[1] *Ber.*, 32, 697 (1899).

and so much harder to detect in small amounts than the red copper carbide, that the formation of the latter is the more useful test even when, as in the presence of carbon bisulfide, the copper solution used cannot be decolorized.

Removal of Acetylene from Calcium Carbide.—Commercial calcium carbide always contains a considerable amount of occluded acetylene, formed by interaction with moist air, which must be removed before any delicate test can be made for water in solution. It is very difficult to remove this acetylene completely even by ignition in an evacuated tube, but it may be completely driven off by boiling the carbide with one or two portions of the anhydrous solvent, the liquid being completely evaporated before the carbide is used. In case it is not desired to use, for this purpose, the solvent which is subsequently employed in the water determination, anhydrous ether may always be used.

Method of Making Test.—The test for water is carried out most simply by adding the substance to be tested, together with the solvent, to a few pieces of calcium carbide which have been "boiled out," as described in the preceding paragraph, in a test tube. The test tube is closed by a dry cork or other stopper and shaken occasionally without allowing the liquid to touch the stopper. Two or three minutes' contact with the carbide is usually sufficient. The tube is allowed to stand long enough for the carbide to settle and the clear solvent decanted into the cuprous solution, with which it is vigorously shaken. It might be supposed that small particles of carbide would be carried into the aqueous solution and that the acetylene so produced would make the test of no value; but very little difficulty is experienced from this source. The high density of the carbide causes even very small pieces to settle rapidly, and particles which are carried into the precipitating solution are immediately surrounded by a dense precipitate which causes them to appear as black specks easily distinguished from the bright red, flocculent precipitate produced by dissolved acetylene.

In case a more rigid examination for water is desired, the method may be very easily modified to permit suitable precautions to be taken to exclude moisture from the air; and the probability of error from particles of calcium carbide carried mechanically into the aqueous solution may be avoided by distilling the solvent, together with the dissolved acetylene, into the precipitating solution. In case the latter method is adopted, it is most convenient to distil in a stream of hydrogen dried over phosphorus pentoxide.

In testing solids, it is preferable to use as a solvent for the acetylene a liquid which also dissolves the solid under examination. This is not absolutely necessary however, since an anhydrous liquid will generally extract water quite readily from a solid containing it, provided the solid is in a fine state of division. Tests for water in powdered sugar have been made successfully by the use of ether, in which sugar is nearly, if not entirely, insoluble. Tests of nonvolatile acids or other compounds, which it is not desirable to bring into contact with carbide, may be made by adding an anhydrous liquid, which is then distilled off and tested for water, either by passing over carbide in vapor form or in the usual manner after condensation. Gases may be tested by simply passing over carbide, which has been freed from acetylene, and into the cuprous chloride solution.

Blank Tests.—Whatever procedure is adopted, it is necessary to make a blank test before using the method to detect water in the sample under examination. When testing an organic liquid by simple contact with carbide and decantation, it is only necessary to insure the removal of all acetylene previously held by the carbide. Boiling out two or three times with the liquid under test or with ether, in the manner already dsecribed, is always sufficient to accomplish this. Any acetylene found in portions of the liquid subsequently added is due to water in the sample. When using an anhydrous solvent or when distilling in hydrogen it is necessary to make the blank test in the same manner as the test for water.

Compounds Interfering with the Test.—The usefulness of any qualitative test is, of course, largely determined by the number of compounds which will give the reaction in question. Masson[1] states that of all the substances dealt with in ordinary circumstances, water is the only one which has any chemical action on carbide. A consideration of the reaction between water and calcium carbide and that occurring in neutralization shows that in the presence of an acid, water might be expected to form as rapidly as it is removed until the hydrogen of the acid has been quantitatively converted into acetylene by the following cycle of reactions:

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

$$Ca(OH)_2 + 2H(A) = Ca(A)_2 + 2H_2O$$

In the case of the weaker organic acids, at least, this does not take place, probably because of the fact that no neutralization occurs in a nearly anhydrous solution, and the formation of acetylene seems to give a good qualitative test for water in spite of the possible reaction between the acid and calcium hydroxide.

Masson found that crystalline acids and acid salts, including those which contain water of crystallization readily removed by calcium carbide, do not react as acids, when treated with calcium carbide, with either the carbide or the calcium hydroxide resulting from reaction with the water of crystallization. Experiments by the author with acids in anhydrous solution showed that in some cases, at least, the acid in solution

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[1] *Chem. News*, 103, 37–8 (1911); *J. Chem. Soc.*, 97, 851 (1910).

is quite as inactive as were the acids in Masson's experiments. Thus a 1 g. sample of fused benzoic acid was dissolved in ether and boiled with calcium carbide under a reflux condenser for fifteen minutes without producing a trace of acetylene. Solutions of oleic and phthalic acids have been found to behave in the same manner. Ordinary glacial acetic acid reacts vigorously with the production of acetylene; but neither acetic anhydride, nor acetic acid containing a considerable excess of acetic anhydride do so. Sulfuric acid of all concentrations, including that containing an excess of sulfur trioxide, causes a continuous slow evolution of acetylene. Even in cases when acetylene is evolved on testing the weaker organic acids, it would, of course, be impossible to say, without first testing acids of known water content, how much, if any, of the acetylene was formed by the acid itself.

In his experiments upon the determination of water by the measurement of the acetylene evolved, McNeil[1] found that a larger volume of gas was evolved from glycerol and from oleic acid than could be accounted for by the amount of water present. In view of the behavior of related compounds, it seemed improbable that this could be due to the production of acetylene from the compounds themselves, except that in the case of oleic acid continuous neutralization and reaction with the water so formed might be expected to take place as with any other acid. In order to test this point, thoroughly dried samples of the two compounds were prepared. The large water content of the best samples available was not materially reduced by heating for three hours at 100°, in a stream of air dried over phosphorus pentoxide and at a pressure of less than half an atmosphere. The oleic acid was therefore dissolved in anhydrous ether, the ether distilled off under reduced pressure, and the acid heated to 110°. This operation was repeated several times. Glycerol was treated in the same way, using alcohol as a solvent instead of ether. By this procedure, both oleic acid and glycerol were obtained which did not give any trace of acetylene after contact with calcium carbide, either when used alone or in solution in ether or alcohol. An elevated temperature (as high as 120°) did not cause any reaction which could be detected.

Sensitiveness of Test.—This method for the detection of water is very sensitive. Numerous tests were made by the simple method of decantation of the solvent after contact with carbide, using samples of gasoline, benzene, and ether, which gave perfect blank tests. Known amounts of water were introduced by adding nearly absolute alcohol, the water content of which had been determined by Mr. E. C. McKelvy of this Bureau by the method of critical solution temperature.[2]

The results indicated about the same degree of sensibility in the case

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[1] *Bureau of Chemistry, Circular* No. 97 (1912).

[2] *Bull. Bur. Standards,* 9, 344.

of the three above-named solvents, 0.01–0.03 mg. of water per cc. of the solution in contact with the carbide being the limit at which the formation of a precipitate could be detected. Other tests made by adding a known weight of water dissolved in anhydrous ether showed about the same sensibility. Tests made upon other solvents, in which a blank test showed a trace of water, indicated that the test made with alcohol was less sensitive than with the solvents mentioned above, but more sensitive than with acetone. Ethyl acetate, chloroform and carbon tetrachloride showed about the same sensibility as ether.

Summary.

A qualitative test for water, sensitive to less than 0.1 mg. may be very easily and quickly made by bringing the substance to be tested into contact with calcium carbide in the presence of a solvent for acetylene, which is then decanted or distilled into an ammoniacal solution of cuprous chloride. Nearly all the common organic liquids are suitable for use, if carefully dried. The method is applicable to a great variety of substances and especially to volatile organic compounds. The only compounds known to interfere with the test are the stronger acids and substances, such as hydrogen sulfide, which precipitate cuprous salts from solution.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE FREE ENERGY OF THE VARIOUS FORMS OF ELEMENTARY SULFUR.

BY GILBERT N. LEWIS AND MERLE RANDALL.

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No other element is known to occur in as many different forms as sulfur. Several solid modifications have been studied, of which we shall, for the present, consider only the familiar rhombic and monoclinic forms, S_R and S_M. Rhombic sulfur, being the stable form at room temperature, will be taken as the standard and will therefore be assumed to possess zero free energy and zero heat content. In the liquid state two distinct substances are present, known as S_λ and S_μ (soluble and insoluble sulfur).[1] In the gaseous state at least four modifications have been studied: S, S_2, S_6 and S_8.

Monoclinic Sulfur.

$S_R = S_M$.—The heat capacity of rhombic sulfur has been determined by numerous investigators.[2] When all their data are plotted the most

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[1] Since this paper was written a third kind of sulfur in the liquid state, S_π, has been described by Aten (*Z. physik. Chem.*, **86**, 1 (1913)). His results do not necessitate any material change in the present calculations, nor do they suffice to warrant us at present in attempting to calculate the standard free energies of the several liquid forms.

[2] Regnault, *Ann. chim. phys.*, [3] **9**, 322 (1843); Kopp, *Trans. Roy. Soc. London*, **155**, I, 71 (1865); Bunsen, *Ann. physik.*, [2] **141**, 1 (1870); Dewar, *Proc. Roy. Soc.*