Iodothymol.—This was first prepared by the method of Willgerodt[1] but later by a simpler method of our own, as follows.

Ten g. (0.066 mol.) of thymol and a small excess of sodium hydroxide were dissolved in 100 cc. of water, dil. acetic acid was added till a slight permanent precipitate was formed, then the solution was filtered into 1000 cc. of water in a 2-liter bottle. A solution of 18.5 g. of iodine and 14 g. of potassium iodide was added rapidly while the mixture was shaken. At this point a brown oil separated. About 150 cc. of petroleum ether and a sufficient quantity of sodium thiosulfate solution to decolorize the mixture were added, and the whole was shaken well. The upper layer which contained the iodothymol was then separated, filtered and placed in a vacuum desiccator attached to a filter pump and left until a good crop of crystals formed. The yield of these first crystals was 6.5 g. and the melting point, without further treatment, 69°, the same as that given by Willgerodt.

This is the only iodothymol described in the literature and is stated by Willgerodt to be the *para* compound.

Summary.

Fresh aristol has been shown to be a mixture of a red substance, insoluble in alcohol, easily reducible, of high molecular weight $(C_{10}H_{11}IO)n$, analogous to Lautemann's Red, and a tarry material, soluble in alcohol, which may be considered at least in part as an intermediate substance.

The red color is inherent in the insoluble fraction and is not due to adsorbed iodine.

The liberation of iodine is caused by the oxidizing action of the red substance.

During this action the red part is reduced to a leuco compound, which can be reoxidized.

The ordinary aristol of commerce consists of the leuco compound together with the soluble part, and more or less of the red substance, according to the length of time it has been kept. On this account it is not capable of giving much iodine.

MINNEAPOLIS, MINNESOTA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRYN MAWR COLLEGE.]

THE PURIFICATION AND SOME PHYSICAL PROPERTIES OF CERTAIN ALIPHATIC ALCOHOLS.

BY ROGER F. BRUNEL, J. L. CRENSHAW AND ELISE TOBIN.

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We have found it necessary to prepare in this laboratory a series of aliphatic alcohols, in which there should be, if possible, no impurity exceeding 0.1 to 0.2%, and have undertaken to purify these alcohols by a somewhat more careful fractional distillation than is usually carried out.

A little examination of the literature will show that there is no criterion for the purity of any except a few of these simple substances. Except in the cases of methyl and ethyl alcohols agreement in boiling points to

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[1] *J. prakt. Chem.*, [2] **39**, 290 (1889).

0.1° and in densities beyond the third decimal is unusual.[1] Since the chief criterion of purity of our own products is in the data obtained in the distillation, it appears necessary to enter into some detail with regard to the stills used and, even more, with regard to the fractions actually obtained, particularly since most common organic compounds have already been fractionated "with great care" by various investigators.

Method of Distillation.—The stills most used have been brass tubes.[2] 1.8 meters tall and 30 mm. in diameter, filled with quartz pebbles which pass through 4-mesh, but not 5-mesh wire netting. These pebbles, obtained under the name of Long Island grit, were cleansed with *aqua regia*, and all markedly pitted or flattened pebbles were picked out.

With alcohols boiling above about 80°, the condensation in such a column, even when wrapped with asbestos, is so great that the vapor can be driven up through it only with difficulty. The columns are therefore wound with resistance wire[3] upon a layer of asbestos, and sufficient current is sent through to overcome some of the loss of heat to the air and keep the distillation in progress with a flame 3 or 4 inches high under the flask at the bottom. Alcohols boiling as high as 130° have thus been distilled. Furthermore, by connecting the heating coil to the 220 v. circuit at the end of the distillation, the column can be heated as hot as desired, and the liquid retained by the pebbles greatly reduced, usually to about 30 cc. Toward the end of this process the fractionating effect is, of course, diminished, but when the alcohol is pure, no change in temperature occurs until the liquid is nearly out of the column, when superheating becomes markedly evident. This point is so well marked that there is never any doubt as to when it is reached.

The effectiveness of the stills is, of course, greater, the slower the rate of distillation. The rate is followed by observing the drops from the end of the adapter on the condenser. The speed of distillation rarely exceeds 40 drops a minute, and during the last few distillations of a pure product it is kept at 15 to 30 drops a minute. With a pure substance the temperature of the vapor should, of course, be independent of the rate of distillation, and this was found to be the case with a 5-fold change in the rate with *iso*-propyl and *iso*-butyl alcohols. It appeared to be the case for all of the alcohols with the small changes in rate which inevitably occur.

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[1] Michael, Scharf, and Voigt (THIS JOURNAL, 38, 653 (1916)); purified *iso*-butyl alcohol with great care, and Orton and Jones (*J. Chem. Soc.*, 115, 1194 (1919)), *n*-butyl alcohol, but the physical properties are not recorded. *Tertiary* butyl alcohol, by reason of its high melting point, has also probably been obtained pure.

[2] Pyrex columns of the same height and 36 mm. in diameter have occasionally been used.

[3] A winding with Advance (constantan) wire, No. 21 gage from the Driver-Harris Wire Co., 6 turns to the inch, is satisfactory with the 110 v. current.

The temperatures are read on thermometers graduated to 0.1°. With our tall stills it is impracticable to use a cathetometer, but a special reading device, magnifying 5 diameters, is supported against the still head in such a way that perpendicular vision is obtained and errors due to parallax are avoided.[1] The temperature is always read to 0.01°, and the barometer read simultaneously. *When products are spoken of as constant boiling, constancy to 0.01°, as nearly as can be read, is to be understood.*

The thermometer is enclosed in a glass still-head at the top of the column, 20 mm. in diameter, and tall enough so that the thermometer can be suspended completely in the vapor. A wire ring prevents contact with the walls.[2] The immersion of the entire thermometer in the vapor is of the greatest importance with thermometers which are not gas-filled. If only the mercury stem is immersed, enough mercury distils and condenses further up the capillary to cause serious error in a short time.[3] The bulb of the thermometer is protected from radiation by black paper around the glass. If there is any difference between the effect of such a shield and one of nickel or iron inside the still-head, it is a matter of less than 0.005° at the temperatures here concerned. The chief purpose which the shield serves is to provide protection from radiation from nearby lights, which may raise the temperature of the thermometer some hundredths of a degree.

Our stills are sufficiently effective so that in many cases, we obtain a considerable quantity of distillate within 0.01° after one or two distillations, but it is, of course, a more difficult matter to obtain products which will redistil entirely, or nearly entirely, at constant temperature.

The extent to which a constant boiling fraction finally again comes over at constant temperature is what we have taken as the chief criterion of purity. Statements that "nearly all" of a product distils constantly appear so inexact that we have given below the boiling-point range and weight of the fractions in many of the final distillations, and in all cases the percentage of the product collected without change of temperature.

Sometimes nearly the whole amount distils at constant temperature, but we have usually had to be satisfied when 70 to 80%, and in a few cases even less of a product collected at constant temperature would again come

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[1] A brass tube, 15 cm. long, with support to fit the still head, is fitted with a Bausch and Lomb 25 mm. triple aplanat lens as objective and a brass cap with 1.5 mm. hole as eyepiece. This device, in improved form, is now offered for sale by the A. H. Thomas Co. of Philadelphia.

[2] The thermometer bulb was thus far below the side arm, but there is no reason to expect change of composition of the vapor in ascending the glass tube above such a tall column, except with impure substances and a device such as that of Richards and Barry (THIS JOURNAL, **36**, 1787 (1914)) appeared unnecessary.

[3] Olivier, *C. A.*, 11, 1927 (1917) has observed such vaporization of the mercury in a thermostat at 30°.

over at the same temperature. In such cases the deviation from constancy has not been great. The distillation rarely begins more than 0.15° below the true boiling point, and, frequently only a few drops come over so low. Sometimes the low boiling portions are all within 0.05 or even 0.02°. The temperature at which the distillation begins can well be determined since the hot vapor is at first driven up through the still head slowly and the thermometer is deeply enough immersed to assume the temperature of the vapor before any passes over.

Since the temperature in the final distillations, when it has once become constant, always remains constant until the distillation ceases, it is evident that high boiling impurities are retained in the still, if they have not been already eliminated in the liquid retained by the still in earlier distillations. In the case of *iso*-propyl and *iso*-butyl alcohols the residues from distillation of a number of nearly pure specimens were united and subjected to further fractionation. Since these residues yielded, with very little further fractionation, specimens which did not differ in density or refractivity from the main products, it appears that high boiling impurities were probably eliminated early in the process of fractionation.

The exact determination of the boiling points of the alcohols was a matter of difficulty. At first the final distillation of each alcohol was carried out with a still-head containing 3 or 4 thermometers. When the corrections were obtained for the thermometers the boiling-point readings agreed within 0.02° at temperatures below 100°, but above 100° no satisfactory results were obtained. Through the courtesy of the Bureau of Standards, it was then arranged that we should take specimens of the alcohols to the Bureau and determine their boiling points with a resistance thermometer. Here it was found that with small specimens of the alcohols in a boiling-point apparatus no constant readings could be obtained when the violence of the boiling was altered. In particular, with the higher boiling alcohols the temperature always fell as the violence of boiling was increased. We were not in position to continue the work there long enough to discover whether the cause of the difficulty lay in the alcohols or in the design of the boiling-point apparatus.

In order to continue the work in our own laboratory, since we were equipped with a potentiometer, a thermoelement was employed.

The Thermoelement.—A 12-junction copper-constantan thermoelement was constructed materially according to the directions of Adams,[1] of No. 36 copper and No. 30 constantan,[2] B. and S. gage. The constantan wire was tested for homogeneity in order to have as small electromotive forces as possible set up at points other than the junctions, and a good deal of wire was rejected. Twelve 120 cm. lengths were selected with 30 cm. at one end and 25 cm. at the other as homogeneous as possible, the former ends being used for the hot junction. Satisfactory junctions were not obtained with

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[1] This Journal, **37**, 484 (1915).

[2] "Ideal" wire from the Electrical Alloys Co. of Morristown, N. J., was used.

ordinary solder, so they were brazed with silver solder in a small flame, with borax as flux. They were then dipped in enamel obtained from a wire insulating company, which was hardened by heating at 230°. The sets of hot and cold junctions were enclosed in glass tubes connected by rubber tubing.

A Leeds and Northrup potentiometer was used, but the coils were first tested, since we wished an accuracy of one microvolt in seventy thousand. No corrections of more than 5 μv. were found necessary.

Three Clark cells and 2 sets of 5 Weston cells served as standards.[1] These were kept in a thermostat at 24.94° ±0.005°. The Clark cells differed by only 0.00004 v. almost from the start and the relation between them within this range remained almost constant. When the Weston cells became constant, they also remained nearly as close together. The ratio between the Weston and Clark cells has remained exactly that found by Guthe[2] and Hulett,[3] $\frac{1.0184}{1.42040}$ at 25°. for several months.

The calibration data for the thermoelement were as follows. Cold junction at 0°. $Na_2SO_4.10H_2O$, transition point 32.384°,[4] 15,779 μv. $SrCl_2.6H_2O$, transition point, 61.341°,[5] 30,814 μv. Water boiling point, 52,127 μv. at 760 mm. Naphthalene boiling point, 217.58° at 753.4 mm.,[6] 12,4459 μv.

These values do not fall on a curve which can be represented by 3 constants. The 3 higher values have, therefore, been used, giving the equation,

$$E = 470.045t + 0.54892t^2 - 0.00042t^3$$

which does not differ greatly from that of White,[7] or that of Adams and Johnston.[8]

The value calculated for the transition point of sodium sulfate from our equation is 15,785 instead of 15,779 found. This corresponds to an error of nearly 0.01°, but we are using the element in the temperature range 78–130° and our equation probably does not introduce an appreciable error there.[9]

The increase in e. m. f. per degree varies from 551 μv. at 77° to 654 μv. at 217°. Since it is readily read to 1 μv., the thermoelement is evidently sensitive to 0.002°. In fact, a change of 0.5 μv. is noticeable on the potentiometer. Although we believe that the boiling point of water is reproduced to better than 0.01°, such accuracy has not been obtainable with the alcohols, but most of these are probably correct to ±0.01°.

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[1] Hulett's directions were followed, *Phys. Rev.*, **32**, 257 (1911).

[2] *Guthe*, Bur. Standards, *Bull.* **2**, 33 (1906).

[3] *Hulett, Phys. Rev.*, **32**, 276 (1911).

[4] Dickinson and Mueller, THIS JOURNAL, **29**, 1381 (1907).

[5] Richards and Yngve, *ibid.*, **40**, 89 (1918).

[6] Jaquerod and Wassner, *J. Chem. Phys.*, **2**, 52 (1904).

[7] White, *Phys. Rev.*, **31**, 162 (1910).

[8] Adams and Johnston, *Am. J. Sci.*, [4] **33**, 538 (1912).

[9] The equation recommended by Adams (*J. Wash. Acad. Sci.*, **3**, 469 (1913)) $E = At + B(1 - e^{-Ct})$ would very likely prove more satisfactory, but we have not, up to the present, had the necessary table of exponentials at hand.

The thermoelement is inferior to the resistance thermometer for the determination of boiling points unless an instrument can be made which is independent of the depth of immersion in the hot vapor. In spite of our care in choice of the constantan wire, the e. m. f. varied with the depth of immersion as much as 8 μv. at 100°, the greatest error occurring when just the tip was heated. But it was found that there was a range of about 7 cm. over which there was no change, and there was only about 3 μv. variation in the immediate neighborhood of this region. The element was therefore used with an immersion of about 14 cm. with the possibility of varying this several centimeters either way without altering the reading.[1]

A nickel or iron shield has been used about the thermoelement. We have not detected any difference between them. A piece of black paper outside the tube has the same effect to within 0.005°. The effect of omitting the shield depends mainly upon the surroundings, the thermoelement being sensitive to changes in the illumination of the room, such as the lowering of a shade in a window some distance away, or switching lights on or off within a meter or two of the apparatus.

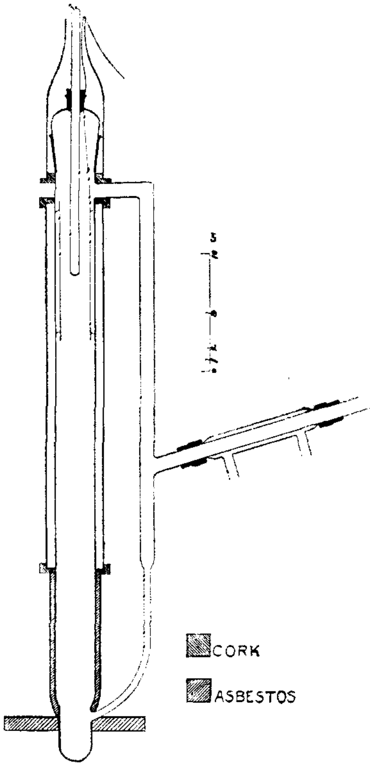

Fig. 1.

The Boiling Point Apparatus.—The apparatus finally adopted is shown in Fig. 1. It is 32 mm. wide in the main part, and 53 cm. high. The air jacket is preferable to an asbestos wrapping since the behavior of the boiling liquid can be watched. The glass stopper is drawn down to a neck of 11 mm. diameter so that a small cork serves to hold the thermoelement. The same cork was used continuously so that any soluble material must soon have been extracted, and any absorbed alcohol could easily be driven out. Gold scraps were usually placed in the apparatus to facilitate boiling, but experiments without them seem to have proved them superfluous. With this apparatus about 20 cc. of alcohol sufficed for a test.

The side arm was made of tubing of 10 mm. internal diameter in order to avoid

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[1] With naphthalene there was variation in the reading even within this best portion of the element. The calibration value was read with what we considered our standard depth of immersion.

rise above atmospheric pressure with vigorous boiling. With a sufficiently narrow outlet tube such changes may occur, but this is a source of error easily avoided. The most persistent difficulty which we had to overcome was the *fall in boiling point* which always occurred with the higher boiling alcohols *when the flame was raised* and the violence of boiling increased. It was suspected that the backflow from the condenser was the cause of this, and the apparatus (Fig. 1) with return tube for condensed liquid was therefore adopted. But this was not the cause of the trouble. The real cause was found to lie in the failure to dry the alcohol thoroughly.[1]

Drying Agents.—The alcohols were all originally boiled with and distilled from lime until no apparent further action occurred before fractionation was begun. The subsequent prolonged boiling during the fractionation appeared to dry them completely. When, however, the boiling points were tested, it was found necessary to repeat the drying.[2] We at first tried to distil the small quantities needed for the tests (about 20 cc.) from a drying agent into the well-dried boiling-point apparatus, but found it impossible to get a constant boiling specimen in this way. The tests have therefore been made with the drying agent in the apparatus. A test of the boiling point in this apparatus apparently shows the presence of the least trace of moisture, at least when the alcohol boils above 100°. With a sufficiently low flame the water, in such a case, gradually accumulates in liquid condensed in the upper part of the apparatus and in the condenser, beyond the point where it can be washed down. The boiling point gradually rises to a maximum, which has proved to be very close to the true boiling point of the alcohol, provided the amount of water present is not too great. *But as soon as the rate of boiling is increased so that the walls are washed down, the temperature drops.* Such fluctuations have often amounted to 0.3° and were always observed with alcohols boiling above 100°.

This explanation of these fluctuations is borne out by the fact that with sufficient drying the boiling point became constant. Furthermore, in

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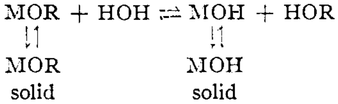
[1] The boiling point of a perfectly pure substance can, as a matter of fact, be determined with very few precautions as regards the apparatus. We finally tested the boiling point of *n*-butyl alcohol in an apparatus consisting of a tube 33 mm. in diameter by 45 cm. high, with a side tube for condenser near the top, with no air jacket or insulation of any sort, but with shield about the thermoelement. The result was identical with that obtained with the other apparatus. It would appear that such an apparatus as that of Edwards (*C. A.*, **12**, 1261 (1918)), in which care is taken to have the inner chamber surrounded by a jacket of vapor at the same temperature, involves somewhat unnecessary precautions. Nevertheless, a jacket of some sort is, of course, desirable since, otherwise, air currents interfere with careful regulation of the rate of boiling.

[2] See Young and Fortey, *J. Chem. Soc.*, **83**, 65 (1903)) in this connection. The remarks of Winkler, *Ber.*, **38**, 3616 (1905), regarding overemphasis which he considers has been placed on the hygroscopicity of ethyl alcohol, appear to us misleading. We find it impossible to keep our compounds dry.

the case of several specimens of alcohols which were not boiling constantly, the apparatus was tipped and the alcohol distilled through the side arm. The first few drops of such distillates in every case turned copper sulfate blue, while water was not detected in the main portion of the distillate by the same test.

The complete drying of these specimens, presumably nearly dry at the start, was, however, so difficult that the action of drying agents was given special consideration. The matter does not appear to have been thoroughly discussed in the literature. When a metal or metallic oxide is used to dry an alcohol, the following set of equilibria must exist as soon as hydroxide is formed:



$$\begin{array}{ccccc} \text{MOR} & + \text{HOH} \rightleftharpoons & \text{MOH} & + \text{HOR} \\ \updownarrows & & \updownarrows & \\ \text{MOR} & & \text{MOH} & \\ \text{solid} & & \text{solid} & \end{array}$$

M being the metal, and R the alcohol radical.

The effectiveness of the drying agent will evidently depend upon (1) the equilibrium constant of the reaction in solution, which, however, should not vary greatly with different metals; (2) the solubility of MOH and MOR. The solubility of the base should obviously be as small as possible, while solubility of the alcoholate will be favorable.

In addition, the dissociation pressure of water over the hydroxide must be taken into account, although this is probably too small with any of the metals concerned to be of any consequence.[1]

The velocity with which a drying agent will act is a different matter. It obviously depends upon the rate of its reaction with water, but when the concentration of water becomes low so that the velocity of its reaction with the drying agent is very small, a rapid action of the drying agent with the alcohol, forming an alcoholate which is appreciably soluble, will be as effective as direct action with the water, since the alcoholate will at once react with the water, precipitating metallic hydroxide.

Sodium, in view of the above considerations, could not be expected to be an effective drying agent, by reason of the high solubility of the hydroxide. The addition of sodium to a specimen of *n*-butyl alcohol in the boiling-point apparatus proved to be quite without effect. The fluctuation of the boiling point was the same after its addition as before, while the maximum temperature attained with a low flame was 0.015° below the true boiling point.

Lime should be much more effective. Lassar-Cohn[2] quotes Smith[3] as having shown that 50 cc. of alcohol in contact with lime contains only 0.0005 g. of solid. Since the hydroxide is probably less soluble than the

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[1] See Johnston, This Journal, 30, 1357 (1908).

[2] Lassar-Cohn, "Arbeitsmethoden," 1, 265 (1906).

[3] Smith, *Arch. Pharm.*, 1876, p. 356.

alcoholate, the equilibrium must be driven far to the right, so that the alcohol is practically dry.

The amount of water which could remain in such a solution, in the presence of lime is, moreover, limited to the amount which would have a vapor pressure equal to the dissociation pressure of water over calcium hydroxide at the temperature concerned. At the boiling point of butyl alcohol, with which we have tested this question, 117°, this pressure would be, according to Johnston's[1] equation, 0.00002 mm. It would appear that such alcohol could reasonably be called dry.

Mendelejeff[2] nevertheless claimed that alcohol could take water from calcium hydroxide, and when difficulty was met with in drying the alcohols completely with lime the matter was tested by addition of calcium hydroxide to thoroughly dried butyl alcohol. In the two most conclusive experiments *n*-butyl alcohol was first dried with aluminum amalgam until it boiled constantly at 117.705° and 117.707° respectively. To the first specimen slightly hydrated lime, to the second freshly slaked lime dried by brief heating to 200° was added. In neither case was the boiling point altered by 1 μv., even after further standing and boiling.

Calcium acts more rapidly than lime, largely because of the rapid formation of alcoholate. In the only case in which we used it, however, a constant boiling point was not obtained, and since both Osborne, McKelvy and Bearce,[3] and Robertson and Acree[4] found that ethyl alcohol had a higher density when dried with calcium than when dried with lime, it appears possible that the calcium usually contains some impurity which renders it unsuitable for use.[5]

Barium oxide appears to act more rapidly than lime, presumably, again, because it forms alcoholate more readily, at least with some alcohols. We have not found that it dries the alcohols more thoroughly than lime, which is not surprising, since any further reduction in the amount of water below what can eventually be reached with lime, probably could not be detected.

Aluminum amalgam, recommended by Wislicenus and Kaufmann,[6] we have found to be very effective. It dries butyl alcohol, with which it forms alcoholate readily, much more rapidly than *iso*-propyl alcohol, with which the alcoholate formation is slow. In view of the fact that aluminum hydroxide dissociates partially at 200°, it would appear that

[1] *Loc. cit.*

[2] *Z. Chem.*, 1865, p. 261.

[3] Osborne, McKelvy and Bearce, *J. Wash. Acad. Sci.*, **2**, 95 (1912).

[4] Robertson and Acree, *Am. Chem. J.*, **49**, 494 (1913).

[5] The trouble may be caused by ammonia. Winkler, *Z. angew. Chem.*, **29**, I, 18 (1916), describes a method of removing this. According to Delépine, *Jahrb. Chem.*, 1892, p. 196, ammonia raises the density of alcohol.

[6] Wislicenus, *Ber.*, **28**, 1323 (1895); Kaufmann, *J. prakt. Chem.*, [2] **54**, 54 (1896).

the dissociation pressure of water might be sufficient at 117° to prevent thorough drying of the alcohol. There is perhaps not conclusive evidence that aluminum oxide rather than hydroxide is not formed, or possibly a partially hydrated oxide. Some of our best tests were made with this drying agent, and although we did not discover that lime or baryta did not eventually produce the same result, the aluminum hydroxide is nevertheless the most satisfactory reagent we found, on account of rapidity of its action.

Densities.—The densities have been determined with a pycnometer of the Sprengel type, with arms bent up and thermometer fused in, with a capacity of 8.2760 cc. at 25°. The thermostat is controlled to ±0.02° or better. To protect the liquid in the pycnometer from a fine, hardly visible spray thrown up by the vigorous stirring of the thermostat, small glass tubes, closed at the outer end, were fitted loosely over the arms. Without these it appeared that the density altered slightly when the pycnometer remained long in the thermostat. The density determinations are accurate to ±0.00002.

Refractivities.—The refractivities were determined with a Zeiss-Pulfrich refractometer. Accuracy to the fourth decimal in absolute value of the refractive index is barely obtainable with our instrument, although occasionally a 5 in the fifth decimal is thought justifiable. Constant temperature was secured by a slow current of water run through a copper coil in the thermostat.

As regards the relative value of the various physical properties as a criterion for the purity or identity of such substances, it is to be noted that we have had no difficulty in preparing specimens agreeing in boiling point to 0.01°. The agreement in refractivity to the fourth decimal has also frequently been satisfactory. Nevertheless, the determination of the density to the fifth decimal has in some cases shown such specimens not to be identical. If these are assumed to be, respectively, the degrees of accuracy easily attainable in the determination of these constants, it is evident that the densities are the best test of the purity of the substances.

Preparation of alcohols.—Ethyl, *n*-propyl, *n*-butyl, and *iso*-butyl alcohols were the best commercial products obtainable.

The secondary alcohols here described, as well as others not yet fractionated, were prepared by catalytic reduction of ketones under pressure, with nickel oxide as catalyst. The method is, in principle, that of Ipatiew,[1] although the apparatus was designed by Bergius.[2]

The bomb is a steel tube, 60 cm. long, and 30 mm. inner diameter, with 1 cm. walls, rotated in a horizontal position in an electric furnace. The capacity is 260 cc. and it is usually half filled with ketone. The reduction goes on rapidly at any pressure above about 45 kg., at temperatures of 150–200°, but in order to accelerate the reaction, as

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[1] *C. A.*, 1, 2878 (1907) and other articles in the *J. Russ. Phys. Chem. Soc.*

[2] Somewhat like that described by Bergius, *Dissertation*, Halle, 1913.

well as from the necessity of introducing the requisite quantity of hydrogen, an initial pressure of 1363 kg. is usually used. This quantity of hydrogen will react completely in less than 10 minutes.

This method has several advantages over that of Sabatier and Senderens and their collaborators, once the apparatus is installed. The catalyst may be prepared with much less care, nickel nitrate being heated to redness; the oxide need not be reduced to metallic nickel; commercial electrolytic hydrogen is pure enough, and oxygen need not be excluded with particular care; by taking care that there is an excess of hydrogen (usually about 230 kg.) during the final heating, the reaction, which is reversible, can be driven practically to completion and 130 cc. of almost pure alcohol can be prepared per day.

Experimental Part.

All of the boiling points recorded have been reduced to 760 mm. to facilitate comparison. Since the values recorded in the literature for dT/dp are not in agreement, even for ethyl alcohol, we have used values deduced from the boiling points of our own specimens on different days. The disagreement in the values found for dT/dp is doubtless due to the fact that this property is very susceptible to the influence of impurities if their boiling point differs greatly from that of the alcohol.

The boiling points in the determinations with the thermoelement were in some cases constant to 1 μv. (0.002°), or less. Where they were not constant, the temperature given is the maximum and the magnitude of the fluctuation is indicated. The values obtained by the authors at the Bureau of Standards are also given. The differences between these values and those eventually obtained are doubtless due to the moisture of the specimens. These values are, however, near enough to those obtained with the thermoelement to show that there is no error of great magnitude in either set of values.

Where distillation with the thermoelement is mentioned, the data refer to the distillation of small specimens from the boiling-point apparatus.

Complete data are given for the final distillation of many of the specimens. In particular, they are given where the constant boiling portion of the distillate was divided into several fractions. The temperature ranges for the fractions are based on the thermometer readings, but the actual temperatures are all corrected in accordance with the best value obtained for the boiling points.

Ethyl alcohol: Boiling point: (1) thermoelement: aluminum amalgam, 78.317° (77.979° at 750.35 mm.); (2) thermometers: 78.31°, 78.32°, 78.33°; mean: 78.32°; (3) obtained by the authors at the Bureau of Standards, 78.42°. The best specimens distilled entirely at constant temperature, except for less than a gram at the beginning.

n-Propyl alcohol: Boiling point: (1) thermoelement: aluminum amalgam, 97.19° (0.01°); (2) thermometers: 97.19°, 97.19°, 97.17°; (3) obtained by the authors at the Bureau of Standards, 97.12°.

In view of the particularly numerous and discordant values for the physical properties of propyl alcohol recorded in the literature, the following data for the distillation of our best specimen are given.

A. Weight before distillation, 216 g. 1. 97.04—97.17°; 5 g. II. 97.17–97.19°; 27 g. III. 97.19°; 114 g.

The temperature remained constant until the distillation stopped, but the amount of alcohol left in the still was much larger than usual. Data for our other specimen are given in Table I below.

Iso-Propyl alcohol: Boiling point: (1) thermoelement: boiled 4 hours with lime and distilled, 82.239–82.263°; boiled 6 hours with lime and distilled, 82.257–82.267°; boiled 4 hours with aluminum amalgam, 82.259° (0.004°); (2) thermometers, 82.27°, 82.28°, 82.29°; mean: 82.28°; (3) obtained by the authors at the Bureau of Standards, 82.25°.

This alcohol was distilled in glass columns for fear of re-oxidation by contact with the brass, but this was later found to be a needless precaution. The data for the best specimen (A) are as follows: wt., 210 g. I, 82.12–82.25°; 8 g. II, 82.25–82.26°; 14 g. III, 82.26°; 147 g. IV, 82.26°; 30 g.

The data for physical properties of other specimens are given below.

n-Butyl alcohol: Gentle boiling with the drying agent does not dry the alcohols boiling above 100°, since the water distils out of the liquid and remains in the condensate in the upper part of the apparatus. It is necessary occasionally to boil the alcohol up vigorously and wash the apparatus down.

Boiling point: (1) thermoelement: boiled with barium oxide, 117.706° (0.003°); same, 117.707°, maximum, not constant; metallic calcium, 117.712° (fluctuations, 0.01°)[1] Aluminum amalgam, 117.705° (0.003°); same, 117.707° constant. (2) obtained by the authors at the Bureau of Standards, 117.686°.

For the alcohols above 110°, the values obtained with the thermometers during the distillation are in such disagreement as to be of no value. In this case they disagreed by over 0.1°.

Data for distillation of two specimens from different sources follow: (A) I, 117.69–117.70°, 19 g.; II, 117.70–117.71°, 16 g.; III, 117.71°; 303 g. (B) wt., 610 g. I, 117.54–117.64°, 9 g.; II, 117.64–117.67°, 36 g.; III, 117.67–117.70°, 45 g.; IV, 117.70–117.71°, 28 g.; V, 117.71°, 251 g.; VI, 117.71°, 103 g.; VII, 117.71°, 65 g. V, VI, VII, total, 419 g.

The low boiling fractions in B are larger than they should have been owing to poor control of the rate, which reached 100 drops a minute at times. To secure small low boiling fractions it is advantageous to conduct that part of the distillation very slowly. The constant boiling portion in B was again divided.

Iso-Butyl alcohol: Boiling point: (1) thermoelement: boiled 4 hours with barium oxide, 107.877°; distilled from barium oxide without long boiling, 107.874–107.888°; aluminum amalgam, 107.881°; (2) obtained by the authors at the Bureau of Standards, 107.89°.

The data for distillation of 2 specimens follow. A third specimen was worked up from residues.

(A) 265 g: I, below 107.86°, 15 g.; II, 107.86–107.89°, 48 g.; III, 107.89, 170 g. (B) I, 107.88–107.89°, 14 g.; II, 107.89°, 66 g.

Particular attention is called to the densities of this alcohol, seen in the table below. In this case the density is of little value as a criterion of purity.

sec.-Butyl alcohol: Since the thermometers gave concordant values for the boiling point and our supply of this alcohol was limited, it was not tested with the thermoele-

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[1] This was not a very reliable determination and does not indicate inferiority of the calcium as a drying agent.

ment. The thermometer readings are especially reliable since they lie so close to the 100° point. (1) Thermometers: 99.52°, 99.53°, 99.53°.

This was one of the alcohols most readily purified. The data in the table below appear to be sufficient.

Methyl iso-butyl carbinol: Aluminum amalgam dries this very slowly, partly, at least, because of the slight reactivity of the drying agent with the alcohol itself. After several hours' boiling a large part of aluminum had still not reacted. In addition to this, the boiling point of the alcohol is so far above 100° that the water has a particular tendency to distil out of the alcohol and collect in the condensed liquid in the cooler parts of the apparatus. It is difficult to prevent this altogether since too prolonged, vigorous boiling causes too much loss of vapor around the ground glass stopper of the apparatus.

The values obtained were from 131.78° to 131.826°, and the higher value is more likely to be correct. The value obtained at the Bureau of Standards was much too low. The values on our thermometers were also unsatisfactory, varying from 131.77° to 131.85°. The value 131.82° must be nearly correct.

This alcohol was easily purified. A good deal came over within 0.01° on the first distillation, and 72% of this, on redistillation, came over constantly. This, and other constant boiling portions were distilled as follows:

(A) wt., 320 g. I, Below 131.79° less than 1 g., total to 131.81°, 12 g.; II, 131.81°, 73 g.; III, 131.81°, 166 g.; IV, 131.81°, 50 g.; II, III and IV, 289 g.

Another specimen (B) distilled nearly as well.

Table I summarizes the distillation data and physical properties of our specimens. Under Col. 2 will be found the per cent. of the material taken for the final distillation, which came over at constant temperature. Values are, however, lacking in some cases due to failure to record the total weight before distillation. These values do not fairly represent the purity of the specimens since they imply that the material remaining in the still would not have come over at the correct temperature, whereas all experiments with these residues indicated that the amount of high boiling impurity in them was small. More significant are the figures in Col. 3, which show the per cent. of the amount actually distilled which was collected at constant temperature.

The "most probable values" are not always averages of the results, but are based upon our judgment as to the relative value of the tests or purity of the specimens. We believe the boiling points to be accurate to ±0.01°, except that of methyl-*iso*-butyl-carbinol. The refractivities appear to be accurate to 0.0001. In the case of the densities, however, while the determinations are accurate to 0.00002, the true densities of the substances have not been established, in most cases, nearer than 0.0001.

The values for dT/dp are given in degrees per mm. pressure. The values of the molecular refractivity are calculated according to the equation:

$$M = \frac{\eta^2 - 1}{\eta^2 + 2} \cdot \frac{M}{D}.$$

In Table II we have quoted for comparison some of the values to be found in the literature. Among the older values we have included only those which were determined with particular care or which are often

TABLE I.

1.	2. Const. boiling portion.	3.	4.	5.	6.	7.	8.
Specimen.	% of total.	% of part distd.	d*t*/d*P*.	B. p. °C.	d_4^{25}	n_{25}^{D}	M_{25}^{D}
Ethyl Alcohol.							
		100	0.035	78.32	0.78505	1.3595	12.93
n-Propyl Alcohol.							
A	56	78	0.036	97.19	0.79975	1.3833	...
B	47	63	...	....	0.79992	1.3832	...
Most probable values:				**97.19**	**0.7998**	**1.3833**	**17.54**
Iso-Propyl Alcohol.							
A-III	84	87	0.033	82.26°	0.78089	1.3750	...
IV			...	....	0.78167	1.3750	...
B	70	81	...	....	0.78071	1.3749	...
C	..	57	...	....	0.78072	1.3748	...
D (Res.)	..	56	...	....	0.78086	1.3749	...
Most probable values:				**82.26**	**0.7808**	**1.3749**	**17.61**
n-Butyl Alcohol.							
A	..	90	0.036	117.71	0.80560	1.3974	..
B-V			...	....	0.80566	1.3974	...
VI	69	78	...	....	0.80571	1.3974	...
VII			...	....	0.80586	1.3973	...
Most probable values:				**117.71**	**0.8057**	**1.3974**	**22.17**
Iso-Butyl Alcohol.							
A	64	73	0.036	107.89	0.79800	1.3938	...
B	..	82	...	....	0.79800	1.3939	...
C (Res.)	72	77	...	....	0.79802	1.3939	...
Most probable values:				**107.89**	**0.79801**	**1.3939**	**22.21**
sec.-Butyl Alcohol.							
A-III			0.036	99.53	0.80270	1.39495	...
IV		over 90	...	....	0.80276	1.39495	...
B	83	97	...	....	0.80267	1.39495	...
Most probable values:				**99.53**	**0.80271**	**1.39495**	**22.13**
Methyl-*iso*-Butyl-carbinol.							
A-II			0.040	131.82	0.80251[a]	1.40895	...
III	88	96			0.80238	1.40895	...
IV	..	..	...	....	0.80250	1.40885	...
B	..	84	...	....	0.80243	1.40895	...
Most probable values:				**131.82**	**0.8025**	**1.40895**	**39.61**

[a] The fractions of Specimen A were tested in very humid weather. Possibly the values should have been identical.

quoted. Densities have been recalculated to 25° where they were not determined at this temperature, and we have indicated in parenthesis the temperature of the original determinations in such cases. For alcohols where there is no basis for such calculation, the values are not given.

The reliability of the calculations of the densities is open to question, but the differences between the values are in most cases greater than the

TABLE II.

Author.	B. p. °C.	d_4^{25}	n_{25}^{D}
		Ethyl Alcohol.	
Mendelejeff[1]	78.303	.....	.....
Ramsay and Young[2]	78.33	.....	.....
Noyes and Warfel[3]	78.30	.....	.....
Andrews[4]	...	0.78510	1.35941
Doroshevski and Dvorzhanchik[5]	...	.....	(24°) 1.35927
Doroshevski and Polianski[6]	78.35	.....	.....
Wade and Merriman[7]	78.39	.....	.....
Osborne, McKelvy, and Bearce[8]	...	0.78506	.....
Robertson and Acree[9]	...	0.785085	.....
Richards and Coombs[10]	78.42	.....	.....
Author's values	78.32	0.78505	1.3595
		n-Propyl Alcohol.	
Brühl[11]	97.3–.5	0.8005 (20°)	1.3836
Naccari and Pagliani[12]	.....	0.8004	....
Perkin[13]	98	0.8001	....
Ramsay and Young[14]	97.4	0.7995	....
Landolt and Jahn[15]	96.1	0.8017 (17.8°)	1.3835
Loomis[16]	97.2	0.8000 (20°)	....
Young and Fortey[17]	97.19	0.7994 (0°)	....
Holmes and Sagemann[18]	97.2–.4	0.79972	....
Doroshevski and Rozhdestvenski[19]	97.26	0.7994 (20°)	....
Doroshevski and Dvorzhanchik[20]	....	....	(20°) 1.38365
Author's values	97.19	0.7998[21]	1.3833
		iso-Propyl Alcohol.	
Brühl[22]	82–83	0.7844 (20°)	1.3756
Zander[23]	82.7–.9	0.7794 (17°)	....
Perkin[13]	....	0.78220	....
Thorpe[24]	81.6–82.1	0.7811 (15°)	....
Louginine[25]	82.04	....	....
Doroshevski	82.42[26]	0.7807[27] (20°)	....
Doroshevski and Dvorzhanchik[20]	....	....	1.37534
Author's values	82.26	0.7808	1.3749
		n-Butyl Alcohol.	
Kahlbaum[28]	117.6°	....	1.39747
Doroshevski and Dvorzhanchik[20]	117.1	....	1.39749
Author's values	117.71	0.8057	1.3974
		iso-Butyl Alcohol.	
Perkin[13]	107.6–8.3°	0.79852	....
Traube[29]	....	0.8000 (20°)	....
Landolt and Jahn[30]	107.25	0.7987 (17.5°)	1.3941
Naccari and Pagliani[12]	....	0.7972	....
Doroshevski and Dvorzhanchik[20]	107.93	0.7976 (15°)	1.39396
Doroshevski[27]	107.5	....	....
Michael and Zeidler[31]	107.67–.75	....	....
Richards[32]	107.2–.3	....	....
Authors' values	107.89	0.79801[33]	1.3939

TABLE II (*Continued*).

Author.	B. p. °C.	d^{25}_4	η^D_{25}
	sec.-Butyl Alcohol.		
Pickard and Kenyon[34]	99°	0.8039	
Dogolenko[35]	....	0.8024–0.8031 (20°)	
Authors' values	99.53	0.80271	....

The temperatures in parenthesis are those of the original determinations, from which the values given were calculated.

References.—(1) *Z. Chem.*, **1865,** 257. (2) *J. Chem. Soc.*, **47,** 654 (1885). (3) THIS JOURNAL, **23,** 465 (1901). These authors state that they consider their value probably less reliable than that of Ramsay and Young. (4) *Ibid.*, **30,** 357 (1908). (5) *C. A.*, **2,** 2181 (1908). (6) *Z. physik. Chem.*, **73,** 192 (1910). (7) *J. Chem. Soc.*, **99,** 1002 (1911). (8) *J. Wash. Acad. Sci.*, **2,** 95 (1912). (9) *Am. Chem. J.*, **49,** 497 (1913). (10) THIS JOURNAL, **37,** 1669 (1915). (11) *Ann.*, **200,** 173 (1879). (12) *Atti. Accad. Sci. Torino,* **16,** 407 (1881). (13) *J. Chem. Soc.*, **45,** 466 (1884). (14) *Phil. Trans.*, **180,** 140 (1889). (15) *Z. physik. Chem.*, **10,** 288 (1892). (16) *Ibid.*, **32,** 594 (1900). (17) *J. Chem. Soc.*, **81,** 725 (1902). (18) *Ibid.*, **95,** 1936 (1909). (19) *J. Russ. Phys. Chem. Soc.*, **40,** 1428 (1910). The formula of De Heen ,which these authors recommend, was tested by them only between 10° and 20°. When tested by the results of Ramsay and Young, and Naccari and Pagliani for 0°, it is not as satisfactory as the formula of the latter authors, which we have used. (20) *C. A.*, **3,** 1355 (1909). (21) Further tests of this value will be made with material now being purified. (22) *Ann.*, **203,** 12 (1880). (23) *Ann.*, **213,** 155 (1882). (24) *J. Chem. Soc.*, **71,** 923 (1897). (25) *Ann. chim. phys.*, [7] **13,** 307 (1898). (26) *Centralbl.*, **1911,** I, p. 465. (27) *C. A.*, **4,** 1404 (1910). (28) *Z. physik. Chem.*, **46,** 628 and 646 (1898). This author gives $d^{20}_4 = 0.80978$. If we assume the temperature coefficient to be the same as that of isobutyl alcohol, we obtain $d^{25}_4 = 0.8059$ (29) *Ber.*, **19,** 883 (1886). (30) *Z. physik. Chem.*, **10,** 317 (1892). (31) *Ann.*, **493,** 93 (1912). (32) THIS JOURNAL, **37,** 1669 (1915). (33) The density appears, in this case, to be easy to duplicate without a high degree of purity. Some years ago one of the authors (*Ber.*, **44,** 1004 (1911) obtained 3 fractions boiling, altogether, over a range of 0.24°, having densites of 0.79890 to 0.79802. (34) *J. Chem. Soc.*, **103,** 1940 (1913). Value for 25° by linear interpolation. (35) *Z. physik. Chem.*, **62,** 505 (1908). Values estimated from those given for 20° by comparison with Pickard and Kenyon's values.

possible errors in calculation. The following appear to be the most reliable formulas (the references will be found in the table).

For *n*-propyl alcohol, a formula of Naccari and Pagliani, $d = 0.8203 - at + bt^2 - ct^3$ where $\log a = 6.90228$, $\log b = 3.66482$, $\log c = 2.10469$ (—10 after each), and 0.8203 is the density at 0°. This equation fits the values of Ramsay and Young (0°, 15°, 25°), Perkin (15°, 25°), Loomis (15°, 20°), and Doroshevski and Rozhdestvenski (10°, 20°) to within 0.0001, after calculation back to a value for d^0_4 in each case.[1]

For *iso*-propyl alcohol, one of the equations given by Zander, $V_t = V_0 (1 + 0.0010743t + 0.06328t^2)$, which very nearly fits the values of Perkin (15°, 25°).

For *iso*-butyl alcohol, the equation of Naccari and Pagliani, $d = 0.81624 - at - bt^2 - ct^3$ where $\log a = 6.87551$, $\log b = 3.43912$, $\log c = 1.86857$

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[1] Although the density of the alcohols is affected by slight impurities, the form of the density-temperature curve is apparently not much affected.

(—10 after each), and 0.81624 is the density at 0°. This equation fits the values of Perkin (15°, 25°) very closely.

The refractivities can be calculated with more certainty, since Doroshevski and Dvorzhanchik showed that the formula $\eta_t = \eta_0/(1 + kt)$ holds for the common alcohols. Where the refractivity has been determined for two temperatures, a value for k can be calculated. We have used for *n*-propyl alcohol, $k = 0.032368$ (values of D. and D.); *iso*-propyl alcohol, 0.0_32850 (authors' values); *iso*-butyl alcohol, 0.0_3269 (D. and D.).

No values are given in Table II for methyl-*iso*-butyl-carbinol. It has been prepared by Skita and Ritter,[1] Pickard and Kenyon,[2] Guerbet,[3] and others, but, although its boiling point has been known to be in the neighborhood of 131°, no determinations of its density or refractivity are recorded.

The authors acknowledge with pleasure the courtesy of the U. S. Bureau of Standards in providing opportunity for the first boiling point tests with one of their resistance thermometers, and, in particular, their indebtedness to Miss Amelia K. Benson, with whose assistance the tests were made.

They also take pleasure in acknowledging their indebtedness to the Warren Fund of the American Academy of Arts and Sciences for a grant which covered the cost of materials for this work as well as for the preparation of several alcohols on which the work is not yet completed.

NITROTARTARIC ACID.

By Arthur Lachman.

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Although nitrotartaric acid is the raw material of the important dye tartrazine, it has not been the subject of much published work; it is, however, a very interesting substance. It was first prepared by Dessaignes,[4] by dissolving tartaric acid in strong nitric acid, and adding sulfuric acid to the mixture. He found it a rather unstable compound, and described its decomposition products quite accurately, although he overlooked the most important one, *viz.*, dioxy-tartaric acid. This reaction was discovered by Kekule.[5] Dihydroxy-tartaric acid behaves like a diketone, and it is a condensation product of this diketone with phenylhydrazine sulfonic acid which forms the dye tartrazine.

There would seem to be little doubt, from its method of preparation, that nitrotartaric acid is really what its name implies, *viz.*, the nitric ester of tartaric acid; yet it is usually referred to with quotation marks around the "nitro," or as "the so-called nitrotartaric acid." Its actual relation-

[1] Skita and Ritter, *Ber.*, **43**, 3397 (1910).

[2] Pickard and Kenyon, *J. Chem. Soc.*, **99**, 56 (1911).

[3] Guerbet, *Compt. rend.*, **149**, 129 (1909).

[4] Dessaignes, *ibid.*, **54**, 731 (1852).

[5] Kekule, *Ann.*, **221**, 245 (1883).