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CALCIUM CARBIDE AS A DEHYDRATING AGENT FOR ALCOHOLS.

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It is well known that almost all alcohols purchased in the market contain considerable water. It varies from five per cent. to fifteen per cent. in methyl and ethyl alcohols and is less in amyl and other alcohols. It was thought that it would be interesting and profitable to determine the degree of dehydration produced by the action of calcium carbide on the water in these alcohols. In the reaction acetylene is evolved and calcium oxide is formed according to the following equation.

$$CaC_2 + 2H_2O = CaO + 2C_2H_2.$$

Several methods have been suggested, and employed to a limited extent, for the quantitative estimation of alcohols, but only one or two of them have come into general use. The method used for determinining the degree of dehydration in this work was to ascertain the specific gravity of the alcohol at 15.5° C., and then compare the result with a specific gravity table. All of the usual precautions as to temperature, etc., that are common to this method, were employed.

Methyl Alcohol. About the only dehydrating agents heretofore used for methyl alcohol are anhydrous copper sulphate, anhydrous potassium carbonate, and calcium oxide. Methyl alcohol combines with calcium chloride and barium oxide to form alcohol of crystallization, similarly to water, which fact prevents their being used as in case of

ethyl alcohol. Calcium carbide also combines with methyl alcohol, but not at the temperature of the boiling alcohol.

In one experiment, 500 grams of methyl alcohol, the specific gravity of which was .820 as shown by the hydrometer (and which was therefore a 91 per cent. alcohol) was treated with powdered, commercial calcium carbide. The amount necessary was calculated from the equation given above, and 20 per cent. was added to this in order to provide for the impurities in the carbide and still leave an excess. An evolution of acetylene began which rapidly increased and the heat of reaction raised the temperature of the alcohol to its boiling point, so that it became necessary to attach a return condenser to prevent the loss of the alcohol. The flask was thoroughly shaken occasionally during the reaction. When the action, which required four or five hours had ceased, the flask and contents were placed on a water bath and the alcohol boiled with a return condenser for some time in order to drive off as much acetylene as possible as it is quite soluble in methyl alcohol. It was then distilled off with the usual precautions to keep out the moisture of the air. All parts of the distillate still contained considerable acetylene and anhydrous copper sulphate was added to remove it. The flask was thoroughly shaken and the alcohol redistilled. The first portion of the distillate was rejected as it still smelled strongly of acetylene. The specific gravity of this specimen was not taken but it must have been completely dehydrated, since it dissolved anhydrous copper sulphate with the formation of the blue solution* of the formula, $CaSO_4 + 2CH_4O$. This takes place only with perfectly anhydrous methyl alcohol.

Dr. Theodore Schuchardts c. p. methyl alcohol (which had a specific gravity of .8187, and which was therefore a 92 per cent. alcohol), when treated with calcium carbide evolved acetylene rapidly. When it had reached the point where calcium carbide ceased to act upon it, it still had a specific gravity of .8046. The density of the absolute

*Klepl, Ber. der Deut. Chem. Ges. p 15, R, 2361; and de Forcrand, *Ibid.*, XIX. R, 236.

alcohol is given as .8021.* This would indicate either that the alcohol was not absolute (the specific gravity obtained corresponds to a 99 per cent. alcohol), or that the specimen experimented upon was not quite pure. From the fact that it gives the reaction of de Forcrand and Klepl mentioned above, one would be justified in concluding that the latter was true, and that the alcohol was entirely anhydrous.

Ethyl Alcohol. It has always been considered difficult to remove the last traces of water from ethyl alcohol. On account of the importance of absolute alcohol it was one of the first subjects to receive the attention of the early chemists and a number of good methods for dehydrating ethyl alcohol were in use more than a century ago. In the year 1788 the British government employed a chemist by the name of Gilpin to work on the subject. He succeeded in obtaining alcohol of specific gravity .7939 at 60 degrees Farenheit. This was a remarkably good result for that time. The specific gravity of ethyl alcohol is now usually considered to be .7938. One experimenter,† however, claims to have prepared an alcohol of specific gravity .7935.

The common dehydrating agents for ethyl alcohol are calcium chloride (for removing the first portion of water), anhydrous potassium carbonate, anhydrous potassium acetate, anhydrous copper sulphate, metallic sodium, phosphoric anhydride, barium oxide, and calcium oxide. Drinkwater,‡ about 1860, and Mendeleeff,§ in 1865, showed that calcium oxide was superior to all dehydrating agents then in use.

The term "absolute alcohol" is frequently used to indicate any alcohol that is stronger than can be obtained by simple fractional distillation and which still contains considerable water. Most of the absolute alcohol of the best grade contains some water. A specimen at hand from Sargent & Company evolves some acetylene when warmed with powdered calcium carbide.

*Allen's Com. Org. Anal., Vol. I, page 71.
†Allen's Com. Org. Anal., Vol. I, page 85.
‡Dr. Sheridan Musprat's Chemistry, Vol. I, pages 51-52.
§Jour. Lond. Chem. Soc., 1871, 133.

In the preparation of absolute ethyl alcohol precisely the same method was used as is given above for methyl alcohol, except that it was not found necessary to use the return condenser during the action of the calcium carbide, on account of the higher boiling point of ethyl alcohol. In one experiment where extra precautions were not taken against loss by evaporation, 700 grams of absolute alcohol were obtained from 1,000 grams of an 89 per cent. alcohol.

A specimen of Sargent's "95 per cent. alcohol," which had a specific gravity of .8183 at 15.5 degrees C. (and which was therefore a 92.7 per cent. alcohol), when dehydrated, had a specific gravity of .79357 on the average. This corresponds with the lowest figures obtained by Squibs and Mendeleeff, and it would indicate that it was entirely dehydrated. The fact that Yvon¶ has also prepared absolute ethyl alcohol by this method was overlooked until after the above work was completed. The yield of alcohol is very much diminished by decanting from the residual calcium hydroxide, as he did, instead of distilling it off, since fully one-third of the alcohol is held mechanically by the bulky residue.

Butyl Alcohol. The specimen of alcohol used was from Merck & Company. It had a boiling point of 104 degrees C. and a specific gravity of .8059. When treated with calcium carbide it evolved acetylene when slightly warmed. When the action was complete it had a specific gravity of .8043 at 15.5 C. It was found very unsatisfactory to compare this result with the specific gravities given, as various investigators have obtained results which differ widely. Of the four specific gravities we find given for butyl alcohol, it is higher than one, but lower than three of them. The burden of evidence is therefore in favor of its being entirely dehydrated.

Amyl Alcohol. A specimen of Dr. Theodore Schuchardt's alcohol, that had a specific gravity of .8163 (which would of itself indicate that it contained considerable water) evolved acetylene rapidly when treated with calcium carbide and heated to 100 degrees C. When the action was

¶Compt. Rend. 1897, 1181, 1182.

complete it had a specific gravity of .8131. The specific gravity of the anhydrous alcohol* is given as .8148.

From the results given above it will readily be seen that calcium carbide affords a good test for water in alcohols, since it acts upon aqueous alcohol as long as any water remains in it with the evolution of acetylene, especially when slightly warmed. One would also be warranted in concluding that calcium carbide deserves to be ranked with calcium oxide as a dehydrating agent for alcohols.

THE SIOUX CITY WATER SUPPLY.

BY ALFRED N. COOK AND C. F. EBERLY.

A good water supply is one of the greatest boons man can possess. Notwithstanding this fact, it is the one thing above all others, almost, which is likely to receive the least attention. It is well known to those who have given the subject some study that the taste is no criterion by which to judge a water. So often have we known men to declare that a certain water was good because of its excellent taste, often due to chlorides, nitrates, etc., derived from sewage, or outhouses not far distant. So often men will provide their families with every comfort that modern applied science has made possible and yet unknowingly be using a contaminated water supply. This was recently well illustrated by a prosperous professional man of Sioux City who not long since built a new home in Morningside and furnished it with every modern convenience at a cost of several thousands of dollars. Instead of tapping the city water supply which was not far distant, he dug a well and within two or three rods of the well sank a large cess-pool which receives the drain from the kitchen and water closet.

*Allen's Com. Org. Anal., Vol. I, page 165.