

LXXXII.—*The so-called Hydrates of Isopropyl Alcohol.*

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ERLENMEYER, in 1863 (*Annalen*, **126**, 307), announced the existence of a hydrate of isopropyl alcohol of the composition $2C_3H_8O, H_2O$. It was stated to be formed when the aqueous alcohol, after being treated with dry pearl-ash, was digested with anhydrous copper sulphate. It was described as boiling at about 80° , and contained, theoretically, 13.0 per cent. of water. This hydrate has the same percentage composition as ethylic alcohol, and boils at very nearly the same temperature.

Two years later, Linnemann (*Annalen*, 1865, **136**, 40) isolated two more hydrates, $3C_3H_8O, 2H_2O$ and $3C_3H_8O, H_2O$. The first was said to be obtained by careful distillation of aqueous isopropyl alcohol from a water bath. It boiled between 78° and 80° (Bar. 738 mm.) and contained theoretically 16.66 per cent. of water. The second hydrate was procured by treating the first hydrate with dehydrated copper sulphate. It boiled at 81° , and its formula implies that it contained 9.09 per cent. of water.

Lastly, Ruhemann and Carnegie (Trans., 1888, 427) found that an aqueous solution of isopropyl alcohol, after saturation with potash, and desiccation over solid potash, yielded a fourth hydrate, C_3H_8O, H_2O , boiling between 78° and 79° ; this theoretically should contain 23.08 per cent. of water.

Pure dry isopropyl alcohol boils at about 82° . On the addition of water, the boiling point falls, and, as shown by the above statement, to an extent depending, within certain limits, on the amount of added water. All the several hydrates are included within a comparatively small range of boiling point—some 3° or 4° at the outside—whereas the amount of water they contain varies from 9 to 23 per cent.

The action of water in depressing the boiling point of an alcohol is, of course, not peculiar to the case of isopropyl alcohol. It has been observed also in the cases of methyl, ethyl, and allyl alcohol, all of which, like isopropyl alcohol, boil below 100° . I am not aware that this fact has been held to indicate the existence, or to be connected with the presence, of definite hydrates of these alcohols.

In the course of an inquiry concerning the validity of certain methods of determining the amount of ethyl alcohol in commercial fusel-oils, it was necessary to have regard to the possible influence of these hydrates of isopropyl alcohol. Some preliminary experiments on the behaviour of isopropyl alcohol containing water led me to doubt their existence as distinct chemical entities, capable of being definitely isolated. The facts appeared to indicate that, within certain fairly wide limits, water and the alcohol would distil together in indefinite proportions, and a study of the original papers served to render this surmise still more probable. Not only were the boiling points of the so-called hydrates very close together, but they were never quite constant in the case of any particular hydrate. Moreover, the analytical data adduced as evidence of the composition of these substances were not always very conclusive. Thus, in the case of the monohydrate, the percentage amount of hydrogen, in presumably different preparations, varied from 12.6 to 13.7. Lastly, it will have been noticed that the two hydrates, $2C_3H_8O, H_2O$ and $3C_3H_8O, H_2O$ —the one containing 13 and the other 9 per cent. of water—were obtained by the same method of dehydration.

About 300 c.c. of isopropyl alcohol containing a small quantity of water was submitted to distillation, and the distillate collected in three fractions. Bar. 772 mm. Fraction I boiled between 80.2° and 81.2° , and had a relative density of 0.8107 at $4^\circ/4^\circ$. Fraction II boiled between 81.2° and 82.2° , and its relative density was 0.8076 at $4^\circ/4^\circ$. Fraction III boiled between 82.2° and 83.5° , and its relative density was 0.8038 at $4^\circ/4^\circ$. It will be seen that the relative density of each fraction diminishes as the boiling point in-

creases—or, in other words, that the water passes over in largest proportion in the first fractions. To each portion a quantity of anhydrous copper sulphate was added. It was quickly evident, from the different intensity of the green tint, that the greater quantity of the water had distilled over in the fraction of lowest boiling-point.

After a week's agitation with the copper sulphate, the liquid was again distilled into three fractions as before, and the relative densities again taken. Bar. 766 mm. The results were as follows :

	Fraction.	Density at 4°/4°.
I.	80·4°—81·6°.	0·8048
II.	81·6°—82·2°.	0·8028
III.	82·1°—83·2°.	8·8008

The range of boiling point, it will be seen, was but slightly affected, whereas that of the relative density is considerably less. Each fraction was again treated with dehydrated copper sulphate. In the last fraction, the colour of the salt was practically unchanged ; whereas in the others it became slightly green, and most markedly so in the first. As before, the water passed over in largest proportion in the fraction of lowest boiling point.

After another week's contact with the copper sulphate, the alcohol was again submitted to distillation, three fractions being collected, of which the boiling points and relative densities were as follows. Bar. 748 mm. :

	Fraction.	Density at 4°/4°.
I.	80·8°—81·2°	0·8009
II.	81·2°—81·5°	0·8001
III.	81·4°—82·2°	0·7999

The range of boiling point is now seen to be smaller, and the densities are more nearly in accord. On treatment with dehydrated copper sulphate, only the first fraction gave any perceptible green tinge to the salt.

After two more repetitions of this treatment, the whole of the liquid was found to boil between 80·7° and 81·7°, by far the greater portion distilling between 81·2° and 81·3°. Bar. 741 mm. It was collected as before in three fractions, of which the relative densities at 4°/4° were, respectively, 0·7992, 0·7990, 0·7991, that is, the whole liquid was of almost uniform density. It had, apparently, no further action on dehydrated copper sulphate ; the salt remained quite white even after standing in contact with the alcohol for nearly a fortnight.

It would appear, however, that copper sulphate, as in the case of ethylic alcohol, is incapable of removing the last traces of water from isopropyl alcohol. By boiling the alcohol over freshly heated lime, in connection with a reflux condenser for some time, and sub-

sequently distilling, the relative density at $4^{\circ}/4^{\circ}$, taken on two separate fractions, was found to be 0.7982 and 0.7982. At $15^{\circ}/15^{\circ}$, it was 0.7903. No further reduction was observed, and the alcohol thus obtained was regarded as practically anhydrous. Zander found 0.7996 at 0° (*Annalen*, 214, 154). The liquid now boiled almost entirely between 80.9° and 81.4° . Bar. 738 mm. The corrected and reduced boiling point may be taken as 82.1° .

The phenomena observed in distilling a mixture of isopropyl alcohol and water are not peculiar to this particular mixture. Ethylic alcohol, which is supposed to retain water with extraordinary tenacity, exhibits, according to Sömmerring, the same behaviour. Le Bel, by fractionating a 98 per cent. ethylic alcohol, obtained a distillate containing 97.4 per cent., whilst the residue in the flask contained 99.5 per cent. of the alcohol.

It is conceivable, of course, that hydrates of isopropyl alcohol may exist at ordinary temperatures but may suffer more or less dissociation when heated.

The following experiments were made to test this supposition. A quantity of anhydrous isopropyl alcohol was mixed with water in the proportion required by the formula C_3H_8O, H_2O . The relative density of this mixture, the so-called monohydrate, was 0.8485 at $15^{\circ}/15^{\circ}$. It was placed in a suitable vessel over sulphuric acid (which readily absorbs both vapours) within a large bell-jar, and allowed to remain at the ordinary temperature until it had lost 52.9 per cent. of its weight. The relative density of the residue at $15^{\circ}/15^{\circ}$ was now 0.8303, or the percentage amount of alcohol had risen from 76.9 to 84.6. Although the substance, to begin with, presumably consisted wholly of the monohydrate, the water was found to have evaporated faster than the alcohol. The substances were therefore not in stable chemical union even at ordinary temperatures.

A similar experiment was made with a mixture corresponding to Linnemann's 'hydrate,' $3C_3H_8O, 2H_2O$. This had a relative density of 0.8332 at $15^{\circ}/15^{\circ}$. After 96 hours' exposure over the oil of vitriol at the ordinary temperature, the mixture having lost 48 per cent. of its weight, the relative density was 0.8127 at $15^{\circ}/15^{\circ}$; or the proportion of alcohol had risen from 83.3 to 91.7 per cent.

Erlenmeyer's 'hydrate,' $2C_3H_8O, H_2O$, which was found to have a density of 0.8244 at $15^{\circ}/15^{\circ}$, was treated in the same way. After 78 hours' exposure, when the mixture had lost 49.3 per cent. of its weight, its density had fallen to 0.8033; or the percentage amount of alcohol had risen from 86.9 to 94.8.

Hence there is no more evidence of the existence of these 'hydrates,' as stable combinations, at ordinary temperatures, than there is of their existence at higher temperatures. Both the constituents

vaporise together at all temperatures in a state of mixture and not in chemical combination, and at rates depending on their vapour pressures and diffusibilities.

A further proof of this fact is seen in the circumstance that when a stream of air is led through the mixture at ordinary temperatures, the proportion of alcohol increases. A mixture of isopropyllic alcohol and water in the ratio demanded by Linnemann's formula, $3C_3H_8O, H_2O$, and having the relative density 0.8146 at $15^\circ/15^\circ$, was subjected to this treatment. After $7\frac{1}{2}$ hours' passage of the air, when the mixture was found to have lost 54.5 per cent. by weight, its density at $15^\circ/15^\circ$ was 0.8103 , or the amount of alcohol had risen from 90.9 to 92.6 per cent.

It seems therefore established that these so-called hydrates are not definite chemical compounds, but are merely mixtures of the alcohol and water.

When the relative densities of these mixtures are plotted in terms of the amount of water they contain, the values are found to lie on what is very nearly a straight line; or, in other words, the density of the aqueous alcohol is, within the limits studied, very nearly a linear function of the amount of contained water. Hence, between these limits, it is easy to determine the percentage amount of alcohol from the relative density of the mixture.

The following table shows the relative density of a mixture of isopropyllic alcohol and water containing amounts of alcohol varying between 100 and 75 per cent. It is from this table that the amounts of alcohol in the partially evaporated mixtures have been deduced:

Table showing the Relative Density of Mixtures of Isopropyllic Alcohol and Water.

Temp. $15^\circ/15^\circ$.

Alcohol, per cent.	Density.	Alcohol, per cent.	Density.	Alcohol, per cent.	Density.
100	0.7903	91	0.8144	82	0.8365
99	0.7931	90	0.8169	81	0.8389
98	0.7958	89	0.8194	80	0.8412
97	0.7985	88	0.8219	79	0.8436
96	0.8012	87	0.8244	78	0.8459
95	0.8039	86	0.8268	77	0.8483
94	0.8066	85	0.8293	76	0.8506
93	0.8092	84	0.8317	75	0.8529
92	0.8118	83	0.8342		

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