as tannin, etc., or such solutions as ammonia, alum, etc., which can be shown by experiment to produce the desired results; and second, weathering, with its mechanical action and its possible addition of colloids by bacteria.

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LIQUID MIXTURES OF MINIMUM BOILING-POINT.

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THREE YEARS ago one of us, C. D. Holley,[1] presented the results of an investigation of sixteen pairs of liquids of which amyl alcohol or its derivatives formed one constituent. Of these sixteen pairs, five gave mixtures having well-defined minimum boiling-points, two showed no relative elevation or depression of the boiling-point and the remaining nine presented no unusual phenomena. In this paper the writer reports the results obtained with a series of pairs of liquids with propyl and isobutyl derivatives as one of the constituents, together with some miscellaneous curves. The investigations made with carbon tetrachloride were carried out under the direction of the writer by J. T. Weaver in the North Dakota Agricultural College Laboratory.

The apparatus and methods of procedure were the same as described in the previous article, a Hite's apparatus provided with a thermometer reading to fifths being used. A weighed amount of the lower boiling constituent was introduced into the bulb and boiled for several minutes, the boiling-point and barometric pressure being noted. Weighed amounts of the other constituent were added and the successive boiling-points recorded until the liquids were present in nearly equal proportions. The process was then reversed beginning with the higher boiling constituent.

The liquids used were supposed to be chemically pure as purchased, but before being used were further purified by distillation, the first and last fourths being rejected. The bulb of the Hite apparatus was kept covered and the distillation carried on in subdued light, and it is believed that the bromides underwent very slight, if any, decomposition. From twenty-five to thirty readings were made with each pair of liquids, and as the minimum point was approached the successive portions of the added con-

[1] This Journal, **24**, 448 (1902).

stituent were diminished in quantity so that the ratio of the constituents which gave the minimum point was definitely obtained.

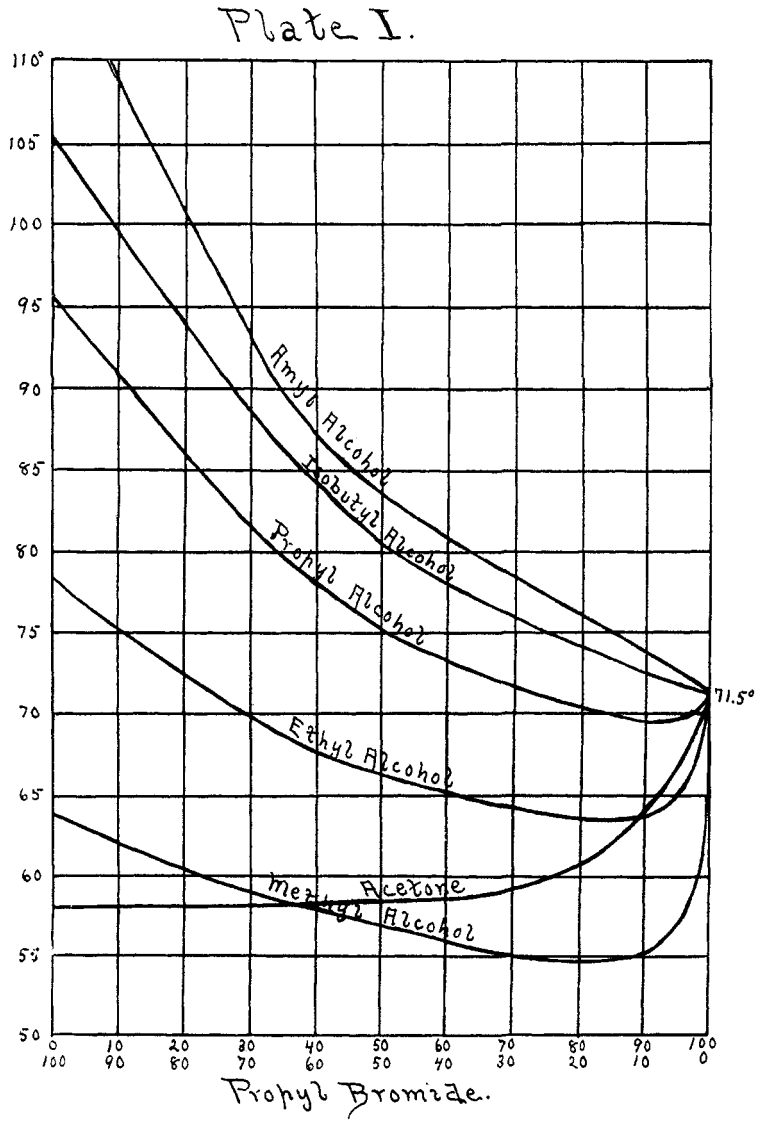
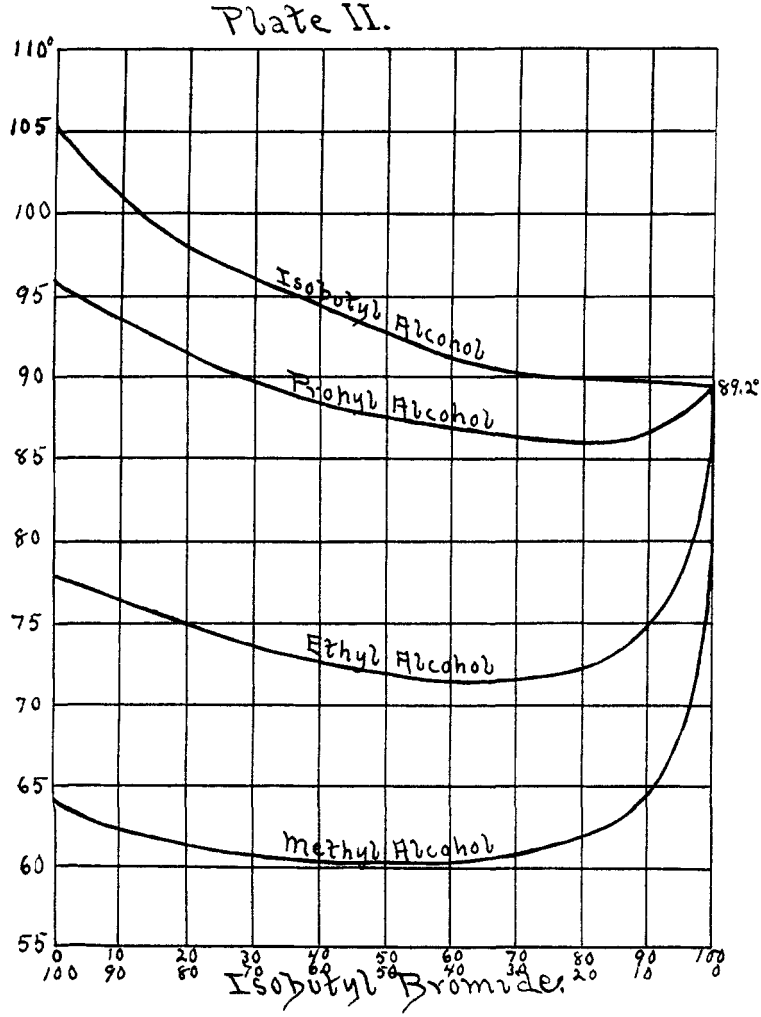


Plate I represents the boiling-point curves for propyl bromide with methyl, ethyl, propyl, isobutyl and amyl alcohols and also

with acetone. The addition of propyl bromide (71.5° C.) to amyl alcohol (129.3° C.) and isobutyl alcohol (105.5° C.) rapidly lowered their boiling-points but did not give a minimum point, though there was a tendency in that direction as indicated by the waviness of the two curves. Propyl alcohol (95.6° C.) gave a mixture having a minimum boiling-point of 69.75° C., in the ratio of 10 parts propyl alcohol to 90 parts propyl bromide, the minimum point being 1.75° below that of propyl bromide, the lower boiling constituent. Ethyl alcohol (78.4° C.) gave a rather interesting curve. It is obvious that the ratio of the constituents can be varied widely and yet give mixtures which have a boiling-point below that of the lower boiling constituent. The minimum point obtained was 63.6° C. or 7.9° below that of the propyl bromide, the ratio at that point being 16.24 parts ethyl alcohol to 83.76 parts propyl bromide. The curve obtained with methyl alcohol (64.0° C.) has the same general characteristics as the preceding ethyl alcohol curve, but much more intensified, the minimum point being 54.8° and the ratio 20.60 parts methyl alcohol to 79.40 parts propyl bromide. The minimum boiling-point obtained was 9.2° below that of the methyl alcohol, the lower boiling constituent. The effect of additions of propyl bromide to acetone was rather odd as it gave neither an appreciable depression nor elevation of the boiling-point until the mixture contained over 60 per cent. propyl bromide, then giving a curve which is characterized by its extreme flatness.

Plate II shows the boiling-point curves of isobutyl bromide (89.2° C.) with methyl, ethyl, propyl and isobutyl alcohols. As in the preceding series of curves isobutyl alcohol does not give a minimum point, though the range between the boiling-points of the isobutyl bromide and isobutyl alcohol is much less than the range between isobutyl alcohol and propyl bromide, the difference being 34° and 15.3° respectively. Isobutyl bromide and propyl alcohol gave a mixture having a minimum boiling-point of 86.1° in the proportions of 19.25 parts propyl alcohol to 80.75 parts isobutyl bromide, the minimum point being 31° below the boiling-point of the isobutyl bromide. Ethyl alcohol gave a mixture with a minimum boiling-point of 71.4° with a ratio of 41.0 parts ethyl alcohol and 59.0 parts isobutyl bromide. As in the preceding series of curves the one obtained with methyl alcohol resembles the ethyl alcohol curve closely, a minimum boiling-point

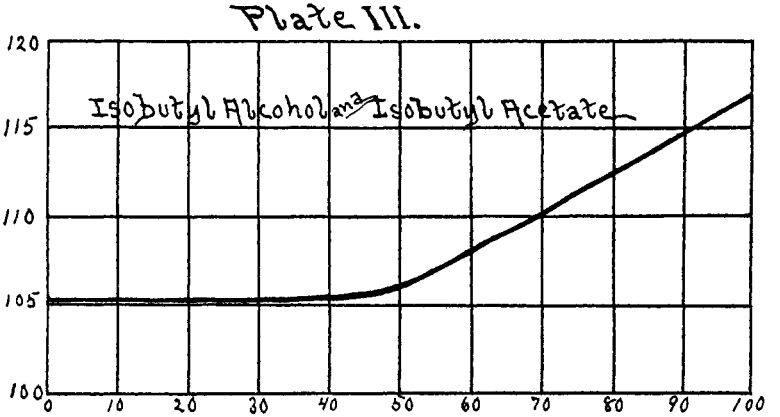
of 60° being obtained, but this point is not definitely located on the curve, as the mixture may contain anywhere from 41 to 56 per cent.



of isobutyl bromide without any resulting change in the boiling-point.

Plate III. Isobutyl alcohol (105.5° C.) and isobutyl acetate (116.3°) as indicatd by the curve did not give a mixture having a minimum boiling-point. The first six additions of isobutyl

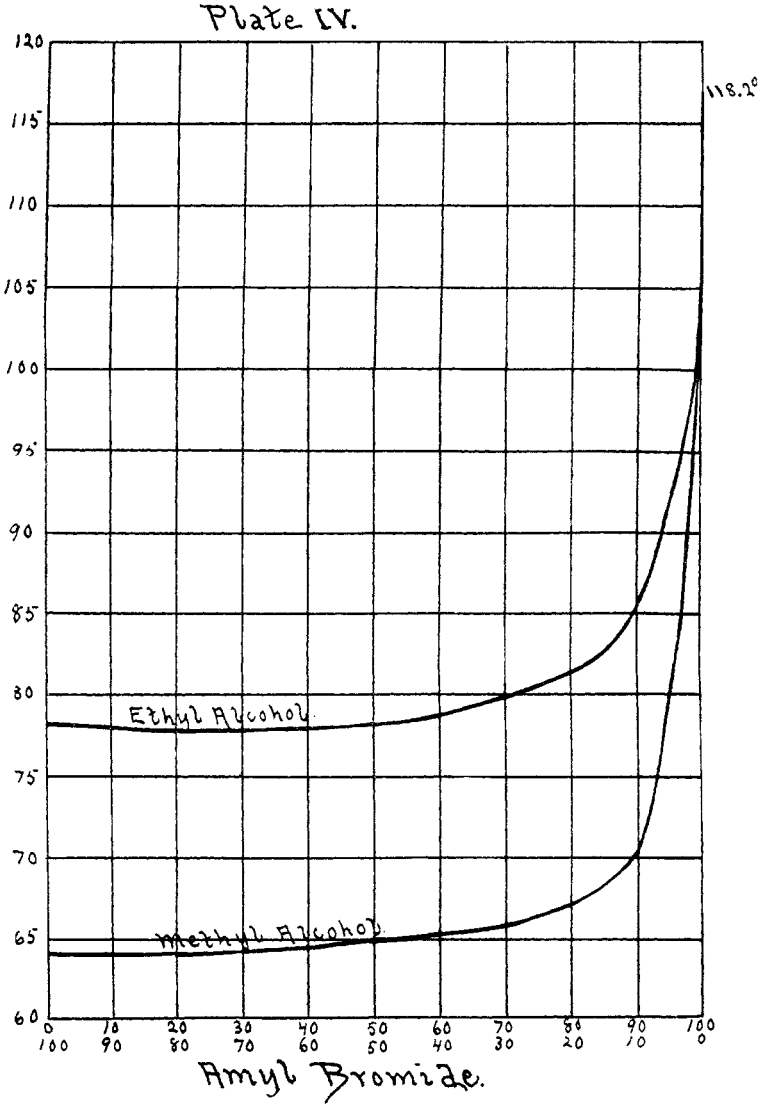
acetate did not lower or raise the boiling-point of the isobutyl alcohol. The mixture contained at this point 40 per cent. isobutyl acetate; further additions of acetate caused a gradual rise of the



boiling-point of the mixture, the remainder of the curve taking the form of a straight line connecting this point with the maximum.

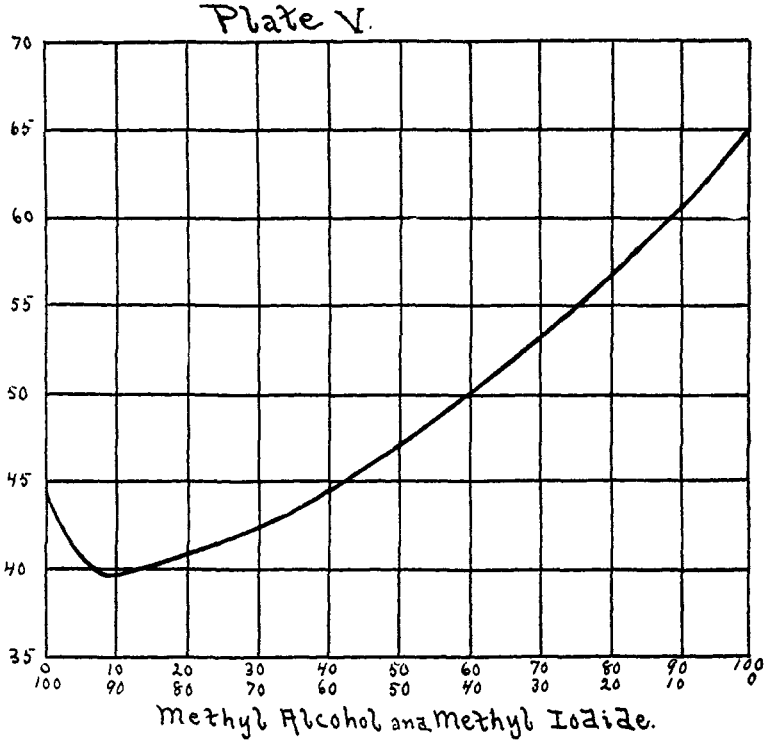
Plate IV represents the completion of the amyl bromide series begun in the writers' previous article. The three higher alcohols, propyl, isobutyl and amyl alcohols, gave mixtures having fairly well-defined minimum boiling-points, though there was the same tendency toward flatness that is exemplified to a marked degree in the two curves here shown; ethyl alcohol (78.3° C.) and amyl bromide (118.2° C.) gave a mixture having a minimum boiling-point of 77.3° C. in the ratio of 72.0 parts ethyl alcohol to 28.0 parts amyl bromide. The minimum point is not as clearly defined as with the higher alcohols. The additions of as much as 10 per cent. of amyl bromide caused no change in the boiling-point of the methyl alcohol (64.0° C.), further additions causing slight elevations of the boiling-point of the mixture. The effect of very small additions of either methyl or ethyl alcohol to pure amyl bromide is to be noticed, the boiling-point of the amyl bromide being lowered nearly (50° C.) by the addition of 5 per cent. of methyl alcohol.

Plate V. Methyl alcohol (64.8° C.) and methyl iodide (44.5° C.) gave a mixture having a minimum boiling-point of 39.6° C. in the ratio of 8 parts methyl alcohol to 92 parts methyl iodide. The



curve drops very abruptly to the minimum, which is very close to the methyl iodide side, then rises in a sweeping curve to the maximum.

Plate VI. Contrary to expectation butyric acid and bromoform gave a mixture having a minimum boiling-point. The

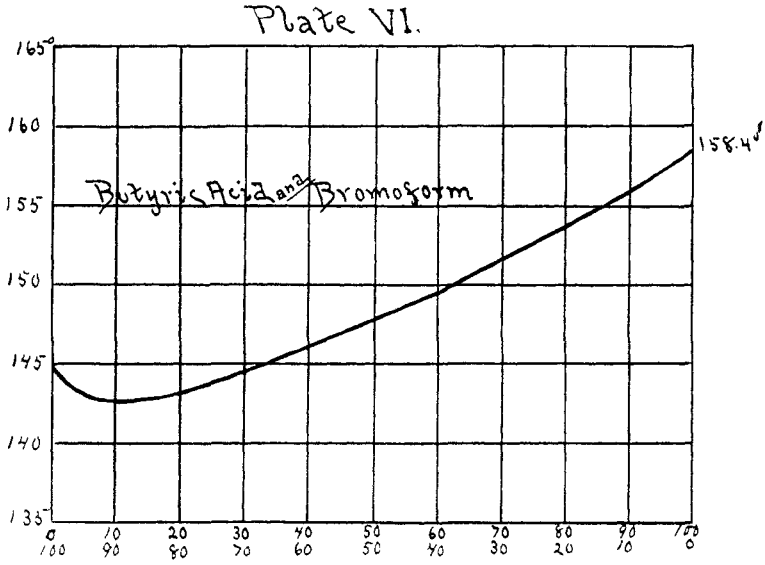


butyric acid used was obtained from Richards & Co., and though marked "C. P." was a very poor article. After several fractional distillations, a portion consisting of about 40 per cent. of the original amount was obtained which distilled between 158° C. and 159° C. The bromoform was obtained from the same company. After several distillations its boiling-point was much lower that it should have been. A portion was obtained finally which distilled uniformly at 145.5° C. A further quantity was procured from Merck & Co. but gave no better results.

The minimum boiling-point obtained was 142.6° C., the proportion being 87.5 parts bromoform and 12.5 parts butyric acid. The curve does not present any unusual characteristics.

Plate VII. Carbon tetrachloride with propyl alcohol, benzene and toluene. This plate shows the boiling-point curves obtained with mixtures of carbon tetrachloride (76.7° C.) with propyl alcohol (95.5° C.), benzene (79.6° C.), and toluene

(110.3° C.), respectively. Propyl alcohol gave a mixture having a minimum boiling-point of 72.6°, the ratio being 11.80 parts



propyl alcohol and 88.20 parts of carbon tetrachloride. The curve drops rapidly to the minimum point and then rises in nearly a straight line to the maximum. Carbon tetrachloride and benzene, which from the closeness of their respective boiling-points might be expected to yield a boiling-point curve with a well-defined minimum point, do not present any unusual phenomena at all, the curve being very nearly a straight line as is also the curve obtained with toluene and carbon tetrachloride.

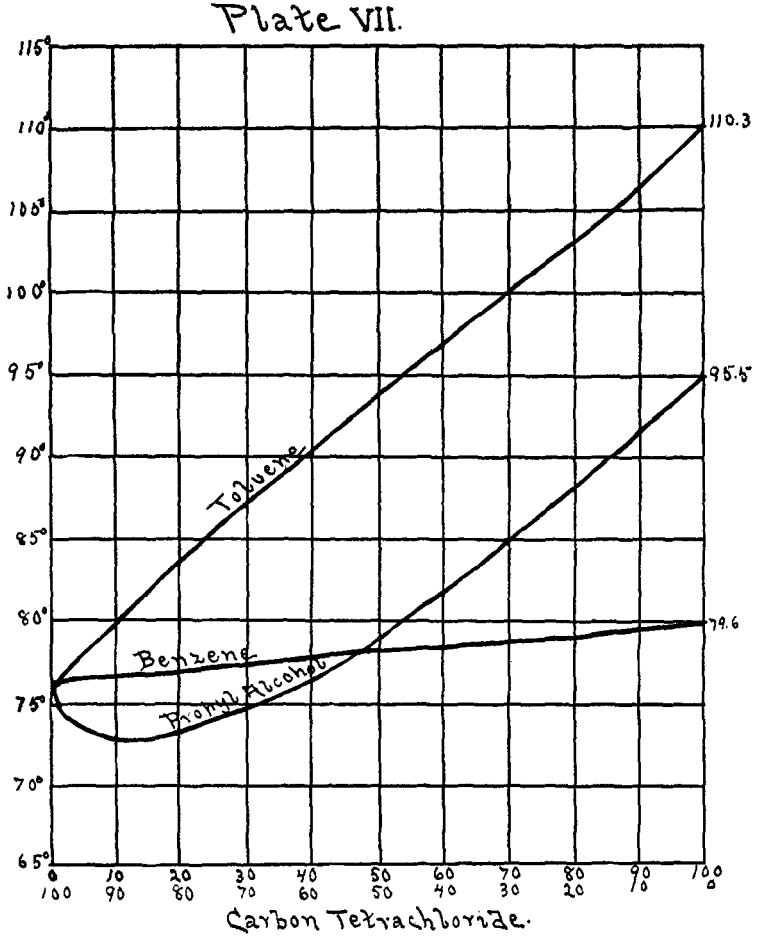
The following pairs of liquids were experimented with but no mixtures giving a minimum boiling-point were obtained:

Isobutyl alcohol (105.5° C.) and ethyl butyrate (120.6° C.).
Isobutyl alcohol (105.5° C.) and amyl acetate (137.5° C.).
Isobutyl iodide (120.4° C.) and bromoform (147.0° C.).
Isobutyl iodide (120.4° C.) and amyl acetate (137.5° C.).
Isobutyl iodide (120.4° C.) and ethylene bromide (129.8° C.).
Brombenzene (129.9° C.) and ethylene bromide (129.8° C.).
Bromoform (147.2° C.) and ethylene bromide (129.8° C.).

CONCLUSION.

Of the twenty-five pairs reported on in this investigation ten

gave mixtures having minimum boiling-points, three showed no relative elevation or depression of the boiling-point, and the remaining twelve pairs presented no unusual phenomena. As shown in the previous investigation, the chemical constitution



exercised a greater influence on the formation of mixtures with minimum boiling-points than the close proximity of the boiling-points of the constituents. One constituent remaining the same, mixtures with substances of similar chemical constitution yield similar boiling-point curves.

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