arated melting at 33°, the melting-point of methyl cinnamate. This product was then distilled, and the boiling-point also agreed with that of methyl cinnamate. The yield after all this treatment was found to be 15 grams or 60 per cent. of the calculated.

The *dibromide from 2,4-dinitrostilbene* (15 grams), when boiled with alcoholic potassium thiocyanate, gave 6 grams of pure 2,4-dinitrostilbene or 64 per cent. of the calculated.

The *dibromide from the nitrile of phenyl cinnamic acid* (60 grams) gave 24 grams of the unsaturated product or 70 per cent. of the calculated. These yields do not represent the total amount of unsaturated material formed, since no special effort was made to obtain the entire amounts.

NEW HAVEN, CONN.,
February 10, 1902.

LIQUID MIXTURES OF MINIMUM BOILING-POINT.

BY CLIFFORD D. HOLLEY.

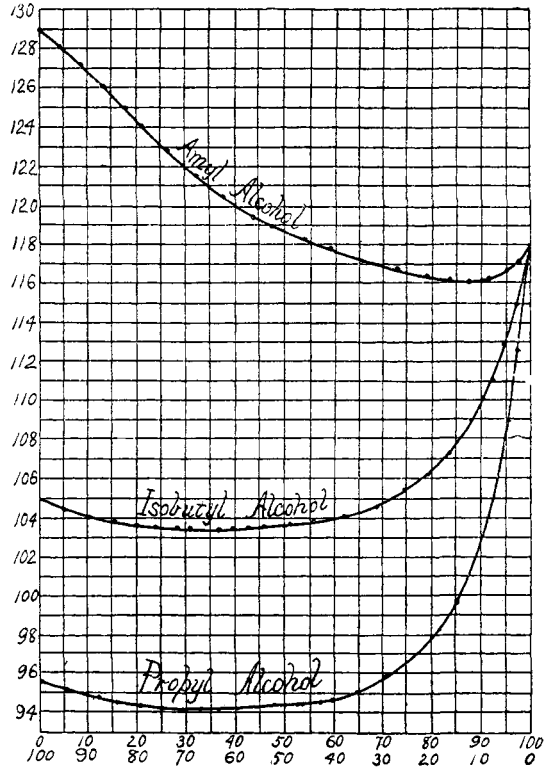
Received January 24, 1902.

IN 1899, Dr. Garnett Ryland[1] reported the results of an investigation of 80 pairs of the more common liquids. He found that 45 furnished mixtures which distilled in the same proportions with a constant boiling-point below the boiling-points of the constituent liquids; one which presented no relative depression or elevation of the boiling-point; and 3 which were of an uncertain character. During the same year, E. F. Thayer[2] and J. K. Haywood[3] investigated several of the same mixtures, but instead of following the method of Ryland, and determining the minimum-point by repeated distillations, they determined the boiling-points of several mixtures of the liquid constituents, and plotted the resulting boiling-point curve. From a comparison of the two methods it is seen that the proportion in which two liquids give a minimum point on the boiling-point curve is the same in which they distil with a constant boiling-point which lies below that of either liquid constituent, and the boiling-points are the same in both cases. But little having been done along this line during the past two years, it seemed desirable to add to our knowledge of such phenomena, and continue the investigations of such systems as would be likely to furnish mixtures of minimum boiling-point.

[1] *Am. Chem. J.*, **22**, No. 5.
[2] *Jour. Phys. Chem.*, **2**, 382; **3**, 32.
[3] *Ibid.*, **2**, 317.

In this paper are presented the results obtained with amyl compounds as one of the liquid constituents.

The boiling-point method was chosen as the more preferable, as in the distillation of bromides and iodides the formation of tarry residues towards the close of the distillation renders the thermometer readings inaccurate. A slightly modified form of Hite's apparatus was used. Instead of a differential thermometer,



Amyl bromide.

one of the ordinary type was provided. It was graduated to fifths of a degree centigrade but with a scale so large that twentieths could be readily estimated.

A weighed amount of the lower boiling constituent was introduced into the bulb of Hite's apparatus, boiled for several minutes and the boiling-point and barometric pressure recorded. Weighed amounts of the other constituents were added, the successive boil-

ing-points noted, and this procedure was continued until the liquids were present in nearly equal proportions. The flask was then emptied and the process reversed, weighed portions of the first being added to a weighed amount of the second constituent. The results obtained are shown in the form of a plot. No corrections were applied to the curves because of variations of barometric pressure, as the error thus introduced is believed to be inappreciable. The liquids used were purified by redistillation, usually the first and last fourth being rejected. The portions reserved distilled at a very nearly uniform temperature.

In experimenting with mixtures of amyl iodide the bulb of Hite's apparatus was covered, and the investigation carried on in very subdued light, but even with these precautions the mixtures were noticeably colored towards the close of the operations from the separation of free iodine.

TABLE I.—AMYL BROMIDE AND AMYL ALCOHOL.

No.	Amyl bromide. Per cent.	Amyl alcohol. Per cent.	Temperature. °C	Barometer. mm.
1	100.00	0.00	117.9	764.1
2	97.68	2.32	117.2	764.1
3	95.04	4.96	116.8	764.1
4	91.39	8.61	116.35	764.0
5	87.33	12.67	116.15	764.0
6	83.40	16.60	116.3	764.0
7	79.22	20.78	116.4	764.0
8	73.12	26.88	116.8	764.0
9	65.58	34.42	117.25	763.9
10	59.38	40.62	117.9	763.9
11	53.98	46.02	118.4	763.9
12	47.44	52.56	118.9	763.8
13	43.00	57.00	119.5	763.8
14	43.29	56.71	119.0	763.8
15	37.91	62.09	120.3	763.8
16	32.40	67.60	121.5	763.8
17	26.86	73.14	122.7	763.7
18	21.03	78.97	124.0	763.7
19	17.32	82.68	124.9	763.7
20	13.28	86.72	126.0	763.6
21	9.02	90.98	127.0	763.5
22	4.23	95.77	128.1	763.5
23	0.00	100.00	129.0	763.4

TABLE II.—ISOBUTYL ALCOHOL AND AMYL BROMIDE.

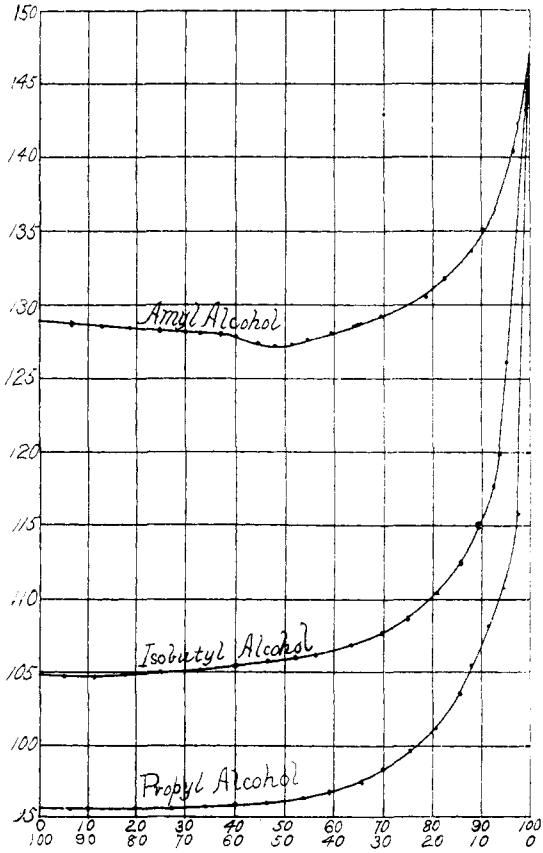
No.	Isobutyl alcohol. Per cent.	Amyl bromide. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	105.0	757.8
2	94.88	5.12	104.3	757.8
3	89.50	10.50	104.0	757.8
4	84.33	15.67	103.8	757.8
5	79.92	20.08	103.65	757.8
6	76.35	23.65	103.6	757.8
7	72.96	27.04	103.55	757.5
8	69.36	30.34	103.5	757.5
9	66.63	33.37	103.45	757.5
10	63.63	36.37	103.4	757.4
11	60.70	39.30	103.45	757.4
12	57.48	42.52	103.5	757.5
13	54.56	45.44	103.6	757.5
14	51.37	48.63	103.7	757.4
15	48.10	51.90	103.75	757.4
16	44.32	55.68	103.8	757.4
17	38.08	61.92	104.1	757.4
18	31.28	68.72	104.6	757.3
19	25.55	74.45	105.4	757.3
20	20.56	79.44	106.2	757.3
21	16.55	83.45	107.4	757.3
22	12.22	87.88	109.0	757.3
23	7.89	92.11	111.2	757.2
24	6.01	93.99	112.9	757.0
25	2.73	97.27	115.0	757.0
26	0.00	100.00	118.1	757.0

Table I. Amyl Alcohol and Amyl Bromide.—In the accompanying plot the left-hand ordinate represents 100 parts amyl alcohol. Amyl bromide (117.9°) and amyl alcohol (129.0° C.) furnish a mixture with a minumum boiling-point of 116.15° C. in the proportion of 12.7 parts amyl alcohol, and 87.3 parts amyl bromide. The minimum point is definitely defined. The first additions of amyl alcohol cause a rapid lowering of the boiling-point followed by a gradual rise until the maximum is reached. The curve exhibits a distinctly wavy tendency.

Table II. Isobutyl Alcohol and Amyl Bromide.—Isobutyl alcohol (105°) and amyl bromide (118.1°) in the proportion of 63.6 parts isobutyl alcohol to 36.4 parts amyl bromide, gives a mixture having a minimum boiling-point of 103.4° C. The major portion of the curve is very flat, and the minimum point is not sharply marked. From the curve it is seen that isobutyl alcohol can be diluted with amyl bromide until it contains nearly 43 per cent. of

the latter before the boiling-point of the mixture is raised above that of isobutyl alcohol.

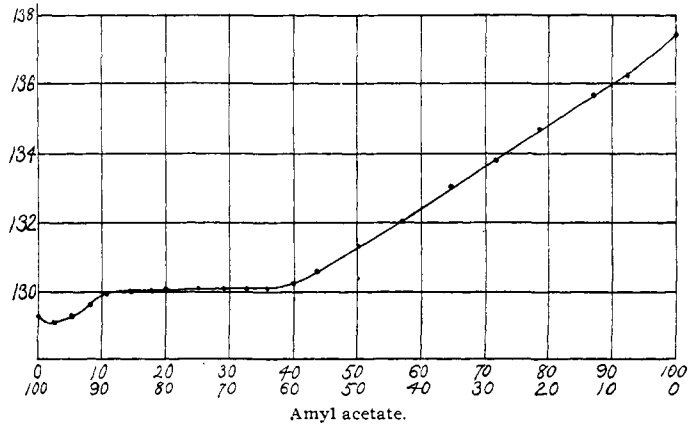
Table III. Propyl Alcohol and Amyl Bromide.—A mixture of propyl alcohol (95.5°), and amyl bromide (118.2°), in the proportions of 70.7 parts propyl alcohol to 29.3 parts amyl bromide, gives



a minimum point of 94°. The curve descends in a nearly straight line to the minimum, then rises very gradually at first, but at last with great abruptness to the maximum. Propyl alcohol may contain as much as 65 per cent. of amyl bromide without raising its boiling-point.

Table IV. Amyl Alcohol and Amyl Iodide.—Amyl alcohol

(128.9°) and amyl iodide (146.5°) furnish a mixture having a minimum boiling-point of 127.3° in the proportion of 52 parts amyl alcohol to 48 parts amyl iodide. The minimum point is



fairly well defined; the major portion of the curve is quite flat, and it is evident that amyl alcohol may contain as much as 65 per cent. of amyl iodide and still have a boiling-point below that of pure amyl alcohol.

TABLE III.—PROPYL ALCOHOL AND AMYL BROMIDE.

No.	Propyl alcohol. per cent.	Amyl bromide. per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	95.5	762.8
2	94.42	5.58	95.2	762.8
3	88.05	11.95	94.8	762.8
4	83.78	16.22	94.6	762.8
5	79.55	20.45	94.4	762.8
6	74.81	25.19	94.2	762.8
7	70.70	29.30	94.0	762.8
8	66.99	33.01	94.1	762.8
9	63.69	36.31	94.15	762.8
10	59.85	40.15	94.2	763.0
11	55.98	44.02	94.25	763.0
12	52.09	47.91	94.3	763.0
13	47.94	52.06	94.4	763.0
14	46.60	53.40	94.4	763.0
15	43.01	56.99	94.5	763.1
16	40.50	59.50	94.7	763.1
17	35.35	64.65	95.2	763.1
18	29.02	70.98	95.9	763.3
19	23.24	76.76	96.9	763.3

No.	Propyl alcohol. Per cent.	Amyl bromide. Per cent.	Temperature. °C.	Barometer mm.
20	18.23	81.77	98.3	763.3
21	14.81	85.19	99.6	963.4
22	11.38	88.62	101.6	763.4
23	8.77	91.23	103.85	763.4
24	6.49	93.51	106.2	763.6
25	4.36	95.64	109.1	763.6
26	2.14	97.86	112.6	763.6
27	0.00	100.00	118.2	763.6

TABLE IV.—AMYL ALCOHOL AND AMYL IODIDE.

No.	Amyl alcohol. Per cent.	Amyl iodide. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	128.9	758.6
2	93.57	6.43	128.6	758.6
3	87.47	12.53	128.4	758.6
4	81.19	18.81	128.3	758.6
5	74.80	25.20	128.2	758.6
6	70.19	29.81	128.18	758.7
7	67.46	32.54	128.05	758.7
8	63.26	36.74	127.9	758.7
9	60.08	39.92	127.7	758.6
10	56.18	43.82	127.4	758.6
11	51.98	48.02	127.3	758.6
12	48.89	51.11	127.4	758.7
13	45.84	54.16	127.6	758.0
14	40.48	59.52	128.0	758.0
15	35.60	64.40	128.6	758.0
16	30.32	69.68	129.3	758.1
17	21.28	78.72	130.6	758.1
18	18.12	81.88	132.0	758.1
19	12.64	87.36	133.7	758.1
20	10.10	89.90	135.2	758.1
21	7.43	92.57	136.5	758.3
22	3.16	96.84	140.5	758.3
23	2.04	97.96	142.3	758.3
24	0.00	100.00	146.5	758.3

TABLE V.—ISOBUTYL ALCOHOL AND AMYL IODIDE.

No.	Isobutyl alcohol. Per cent.	Amyl iodide. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	104.8	747.4
2	94.88	5.12	104.7	747.4
3	83.36	11.64	104.7	747.4
4	82.35	17.65	104.8	747.3
5	74.99	25.01	105.0	747.5
6	67.56	32.44	105.3	747.5
7	59.67	40.33	105.5	747.5

No.	Isobutyl alcohol. Per cent.	Amyl iodide. Per cent.	Temperature. °C.	Barometer. mm.
8	53.87	46.13	105.8	747.5
9	47.88	52.12	106.1	747.5
10	43.40	56.60	106.2	747.5
11	36.86	63.14	106.9	747.8
12	29.92	70.08	107.8	747.8
13	25.39	74.61	108.7	747.8
14	19.20	80.80	110.4	747.8
15	14.48	85.52	112.6	747.8
16	11.00	89.00	115.0	747.8
17	7.73	92.27	117.8	748.0
18	5.26	94.74	121.0	748.0
19	2.32	97.68	126.0	748.0
20	0.00	100.00	146.5	748.1

Table V. Isobutyl Alcohol and Amyl Iodide.—Isobutyl (104.8°) alcohol and amyl iodide (146.5°) do not give a mixture having a definite minimum boiling-point. The first two additions of amyl iodide caused a lowering of the boiling-point of 0.1° C. This was followed by a gradual rise until the mixture contained about 70 per cent. of amyl iodide, when the boiling-point rose with great abruptness to the maximum.

TABLE VI.—PROPYL ALCOHOL AND AMYL IODIDE.

No.	Propyl alcohol. Per cent.	Amyl iodide. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	95.7	753.8
2	93.36	6.64	95.6	753.8
3	89.94	10.06	95.65	753.8
4	79.91	20.09	95.7	753.8
5	73.06	26.94	95.8	753.8
6	66.16	33.84	95.9	753.8
7	59.90	40.10	96.1	753.8
8	54.38	45.62	96.3	753.7
9	46.15	53.85	96.6	753.4
10	41.08	58.92	96.9	753.4
11	36.50	65.40	97.6	753.4
12	30.27	69.73	98.4	753.4
13	24.90	75.10	99.7	753.4
14	19.19	80.81	101.4	753.4
15	14.78	85.22	103.4	753.5
16	11.48	88.52	105.6	753.5
17	8.64	91.36	108.2	753.2
18	5.95	94.05	110.8	753.2
19	3.07	96.93	115.6	753.2
20	0.00	100.00	146.5	753.2

TABLE VII.—AMYL ALCOHOL AND AMYL ACETATE.

No.	Amyl alcohol. Per cent.	Amyl acetate. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	129.3	770.4
2	97.36	2.64	129.1	770.4
3	94.58	5.42	129.3	770.4
4	91.84	8.16	129.55	770.4
5	89.10	10.90	129.9	770.4
6	85.42	14.58	129.95	770.3
7	82.06	17.94	130.0	770.3
8	78.48	21.52	130.0	770.3
9	74.80	25.20	130.05	770.3
10	71.27	28.73	130.01	770.3
11	67.62	32.38	130.01	770.1
12	64.16	35.84	130.1	770.0
13	60.08	39.92	130.2	770.0
14	56.87	43.13	130.5	770.0
15	50.04	49.96	131.3	769.6
16	42.88	57.12	132.0	769.6
17	35.21	64.79	133.0	769.7
18	27.83	72.17	133.8	769.8
19	20.85	79.15	134.55	769.8
20	17.80	82.20	135.5	769.9
21	7.49	92.51	136.2	769.9
22	0.00	100.00	137.5	770.0

Table VI. Propyl Alcohol and Amyl Iodide.—Propyl alcohol (95.7°) and amyl iodide (146.5) give results very similar to those obtained with isobutyl alcohol and amyl iodide. There is a slight lowering of the boiling-point, 0.1°, by the first two additions of propyl alcohol. The major portion of the curve is slightly flatter than with isobutyl alcohol and the abrupt ascent to the maximum more marked.

Table VII. Amyl Alcohol and Amyl Acetate.—Amyl alcohol (129.3°) and amyl acetate (137.5°) give a mixture having a minimum boiling-point of 129.1° in the ratio of 97.4 parts amyl alcohol to 2.6 parts amyl acetate. A second determination was made, and the same result obtained. The curve exhibits some marked peculiarities. There is at first a slight lowering of the boiling-point followed by a corresponding rise; the curve then becomes perfectly flat until the mixture contains 40 per cent. amyl acetate, when the curve rises in a straight line to the maximum.

The following pairs of liquids were investigated, but no mixtures of minimum boiling-point were obtained:

Amyl alcohol	129°	and ethyl butyrate	120.6°
Amyl alcohol	129°	and bromoform	147.1°
Amyl acetate	137.5°	and ethylene bromide	129°
Amyl acetate	137.5°	and amyl bromide	118°
Amyl acetate	137.5°	and amyl iodide	146.5°
Amyl acetate	137.5°	and bromoform	147.1°
Amyl acetate	137.5°	and ethyl butyrate	120.6°
Amyl bromide	118°	and ethyl butyrate	120.6°
Amyl bromide	118°	and toluene	109.5°

Of the 16 pairs of liquids investigated, 5 gave mixtures having well-defined minimum boiling-points, while 2 showed no relative elevation or depression of the boiling-point.

The chemical constitution of the constituents exercises a greater influence in the formation of mixtures with minimum boiling-points than the close proximity of the boiling-points of the constituents. One constituent remaining the same, or with constituents closely related, mixtures with substances of similar chemical constitution yield similar boiling-point curves.

In the next paper the writer hopes to present the results obtained with propyl and isobutyl compounds.

UNIVERSITY OF MAINE.

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

THE VOLUMETRIC ESTIMATION OF ALUMINA, AND FREE AND COMBINED SULPHURIC ACID IN ALUMS.

BY ALFRED H. WHITE.

Received January 25, 1902.

IN judging the quality of an alum, among the important determinations are those which give the amount of soluble alumina and the amount of sulphuric acid in combination with it or existing as free acid. The alumina may be satisfactorily estimated gravimetrically, but the method is tedious. A gravimetric estimation of the sulphuric acid gives not only that combined with aluminum plus that present as free sulphuric acid, but also that present as sodium sulphate, etc., and the amount of alkalies must be known before the amount of sulphuric acid combined with aluminum can be determined.

The determination of free sulphuric acid in alums by volumetric means has been repeatedly attempted. The hydrolysis of aluminum sulphate prevents direct titration with an alkali, since as fast as the free acid present is neutralized, more is formed by hydrol-