due to Dr. W. Frear of this experiment station for advice and suggestions in the preparation of these papers; to Dr. G. G. Pond of the Pennsylvania State College for the use of a refractometer, and to Dr. F. E. Tuttle of the same institution for assistance in making combustions; also to Mr. C. W. Norris of this experiment station, who made many of the determinations of specific gravity and melting-point contained in the tables of these articles, and who also rendered valuable assistance in determining calories of combustion. We also wish to express our indebtedness to Messrs. A. N. Diehl and C. P. Beistle of this station for their kindly aid at various stages of the laboratory work.

[CONTRIBUTION FROM THE CHEMICAL DIVISION, UNITED STATES DEPARTMENT OF AGRICULTURE, No. 35.]

SOME BOILING-POINT CURVES.

PAPER II.

J. K. HAYWOOD.

Received July 10, 1899.

In a recent paper on boiling-point curves[1] I presented the results of my work on mixtures of organic liquids in which alcohol, acetone and chloroform respectively was one of the constituents. In the following paper I have worked out the curves for mixtures in which benzene and methyl alcohol, respectively, is one of the constituents.

The apparatus and thermometer used were the same as those employed in my previous work and, therefore, need no description. All of the chemicals used were purified as I have already described, with the addition of benzene, which was first allowed to stand over sulphuric acid to both dry and remove any possible traces of thiophene and then decanted and distilled through a high column. None of the purified materials varied more than 0.5° C. in their boiling-point and nearly all not more than 0.1° C.

All readings were made at the prevailing atmospheric pressure and in no case was the variation great enough to seriously affect the accuracy of the results. For purposes of comparison the curve for benzene and alcohol by Thayer,[2] for benzene and carbon

[1] *J. Phys. Chem.*, **3**, 317 (1899).

[2] *Ibid.*, **2**, 382 (1898).

disulphide by Carveth,[1] for methyl alcohol and acetone and methyl alcohol and chloroform by myself, are included.

Following are the analytical data and charts, in which the temperatures are plotted as ordinates and the percentage compositions by weight as abscissas:

BENZENE AND CHLOROFORM.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.3	761.5	45.2	72.65	761.5
85.1	78.85	761.5	40.5	71.7	761.4
70.4	76.9°	761.5	34.1	70.35	761.4
61.9	75.65	761.5	27.7	68.9	761.4
55.9	74.6	761.5	18.8	66.7	761.4
52.0	73.9°	761.5	8.2	63.9	761.4
47.3	73.025	761.4	0.0	61.6	761.4

BENZENE AND CARBON TETRACHLORIDE.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.35	763.1	45.5	78.3	763.6
82.1	79.8	763.1	40.2	78.1	763.6
73.5	79.4	763.1	35.2	77.9	763.6
66.1	79.15	763.1	28.6	77.65	763.6
59.4	78.9	763.0	19.7	77.35	763.6
51.9	78.6	763.0	10.7	77.1	763.6
47.7	78.4	763.0	0.0	76.925	763.7

BENZENE AND ETHER.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.3	762.9	46.4	47.8	760.7
83.2	67.5	762.9	41.4	46.1	760.7
72.8	60.65	762.9	36.0	44.35	760.8
64.3	55.95	762.7	29.3	42.3	760.9
56.1	52.0	762.4	14.4	38.15	761.0
51.4	50.05	762.0	0.0	34.75	761.1
47.4	48.5	762.0	....	....	....

BENZENE AND ACETONE.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.5	767.2	49.8	62.0	766.5
87.1	72.2	767.1	47.2	61.6	766.5
78.2	68.55	767.0	41.1	60.75	766.6
68.9	65.85	76.70	33.6	59.8	766.6
60.2	63.9	76.70	23.8	58.75	766.6
54.3	62.8	767.0	9.9	57.5	766.6
50.3	62.1	767.0	0.0	56.7	766.7

[1] *J. Phys. Chem.*, 3, 193 (1899).

BENZENE AND METHYL ALCOHOL.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.25	760.8	56.8	58.3	760.5
92.7	60.95	760.8	51.4	58.4	760.5
89.7	59.85	760.8	49.3	58.42	760.4
87.5	59.4	760.8	46.8	58.45	759.5
83.4	58.92	760.8	42.5	58.6	759.5
81.2	58.8	760.8	35.3	59.0	759.6
76.2	58.525	760.8	26.3	59.8	759.7
73.9	58.475	760.8	16.5	61.2	759.8
69.7	58.4	760.8	6.9	63.2	759.8
65.7	58.3	760.8	0.0	65.0	759.9
61.8	58.3	760.7	....	....	....

METHYL ALCOHOL AND ETHYL ALCOHOL.

Per cent. methyl alcohol.	Temperature.	Barometer.	Per cent. methyl alcohol.	Temperature.	Barometer.
100.	65.1	762.7	46.0	70.65	762.5
88.1	66.1	762.7	42.4	71.15	762.5
74.6	67.35	762.7	36.5	72.0	762.5
65.4	68.3	762.7	24.9	73.9	762.5
55.9	69.4	762.7	11.1	76.5	762.5
50.0	70.1	762.7	0.0	78.75	762.5
46.2	70.6	762.7	....	....	....

METHYL ALCOHOL AND CARBON TETRACHLORIDE.

Per cent. methyl alcohol.	Temperature.	Barometer.	Per cent. methyl alcohol.	Temperature.	Barometer.
100.	65.2	765.1	40.6	56.6	765.3
93.9	64.0	765.1	38.5	56.475	765.5
87.2	62.7	765.1	31.8	56.2	765.5
75.0	60.5	765.2	24.9	56.0	765.5
64.0	58.85	765.2	20.7	55.97	765.5
59.6	58.3	765.3	18.4	55.95	765.5
54.9	57.8	765.3	15.0	56.0	765.5
51.6	57.45	765.4	11.1	56.1	765.3
48.6	57.2	765.4	7.4	56.35	765.3
45.6	56 9	765.4	5.9	56.6	765.3
42.1	56.7	765.4	0.0	77.2	765.3

METHYL ALCOHOL AND ETHER.

Per cent. methyl alcohol.	Temperature.	Barometer.	Per cent. methyl alcohol.	Temperature.	Barometer.
100.	65.15	765.3	39.1	40.1	765.3
85.3	57.7	765.3	36.5	39.55	765.3
70.4	50.2	765.3	36.2	39.42	765.1
63.1	47.1	765.3	30.7	38.5	765.1
56.2	44.7	765.3	18.4	36.6	765.1
49.7	42.7	765.3	0.0	34.85	765.1
44.5	41.4	765.3	....	....	....

Chart I represents the results obtained in mixtures where benzene was one constituent. The curve for carbon tetrachloride has already been worked out by Lehfelt,[1] by measuring the vapor-pressure with varying composition, the temperature being kept constant. Since it rested on so few measurements, however, I have thought it worth while to repeat his work. The results obtained were very much the same as those already given by Lehfelt. The curve has no maximum or minimum point and presents no unusual features other than the absence of such a point when the boiling-point of the constituents lie so close together.

The curves for chloroform, acetone, carbon disulphide and ether have neither maximum nor minimum point and present no unusual features. The curve for methyl alcohol, like that for ethyl alcohol, has a minimum point at about 58.3° C. Owing to the flatness of the curve at this point, however, the exact composition of the constant boiling mixture can not be given from my work. We can only say that it lies somewhere between 53 and 67 per cent. of benzene. The methyl alcohol curve cuts the ether curve at a composition of about sixty-nine per cent. benzene, the carbon disulphide curve at a composition of about fifty-five per cent. benzene, the acetone curve at a composition of about thirty-one per cent. benzene, and the chloroform curve at a composition of about six per cent. benzene.

In Chart II the results are given for mixtures of the various liquids with methyl alcohol. The curve for ethyl alcohol has neither maximum nor minimum point, which we might expect since the boiling-points of these two liquids are rather close together. But, here again, as in the carbon tetrachloride and chloroform curve, presented in my first paper, the close chemical relationship of these two compounds may be a strong modifying influence.

The curve for benzene has a minimum point at about 58.3° C. and a composition of fifty-three to sixty-seven per cent. benzene. The curve for carbon tetrachloride has a minimum point at about 55.95° C. and a composition of 18.4 per cent. methyl alcohol. The curve for ether has neither maximum nor minimum point and presents no unusual features. The curves for chloroform

[1] *Phil. Mag.*, and *J. of Science*, **46**, No. 278 (1898).

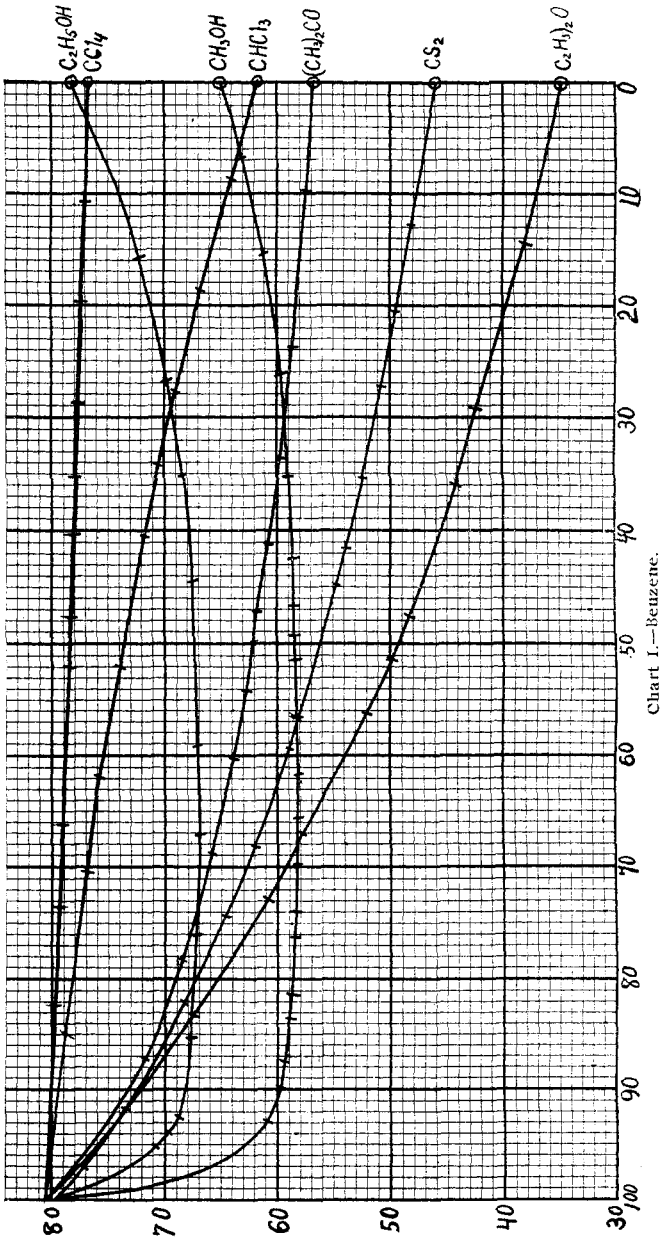

Chart 1.—Benzene.

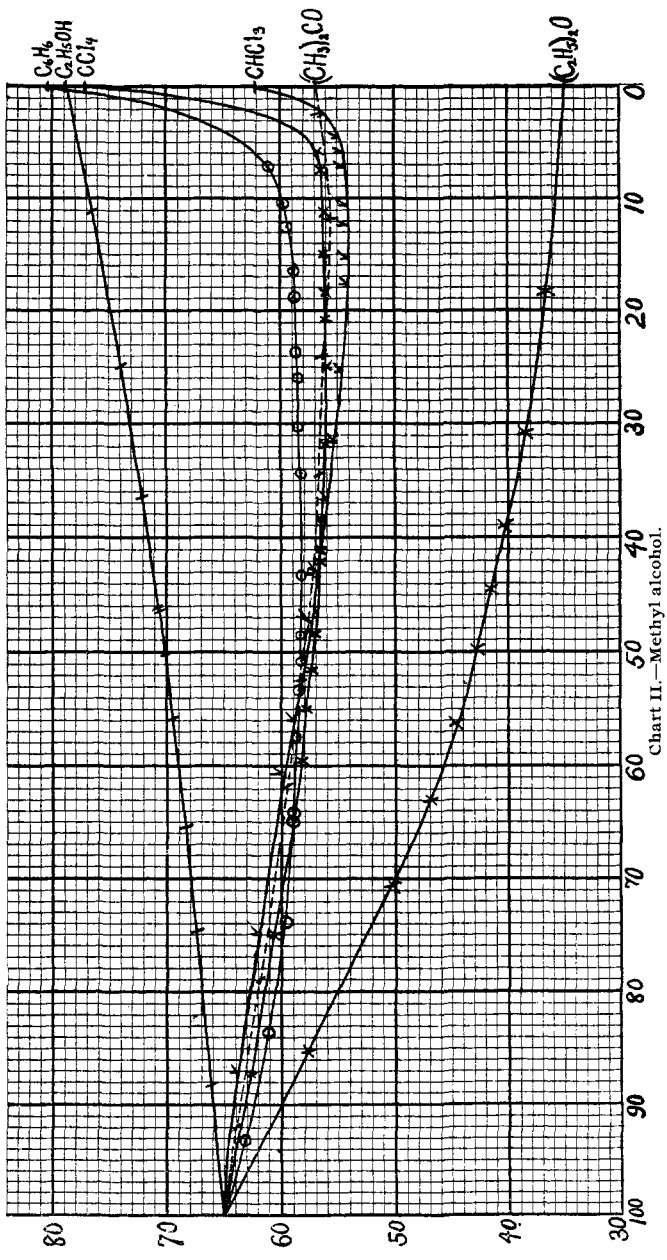

Chart II.—Methyl alcohol.

and carbon tetrachloride respectively both have minimum points, but need no further mention, as they have been fully discussed in my first paper.

If now the above chart representing the curves for methyl alcohol, is compared with the chart in paper I representing the curves for ethyl alcohol, it will at once be seen that the curves for the several liquids with methyl alcohol are quite similar to the curves for the same liquids with ethyl alcohol, each to each. Thus, the statement made in paper I, "In general, one constituent remaining the same, mixtures with substances of similar chemical constitution yield similar boiling-point curves," is borne out. The only exception one might pick out in these two sets of curves is when the methyl alcohol and acetone curve and the ethyl alcohol and acetone curve are compared. The first of these has a minimum point and the second has not. Granting, however, that this is the case, the minimum point of the methyl alcohol and acetone curve is only 0.8° C. below the boiling-point of the pure acetone, and the general shape of the curve is exactly the same as that of the ethyl alcohol and acetone curve.

From the data here presented the following conclusions may be drawn:

1. All mixtures of the following pairs of liquids boil at temperatures between the boiling-points of the constituents: Benzene and chloroform, benzene and carbon tetrachloride, benzene and ether, benzene and acetone, methyl alcohol, ethyl alcohol, and methyl alcohol and ether.

2. A solution containing 33 to 47 per cent. methyl alcohol in benzene distils without change at about 58.3° C. under a pressure of 760.7 mm. of mercury.

3. A solution containing about 18.4 per cent. methyl alcohol in carbon tetrachloride distils without change at 55.95° C. approximately under a pressure of 765.5 mm. of mercury.

4. The statement of paper I is borne out that "In general one constituent remaining the same, mixtures with substances of similar chemical constitution yield similar boiling-point curves."

5. Further, the statement in paper I is also borne out that: "The close proximity of the boiling-points of the constituents appears to be a favorable condition for the existence of a maximum or a minimum point on the boiling-point curve,

similarity of constituents seems to be a strongly modifying condition however.

Note.—Since sending the above article to press I am in receipt of a reprint of a paper entitled, "A Contribution to the Study of Liquid Mixtures of Constant Boiling-point," by Dr. Garnett Ryland,[1] in which are described his investigations of some of the same mixtures as are given in the above paper and paper I. They are benzene and chloroform, benzene and methyl alcohol, methyl alcohol and ether, methyl alcohol and acetone, and methyl alcohol and chloroform. His results are in the main the same as those obtained by myself, except in the case of methyl alcohol and acetone. He finds that this mixture can be separated by fractional distillation, while I find that the mixture has a minimum point about 0.8° C. below the boiling-point of the pure solvent.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 49.]

THE ELECTROLYSIS OF METALLIC PHOSPHATE SOLUTIONS.

BY HARRY M. FERNBERGER AND EDGAR F. SMITH.

Received August 2, 1899.

THE action of the current upon metallic phosphates, has received considerable attention in this laboratory. The frequent satisfactory repetition of these methods has only served to convince us that they deserve a permanent place in electrolytic literature, hence we take the present opportunity of again calling attention to them in their modified forms as to current density, voltage, etc., factors which were not especially emphasized in the earlier communications. Furthermore, other interesting behaviors of various metals in phosphate solutions, having come to light, we shall include them here. They are at least suggestive.

COPPER.

To a solution of copper sulphate, equivalent to 0.1239 gram of metal, were added twenty cc. of disodium hydrogen phosphate (sp. gr. 1.0358), and the precipitate produced was dissolved in five cc. of phosphoric acid (sp. gr. 1.347). The electrolytic

[1] Dissertation, Johns Hopkins University, 1898.