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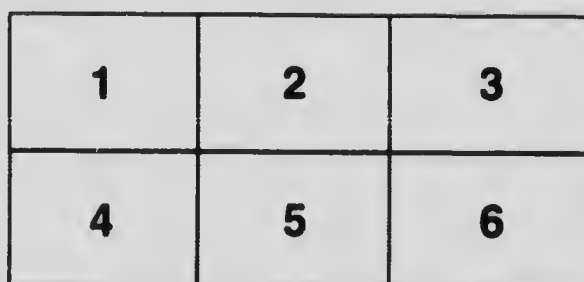
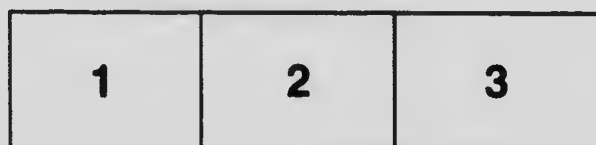
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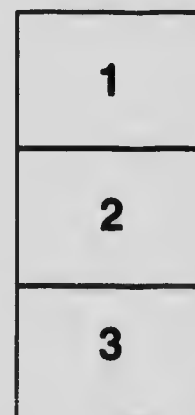
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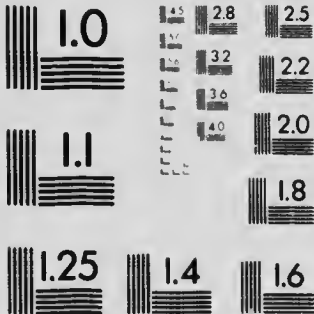
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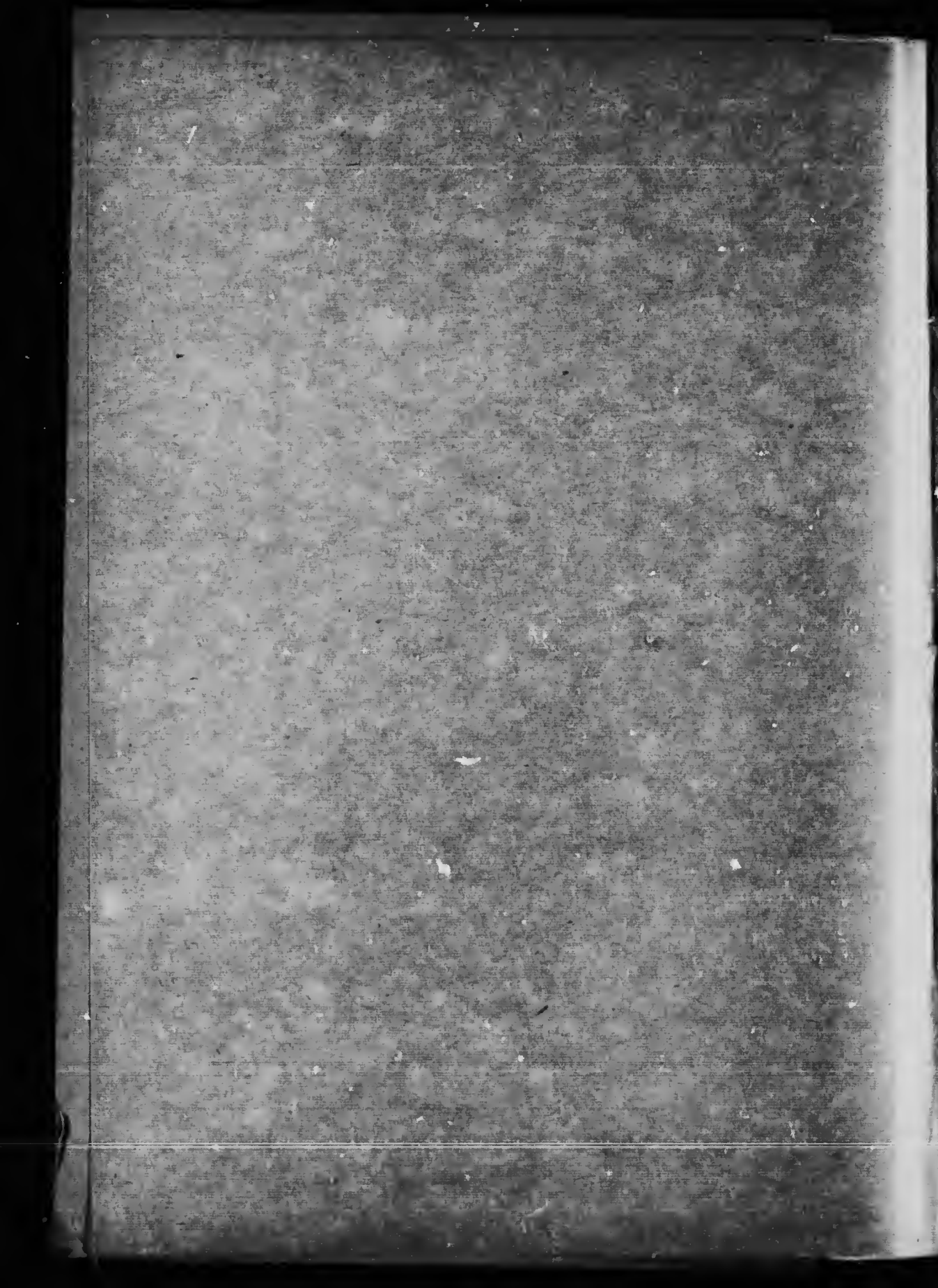
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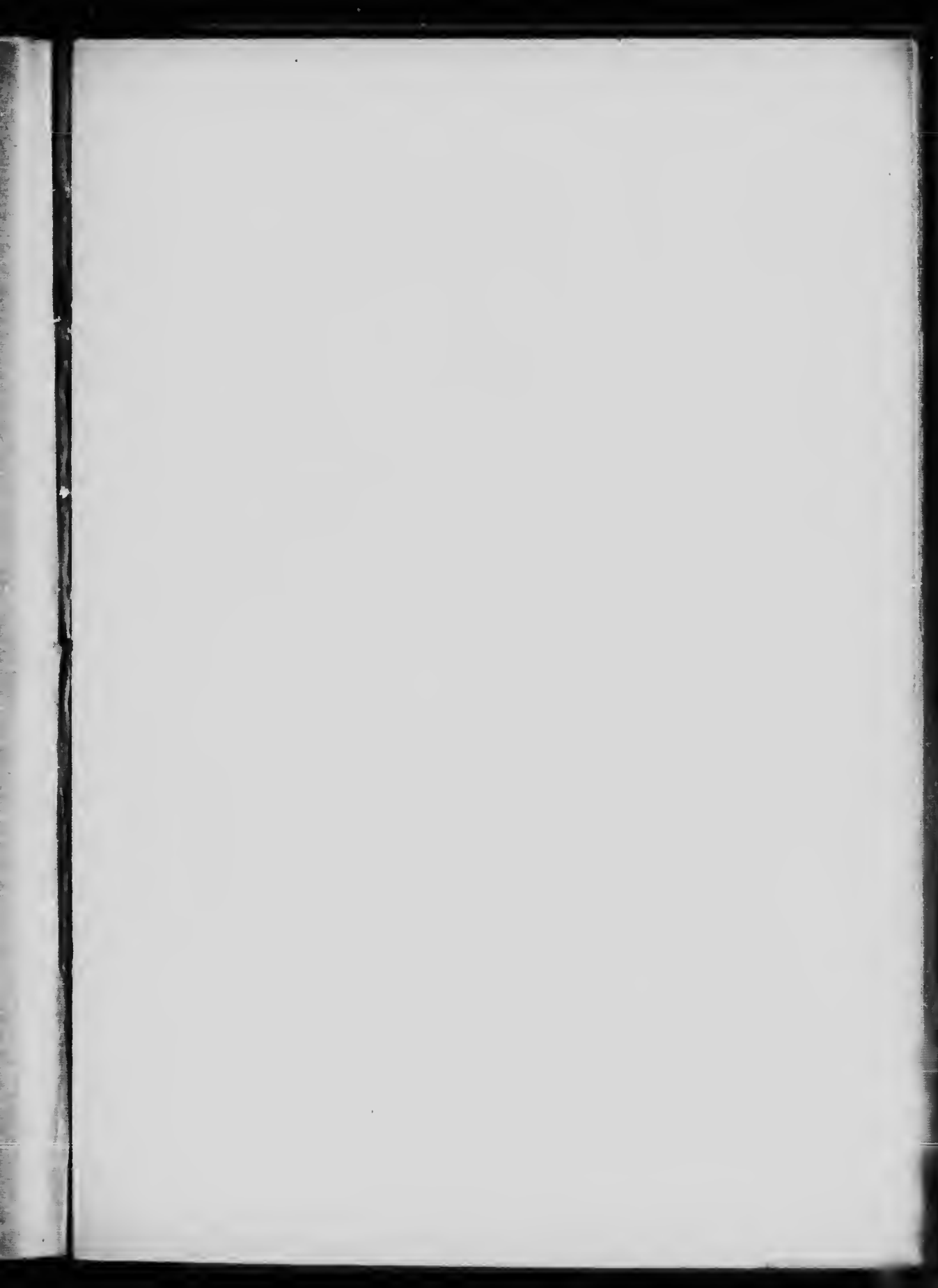
PAPERS FROM THE CHEMICAL
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No. 91: EXPERIMENTAL DETERMINATION OF BINODAL
CURVES, PLAIT POINTS, AND TIE LINES, IN FIFTY
SYSTEMS, EACH CONSISTING OF WATER AND TWO
ORGANIC LIQUIDS, BY WALTER D. BONNER

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EXPERIMENTAL DETERMINATION OF BINODAL CURVES, PLAIT POINTS, AND TIE LINES, IN FIFTY SYSTEMS, EACH CONSISTING OF WATER AND TWO ORGANIC LIQUIDS

BY WALTER D. BONNER

Comparatively little is known of the compositions of the two coexistent liquid phases which are often formed when three liquids are mixed together. The earliest determinations seem to have been made by Tuschmidt and Follenius in 1871, but the only considerable experimental research on the subject is that published by W. D. Bancroft in 1895. Now that the graphic methods of the Phase Rule have been applied to problems of this sort, more particularly by van Rijn van Alkemade, Schreinemakers, and Roozeboom, it seemed desirable to add to the stock of experimental data, and accordingly the present investigation was undertaken.

When alcohol, for example, is gradually added to a mixture of ether and water, at some constant temperature, the compositions and quantities of the two layers of liquid gradually change, and finally a homogenous solution is obtained. The points of the "Binodal Curve" give the quantity of alcohol which must be added to any given quantities of ether and water in order to bring about homogeneity, and the extremities of the "tie lines" give the compositions of the various pairs of liquids which may exist in equilibrium. When the two layers are practically of the same composition, the tie line is reduced to a point, the "plait point," on the binodal curve.

The experimental researches hitherto published have dealt mainly with the data for the binodal curve; the positions of tie lines, that is the compositions of the various pairs of coexistent liquids, have been determined in but few cases.¹

¹ By Waddell, Schreinemakers, Roozeboom, Wright. See Bibliography, p. 787. The paper by Duclaux contains data enough for the calculation of the tie lines.

As I wished to study as many different systems as was possible, and as organic liquids are in general costly, it was necessary to develop a method of working which would not necessitate the use of more than a few grams of material in each experiment. The difficulties of analysis were avoided by adopting a modification of the method of "quantitative synthesis" employed by Bancroft,¹ and the positions of the tie lines and plait points were determined by the graphic method described by W. Lash Miller and R. H. McPherson,² and applied by them in a few cases.

Method of Working

My method of working may best be described by reference to a particular case. Three Ostwald-Sprengel pyknometers with long capillary discharge tubes³ were filled with ether, water, and alcohol, respectively, and from these 0.354 gram ether and 0.501 gram water were weighed into a cylindrical glass tube about 12 cm long and 1 cm in diameter, to the upper part of which a tube of larger bore (1.5 cm diameter and 3 cm long) had been sealed for convenience of corking. This tube was at once corked and immersed in a well stirred mixture of ice and water contained in a covered rectangular glass "aquarium" (such as is often used for gold fish) the sides of which were jacketed with felt except for a space of about 10 cm square at each end. One of these openings could be illuminated by an electric light which was extinguished except during an observation, while the other served as a window, to enable the tube to be observed through the telescope of a cathetometer. The contents of the tube were stirred by a bent wire which projected through a hole in the cork, and alcohol was gradually added from the third pyknometer (by lifting the cork and dropping in a little at a time) until a homogeneous solution was obtained. This needed 0.326 gram alcohol. The total weight of liquid in

¹ Phys. Rev., 3, 27 (1895).

² Jour. Phys. Chem., 12, 709 (1908).

³ Such as are used to introduce liquids into a boiling point apparatus. See Ostwald-Luther, *Physico Chemische Messungen*, 2nd edition, p. 305.

the tube was thus 1.181 grams; the cathetometer gave the height of the liquid in the tube, hence from a previous calibration, its volume; from these data its specific gravity was obtained.

The three numbers: ether 0.354, water 0.501, alcohol 0.326, fix a point on the binodal curve; but as in the graphic representation which I have adopted, the sum of the weights of ether and water is represented always by 1.00, the three numbers must each be multiplied by $1.000/0.855$, giving ether 0.414, water 0.586, alcohol 0.381, as the coordinates of the point in question. In the diagram, Fig. 1, the abscissa gives the amount of ether and the ordinate the amount of alcohol; the amount of water may be obtained by subtracting the value of the abscissa from unity.¹ The other points on the binodal curve (Fig. 1) were similarly obtained.

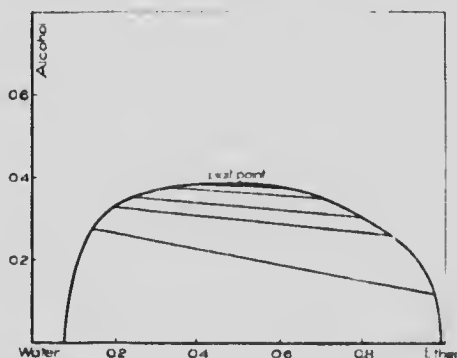


Fig. 1

The actual amount of ether used in determining the eleven points of the figure was 4.008 grams, and of alcohol 2.680 grams. About four hours work was required.

¹ This representation, while not so symmetrical as the triangular diagram, has the advantage that the ordinates are directly proportional to the weights of alcohol used in the experiments. The vertical displacement of the points of the graph due to an error of one drop of alcohol per gram of ether and water, is thus the same in every region of the diagram.

Effect of Temperature

After measuring the volume, the tube was removed from the ice bath and placed for a few minutes in a beaker of water at about 20° C. In the experiments with ether-water-alcohol, the homogeneous solutions clouded on warming and separated into two layers. In all other cases they remained clear.¹

Determination of Plait Point and Tie Lines

As the alcohol was added in the experiment just described, the lower (aqueous) layer increased in volume, while the upper (etheral) decreased and finally disappeared. In a subsequent experiment in which the proportions of ether and water were 0.601 and 0.399, respectively, the reverse was observed, the lower layer diminishing and ultimately disappearing. The abscissa of the plait point consequently lies between 0.414 and 0.601. To determine it more closely, 0.556 gram of ether and 0.541 gram of water were weighed out, alcohol added in successive portions and the volumes of the two layers determined by the cathetometer after each addition. The results were as follows:

TABLE I

Alcohol gram	Ether 0.556 g lower layer cc	Water 0.541 g upper layer cc	Volume ratio
0.226	0.783	0.739	0.94
0.331	0.800	0.800	1.01
0.358	0.807	0.815	1.01
0.394	0.814	0.842	1.03
0.412	0.822	0.850	1.05
0.432	Homogeneous		—

¹ Except in the case ether-water-alcohol, mixtures to which almost enough alcohol (or other consolute liquid) has been added to make them homogeneous, become so on removing from the ice bath and cloud again when replaced. Experiments numbered 38, 39, 40 were carried out at 15° C. because of the high melting point of one of the constituents. In these cases the homogeneous solutions clouded on cooling, and cleared again on warming. In Meerburg's study of the binodal curves of systems containing trimethylamine, cases analogous to that of ether-water-alcohol were met with.

If it be assumed, as a *first approximation*, that the specific gravities of the two layers are the same, the volume ratio will be the ratio of their weights. If then a straight line be drawn through the point which represents the composition ether 0.556, water 0.541, alcohol 0.226 (or ether 0.507, water 0.493, alcohol 0.206) to meet the binodal curve at each side so that the length of the portion of the line to the left of the point is 0.94 times the length of the portion of the line to the right, the points at which this line meets the binodal curve will give the compositions of the lower and upper layers, respectively, and the line will be a "tie line." The abscissa of the two ends of this line are 0.100 and 0.935, respectively. To make a *second approximation*, the volume of the lower and upper layers (0.783 cc and 0.739 cc) may be multiplied by the specific gravities of the solutions (abscissa 0.100 and 0.935), viz.: 0.98 and 0.79 respectively, giving 0.768 gram and 0.584 gram as the weights of the two layers, and 0.760 as the weight ratio. Shifting the line to correspond, gives 0.130 and 0.990 as the abscissa of the end points. A further approximation is in general unnecessary. Each line of Table I thus serves to place a tie line; their positions were checked by three further sets¹ of experiments with different relative quantities of ether and water. As near the plait point the tie lines are roughly parallel, the position of the plait point may be obtained graphically with fair accuracy. In the present instance its coordinates are ether 0.51, alcohol 0.39, indicated by a dot on the binodal curve (Fig. 1).

Source of Error and Precautions Taken

Nearly all the chemicals used were Kahlbaum's best, mostly from bottles opened for the occasion. In a few cases, however, where the guarantee of purity was not so good, the liquid was dried and fractionated until a satisfactory preparation was obtained.

The pycnometers were weighed to four places of deci-

¹ In general only two sets of tie line determinations were made.

mals, but only three are recorded. They were always weighed immediately before and immediately after using, even where a series of measurements with the same liquids was in progress. In some cases the liquid was blown from the pyknometer, a tube 15 cm long of calcium chloride and soda-lime being used to prevent contamination by the breath; generally, however, it was found easier to add small definite amounts by squeezing a short piece of rubber tubing attached to the upper tube of the pyknometer and plugged with a bit of glass rod.

The attempt to substitute small burettes for the pyknometers was abandoned, as it was found impossible to keep the liquids in them at constant temperature.

To guard against evaporation, the tube in which the liquids were mixed was kept stoppered. In a number of cases it was weighed after the experiment and the loss thus determined directly; with volatile liquids on long standing (as in tie line determinations) this might reach as high as one percent. Table II gives the total weights and the losses in the experiments to determine the binodal curves for toluene-water-alcohol and for chloroform-water-carbinol respectively:

TABLE II

Toluene-water-alcohol		Chloroform-water-carbinol	
Added	Loss	Added	Loss
1 3594	0 0024	1 3122	0 0118
1 6416	0 0116	1 5174	0 0120
1 7512	0 0056	1 8742	0 0088
1 5764	0 0050	2 1664	0 0140
2 4756	0 0112	2 4426	0 0153
2 5866	0 0076	2 1092	0 0110
1 8362	0 0062	1 3517	0 0067
1 6854	0 0046		
0 9570	0 0070		

As in all the experiments the tube was at least one-third full of liquid, the composition of the liquid was not ap-

preciably affected by the formation of vapor (at zero centigrade) within the tube.

In general there was no difficulty in deciding whether one phase was present, or two; the contents of the tube forming a more or less translucent, milky emulsion until the last drop of the consolute liquid suddenly cleared it. In a few cases,¹ ether-water-alcohol, for example, no such emulsion was formed and the end point was harder to determine. If a little lampblack² were added, however, it collected at the boundary between the two liquids, which thus became easily visible even when the amount of one phase was very small.

In order to get an idea of the probable accuracy with which the end point could be determined in such cases, saturated solutions of ether in water and of water in ether were made by shaking together equal volumes of water and ether. Some of the lower layer was pipetted off into a tared tube, weighed, and then the least amount of the upper layer of whose presence I could be positive was determined by adding it in very small drops until plainly visible, and then weighing. The same procedure was followed in the case of the upper layer, adding a small amount of the lower, and in both cases experiments were made with and without addition of lampblack. Using about one gram of the lower layer, and adding the upper in very small drops, I found as the mean of several trials that six or eight milligrams was the least amount of which I could be quite certain. The presence of the black does not greatly lessen the amount of the upper layer needed, but it facilitates its detection very decidedly. Before adding the upper layer the black is scattered in loose flakes over the surface or climbing up the sides of the tube; but the addition of a very small drop of the upper layer causes it to form a pronounced film on the surface, and to come down from the sides. This film forms again at once if dis-

¹ Other experiments in which this occurred were Nos. 5, 11, 21, 31, 32, 33 and 34 (see Table V).

² Lycopodium will not go into the boundary. Indigo, carmine, and ultramarine dissolve, or seem to, in some of the liquids used.

turbed by stirring, but on the addition of a drop or two of alcohol, enough to render the system homogeneous, it is immediately dissipated, the black for the most part settling into the liquid and slowly to the bottom of the tube.

Using about the same amount (one gram) of the upper phase and adding small drops of the lower, I found that about twenty milligrams was the least amount of which I could be positive.

Another method of detecting the end point that proved useful with some substances¹ was to warm the liquid slightly until it became homogeneous and then to cool it again in the ice bath, when the second phase would separate as an emulsion, whose disappearance on addition of the consolute liquid could easily be noted.

In determining the tie lines it was usually necessary to let the mixture stand from a half hour to several hours before it separated into two layers whose volumes could be measured. In a number of cases complete separation did not occur in six or eight hours and recourse was had to a centrifuge.²

On addition of alcohol to mixtures of water and *o*-xylene, the densities of the upper and lower layers approach, finally become equal, and then when more alcohol is added the "upper" layer becomes the heavier, and the two change places.³ In this case I could not obtain good separation on standing, even for twenty-four hours, or on centrifuging. Water, mesitylene and alcohol behave in an analogous manner, but separation is not so difficult.

The tubes used were calibrated by adding weighed amounts of water (of chloroform) a duplicate calibration) and determining with a cathetometer the distance from the bottom of the glass tube to the lowest and the highest points of the meniscus.

¹ This plan was used in experiments Nos. 24, 25, 26, 27, 28, 29 and 37 (Table V).

² Experiments Nos. 3, 4, 26, 27, 28, 35, 37, 39, 42, 45 and 48.

³ This occurred in experiments Nos. 4, 8, 28, 35, 39, 41, 43 and 49.

The volume of the meniscus cannot be neglected; it was calculated from the height of the meniscus by assuming¹ that the perpendicular section of the boundary liquid-air is an ellipse. From this assumption it follows that the volume of the meniscus is directly proportional to its height. With one of the tubes, for example, the volume was 0.025 cc per mm, and the height varied from about 1.8 mm to 2.5 mm, depending on the liquids used. On a total volume of one cc the "meniscus correction" thus amounts to five or six percent.

The cathetometer was a good instrument with glass scale, each division of the scale corresponding to one mm, the tenths being easily read with a vernier. With the tubes used, 0.1 mm corresponded to about 0.01 cc, or one percent on a volume of one cc. An error of one or two percent in the density might thus easily be made. Any greater accuracy, however, would be superfluous, as the densities were only used in placing the tie lines (see page 742).

As the object of the investigation was to study a large number of substances, extreme accuracy had to be sacrificed to the necessity for working with small quantities. The abscissa of points on the binodal curve are, of course, fairly accurate, probably well within one-half percent. But since a drop of alcohol, or of the other consolute liquids used in the experiments, weighs about 0.01 gram, the ordinates may be one or two percent out. From the agreement between duplicate experiments, and from the smoothness of most of the curves, I do not believe that the error in general exceeds this amount.

In placing the tie lines, much depends on the form of the curve. The nearer the "volume ratio" approaches unity, the less the error, and I have borne this in mind when planning the experiments.

The results furnish a view of a very extensive field. If it should prove necessary to examine any portion of it more

¹ Ostwald, *Lehrbuch*, 1, 481

minutely, the necessary experiments can be repeated on a larger scale. The experimental data are collected in Table V, and additional experimental details are given under "Notes on Table V," p. 757.

Discussion of the Results

Examination of Table III in which the coordinates of the plait points are collected, shows obvious stoichiometric regularities: With alcohol as consolute liquid, the three esters, ethyl acetate, propionate and isobutyrate, come together, in the order given; similarly with the three alcohols, benzyl, isobutyl and isoamyl. The hydrocarbons pinene, mesitylene, *o*- and *p*-xylene, and toluene come in the order given, but *m*-xylene stands out of its place at the head of the series. Amyl, isobutyl, propyl, and ethyl bromides follow in the order named. Speaking roughly, the latter half of the table includes the liquids noticeably soluble in water, and with the exception of chloroform, only such; while the first half is taken up with hydrocarbons, brom and nitro derivatives. Except in the case of chloroform-propyl alcohol, the plait point is shifted to the right (less water) when carbinol is replaced by ethyl alcohol and the latter by propyl alcohol.

Table V. Inspection of Figs. 2, 3 : ' ' shows, however, that there is no such regularity to be observed in the relative positions of the three binodal curves: in the case of brom-benzene, the highest curve is that for methyl alcohol, then ethyl alcohol, and propyl alcohol lowest; with chloroform the order is propyl, methyl, ethyl; and with carbon tetrachloride, methyl, propyl, ethyl; at the extreme left of the figures, however, the order is methyl, ethyl, propyl, in every case. In the systems hexane-water-carbinol and heptane-water-carbinol the plait point is situated practically at the origin of coordinates; in other words, no matter what the proportions of carbinol, water and hexane (heptane) may be, if two layers are formed the upper layer

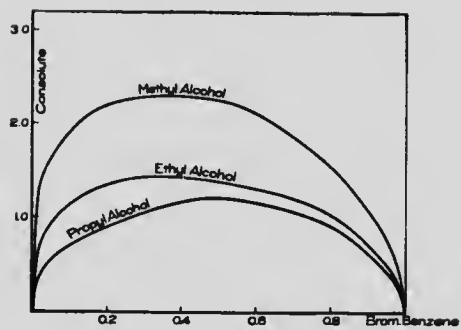


Fig. 2

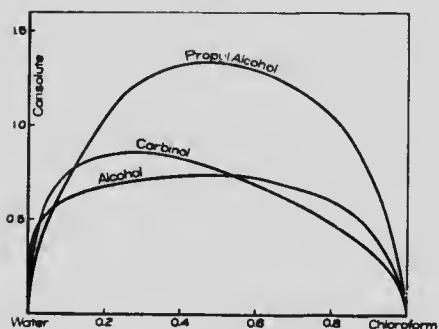


Fig. 3

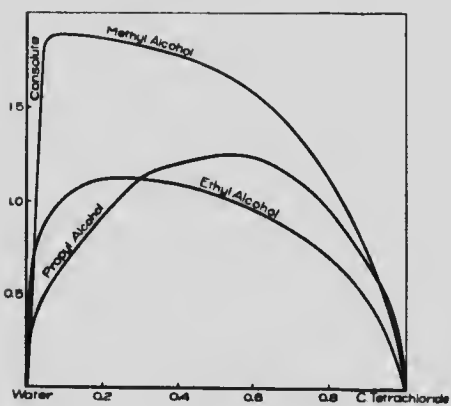


Fig. 4

will be practically pure hexane (heptane). The behavior of hexane and heptane is thus analogous to that of a solid (e. g. common salt) with carbinol and water; the amount

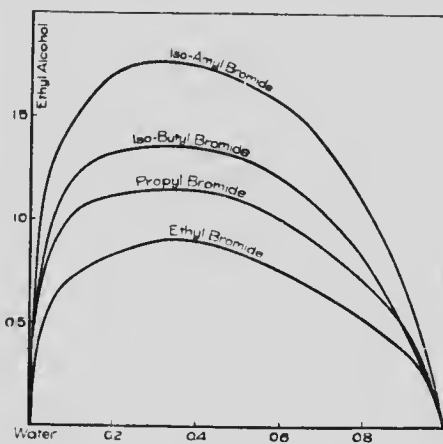


Fig. 5

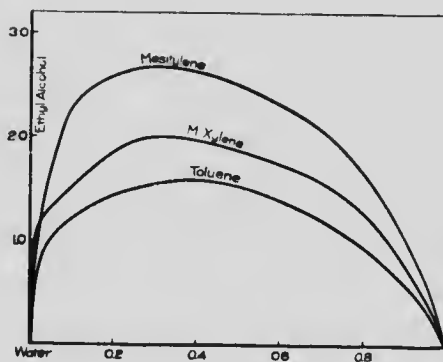


Fig. 6

dissolved varies with the proportion of water to carbinol, but neither of the latter substances is dissolved in the hydrocarbon or in the salt.

TABLE III—(Continued)

System number	Acetone		Alcohol		
	Water	Acetone	System number	Water	Alcohol
20	0.51	1.6	25	0.32	0.60
5	0.58	1.65	Benzyl acetate	0.33	0.71
			Benz. ethyl ether	0.33	0.72
			Ethylidene chlor.	0.34	0.72
			Methyl aniline	0.35-0.50	1.4
			Toluene	0.43	0.61
			Benzaldehyde	0.49	0.38
			Ether	0.50	0.41
			Ethyl ketone	0.52	0.30
			Ethyl acetate	0.54	0.53
			Ethyl propionate	0.54	0.67
			Ethyl butyrate	0.50-0.60	0.49
			o-Toluidene	0.58	0.73
			Chloroform	0.62	0.42
			Benzyl alcohol	0.65	0.21
			Isobutyl alcohol	0.73	0.43
			Isoamyl alcohol	Acetone	
			Alcohol	Propyl alcohol	
Heptane	0	0.02	0.38		
Hexane	0	0.03	0.59		
Carbon tetrachloride	0.015	0.08	0.39	0.75	1.06
Bromtoluene	—	0.02	0.33	0.75	0.97
Brombenzene	0.02	0.04	0.42	0.75-0.85	0.90
Ethyl bromide	0.05	0.17	0.45	0.96	0.20
Chloroform	0.05	0.5	0.73	0.49-0.56	1.3
				0.51	1.6
				0.58	1.65

Equations for the Binodal Curve

The first attempt to set up an algebraical equation for a binodal curve was made by Tschischmidt and Follenius,¹ who found that values of x calculated from the expression

$$x = \frac{c}{y + b}$$

(where y gives the number of cc of carbon bisulphide which will dissolve in 10 cc of a spirit containing x percent alcohol by weight) agreed "beinahe vollständig" with the results of their experiments.

Pfeiffer² expected to be able to express the equilibrium by the formula

$$(a - x)(a - y)^2 = (a - z)(x)$$

but the calculations were far from agreeing with the experiments."

Beginning in 1894³ Bancroft published a series of papers on "Ternary Mixtures." He found that in a number of cases, including those investigated by himself and the alloys of Wright,⁴ the curves were represented by the formula

$$x^a y^b = \text{const.},$$

where x and y are the amounts of the two immiscible liquids to a definite amount of consolute. In most cases, however, two equations with different constants were necessary to express the whole curve. It was thought that the corresponding logarithmic lines might cross at the plait point, but this is shown not to be the case by Waddell's experiments⁵ on the system benzene-water-acetic acid and by my own measurements. Lincoln,⁶ in repeating Waddell's ex-

¹ Ueber die Löslichkeit des CS₂ in Alcohol. Ber. chem. Ges. Berlin, **4**, 583 (1871).

² Ueber Lösungen von begrenzter Mischbarkeit. Zeit. phys. chem., **9**, 444 (1892); see page 470 of his paper.

³ Phys. Review, **3**, 21 (1895), etc.

⁴ See Bancroft's fourth paper, Jour. Phys. Chem., **3**, 217 (1899).

⁵ Jour. Phys. Chem., **2**, 233 (1898).

⁶ Ibid., **8**, 248 (1904).

periments, found, contrary to that author, two straight lines; but the point of intersection does not correspond with the plait point given in Waddell's paper. Furthermore, in a number of the systems investigated by Bell¹ the lines plotted in logarithmic coordinates are distinctly curved, a fact that is true also in a number of my own results.

I have calculated the logarithmic coordinates for the present measurements, taking $\log \frac{w}{a}$ as ordinates and $\log \frac{1-w}{a}$ as abscissa, where w represents the weight of water and a the weight of consolute, to a total of one gram of water plus third liquid. The results are given under the various systems in Table V. The following list indicates the form of the corresponding graphs, the numbers referring to the System No. given in Table V.

Straight lines (between the limits of w given in the last col. of Table IV) Nos. 1, 3, 9, 11, 12, 14, 22, 25, 29, 32, 35, 36, 38, 39, 40, 41, 43, 44.

Concave upwards. Nos. 4, 8, 13, 19, 23, 28, 33, 39, 50.

Convex upwards. Nos. 2, 5, 6, 7, 10, 15, 16, 17, 18, 20, 26, 27, 28, 31, 37, 42.

Irregular. Nos. 24, 34, 45, 46, 47, 48.

In all cases where the logarithmic curve, or part of it, is straight, I have calculated, from the graphs, the two constants for the equation to the line, which for convenience has been written

$$\log \frac{w}{a} = -p \log \frac{1-w}{a} + \log \gamma \dots \dots (\Lambda).$$

The values of p and $\log \gamma$, calculated in this way, are given in the fifth and sixth columns in Table IV, the last column in the table showing the range of the values of w over which the line is straight.

¹ Jour. Phys. Chem., 9, 531 (1905).

TABLE IV—EQUATION CONSTANTS

System number in Table V	System: Water and	$\frac{p}{1-x}$ calcd. from	$\log \left(\frac{0.5}{a} \right)^{p-1}$	p	Log γ	Range of x over which log. line is straight
				Calcd. from log graphs.		
1	Ether-alcohol	0.92	0.21	0.965	0.227	0.1-0.9
2	Chloroform-alcohol	0.89	1.68	—	—	—
3	Chloroform-carbinol	0.37	1.74	0.40	1.72	0.2-0.9
4	Chloroform-propyl alcohol	0.89	1.19	—	—	—
5	Chloroform-acetone	1.67	2.57	—	—	—
6	Carbon tetrachloride-carbinol	0.11	1.41	—	—	—
7	Carbon tetrachloride-alcohol	0.33	1.58	—	—	—
8	Carbon tetrachloride-prop. alcohol	1.08	1.18	—	—	—
9	Ethylene chloride-alcohol	0.72	1.49	0.598	1.522	0.1-0.9
10	Ethylene chloride-carbinol	0.49	1.68	—	—	—
11	Ethyl bromide-carbinol	0.61	1.35	0.603	1.354	0.1-0.9
12	Ethyl bromide-alcohol	0.51	1.67	0.479	1.679	0.2-0.9
13	Ethyl bromide-prop. alcohol	0.89	1.34	—	—	—
14	Propyl bromide-alcohol	0.57	1.46	0.553	1.467	0.1-0.8
15	Isobutyl bromide-alcohol	0.49	1.37	—	—	—
16	Isamyl bromide-alcohol	0.45	1.24	—	—	—
17	Brombenzene-carbinol	0.64	2.93	—	—	—
18	Brombenzene-alcohol	0.47	1.35	—	—	—
19	Brombenzene-prop. alcohol	0.85	1.29	—	—	—
20	Brombenzene-acetone	0.82	1.08	—	—	—
21	—	—	—	—	—	—
22	Bromtoluene-alcohol	0.54	1.14	0.645	1.056	0.1-0.8
23	Bromtoluene-prop. alcohol	0.82	1.36	—	—	—
24	Ethyl acetate-alcohol	0.64	0.28	—	—	—
25	Benzyl acetate-alcohol	0.37	1.73	0.351	1.734	0.2-0.9

TABLE IV—(Continued)

System number in Table V	System: Water and	$\frac{p}{1-w}$ calc'd from $\log \frac{r}{w}$	$\log \frac{r}{w}$ calc'd from $\log \left(\frac{0.5}{d} \right)^{p-1}$	p Calc'd from log. graphs	Log. r	Range of w over which log. line is straight
26	Ethyl propionate—alcohol	0.51	1.97	—	—	—
27	Ethyl butyrate—alcohol	0.47	1.82	—	—	—
28	Benzyl ethyl ether—alcohol	0.39	1.67	—	—	—
29	Isoamyl ether—alcohol	0.43	1.12	0.407	1.141	0.2-0.9
30	Diethyl ketone—alcohol	—	—	—	—	—
31	Hexane—carbinol	0.92	3.88	—	—	—
32	Hexane—alcohol	0.72	2.67	0.666	2.728	0.2-0.9
33	Heptane—carbinol	0.85	3.70	—	—	—
34	Heptane—alcohol	0.79	2.57	—	—	—
35	Benzene—alcohol	0.59	1.40	0.540	1.439	0.1-0.9
36	Toluene—alcohol	0.61	1.22	0.566	1.258	0.2-0.9
37	<i>o</i> -Xylene—alcohol	0.59	1.00	—	—	—
38	<i>m</i> -Xylene—alcohol	0.47	1.15	0.60	1.060	0.1-0.9
39	<i>p</i> -Xylene—alcohol	0.57	1.17	0.552	1.118	0.3-0.9
40	Mesitylene—alcohol	0.43	2.99	0.549	2.911	0.1-0.9
41	Pinene—alcohol	0.69	2.66	0.69	2.650	0.1-0.9
42	Benzaldehyde—alcohol	0.43	1.85	—	—	—
43	Methyl aniline—alcohol	0.45	1.67	0.503	1.647	0.1-0.9
44	<i>p</i> -Nitrotoluene—alcohol	0.67	1.06	0.749	1.031	0.2-0.9
45	<i>o</i> -Toluidin—alcohol	0.54	0.93	—	—	—
46	Isobutyl alcohol—alcohol	0.54	0.61	—	—	—
47	Isoamyl alcohol—alcohol	0.67	0.68	—	—	—
48	Benzyl alcohol—alcohol	0.64	0.10	—	—	—
49	Phenol—alcohol	0.61	1.23	—	—	—
50	Nitrobenzene—alcohol	0.72	1.28	—	—	—

The following considerations will give a clearer idea of the signification of these constants in the corresponding binodal curves.

From equation (A)

$$a^{p+1} = \frac{w}{r} (1-w)^p \dots \dots \dots (B).$$

For the condition $da/dw = 0$, i. e., for maximum a ,

$$p = \frac{1-w}{w}$$

p , therefore, gives the ratio of the weight of immiscible liquid to water at the maximum point in the binodal curve.

For $w = 0.5$, i. e., for the mixture of 0.5 gram water to 0.5 gram immiscible liquid, equation (B) becomes

$$a^{p+1} = \frac{(0.5)^{p+1}}{r}$$

or

$$r = \left(\frac{0.5}{a} \right)^{p+1} \dots \dots \dots (C)$$

where a is the amount of consolute necessary to make a half and half mixture of water and second immiscible liquid homogeneous.

The constants have been calculated in this way for all the experiments (including those for which the logarithmic curve is not straight) and are given in the third and fourth columns of Table IV. The logarithmic lines plotted by the use of these constants will correspond only approximately with the experiments, but will necessarily pass through the right point for $w = 0.5$. Even in the cases where the logarithmic graphs are straight the slope given by the interpolation formula may be slightly inaccurate owing to the difficulty of determining exactly the maximum point of the binodal curve.

Writing equation C in the form

$$\frac{\log r}{p+1} = \log (0.5) - \log a,$$

it will be noted that the left-hand term of the equation increases with decrease of a and *vice versa*. Since $\log \gamma$ varies in the different systems over a much wider range than $p + 1$, which with two exceptions lies between 1.3 and 2, $\log \gamma$ itself may be taken as a rough indication of the variation of a . Since, as was shown above, a is the amount of consolute required to make equal quantities of the two immiscibles homogeneous it might be expected that $\log \gamma$ would be small for the very insoluble pairs and *vice versa*. That this is approximately true is shown by the following list in which the systems are arranged in ascending order of $\log \gamma$ (the numbers refer to the System Nos. in Table IV):

Ascending order of $\log \gamma$: Nos. 33, 31, 34, 5, 41, 32, 17, 40, 44, 20, 37, 22, 38, 39, 8, 4, 49, 36, 16, 50, 19, 13, 11, 18, 23, 15, 35, 14, 9, 7, 28, 12, 43, 2, 10, 25, 3, 27, 42, 26, 45, 47, 48, 1, 24, 46.

It will be noted that the first part of the list contains heptane, hexane, pinene, brombenzene, mesitylene, etc., while in the latter part there are isobutyl alcohol, ethyl acetate, ether, etc.

Notes on Table V

Table V contains the data from the various measurements made. In all the experiments water was one of the non-miscible pair and so has been omitted in the headings, the names of the second non miscible liquid and of the consolute liquid being used to designate the system. The columns headed "water" give the weight of water; the weight of the second non-miscible liquid in the system, and hence the abscissa in the graphs, may be found by subtracting the amount of water from unity. The second column (headed carbinol, alcohol, propyl alcohol or acetone) gives the weight of the consolute liquid necessary to make a homogeneous solution, *i. e.*, the ordinate in the graphs. These two numbers fix a point on the binodal curve. The figures in the "density" column are the densities of the homogeneous systems as determined by the cathetometer. For the convenience of any who may desire to use these results, interpo-

lations of the even decimals have been made and inserted in the table; these interpolations which have been made from the plotted curves are given to two decimal places only, and are marked by an asterisk. The plait points are inserted in the tables in their proper places, and are indicated by the letters P. P. The two small columns headed "water-water," which appear at the bottom of most of the tables give the abscissa of the two ends of the tie lines. The lower, denser, phase is always given in the first column. The tables of logarithmic coordinates are referred to under "Equations for binodal curve," p. 752.

The temperature of the experiments was zero centigrade except where otherwise stated.

(4) Near the plait point separation was very slow; no even dividing line between the phases could be obtained.

Plait point between water 0.49 and 0.56:

(5) These mixtures do not become cloudy to any great extent. Near the plait point the two phases are so nearly the same in appearance that without the lamp black it was very difficult to see the dividing line.

(7) Kahlbaum's preparation, freshly distilled, b. p. 78°.

(9) The ethylene chloride was dried and redistilled, b. p. 83°-84°.

(11) The ethyl bromide was prepared in the laboratory. It was dried and fractionated, b. p. 38°-39°.

(13) The plait point seems to lie between the points water 0.950 and water 0.969, but though repeated attempts were made no tie lines were obtained.

(14) The first three tie lines are a first approximation only, but the radiation from the origin indicates that the bottom layer during the first part of the experiment was practically pure propyl bromide.

(17) The brombenzene was prepared by students in the organic laboratory. A fraction of 100 cc boiling at 154° was used for these measurements.

(19) Separated very slowly near the plait point. Did

not separate on standing twenty-four hours. Centrifuging was of no help.

Plait point between water 0.75 and 0.85:

(21) It was impossible to determine the end point accurately because the bromtoluene phase settles to the bottom as oily drops in a perfectly clear liquid, and the end could be determined only by the disappearance of the oily drops. The bromtoluene was freshly distilled, b. p. 182° – 183° .

(24) At 0° , 10 grams ethyl acetate dissolve 0.301 gram of water. Ten grams of water at 0° dissolve 1.086 grams of ethyl acetate.

(28) Benzyl ethyl ether forms at first the upper layer. After the addition of a little alcohol it forms the bottom layer.

(29) The first two tie lines given are first approximation only.

(30) It was not found possible to carry this curve beyond the point water 0.70. From this point on, after the addition of a small amount of alcohol the mixture no longer separates into two layers but remains turbid and a great excess of alcohol does not remove this turbidity.

Plait point only near water 0.50:

(31) The hexane and heptane used were Kahlbaum's, "aus Petroleum." When carbinol is used as the consolute liquid the plait points lie so near the paraffine end of the graphs that tie line measurements are impossible. This means that the tie lines radiate from the origin and that hence all the solutions obtained by adding carbinol to any mixture whatever of hexane or heptane and water, are in equilibrium with practically pure hexane. To check this conclusion the following measurements of the refractive index were made:

(1) Three cc of hexane, 3 cc of carbinol, and one drop water were shaken well together, let stand to separate and the top layer (about 2 cc) was then transferred to the chamber of the refractometer and its index of refraction determined.

(2) Five cc of hexane, 7 cc of carbinol and 4 drops water, treated as before. The top layer was approximately 3 cc. The refractive index of both top and bottom layers was determined. Upper layer $n_{11} = 1.38343$, lower layer $n_{11} = 1.33935$.

(3) Three cc of hexane, 1 cc of water, well shaken and separated by centrifuging, upper layer $n_{11} = 1.38381$.

(4) Three cc. of hexane and an excess (about 2 drops) of carbinol, allowed to settle. Used the clear solution. $n_{11} = 1.38334$.

The refractometer used (Pulfrich's "Refractometer für Chemiker") gave as the value of n_{14} for distilled water at 14° C. 1.33295 as against 1.33232 given in the Landolt-Bornstein tables; for benzene it gave 1.50139 as against 1.50137 in the tables; pure hexane gave 1.38382 and carbinol 1.33070, all at 14° C.

(34) Plait point is about water 0.02, alcohol 0.38.

(36) Through an oversight no tie line measurements were made:

Plait point between water 0.35 and 0.50:

(37) In this case (as also in the cases of experiments numbered 4, 8, 28, 35, 39, 41, 43 and 49) while the xylene is at first the upper layer, after the addition of a small amount of alcohol, the xylene layer sinks through the watery layer and becomes the lower. This gives another method of obtaining approximately the tie lines in these mixtures. Just before the point at which the "top" layer becomes the "bottom" there is a point at which the densities of the two are identical and the density of either is the density of the total mixture. Add alcohol until the "top" layer just begins to sink into the "bottom" and determine the density of the total mixture at this point. The tie line will be represented by a line passing through the point which gives the composition of the system and cutting the binodal curve at a point on either side which has the density of the given system. The last tie line in the table above was obtained in this way.

The composition of the system was water 0.295, alcohol 0.740, density 0.89.

(38) The plait point lies to the right of the point water 0.010.

(43) The first tie line is a first approximation only. Kahlbaum's best preparation, fractionated twice, b. p. 195° .

(44) The sample of *o*-nitrotoluene was prepared in the laboratory, b. p. 223° - 224° .

(45) B. p. 199° .

It was impossible to get a satisfactory tie line measurement because the layers would not separate well enough to enable one to read the volumes, even up to the point where one drop of alcohol made the mixture homogeneous.

The plait point comes between 0.50 and 0.60.

(46) Kahlbaum's preparation, slightly discolored.

Boiled with calcium turnings under reflux and fractionated. B. p. 107° - 109° . The solubility of water in isobutyl alcohol at zero is 2.17 g water in 10 g and that of isobutyl alcohol in water is 1.15 g in 10 g water. The solubility decreases with rise of temperature.

(47) Kahlbaum's preparation free from pyridine. Dried over calcium turnings and distilled. B. p. 130° . The solubility in water at zero is 0.42 g in 10 g water and the solubility of water in isoamyl alcohol at zero is 0.81 g in 10 g alcohol.

TABLE V
(1) ether alcohol (2) chloroform alcohol

Water	Alcohol	Density	Water	Alcohol	Density
0.041	0.161	0.78	0.093	0.434	1.19
0.087	0.224	0.79	*0.10	0.45	1.18
*0.10	0.28	0.80	0.185	0.587	1.13
0.186	0.299	0.82	*0.20	0.60	1.12
*0.20	0.305	0.82	*0.30	0.68	1.07
0.209	0.354	0.85	0.317	0.692	1.06
0.399	0.376	0.86	0.407	0.726	1.04
P. P. 0.49	0.38	0.88	0.499	0.729	1.03
*0.50	0.39	0.88	P. P. 0.58	0.73	—
0.586	0.381	0.90	0.596	0.733	1.01
*0.60	0.38	0.91	0.689	0.710	0.99
*0.70	0.37	0.93	*0.70	0.70	0.99
0.712	0.365	0.93	0.803	0.672	0.98
*0.80	0.34	0.95	*0.90	0.61	0.98
0.826	0.331	0.96	0.912	0.608	0.98
0.875	0.238	0.97	—	—	—
*0.90	0.16	0.97	—	—	—

Tie-lines

Tie-lines

Water	Water	Water	Water
0.86	0.02	0.10	0.97
0.81	0.12	0.22	0.90
0.77	0.18	0.43	0.72
0.68	0.30		
0.61	0.38		

(1) Logarithmic coordinates

(2) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$	Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	1.638	0.593	0.10	1.347	0.301
0.20	0.810	0.412	0.20	0.523	0.125
0.30	0.933	0.301	0.30	0.645	0.013
0.40	0.934	0.210	0.40	0.742	1.918
0.50	0.108	0.108	0.50	0.836	1.836
0.60	0.198	0.022	0.60	0.913	1.737
0.70	0.277	1.909	0.70	0.000	1.632
0.80	0.372	1.770	0.80	0.076	1.474
0.90	0.750	1.796	0.90	0.169	1.215
P. P. —	0.505	1.720	P. P. —	1.900	1.760

Experimental Determination of Binodal Curves, Etc. 763

TABLE V—(Continued)
(3) chloroform carbinol (4) chloroform propyl alcohol

Water	Carbinol	Density	Water	Propyl alcohol	Density
0.021	0.161	—	0.023	0.304	1.28
*0.10	0.35	1.17	0.074	0.631	1.13
0.132	0.400	1.16	*0.10	0.76	1.11
*0.20	0.49	1.12	*0.20	1.06	1.04
P. P. 0.27	0.57	—	0.240	1.128	1.02
0.276	0.572	1.09	*0.30	1.20	1.01
*0.50	0.60	1.08	0.346	1.250	1.02
0.368	0.660	1.07	*0.40	1.30	0.98
*0.40	0.70	1.05	*0.50	1.34	0.97
*0.50	0.77	1.02	0.511	1.340	0.96
0.519	0.783	1.01	0.606	1.320	0.98
*0.60	0.83	1.00	0.707	1.235	0.96
0.628	0.843	0.99	0.806	0.996	0.95
*0.70	0.86	0.98	0.903	0.672	0.97
*0.80	0.84	0.97	0.970	0.390	0.97
0.822	0.834	0.97	—	—	—
*0.90	0.74	0.96	—	—	—
0.943	0.622	—	—	—	—
0.987	0.267	0.98	—	—	—

Tie-lines

Water	Water
0.00	0.70
0.01	0.58
0.03	0.55
0.05	0.51
0.11	0.45

(3) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	1.456	0.410
0.20	1.611	0.213
0.30	1.699	0.067
0.40	1.757	1.933
0.50	1.813	1.813
0.60	1.859	1.683
0.70	1.911	1.543
0.80	1.979	1.377
0.90	1.085	1.131
P. P. —	1.676	0.107

Tie-lines

Water	Water
0.10	1.00
0.13	1.00
0.24	1.00
0.27	1.00
—	—

(4) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	1.119	0.073
0.20	1.276	1.878
0.30	1.398	1.766
0.40	1.488	1.664
0.50	1.572	1.572
0.60	1.650	1.482
0.70	1.755	1.387
0.80	1.908	1.305
0.90	0.128	1.174
—	—	—

TABLE V—(Continued)

(5) chloroform acetone

(6) carbontetrachloride carbinol

Water	Acetone	Density	Water	Carbinol	Density
0.012	0.501	1.18	P. P. 0.015	0.215	—
0.087	1.221	1.02	0.026	0.328	1.30
*0.10	1.30	1.01	*0.10	0.74	1.13
0.208	1.633	0.98	0.156	0.974	1.06
0.304	1.750	0.96	*0.20	1.10	1.04
0.344	1.742	0.96	0.235	1.268	1.03
*0.40	1.77	0.95	*0.30	1.40	1.00
0.481	1.738	0.94	0.316	1.403	0.99
*0.50	1.72	0.94	*0.40	1.68	0.97
P. P. 0.58	1.65	—	0.490	1.700	0.95
0.592	1.630	0.93	*0.50	1.71	0.95
*0.60	1.63	0.93	*0.60	1.77	0.93
*0.70	1.53	0.94	0.702	1.825	0.93
0.737	1.483	0.95	*0.80	1.88	0.92
0.800	1.321	0.95	0.852	1.890	0.92
0.900	1.144	0.97	*0.90	1.90	0.92
0.982	0.464	0.98	0.951	1.870	0.91
	—	—	0.974	1.045	0.93

Tie lines

Tie lines

Water	Water	Water	Water
0.15	0.99	0.000	0.110
0.17	0.98	0.005	0.035
0.18	0.97		
0.19	0.96		
0.20	0.96		
0.21	0.95		
0.22	0.93		
0.25	0.91		
0.30	0.85		
0.51	0.66		

(5) Logarithmic coordinates

(6) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$	Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	2.886	1.840	0.10	1.131	0.085
0.20	1.089	1.601	0.20	1.260	1.862
0.30	1.234	1.602	0.30	1.331	1.699
0.40	1.354	1.530	0.40	1.403	1.580
0.50	1.464	1.464	0.50	1.466	1.466
0.60	1.566	1.390	0.60	1.530	1.354
0.70	1.660	1.292	0.70	1.583	1.215
0.80	1.783	1.180	0.80	1.630	1.027
0.90	1.897	2.943	0.90	1.675	2.721
P. P.	1.550	1.406	P. P.	2.844	0.661

Experimental Determination of Binodal Curves, Etc. 765

TABLE V—(Continued)
(7) carbontetrachloride alcohol (8) carbontetrachloride propyl alcohol

Water	Alcohol	Density	Water	Propyl alcohol	Density
0.039	0.224	1.36	0.025	0.317	1.31
0.072	0.347	1.23	0.069	0.536	1.17
P. P. 0.08	0.39	—	*0.10	0.65	1.14
*0.10	0.45	1.20	0.200	0.949	1.07
0.156	0.598	1.10	0.270	1.070	1.03
*0.20	0.67	1.15	*0.30	1.12	1.02
0.238	0.746	1.10	0.40	1.20	0.99
*0.30	0.82	1.07	0.414	1.208	0.99
0.361	0.891	1.05	0.501	1.234	0.98
*0.040	0.94	1.03	0.600	1.195	0.97
0.501	1.040	1.00	*0.70	1.13	0.96
0.518	1.046	0.97	0.710	1.119	0.96
*0.60	1.00	0.97	P. P. 0.75	1.06	—
*0.70	1.11	0.96	0.806	0.912	0.96
0.750	1.105	0.95	*0.90	0.68	0.96
*0.80	1.10	0.94	0.911	0.645	0.96
0.887	1.104	0.95	0.987	0.554	0.96
*0.90	1.00	0.92	—	—	—
0.945	0.850	0.91	—	—	—
0.955	0.838	0.92	—	—	—
0.968	0.745	0.93	—	—	—

Tie-lines

Tie-lines

Water	Water	Water	Water
0.01	0.30	0.21	0.99
0.02	0.22	0.47	1.00
0.03	0.16	0.56	0.99
0.05	0.13	0.52	0.90

(7) Logarithmic coordinates

(8) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$	Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	1.347	0.301	0.10	1.187	0.141
0.20	1.475	0.077	0.20	1.330	1.030
0.30	1.597	1.931	0.30	1.428	1.796
0.40	1.629	1.805	0.40	1.523	1.600
0.50	1.683	1.683	0.50	1.600	1.600
0.60	1.741	1.565	0.60	1.690	1.523
0.70	1.800	1.432	0.70	1.792	1.424
0.80	1.863	1.260	0.80	1.944	1.342
0.90	1.954	1.000	0.90	0.121	1.168
P. P.	1.312	0.373	P. P.	1.850	1.373

TABLE V—(Continued)

(9) ethylene chloride alcohol			(10) ethylidene chloride alcohol		
Water	Alcohol	Density	Water	Alcohol	Density
0 029	0 191	1 15	0 015	0 226	1 10
0 050	0 266	1 12	*0 10	0 43	1 03
*0 10	0 42	1 08	0 109	0 436	1 02
P. P. 0 12	0 46	—	0 195	0 586	1 01
0 208	0 670	1 01	*0 30	0 69	0 98
0 290	0 789	0 98	0 316	0 705	1 00
*0 30	0 80	0 98	P. P. 0 33	0 72	—
*0 40	0 93	0 96	*0 40	0 77	0 96
0 486	0 983	0 95	0 423	0 770	0 96
*0 50	0 99	0 95	*0 50	0 82	0 95
0 580	1 000	0 95	0 563	0 857	0 94
*0 60	1 01	0 94	0 607	0 87	0 94
*0 70	0 99	0 94	*0 70	0 88	0 93
0 790	0 958	0 94	0 765	0 864	0 93
*0 80	0 95	0 94	*0 80	0 86	0 93
0 905	0 842	0 96	*0 90	0 79	0 94
0 980	0 514	0 97	0 910	0 774	0 94
			0 970	0 576	0 95
Tie-lines			Tie lines		
Water	Water		Water	Water	
0 00	0 48		0 00	0 79	
0 01	0 36		0 01	0 77	
0 03	0 22		0 03	0 70	
			0 11	0 61	
			0 20	0 47	
(9) Logarithmic coordinates			(10) Logarithmic coordinates		
Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$	Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0 10	1 377	0 331	0 10	1 367	0 321
0 20	1 475	0 077	0 20	1 533	0 135
0 30	1 574	1 942	0 30	1 638	0 006
0 40	1 634	1 810	0 40	1 716	1 892
0 50	1 703	1 703	0 50	1 785	1 785
0 60	1 774	1 598	0 60	1 839	1 663
0 70	1 850	1 482	0 70	1 901	1 533
0 80	1 925	1 323	0 80	1 969	1 367
0 90	0 029	1 076	0 90	0 057	1 102
P. P. —	0 416	0 282	P. P. —	1 661	1 969

TABLE V—(Continued)
 (11) ethyl bromide carbinol (12) ethyl bromide alcohol

Water	Carbinol	Density	Water	Alcohol	Density
0.027	0.202	1.27	0.033	0.240	1.23
P. P. 0.05	0.33	—	*0.10	0.37	1.15
0.064	0.393	1.18	P. P. 0.17	0.45	—
*0.10	0.54	1.14	0.189	0.493	1.09
0.194	0.868	1.08	*0.20	0.51	1.09
*0.20	0.86	1.05	*0.30	0.64	1.06
0.291	1.023	1.01	0.365	0.720	1.04
*0.30	1.04	1.01	*0.40	0.754	1.03
0.398	1.180	1.00	0.476	0.807	1.01
*0.40	1.18	0.99	*0.50	0.83	1.00
0.498	1.250	0.97	*0.60	0.89	0.99
*0.50	1.26	0.97	0.657	0.900	0.98
0.600	1.310	0.96	*0.70	0.89	0.97
*0.70	1.29	0.95	*0.80	0.83	0.96
0.750	1.270	0.95	0.837	0.797	0.96
*0.80	1.21	0.94	*0.90	0.73	0.97
0.816	1.100	0.95	0.948	0.623	0.98
*0.90	0.94	0.94	0.983	0.182	0.99
0.919	0.870	0.94	—	—	—
0.978	0.194	0.98	—	—	—

Tie-lines

Water	Water
0.00	0.21
0.01	0.14
0.02	0.11
0.02	0.08

Tie-lines

Water	Water
0.00	0.63
0.01	0.46
0.06	0.27

(11) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	1.268	0.222
0.20	1.367	1.969
0.30	1.460	1.828
0.40	1.530	1.706
0.50	1.599	1.599
0.60	1.661	1.485
0.70	1.735	1.361
0.80	1.820	1.241
0.90	1.981	0.027
P. P. —	1.181	0.459

(12) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	1.432	0.386
0.20	1.593	0.196
0.30	1.671	0.039
0.40	1.727	1.903
0.50	1.780	1.780
0.60	1.829	1.653
0.70	1.896	1.527
0.80	1.984	1.382
0.90	0.091	1.137
P. P. —	1.577	0.266

TABLE V (Continued)

13 Ethyl bromide-propyl alcohol

Water	Propyl alcohol	Density
0.039	0.807	1.21
0.088	0.618	1.11
0.10	0.63	1.10
0.20	0.88	1.08
0.215	0.800	1.05
0.30	1.00	1.02
0.334	1.004	1.03
0.40	1.00	1.00
0.413	1.002	1.01
0.500	1.124	0.98
0.584	1.115	0.96
0.60	1.10	0.97
0.604	0.968	0.97
0.70	0.90	0.96
0.80	0.81	0.96
0.860	0.671	0.96
0.90	0.80	0.97
0.977	0.227	0.99

P. 1°	0.025	0.100	1.20
	0.08	0.42	
	0.10	0.50	1.12
	0.107	0.508	1.12
	0.20	0.72	1.06
	0.234	0.700	1.04
	0.30	0.88	1.02
	0.328	0.920	1.01
	0.40	1.01	0.99
	0.432	1.181	1.00
	0.496	1.096	0.98
	0.50	1.10	0.98
	0.803	1.134	0.96
	0.60	1.15	0.99
	0.608	1.140	0.95
	0.70	1.14	0.98
	0.706	1.120	0.94
	0.904	1.020	0.94
	0.973	0.687	0.95

Tie lines

Water	Water
0.00	0.96
0.00	0.80
0.00	0.53
0.00	0.34
0.01	0.27
0.02	0.21
0.03	0.16
0.04	0.14

13 Logarithmic coordinates

Water	$\log \frac{a}{d}$	$\log \frac{1-a}{d}$
0.10	1.194	0.148
0.30	1.372	1.074
0.30	1.477	1.848
0.40	1.808	1.741
0.80	1.68	1.650
0.60	1.78	1.861
0.70	1.80	1.7
0.80	1.998	1.73
0.90	0.200	1.752

14 Logarithmic coordinates

Water	$\log \frac{a}{d}$	$\log \frac{1-a}{d}$
0.10	1.301	0.255
0.20	1.444	0.046
0.30	1.533	1.001
0.40	1.598	1.774
0.50	1.688	1.658
0.60	1.718	1.541
0.70	1.788	1.470
0.80	1.834	1.282
0.90	1.946	2.091
P. 1°	1.280	0.341

TABLE V (Continued)

(15) isobutyl bromide alcohol

(16) isomyl bromide alcohol

Water	Alcohol	Density	Water	Alcohol	Density
0.024	0.200	1.18	0.025	0.251	1.10
P. P. 0.07	0.42		P. P. 0.04	0.30	
*0.10	0.52	1.09	0.189	0.636	1.01
0.124	0.607	1.06	*0.10	0.68	1.01
0.20	0.83	1.01	*0.20	1.01	0.96
0.218	0.887	1.00	0.223	1.178	0.97
0.293	1.030	0.98	0.30	1.37	0.94
0.30	1.05	0.98	0.324	1.432	0.93
0.386	1.194	0.96	0.40	1.57	0.93
0.40	1.21	0.96	0.414	1.594	0.93
0.499	1.300	0.94	0.502	1.676	0.91
0.598	1.359	0.93	0.873	1.744	0.91
0.60	1.35	0.93	0.60	1.75	0.91
0.696	1.356	0.93	0.692	1.747	
0.70	1.39	0.93	0.70	1.75	0.91
0.80	1.32	0.92	0.80	1.71	0.91
0.804	1.316	0.92	0.809	1.713	0.91
0.896	1.215	0.93	0.895	1.463	0.92
0.90	1.20	0.93	*0.90	1.40	0.92
0.953	0.937	0.91	0.978	1.027	0.93

Tie lines

Tie lines

Water	Water	Water	Water
0.00	0.51	0.00	0.43
0.00	0.24	0.01	0.11
0.03	0.13	0.02	0.06

(15) Logarithmic coordinates

(16) Logarithmic coordinates

Water	$\log \frac{w}{a}$	$\log \frac{1-w}{a}$	Water	$\log \frac{w}{a}$	$\log \frac{1-w}{a}$
0.10	1.284	0.238	0.10	1.168	0.132
0.20	1.382	1.084	0.20	1.264	1.866
0.30	1.456	1.824	0.30	1.340	1.708
0.40	1.519	1.608	0.40	1.400	1.582
0.50	1.586	1.580	0.50	1.470	1.470
0.60	1.618	1.472	0.60	1.533	1.339
0.70	1.712	1.344	0.70	1.602	1.234
0.80	1.783	1.180	0.80	1.670	1.068
0.90	2.878	2.920	0.90	1.700	2.836
P. P.	1.222	0.545	P. P.	1.040	0.420

TABLE V—(Continued)

(17) brombenzene carbinol (18) brombenzene alcohol

Water	Carbinol	Density	Water	Alcohol	Density
0 009	0 230	—	0 010	0 115	1 34
0 015	0 314	1 24	P. P. 0 04	0 32	—
P. P. 0 02	0 40	—	*0 10	0 65	1 07
0 031	0 453	1 16	0 109	0 641	1 09
*0 10	1 01	1 04	0 195	0 988	0 96
0 127	1 170	1 01	*0 20	1 00	0 96
0 198	1 491	0 98	*0 30	1 19	0 96
*0 20	1 50	0 98	0 354	1 240	0 97
0 237	1 751	0 96	*0 40	1 30	0 98
*0 30	1 84	0 95	0 414	1 326	0 98
0 357	1 932	0 93	0 498	1 385	—
0 400	2 065	0 94	*0 50	1 39	0 95
*0 50	2 24	0 91	0 593	1 420	0 91
0 551	2 290	0 90	*0 60	1 43	0 91
*0 60	2 30	0 90	0 695	1 434	0 90
0 633	2 295	0 90	*0 70	1 43	0 92
*0 70	2 28	0 89	*0 80	1 36	0 93
*0 80	2 20	0 89	0 840	1 305	0 92
0 812	2 185	0 91	*0 90	1 16	0 93
0 905	1 927	0 90	0 903	1 150	0 94
0 984	1 332	0 91	0 976	0 803	0 92

Tie lines

Tie lines

Water	Water	Water	Water
0 00	0 07	0 00	0 22
		0 00	0 16
		0 01	0 09
		0 02	0 06

(17) Logarithmic coordinates

(18) Logarithmic coordinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0 10	2 906	1 950	0 10	1 187	0 141
0 20	1 125	1 727	0 20	1 301	1 903
0 30	1 212	1 580	0 30	1 402	1 770
0 40	1 287	1 463	0 40	1 488	1 664
0 50	1 349	1 349	0 50	1 556	1 556
0 60	1 416	1 240	0 60	1 623	1 447
0 70	1 487	1 119	0 70	1 690	1 322
0 80	1 560	2 958	0 80	1 770	1 168
0 90	1 669	2 714	0 90	1 890	2 935
P. P.	2 699	0 389	P. P.	1 097	0 477

Experimental Determination of Binodal Curves, Etc. 771

TABLE V—(Continued)

(19) brombenzene propyl alcohol (20) brombenzene acetone

Water	Alcohol	Density	Water	Acetone	Density
0.017	0.186	1.29	0.023	0.685	1.12
0.091	0.560	1.11	*0.10	1.13	1.01
*0.10	0.58	1.11	0.107	1.175	1.01
*0.20	0.87	1.05	*0.20	1.41	0.98
0.23	0.936	1.04	0.236	1.470	1.00
*0.30	1.05	1.02	*0.30	1.52	0.97
0.358	1.110	1.01	0.319	1.535	0.96
*0.40	1.15	1.00	*0.40	1.57	0.96
*0.50	1.19	0.97	0.402	1.570	0.96
0.512	1.195	0.97	*0.50	1.60	0.95
0.573	1.208	0.97	P. P. 0.51	1.60	—
*0.60	1.19	0.95	0.547	1.600	0.95
*0.70	1.09	0.95	*0.60	1.59	0.94
0.708	1.071	0.95	*0.70	1.55	0.93
*0.80	0.93	0.95	0.715	1.540	0.94
0.815	0.890	—	0.792	1.454	0.93
*0.90	0.71	0.96	*0.80	1.46	0.93
0.906	0.687	0.96	0.874	1.365	0.93
0.979	0.457	0.98	*0.90	1.30	0.93
	—	—	0.980	0.849	0.95

Tie-lines

Water	Water
0.35	1.00
0.54	1.00
0.51	0.00
0.33	0.77

(19) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	1.237	0.191
0.20	1.362	1.064
0.30	1.456	1.824
0.40	1.541	1.718
0.50	1.624	1.624
0.60	1.703	1.527
0.70	1.808	1.440
0.80	1.935	1.333
0.90	0.103	1.149

Tie-lines

Water	Water
0.11	0.94
0.15	0.86
0.29	0.73
0.38	0.64

(20) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	2.947	1.001
0.20	1.152	1.754
0.30	1.295	1.663
0.40	1.406	1.582
0.50	1.495	1.495
0.60	1.577	1.400
0.70	1.655	1.287
0.80	1.730	1.137
0.90	1.840	2.886
P. P.	1.504	1.486

TABLE V—(Continued)

(21) bromtoluene carbinol

(22) bromtoluene alcohol

Water	Alcohol	Density
0 02	0 33	—
0 049	0 522	1 00
*0 10	0 87	1 06
0 146	1 086	1 01
*0 20	1 28	0 97
0 232	1 352	0 95
*0 30	1 54	0 94
0 386	1 700	—
*0 40	1 71	0 93
*0 50	1 81	0 92
0 534	1 850	0 92
*0 60	1 80	0 91
0 620	1 900	0 91
*0 70	1 80	0 90
0 785	1 800	0 91
*0 80	1 78	0 90
0 900	1 533	0 91
0 967	1 307	0 92

Tie lines

Water	Water
0 00	0 13
0 00	0 10
0 00	0 07
0 01	0 06

(22) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0 10	1 061	0 015
0 20	1 104	1 790
0 30	1 290	1 658
0 40	1 360	1 545
0 50	1 441	1 441
0 60	1 502	1 326
0 70	1 560	1 201
0 80	1 653	1 041
0 90	1 770	2 815
P P.	2 783	0 473

TABLE V —(Continued)

(23) bromtoluene propyl alcohol

(24) ethyl acetate alcohol

Water	Alcohol	Density	Water	Alcohol	Density
0 032	0 252	1 23	0 080	0 100	0 91
*0 10	0 52	1 11	*0 10	0 13	0 91
0 104	0 529	1 10	0 201	0 228	0 93
0 188	0 755	1 04	0 203	0 222	0 93
*0 20	0 78	1 03	0 301	0 205	0 92
0 30	0 96	1 01	0 396	0 200	0 95
0 303	0 955	1 01	*0 40	0 20	0 95
*0 40	1 07	0 99	0 50	0 30	0 95
0 407	1 075	0 99	0 507	0 297	0 94
0 496	1 127	0 98	P. P. 0 52	0 30	
*0 50	1 13	0 97	*0 60	0 31	0 96
0 560	1 124	0 96	0 611	0 310	0 96
0 598	1 139	0 96	0 689	0 304	0 96
*0 60	1 13	0 96	*0 70	0 31	0 95
0 677	1 075	0 95	0 803	0 282	0 97
*0 70	1 03	0 95	0 898	0 143	0 99
P. P. 0 75	0 97				
0 797	0 909	0 94			
*0 80	0 90	0 94			
*0 90	0 72	0 95			
0 925	0 660	0 95			
0 987	0 424	0 96			

Tie lines

Tie lines

Water	Water	Water	Water
0 19	0 99	0 88	0 05
0 33	0 99	0 86	0 15
0 43	0 99	0 78	0 20
0 52	0 92	0 73	0 30

(23) Logarithmic coordinates

(24) Logarithmic coordinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0 10	1 284	0 238	0 10	1 886	0 840
0 20	1 409	0 011	0 20	1 943	0 545
0 30	1 495	1 863	0 30	0 054	0 422
0 40	1 573	1 749	0 40	0 140	0 316
0 50	1 646	1 646	0 50	0 222	0 222
0 60	1 725	1 549	0 60	0 287	0 110
0 70	1 832	1 404	0 70	0 354	1 986
0 80	1 949	1 347	0 80	0 450	1 854
0 90	0 097	1 143	0 90	0 799	1 845
P. P.	1 888	1 411	P. P.	—	0 204

TABLE V—(Continued)
 (25) benzyl acetate alcohol (26) ethyl propionate alcohol

Water	Alcohol	Density	Water	Alcohol	Density
0.023	0.120	1.05	0.023	0.138	0.90
0.099	0.317	1.03	0.085	0.257	0.91
0.197	0.459	0.97	*0.10	0.27	0.90
*0.20	0.46	0.99	0.102	0.373	0.90
*0.30	0.58	0.97	*0.20	0.38	0.90
0.38	0.601	0.96	0.305	0.453	0.92
P. P. 0.32	0.60	—	*0.40	0.49	0.91
*0.40	0.69	0.95	0.494	0.520	0.92
0.415	0.705	0.95	*0.50	0.52	0.92
0.489	0.770	0.95	P. P. 0.54	0.53	—
*0.50	0.78	0.94	0.602	0.532	0.93
0.593	0.841	0.94	0.608	0.547	0.94
*0.60	0.85	0.94	*0.70	0.55	0.94
0.700	0.880	0.93	0.799	0.517	0.95
0.781	0.883	—	*0.90	0.46	0.96
*0.80	0.88	0.93	0.914	0.443	0.97
0.888	0.818	0.94	—	—	—
*0.90	0.80	0.94	—	—	—
0.959	0.665	0.95	—	—	—

Tie-lines

Water	Water
0.00	0.93
0.03	0.73
0.11	0.58
0.17	0.47

Tie-lines

Water	Water
0.95	0.02
0.92	0.13
0.86	0.14
0.83	0.24
0.76	0.34
0.67	0.41

(25) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	1.499	0.453
0.20	1.638	0.240
0.30	1.714	0.082
0.40	1.763	1.939
0.50	1.807	1.807
0.60	1.849	1.673
0.70	1.901	1.533
0.80	1.959	1.356
0.90	0.051	1.097
P. P. —	1.727	0.054

(26) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	1.569	0.523
0.20	1.721	0.323
0.30	1.824	0.192
0.40	1.912	0.088
0.50	1.983	1.983
0.60	0.054	1.878
0.70	0.105	1.737
0.80	0.190	1.587
0.90	0.291	1.337
P. P. —	0.008	1.939

TABLE V—(Continued)
(27) ethyl butyrate alcohol (28) benzyl ethyl ether alcohol

Water	Alcohol	Density	Water	Alcohol	Density
0.030	0.166	0.90	0.029	0.189	0.94
0.097	0.314	0.90	*0.10	0.37	0.92
*0.10	0.32	—	0.108	0.381	0.92
0.200	0.483	0.88	0.191	0.528	0.92
0.300	0.567	0.89	*0.20	0.54	0.92
0.401	0.628	0.90	0.274	0.648	0.92
0.506	0.659	0.91	*0.30	0.67	0.91
P. P. 0.54	0.67	—	P. P. 0.33	0.71	—
0.598	0.684	0.92	*0.40	0.78	0.91
*0.60	0.69	0.92	0.410	0.790	0.91
0.703	0.693	0.93	0.494	0.874	—
0.807	0.684	0.94	*0.50	0.87	0.91
*0.90	0.63	0.94	0.594	0.930	0.92
0.910	0.603	0.95	*0.60	0.93	0.92
—	—	—	*0.70	0.96	0.92
—	—	—	0.711	0.960	0.92
—	—	—	0.802	0.952	0.92
—	—	—	*0.90	0.86	0.93
—	—	—	0.920	0.793	0.94

Tie lines

Tie lines

Water	Water	Water	Water
0.96	0.00	0.00	0.73
0.93	0.05	0.03	0.70
0.89	0.11	0.15	0.52
0.81	0.25		
0.72	0.36		
0.62	0.45		

(27) Logarithmic coordinates

(28) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$	Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	1.495	0.449	0.10	1.432	0.386
0.20	1.617	0.219	0.20	1.560	0.171
0.30	1.723	0.091	0.30	1.651	0.019
0.40	1.804	1.980	0.40	1.710	1.886
0.50	1.880	1.880	0.50	1.759	1.759
0.60	0.939	1.763	0.60	1.810	1.634
0.70	0.004	1.636	0.70	1.863	1.495
0.80	0.008	1.475	0.80	1.924	1.322
0.90	0.155	1.201	0.90	0.020	1.005
P. P. —	1.906	1.837	P. P. —	1.667	1.975

TABLE V (Continued)

(20) isoamyl ether alcohol

(30) diethyl ketone alcohol

Water	Alcohol	Density	Water	Alcohol	Density
0.042	0.308	0.81	0.062	0.136	0.85
0.10	0.70	0.82	0.10	0.19	0.85
P. P. 0.11	0.74		0.105	0.201	0.86
0.121	0.793	0.82	0.20	0.31	0.87
0.20	1.20	0.83	0.219	0.317	0.87
0.233	1.324	0.83	0.298	0.356	0.88
0.298	1.573	0.83	0.400	0.392	0.89
0.406	1.876	0.84	0.453	0.410	0.90
0.50	1.98	0.84	0.501	0.411	0.91
0.599	2.188	0.85	0.542	0.415	0.92
0.60	2.19	0.85	0.593	0.404	0.91
0.698	2.240	0.86			
0.80	2.14	0.87			
0.819	2.102	0.88			
0.90	1.87	0.89			
0.914	1.792	0.89			

Tie lines

(30) Logarithmic coordinates

Water	Water	Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.72	0.00	0.10	1.721	0.675
0.50	0.00	0.20	1.810	0.412
0.38	0.00	0.30	1.921	0.289
0.24	0.01	0.40	0.008	0.185
0.21	0.02	0.50	0.085	0.085
0.10	0.03	0.60	0.167	0.004

(20) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	1.174	0.129
0.20	1.222	1.824
0.30	1.281	1.640
0.40	1.330	1.506
0.50	1.402	1.402
0.60	1.438	1.262
0.70	1.495	1.127
0.80	1.573	2.971
0.90	1.682	2.728
P. P.	1.172	0.080

Experimental Determination of Binodal Curves, Etc. 777

TABLE V—(Continued)

(31) hexane carbinol

(32) hexane alcohol

Water	Carbinol	Density	Water	Alcohol	Density
0 067	4 280		P. P. 0 03	0 50	
*0 10	4 60	0 80	0 035	0 64	0 75
0 160	5 090	0 80	*0 10	1 39	0 77
*0 20	5 26	0 80	0 134	1 54	0 79
0 309	5 710	0 82	0 173	1 899	0 79
*0 40	6 17	0 81	0 20	2 04	0 79
0 414	6 240	0 82	0 272	2 415	0 81
0 509	6 365	0 83	*0 30	2 45	0 81
*0 60	6 33	0 83	0 380	2 712	0 82
0 652	6 241	0 83	*0 40	2 73	0 82
0 670	6 222		*0 50	2 93	0 83
0 70	6 13	0 84	0 525	2 960	0 83
0 80	5 49	0 85	0 575	3 000	0 83
0 830	5 012	0 85	*0 60	3 00	0 83
*0 90	4 01	0 86	0 702	2 918	0 83
0 905	3 912	0 87	*0 80	2 75	0 85
0 984	1 759	0 91	0 815	2 720	0 86
			0 895	2 278	0 86
			*0 90	2 23	0 86
			0 986	1 056	

(31) Logarithmic coordinates

Tie lines

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0 10	2 329	1 283
0 20	2 580	1 182
0 30	2 720	1 088
0 40	2 812	2 988
0 50	2 896	2 896
0 60	2 977	2 801
0 70	1 058	2 690
0 80	1 164	2 551
0 90	1 351	2 397

Water	Water
0 11	0 00
0 07	0 00
0 05	0 01

TABLE V—(Continued)

(32) Logarithmic coordinates

(34) heptane alcohol

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	2.886	1.840
0.20	2.991	1.594
0.30	1.088	1.456
0.40	1.166	1.342
0.50	1.232	1.232
0.60	1.301	1.125
0.70	1.383	1.015
0.80	1.464	0.862
0.90	1.606	0.652
P. P. —	2.706	0.216

(33) heptane carbinol

Water	Carbinol	Density
0.034	4.78	—
*0.10	5.55	0.80
0.126	5.93	0.80
0.207	6.30	0.82
*0.30	7.30	0.82
0.321	7.40	0.82
0.400	8.22	0.82
*0.50	8.76	0.82
0.520	8.80	0.83
*0.60	8.65	0.83
0.672	8.05	0.83
*0.70	7.78	0.83
0.802	6.71	0.84
*0.90	4.40	0.87
0.962	2.96	0.91

(33) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	2.256	1.210
0.20	2.497	1.100
0.30	2.614	2.982
0.40	2.687	2.863
0.50	2.757	2.757
0.60	2.841	2.665
0.70	2.954	2.586
0.80	1.076	2.474
0.90	1.311	2.357

Water	Alcohol	Density
0.038	0.704	0.79
*0.10	1.44	0.80
0.118	1.685	0.80
0.202	2.375	0.82
*0.30	2.82	0.81
0.341	2.940	0.82
0.388	3.015	0.82
*0.40	3.00	0.82
*0.50	3.16	0.83
0.545	3.168	0.83
*0.60	3.17	0.84
*0.70	3.10	0.85
0.725	3.080	0.85
0.804	2.960	0.87
0.907	2.305	0.88

(34) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	2.842	1.796
0.20	2.926	1.528
0.30	1.027	1.395
0.40	1.116	1.293
0.50	1.199	1.199
0.60	1.277	1.101
0.70	1.354	2.986
0.80	1.432	2.830
0.90	1.593	2.638

TABLE V—(Continued)

(35) benzene alcohol (temp. 15°)

(36) toluene alcohol

	Water	Alcohol	Density	Water	Alcohol	Density
	0.013	0.170	0.86	0.052	0.388	0.87
	0.063	0.356	0.87	0.083	0.538	0.86
P. P.	0.10	0.50	0.86	*0.10	0.61	0.86
	0.183	0.708	0.85	0.121	0.705	0.86
	*0.20	0.86	0.86	*0.20	0.95	0.86
	0.298	0.917	0.88	*0.30	1.21	0.86
	*0.30	0.91	0.88	0.351	1.323	0.86
	*0.40	1.07	0.87	*0.40	1.41	0.86
	0.409	1.080	0.87	*0.50	1.53	0.87
	*0.50	1.18	0.87	0.530	1.551	0.87
	0.517	1.188	0.88	*0.60	1.59	0.87
	*0.60	1.22	0.88	*0.70	1.56	0.88
	0.614	1.200	0.88	0.759	1.494	0.89
	0.681	1.210	0.89	*0.80	1.44	0.89
	*0.70	1.21	0.89	0.837	1.380	0.89
	0.799	1.130	0.89	*0.90	1.23	0.91
	0.898	0.972	0.92	0.930	1.148	0.92
	*0.90	0.97	0.92	0.972	0.817	0.94
	0.980	0.590	0.94	—	—	—

Tie-lines

(36) Logarithmic coordinates

Water	Water		Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.04	0.18		0.10	1.215	0.169
(35) Logarithmic coordinates			0.20	1.323	1.925
Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	0.30	1.394	1.762
			0.40	1.453	1.629
			0.50	1.514	1.514
0.10	1.301	0.255	0.60	1.577	1.401
0.20	1.438	0.040	0.70	1.652	1.284
0.30	1.518	1.886	0.80	1.745	1.143
0.40	1.573	1.749	0.90	1.864	2.910
0.50	1.627	1.627			
0.60	1.692	1.516			
0.70	1.762	1.394			
0.80	1.850	1.248			
0.90	1.967	1.013			
P. P. —	1.301	0.255			

TABLE V (Continued)
 (37) *o*-xylene alcohol (38) *m*-xylene alcohol

Water	Alcohol	Density	Water	Alcohol	Density
P. P. 0 020	0 352	0 89	0 033	0 388	0 88
0 04	0 53		0 098	0 800	0 87
0 10	0 93	0 87	*0 10	0 81	0 87
0 129	1 075	0 87	0 162	1 125	0 85
0 214	1 320	0 87	*0 20	1 30	0 85
*0 30	1 53	0 87	0 289	1 590	0 85
0 312	1 560	0 86	*0 30	1 61	0 86
*0 40	1 72	0 87	*0 40	1 77	0 86
0 484	1 845	0 87	0 408	1 775	0 86
*0 50	1 87	0 87	*0 50	1 90	0 87
*0 60	1 96	0 88	0 588	1 965	0 87
0 628	1 955	0 88	*0 60	1 98	0 87
0 70	1 94	0 88	*0 70	2 01	0 88
0 792	1 813	0 89	0 724	2 000	0 88
*0 80	1 81	0 89	0 795	1 870	0 89
0 900	1 640	0 90	*0 80	1 87	0 89
0 969	1 190	0 93	0 898	1 530	0 90
Tie lines			*0 90	1 530	0 90
			0 977	1 168	0 92

Water Water

0 00	0 64
0 00	0 21
0 00	0 16
0 00	0 13
0 00	0 11
0 02	0 88

(37) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0 10	1 032	1 986
0 20	1 180	1 783
0 30	1 292	1 660
0 40	1 367	1 543
0 50	1 427	1 427
0 60	1 486	1 310
0 70	1 537	1 189
0 80	1 645	1 043
0 90	1 739	2 785
P. P. —	1 878	0 054

(38) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0 10	1 092	0 046
0 20	1 187	1 789
0 30	1 271	1 639
0 40	1 354	1 530
0 50	1 420	1 420
0 60	1 482	1 305
0 70	1 542	1 174
0 80	1 631	1 029
0 90	1 770	2 815

Experimental Determination of Binodal Curves, Etc. 781

TABLE V—(Continued)
(39) *p*-xylene alcohol (temp. 15°) (40) mesitylene alcohol

Water	Alcohol	Density	Water	Alcohol	Density
	0.034	0.84	P. P. 0.03	0.48	—
	0.074	0.85		0.037	0.516
P. P. 0.08	0.57	—		0.090	0.981
	*0.10	0.85		*0.10	1.09
	0.121	0.86		0.164	1.473
	*0.20	0.85		*0.20	1.66
	0.211	0.85		0.298	2.030
	0.286	0.85		*0.30	2.04
	*0.30	0.85		*0.40	2.32
	*0.40	0.85		0.429	2.365
	*0.50	0.86		*0.50	2.52
	0.524	0.86		*0.60	2.64
	*0.60	0.86		*0.70	2.68
	0.622	0.86		0.714	2.670
	0.702	0.87		0.801	2.490
	0.807	0.88		0.890	2.325
	*0.90	0.89		*0.90	2.28
	0.912	0.89		0.949	1.615
	0.985	0.93			
Tie-lines			Tie-lines		
Water		Water	Water		Water
0.00		0.26	0.00		0.15
0.01		0.19	0.00		0.10
0.02		0.16	0.00		0.08
0.04		0.14			
(39) Logarithmic coordinates			(40) Logarithmic coordinates		
Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
	0.10	1.187		0.10	2.963
	0.20	1.280		0.20	1.681
	0.30	1.347		0.30	1.168
	0.40	1.409		0.40	1.237
	0.50	1.474		0.50	1.298
	0.60	1.530		0.60	1.357
	0.70	1.605		0.70	1.417
	0.80	1.694		0.80	1.507
	0.90	1.811		0.90	1.596
P. P. —	1.147	0.208	P. P. —	2.796	0.306

TABLE V—(Continued)

(41) pinene alcohol

(42) benzaldehyde alcohol

Water	Alcohol	Density	Water	Alcohol	Density
0 010	0 268	0 87	0 043	0 150	1 02
P. P. 0 015	0 47	—	0 102	0 283	1 01
0 055	1 001	0 85	*0 20	0 42	0 99
0 103	1 595	0 85	0 211	0 441	0 99
0 205	2 268	0 84	0 295	0 520	0 98
*0 30	2 67	0 84	*0 30	0 55	0 98
0 317	2 704	0 85	0 402	0 601	0 97
0 395	2 924	0 84	P. P. 0 43	0 61	—
*0 40	2 94	0 85	0 504	0 643	0 96
0 507	3 135	0 85	0 606	0 681	0 95
0 607	3 126	0 86	0 702	0 701	0 95
0 707	3 038	0 86	*0 80	0 67	0 95
0 806	2 799	0 87	0 817	0 675	0 95
0 906	2 331	0 89	0 898	0 615	0 96
0 965	1 639	0 91	*0 90	0 61	0 96
			0 969	0 461	0 97

Tie lines

Tie lines

Water	Water	Water	Water
0 00	0 06	0 04	0 98
0 00	0 05	0 09	0 96
0 00	0 04	0 10	0 82
0 00	0 03	0 15	0 76
0 01	0 02	0 26	0 63
		0 31	0 57

(41) Logarithmic coordinates

(42) Logarithmic coordinates

Water	$\log \frac{u}{a}$	$\log \frac{1-u}{a}$	Water	$\log \frac{u}{a}$	$\log \frac{1-u}{a}$
0 10	2 799	1 752	0 10	1 548	0 502
0 20	2 945	1 547	0 20	1 648	0 250
0 30	1 051	1 419	0 30	1 737	0 105
0 40	1 134	1 310	0 40	1 823	1 999
0 50	1 203	1 203	0 50	1 893	1 893
0 60	1 283	1 107	0 60	1 946	1 770
0 70	1 362	2 994	0 70	1 999	1 631
0 80	1 456	2 854	0 80	0 077	1 475
0 90	1 587	2 633	0 90	0 169	1 215
P. P.	2 504	0 321	P. P.	1 848	1 971

Experimental Determination of Binodal Curves, Etc. 783

TABLE V—(Continued)

(43) methyl aniline alcohol

(44) *p*-nitrotoluene alcohol

Water	Alcohol	Density	Water	Alcohol	Density
0.041	0.218	0.96	0.022	0.253	1.08
*0.10	0.37	0.95	P. P. 0.05	0.50	—
0.111	0.405	0.95	0.090	0.781	0.98
0.205	0.555	0.93	*0.10	0.84	0.97
*0.30	0.68	0.93	*0.20	1.29	0.96
0.331	0.721	0.93	0.235	1.40	0.93
P. P. 0.34	0.72	—	*0.30	1.57	0.92
0.392	0.756	0.93	0.337	1.649	0.92
*0.40	0.76	0.93	*0.40	1.73	0.91
0.498	0.835	0.93	0.411	1.767	0.91
*0.50	0.84	0.93	0.494	1.782	0.91
0.509	0.892	0.93	0.602	1.868	0.91
*0.60	0.89	0.93	0.706	1.816	0.91
0.697	0.901	0.93	*0.80	1.63	0.91
*0.70	0.91	0.93	0.809	1.607	0.91
*0.80	0.87	0.94	0.898	1.395	0.92
0.813	0.856	0.94	*0.90	1.30	0.92
0.902	0.734	0.95			
0.959	0.581	0.96	0.944	1.105	0.93

Tie lines

Tie lines

Water	Water	Water	Water
0.67	0.00	0.00	0.14
0.59	0.05	0.02	0.10
0.55	0.12	0.03	0.08
0.51	0.16		
0.42	0.23		

(43) Logarithmic coordinates

(44) Logarithmic coordinates

Water	$\text{Log } \frac{x}{a}$	$\text{Log } \frac{1-x}{a}$	Water	$\text{Log } \frac{x}{a}$	$\text{Log } \frac{1-x}{a}$
0.10	1.432	0.386	0.10	1.076	0.030
0.20	1.561	0.163	0.20	1.090	1.793
0.30	1.645	0.013	0.30	1.281	1.649
0.40	1.721	1.897	0.40	1.364	1.540
0.50	1.775	1.775	0.50	1.449	1.449
0.60	1.829	1.653	0.60	1.509	1.333
0.70	1.886	1.518	0.70	1.585	1.217
0.80	1.964	1.362	0.80	1.691	1.089
0.90	0.091	1.137	0.90	1.840	2.886
P. P.	1.674	1.962	P. P.	1.000	0.279

TABLE V—(Continued)

(45) *o*-toluidine alcohol

(46) isobutyl alcohol alcohol

Water	Alcohol	Density	Water	Alcohol	Density
0.046	0.025	1.01	*0.30	0.13	0.87
*0.10	0.21	0.93	0.313	0.141	0.87
0.105	0.219	0.93	0.411	0.177	0.89
*0.20	0.32	0.97	0.498	0.194	0.90
0.222	0.346	0.97	*0.50	0.20	0.90
0.298	0.404	0.96	*0.60	0.20	0.92
*0.30	0.41	0.96	0.613	0.204	0.92
0.402	0.455	0.96	P. P. 0.65	0.21	—
*0.50	0.48	0.96	0.696	0.205	0.94
0.546	0.492	0.95	*0.70	0.21	0.94
0.580	0.493	0.95	*0.80	0.20	0.95
*0.60	0.50	0.96	0.868	0.189	0.96
0.698	0.499	0.96			—
*0.70	0.50	0.96			—
*0.80	0.49	0.96			—
0.810	0.485	0.96			—
0.902	0.462	0.98			—
0.973	0.262				—

Tie lines

Water	Water
0.87	0.28
0.83	0.41
0.81	0.46
0.80	0.50

(45) Logarithmic coordinates

(46) Logarithmic coordinates

Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$	Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0.10	1.678	0.632	0.30	0.303	0.731
0.20	1.796	0.398	0.40	0.372	0.548
0.30	1.864	0.232	0.50	0.398	0.398
0.40	1.944	0.120	0.60	0.477	0.301
0.50	0.018	0.018	0.70	0.533	0.165
0.60	0.079	1.903	0.80	0.602	0.000
0.70	0.146	1.778	0.868	0.662	1.844
0.80	0.213	1.611	P. P.	0.491	0.222
0.90	0.291	1.337		—	—

TABLE V—(Continued)
(47) isoamyl alcohol alcohol (48) benzyl alcohol alcohol

Water	Alcohol	Density	Water	Alcohol	Density
0.097	0.116	0.84	*0.10	0.13	1.03
*0.10	0.12	0.84	0.130	0.153	1.02
0.203	0.258	0.85	*0.20	0.26	1.00
0.306	0.396	0.86	0.209	0.268	1.00
0.398	0.427	0.88	0.295	0.347	0.98
0.503	0.449	0.89	*0.30	0.35	0.98
0.601	0.453	0.90	*0.40	0.39	0.98
0.706	0.434	0.92	0.422	0.392	0.98
P. P. 0.73	0.43	—	*0.50	0.40	0.97
0.804	0.411	0.94	0.512	0.403	0.97
0.900	0.369	0.96	*0.60	0.41	0.97
—	—	—	P. P. 0.62	0.42	—
—	—	—	0.621	0.417	0.98
—	—	—	*0.70	0.41	0.97
—	—	—	0.712	0.404	0.97
—	—	—	0.806	0.388	0.97
—	—	—	0.898	0.352	0.97
—	—	—	*0.90	0.35	0.98
—	—	—	0.960	0.139	0.99

Tie lines

Tie lines

Water	Water	Water	Water
0.95	0.10	0.33	0.92
0.94	0.31	0.41	0.83
0.92	0.40		
0.87	0.53		
0.83	0.63		

(47) Logarithmic coordinates

(48) Logarithmic coordinates

Water	$\text{Log} \frac{w}{a}$	$\text{Log} \frac{1-w}{a}$	Water	$\text{Log} \frac{w}{a}$	$\text{Log} \frac{1-w}{a}$
0.10	1.021	0.875	0.10	1.886	0.840
0.20	1.891	0.493	0.20	1.880	0.488
0.30	1.921	0.288	0.30	1.933	0.301
0.40	1.972	0.148	0.40	0.011	0.187
0.50	0.047	0.047	0.50	0.097	0.097
0.60	0.122	1.946	0.60	0.195	1.080
0.70	0.209	1.841	0.70	0.232	1.864
0.80	0.290	1.688	0.80	0.312	1.710
0.90	0.387	1.433	0.90	0.410	1.456
P. P.	0.230	1.798	P. P.	0.169	1.957

TABLE V—(Continued)

(49) phenetol alcohol (50) nitrobenzene alcohol (temp. 15°)

Water	Alcohol	Density	Water	Alcohol	Density
0 018	0 157	0 96	0 035	0 248	1 08
P. P. 0 10	0 55		P. P. 0 09	0 49	—
0 103	0 554	0 93	*0 10	0 53	1 02
0 202	0 916	0 90	0 109	0 558	1 02
0 203	1 170	0 90	*0 20	0 86	0 97
*0 30	1 18	0 90	0 214	0 901	0 97
0 304	1 380	0 89	*0 30	1 09	0 94
*0 40	1 39	0 89	0 316	1 112	0 94
0 505	1 518	0 89	0 406	1 238	0 93
0 601	1 560	0 89	0 494	1 300	0 92
0 604	1 545	0 90	*0 50	1 31	0 92
*0 70	1 54	0 90	*0 60	1 34	0 92
0 802	1 449	0 91	0 636	1 333	0 92
*0 90	1 21	0 92	0 694	1 305	0 91
0 918	1 150	0 93	*0 70	1 30	0 91
			0 806	1 212	0 92
			*0 90	0 98	0 93
			0 909	0 940	0 93
			0 980	0 601	0 95

Tie-lines

Tie-lines

Water	Water	Water	Water
0 00	0 38	0 00	0 42
0 01	0 26	0 00	0 33
0 04	0 18	0 01	0 24
0 05	0 17	0 03	0 16
0 06	0 15	0 05	0 14

(49) Logarithmic coordinates

(50) Logarithmic coordinates

Water	$\text{Log } \frac{u}{a}$	$\text{Log } \frac{1-u}{a}$	Water	$\text{Log } \frac{w}{a}$	$\text{Log } \frac{1-w}{a}$
0 10	1 260	0 214	0 10	1 276	0 230
0 20	1 337	1 939	0 20	1 367	1 969
0 30	1 405	1 773	0 30	1 440	1 807
0 40	1 459	1 636	0 40	1 512	1 688
0 50	1 517	1 517	0 50	1 582	1 582
0 60	1 585	1 409	0 60	1 651	1 475
0 70	1 658	1 290	0 70	1 731	1 363
0 80	1 742	1 140	0 80	1 820	1 218
0 90	1 871	2 917	0 90	1 903	1 009
P. P.	1 260	2 214	P. P.	—	1 269

Experimental Determination of Binodal Curves, Etc. 787

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|--|---|
| <i>Schijf</i> : Liebig's Ann., 118 , 370 (1861). | Water, alcohol, MnSO_4 . |
| <i>Tuchschmidt and Follenius</i> : Ber. chim. Ges. Berlin, 4 , 583 (1871). | Water, alcohol, carb. bisulphide. |
| <i>Berthelot and Jungblut</i> : Ann. Chim. Phys., (4) 26 , 396 (1872). | Acetic acid, water, ether; bromine, water, carb. bisulphide. |
| <i>Duclaux</i> : Ann. Chim. Phys., (5) 7 , 264 (1876). | Benzene, water, acetic acid; amyl alcohol, water, alcohol; amyl alcohol, water, acetic acid; ether, water, acetic acid. |
| <i>Duport</i> : Chem. News, 35 , 87 (—). | Water, ether, hydrochl. acid. |
| <i>Toussie and Neuberg</i> : Zeit. Phys. Chem., 1 , 509 (1887). | Water, alcohol, ammon. sulph., etc. |
| <i>Haight and Collaborators</i> : Proc. Roy. Soc., 45 , 461 (1889); 48 , 25 (1890); 49 , 156 and 174 (1891); 50 , 372 (1891); 52 , 11 (1892); 55 , 130 (1894). | Alloys. |
| Proc. Roy. Soc., 49 , 183 (1891). | Water, chloroform, acetic acid. |
| <i>Bodländer</i> : Zeit. phys. Chem., 7 , 318 (1891). | Water, alcohol, amm. sulph. |
| <i>Pfaff</i> : Zeit. phys. Chem., 9 , 469 (1892). | Water and alcohol with the following: mono-, di- and triethylacetic ester; amyl alcohol; methyl, ethyl, propyl, butyl and amyl formate; methyl, ethyl, propyl, butyl and amyl acetate; methyl, ethyl and propyl propionate; methyl, ethyl and propyl butyrate; methyl and ethyl valerate. |
| <i>Schunke</i> : Zeit. phys. Chem., 14 , 331 (1894). | Water, ether, hydrochl. acid. |
| <i>Linbarger</i> : Am. Chem. Jour., 14 , 380 (1892). | Water and alcohol with pot. carbonate, sod. carbonate, amm. sulphate, manganoous sulphate; water and acetone with the same salts. |
| <i>Krug and McLeod</i> : Jour. Anal. Chem., 6 , 153 (1892). | Water and acetone with sugar, dextrose, maltose, sucrose. |
| <i>Bancroft</i> : Phys. Review, 3 , 21, 114 and 193 (1895); Jour. Phys. Chem., 1 , 34, and 760 (1896); 3 , 217 (1899). | Chloroform and water with alcohol, carbinol and acetone; benzene and water with alcohol, carbinol and ace- |

Author and reference.

Taylor: Jour. Phys. Chem., **1**, 301
(1896); *Ibid.*, **1**, 461.

Schreinmakers: Zeit. phys. Chem.,
22, 93 and 515 (1897).
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(1898).

Snell: Jour. Phys. Chem., **2**, 457
(1898).

Lincoln: Jour. Phys. Chem., **4**, 161
(1900); *Ibid.*, **8**, 248 (1904).

Ternary system.

tone; ether and water with alcohol
and carbinol; ethyl acetate and water
with alcohol, carbinol and acetone;
alcohol and water with the following:
carbon bisulphid, methyl valerate,
ethyl valerate, methyl butyrate, ethyl
butyrate, amyl alcohol, mono-, di-
and trichloroacetic ester, ethyl iso-
valerate, isoamyl acetate, propyl
butyrate, ethyl propionate, propyl
propionate, propyl acetate, butyl ace-
tate, amyl acetate, propyl formate,
butyl formate, amyl formate.

Water, benzene, alcohol (Binodal
curve); water, benzene, alcohol (Tie-
lines).

Theory.

Water, sod. chloride, succinonitrile
(Tie-lines and binodal curve).

Water, ether, hydrochl. acid (exp. data
of Draper and Schunke); water,
alcohol, amm. sulphate (exp. data of
Bodlander and Traube and Nen-
berg).

Water, ether, succinonitrile.

Water, benzoic acid, succinonitrile.

Water, alcohol, succinonitrile.

Water, phenol, aniline.

Water, phenol, salt.

Water and phenol with tartaric and
racemic acids.

Water, phenol, acetone

Water, phenol, acetone (Tie-lines).

Water, silver nitrate, succinonitrile.

Benzene, water, acetic acid.

Pot. chloride, acetone, water; water,
alcohol, mang. sulphate (exp. data
of Schiff and Linebarger); water,
alcohol, amm. sulphate (exp. data of
Traube and Neuberg).

Water, benzene, alcohol; water, ben-
zene, acetic acid.

Experimental Determination of Binodal Curves, Etc. 789

Author and reference.

Meerburg: *Zeit. phys. Chem.*, **40**, 64 (1902).

Bell: *Jour. Phys. Chem.*, **9**, 531 (1905).

Miller and McPherson: *Jour. Phys. Chem.*, **12**, 709 (1908).

Ternary system.

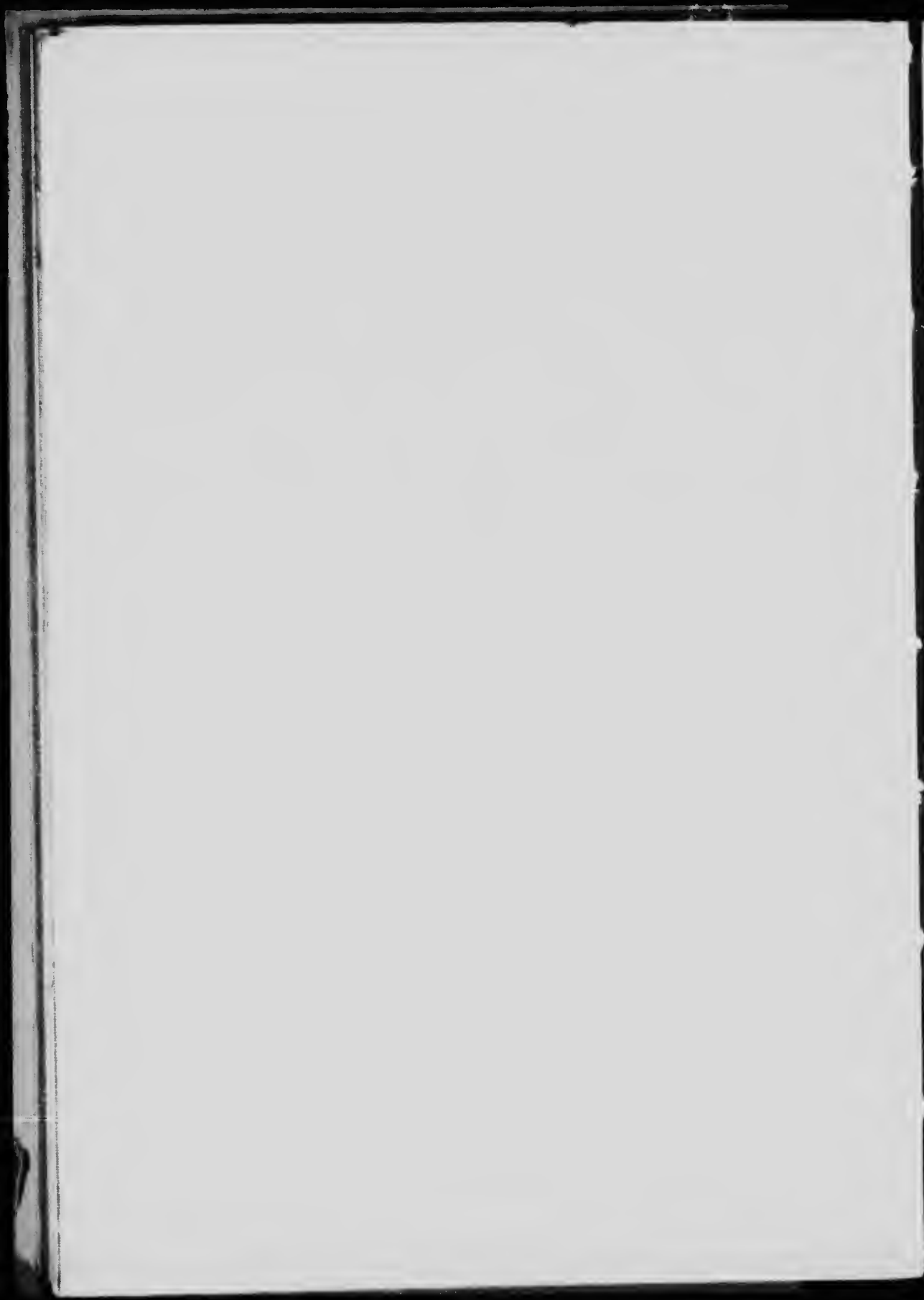
Triethylamine and water with alcohol, ether, phenol.

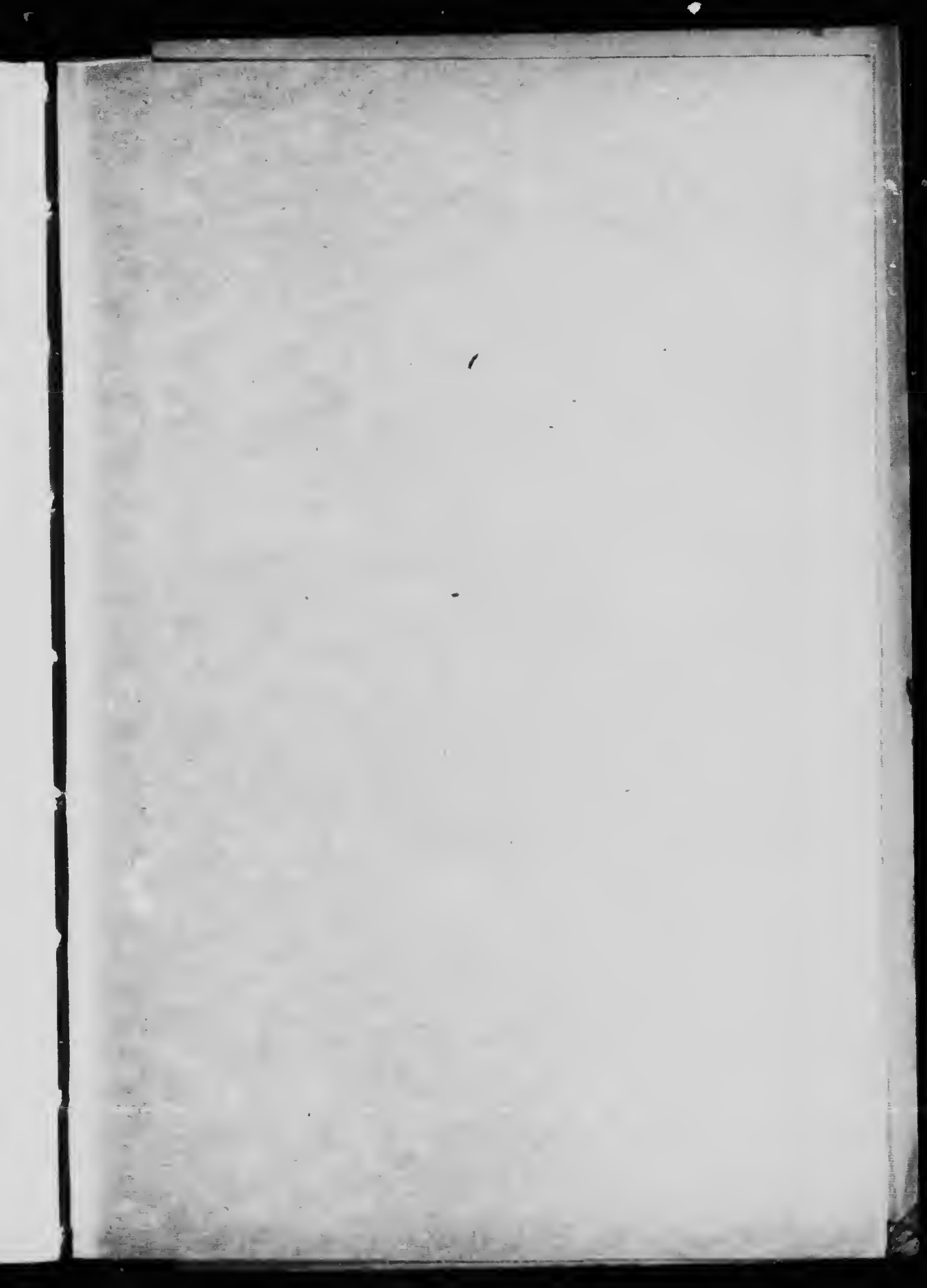
Water, alcohol, pot. carb., etc. (exp. data of Linebarger); water, acetone, sugar, etc. (exp. data of Krug and McElroy); water, acetone, pot. carbonate; water, alcohol, pot. carbonate; water, acetic acid, sod. carbonate; water, acetic acid, sugar; water, acetic acid, naph.; water, acetic acid, anethol; water, alcohol, benzophenone; water, acetic acid, benzophenone.

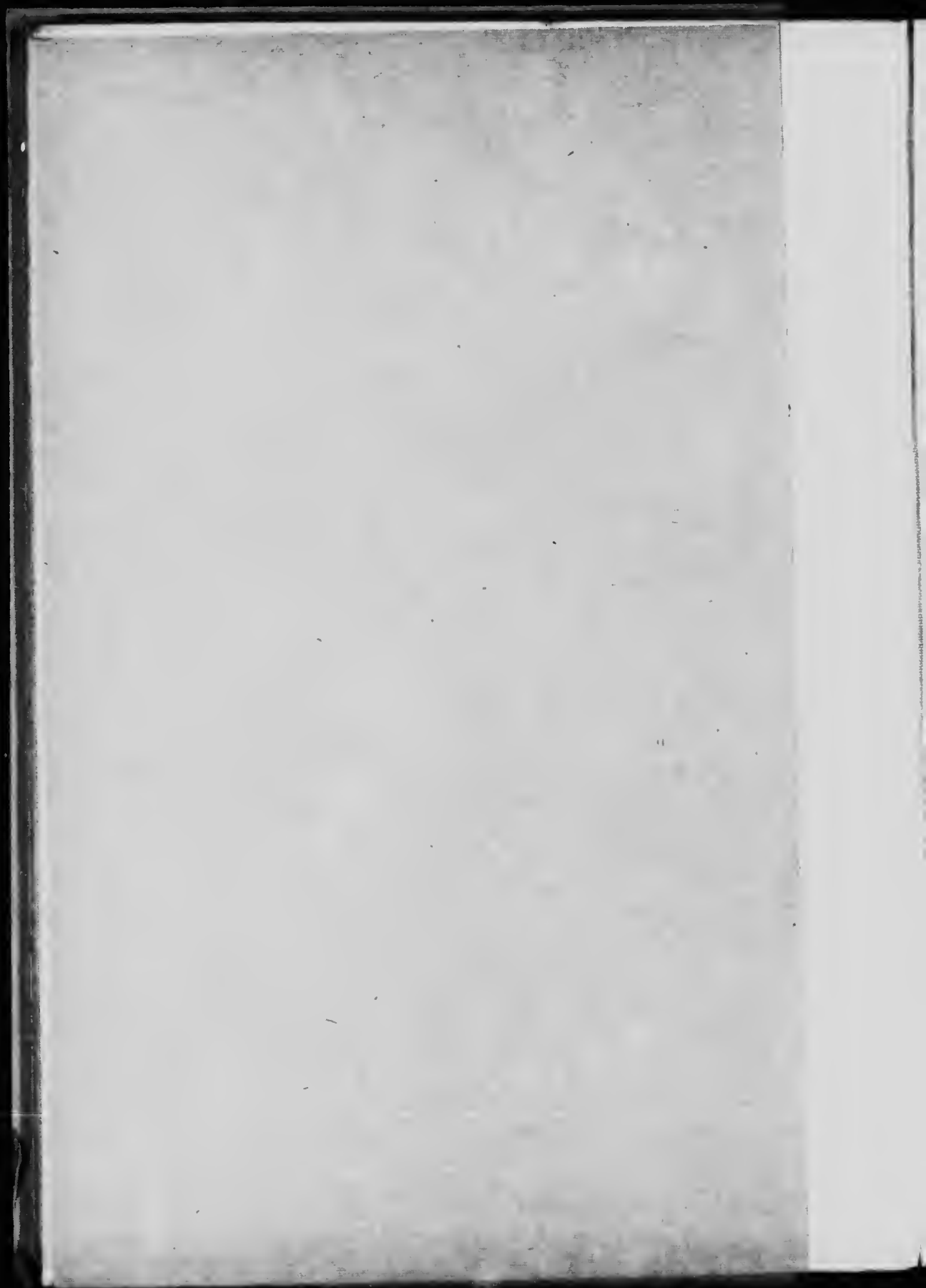
Water, chloroform, alcohol.

My thanks are due to Professor W. Lash Miller, at whose suggestion and under whose direction this work was carried out.

University of Toronto,
May, 1910







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