

This reaction is analogous to that occurring with potassium hydroxide and sulfur¹ except that with the potassium hydroxide the trisulfide (K_2S_3) is formed.

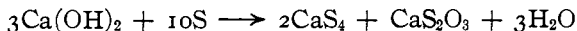
In Experiments 5 and 6 the calcium hydroxide and sulfur were used in amounts proportionate to those required in the equation given in the preceding paragraph. The analytical results show that there was but a slight loss of calcium and sulfur due to the formation of the more insoluble calcium sulfite. Since there was no uncombined calcium hydroxide present, all of this substance had reacted with the sulfur. This fact and the general relationships of the amounts of the different forms of combined sulfur with each other, confirm the conclusions drawn from the preceding experiments.

In solutions A and B where an excess of sulfur was used in preparation, some calcium pentasulfide was present. This justifies the conclusion that a secondary reaction took place in which sulfur combined with the tetrasulfide to form pentasulfide.

In conclusion, it may be well to state that a discussion of the commercial application of the results here reported, will soon be presented for publication in the *Journal of Industrial and Engineering Chemistry*.

Summary.

1. The primary reaction between calcium hydroxide and sulfur in heated aqueous solution takes place as represented by the following equation:



2. When sulfur is used in excess, a secondary reaction occurs in which it combines with the tetrasulfide to form pentasulfide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

SOME PHYSICAL PROPERTIES AND THE ANALYSIS OF TERNARY MIXTURES OF TOLUENE, CARBON TETRACHLORIDE AND ETHYLENE BROMIDE.

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Received December 20, 1913.

The literature of ternary systems appears to contain only two² cases in which unknown ternary mixtures of organic substances have been

¹ *Loc. cit.*

² After this communication had been sent to the editor my attention was called to a case in which the composition of certain ternary mixtures was ascertained by determining their physical properties. Shinkichi Horiba has, namely, analyzed mixtures of water, ethyl alcohol, and ethyl ether by determining their specific gravities, indices of refraction, and specific viscosities. The original paper was published in the *Memoirs, Imperial University, Kyoto*, 3, 3, p. 63, (1911), and a brief abstract of it in the

analyzed. Schreinemakers,¹ in connection with his work on the system phenol–water–aniline, used an analytical method which was purely chemical. The other case is in the work of Barrell, Thomas, and Young,² who resorted to the laborious and inexact method of fractional distillation to determine the unknown composition of certain ternary mixtures,

The method described in this communication is based on the obvious principle that two measurements are necessary and sufficient to determine the composition of a ternary mixture. Ordinary physical properties being chosen, the measurements are simple and the method is very rapid, after the two physical properties have been fully enough ascertained for mixtures of a given set of three substances. The tables below reproduce a complete set of such preliminary measurements for mixtures of toluene, carbon tetrachloride, and ethylene bromide. These data were needed in this laboratory in connection with a quantitative study of fractional distillation. They will, I believe, prove valuable in other physico-chemical studies as well, particularly in connection with the theory of liquid mixtures, and are, therefore, reproduced in full. It will be seen that instead of determining only two physical properties, which would have been sufficient for purely analytical purposes, I determined three, *viz.*, the specific volumes, the boiling points, and the indices of refraction. Experience has taught that even in analytical work a knowledge of the third property is not useless.

Ternary mixtures are now generally represented by means of an equilateral triangle, and in part of my work this was the mode of representation employed. However, different modes of graphic representation were employed in the more essential parts of the work.

If, in an equilateral triangle (Fig. 1) each of whose sides represents 100 units, a straight line be drawn from a vertex, *A*, to any point on the side opposite, then all points on the line will represent mixtures containing two of the components, *B* and *C*, in a fixed ratio. Such mixtures may be consid-

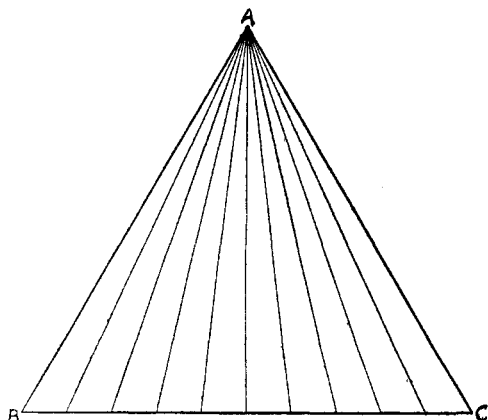


Fig. 1.

Chemisches Zentralblatt, 2, 7, p. 437 (1911). The method employed by Horiba is, however, different in many respects from that described in the present communication and has yielded much less accurate results. This footnote is added in the proof.

¹ Schreinemakers, *Z. physik. Chem.*, 35, 459 (1900).

² Barrell, Thomas and Young, *Phil. Mag.*, [5] 37, 8 (1894).

ered as made up by mixing one of the three substances, *A*, with varying amounts of a binary mixture containing the other two substances *B* and *C*, in the fixed ratio just referred to. In other words, each line within the triangle in Fig. 1 may be thought of as representing all possible *binary* mixtures of the component *A* with a certain liquid which is itself a certain binary mixture of *B* and *C*.

If now some physical property, say the specific volumes, were determined for a set of mixtures along any such line within the triangle, then the graphic representation may be transferred to ordinary rectangular coördinates as follows: The origin of the abscissa may represent 0% and the farthest point to the right 100% of component *A*. At the same time these points will represent, respectively, 100 and 0% of the binary mixtures of *B* and *C* involved. The ordinates corresponding to the various abscissae may represent the physical property on a suitable scale. Then the same diagram may be used with reference to a second of the straight lines within the triangle. Now, the abscissa will represent the same percentages of *A* as before; only the new binary mixture will, of course, have a different composition than in the first case. The new ordinates will give a second curve on the diagram. In this manner a curve may be obtained corresponding to each of the straight lines within the triangle. Such sets of curves will be shown in Figs. 3, 4 and 5 further on. On such a diagram the two extreme curves may correspond to the two sides *AB* and *AC* of the equilateral triangle, and, therefore, represent binary mixtures in the true sense of the term. The data corresponding to each physical property measured will thus be represented by a separate set of curves.

Two sets of curves having been determined, the analysis of any ternary mixture of the components *A*, *B*, and *C* is very simple. The two physical properties are measured for the unknown mixture. Assuming that we deal with the boiling points and the specific volumes, it is evident that we may have an infinite number of mixtures that have the same boiling point as the unknown mixture, and likewise we may have an infinite number of mixtures that have the same specific volume as the unknown mixture. But usually only one mixture can have that boiling point and at the same time that specific volume. The composition of this mixture is determined as follows: At the level representing the boiling temperature of the unknown mixture a line is drawn across the curves parallel to the abscissa. This line will cut a certain number of curves. The percentage of *A* is read where the line cuts each curve, and, since the ratio of *B* to *C* is known for each curve, the percentages of these two components are readily calculated. Then on coördinate paper the per cents. of *B* are plotted as the ordinates, and the per cents. of *A* as the abscissae. In this manner, a curve is obtained representing all mixtures that have the same boiling point as the unknown mixture. This procedure is repeated for the specific

volume, and thus a second curve is obtained representing all mixtures having the same specific volume as the unknown mixture. The two curves will intersect as shown, for example, in Fig. 2. At the point of intersection the per cents. of A and B are read off, and the per cent. of C is obtained by difference. And this is the composition of the unknown mixture. It is obvious that the accuracy of the method is greatest when physical properties are chosen that differ most widely for the three components.

In order to increase the reliability of the method, I decided to determine, as already stated, not two, but three physical properties, namely, the boiling points, the specific volumes, and the refractive indices. In connection with the latter, however, it was found more convenient to plot the angles as directly observed on a Pulfrich refractometer.

The liquids chosen for the experiments were toluene, carbon tetrachloride, and ethylene bromide. These liquids exhibit sufficiently wide differences in the three physical properties to permit of accurate analysis, as is evident from the following table:

TABLE I.

Substance.....	$C_6H_5CH_3$.	CCl_4 .	$C_2H_4Br_2$.
Refractive angle at 25°	39.366°	45.367°	31.350°
Specific volume at 25°	1.1594	0.6297	0.4593
Boiling point under 749.0 mm.....	110.11°	76.87°	130.23°

Great care was observed in the purification of the substances. The carbon tetrachloride and the toluene were Kahlbaum's. They were dried over calcium chloride and distilled with the aid of a five-bulb LeBel-Henninger column. Only the large middle fractions that passed over within 0.1° were taken. The ethylene bromide was made in this laboratory. After drying for several days over calcium chloride, it was distilled three times with the LeBel-Henninger column. Since ethylene bromide absorbs moisture very rapidly from the atmosphere, care was taken that the distillate did not come into contact with the air. Only the large middle fraction that passed over within 0.2° was taken.

The boiling points of the mixtures were determined in an Oddo ebullioscope, which was connected with a 100-liter manostat tank. The manostat was connected, in turn, with a source of compressed air, with suction, and with a large mercury manometer. This permitted the various boiling points to be observed under the same pressure. The pressure em-

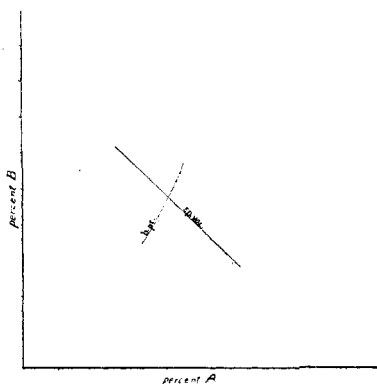


Fig. 2.

ployed in these determinations was 749 mm. (corrected to 0°), which happens to be the average atmospheric pressure at Worcester.

The refractive angles of the mixtures were found by means of an excellent Pulfrich refractometer (new construction). The cup of the refractometer was kept at 25° by a stream of water from the same thermostat in which the mixtures to be analyzed were kept. The washer on the cap consisted of rubber which was painted over with collodion. The collodion was denitrated by treating the washer with ammonium sulphide. This made the washer elastic, and permitted the closing of the cup so that no measurable loss by evaporation could occur. The mixtures were allowed to remain in the cup for five minutes before the final reading was taken. In order to transform the angles given in my tables into the indices, the usual formula should be employed: $n = \sqrt{N^2 - \sin^2 e}$, where n denotes the index of refraction, $N = 1.62197$, and e is the angle observed.

The specific volumes of the mixtures were determined in 50 cc. specific gravity bottles at 25°.

The following procedure was used in making up the desired mixtures: The binary mixtures corresponding to those of the base of the triangle in Fig. 1 were made up of toluene and ethylene bromide, since these were the less volatile components. These binary mixtures will be referred to below as "fundamental mixtures." Carbon tetrachloride was considered as the third component, and altogether 111 samples were examined, including the three pure substances and an evenly graded set of binary and ternary mixtures. The measurements are reproduced in Tables II to XII, inclusively, the composition of each fundamental binary mixture which was mixed with increasing proportions of carbon tetrachloride being given at the head of each table.

In plotting the sets of curves for the boiling points, refractive angles, and specific volumes with the percentage of carbon tetrachloride as the abscissa in each case, the first two cases were found to give rather disappointing results; the curves, namely, ran closely together and finally

TABLE II.—FIRST FUNDAMENTAL MIXTURE: 100% $C_6H_5CH_3$, 0% $C_2H_4Br_2$.

% CCl ₄ .	Boiling point.	Refractive angle.	Specific volume.
0	110.11°	39.366°	1.1594
9.66	107.09	39.650	1.1079
20.00	103.87	40.017	1.0528
31.21	100.68	40.383	0.9996
39.88	97.85	40.733	0.9552
49.88	94.26	41.300	0.8952
60.29	90.72	41.833	0.8391
69.94	87.48	42.517	0.7882
80.04	84.00	43.300	0.7344
89.89	80.52	44.250	0.6821
100.0	76.87	45.367	0.6297

TABLE III.—SECOND FUNDAMENTAL MIXTURE: 90% $C_6H_5CH_3$, 10% $C_2H_4Br_2$.

% CCl_4 .	Boiling point.	Refractive angle.	Specific volume.
0	110.80°	39.117°	1.0876
9.64	107.44	39.450	1.0412
19.79	104.07	39.817	0.9965
29.93	100.75	40.233	0.9501
39.97	97.21	40.717	0.9034
49.97	93.92	41.233	0.8596
59.99	90.49	41.850	0.8124
69.91	87.12	42.533	0.7662
79.93	83.71	43.333	0.7203
90.14	80.19	44.283	0.6739

 TABLE IV.—THIRD FUNDAMENTAL MIXTURE: 80% $C_6H_5CH_3$, 20% $C_2H_4Br_2$.

% CCl_4 .	Boiling point.	Refractive angle.	Specific volume.
0	111.61°	38.833°	1.0184
10.65	107.69	39.250	0.9770
20.09	104.17	39.650	0.9401
29.84	100.72	40.083	0.9021
40.27	96.90	40.617	0.8615
50.41	93.49	41.183	0.8223
60.42	90.03	41.817	0.7836
70.24	86.71	42.550	0.7451
79.93	83.49	43.333	0.7076
90.06	80.08	44.300	0.6674

 TABLE V.—FOURTH FUNDAMENTAL MIXTURE: 70% $C_6H_5CH_3$, 30% $C_2H_4Br_2$.

% CCl_4 .	Boiling point.	Refractive angle.	Specific volume.
0	112.63°	38.502°	0.9507
10.05	108.44	38.967	0.9180
20.05	104.50	39.400	0.8863
30.57	100.41	39.933	0.8626
39.93	96.69	40.450	0.8220
50.37	93.18	41.100	0.7884
59.84	89.84	41.733	0.7583
69.90	86.60	42.467	0.7264
79.99	83.21	43.350	0.6930
89.51	79.99	44.333	0.6602

 TABLE VI.—FIFTH FUNDAMENTAL MIXTURE: 60% $C_6H_5CH_3$, 40% $C_2H_4Br_2$.

% CCl_4 .	Boiling point.	Refractive angle.	Specific volume.
0	113.80°	38.083°	0.8785
9.70	109.37	38.583	0.8543
19.91	104.79	39.117	0.8289
29.89	100.64	39.667	0.8040
40.06	96.52	40.333	0.7781
49.95	93.00	40.967	0.7537
59.99	89.47	41.683	0.7293
70.03	86.14	42.467	0.7035
79.90	82.99	43.333	0.6790
89.60	79.79	44.350	0.6533

TABLE VII.—SIXTH FUNDAMENTAL MIXTURE: 50% $C_6H_5CH_3$, 50% $C_2H_4Br_2$.

% CCl_4 .	Boiling point.	Refractive angle.	Specific volume.
0	115.05°	37.600°	0.8113
9.87	109.87	38.167	0.7935
20.34	104.60	38.817	0.7744
29.82	100.63	39.383	0.7573
39.87	96.33	40.100	0.7386
50.06	92.51	40.850	0.7199
59.90	88.68	41.650	0.7026
69.93	85.62	42.417	0.6865
79.95	82.61	43.350	0.6658
90.15	79.70	44.350	0.6472

TABLE VIII.—SEVENTH FUNDAMENTAL MIXTURE: 40% $C_6H_5CH_3$, 60% $C_2H_4Br_2$.

% CCl_4 .	Boiling point.	Refractive angle.	Specific volume.
0	116.68°	36.933°	0.7390
9.80	110.71	37.633	0.7283
19.91	105.12	38.350	0.7170
29.85	100.27	39.083	0.7061
40.06	95.91	39.867	0.6952
49.94	92.46	40.683	0.6840
59.87	88.68	41.517	0.6734
69.93	85.37	42.400	0.6625
79.91	82.42	43.333	0.6515
90.06	79.48	44.367	0.6398

TABLE IX.—EIGHTH FUNDAMENTAL MIXTURE: 30% $C_6H_5CH_3$, 70% $C_2H_4Br_2$.

% CCl_4 .	Boiling point.	Refractive angle.	Specific volume.
0	118.54°	36.133°	0.6699
10.11	111.39	36.967	0.6660
19.76	105.32	37.833	0.6618
29.71	100.01	38.700	0.6577
39.99	95.42	39.600	0.6537
50.05	92.00	40.617	0.6494
60.16	88.03	41.450	0.6455
69.95	84.99	42.367	0.6414
79.88	82.12	43.350	0.6373
89.52	79.49	44.350	0.6333

TABLE X.—NINTH FUNDAMENTAL MIXTURE: 20% $C_6H_5CH_3$, 80% $C_2H_4Br_2$.

% CCl_4 .	Boiling point.	Refractive angle.	Specific volume.
0	121.04°	35.033°	0.6002
9.88	112.51	36.083	0.6032
20.03	105.33	37.167	0.6059
30.47	99.55	38.217	0.6088
40.14	94.79	39.250	0.6118
49.93	90.95	40.267	0.6146
59.85	87.69	41.317	0.6177
69.92	84.51	42.333	0.6207
80.11	81.61	43.383	0.6236
89.83	79.33	44.367	0.6264

TABLE XI.—TENTH FUNDAMENTAL MIXTURE: 10% $C_6H_5CH_3$, 90% $C_2H_4Br_2$.

% CCl_4 .	Boiling point.	Refractive angle.	Specific volume.
0	124.33°	33.550°	0.5310
10.21	113.49	34.917	0.5408
20.21	105.04	36.300	0.5508
29.96	98.98	37.583	0.5604
39.91	94.31	38.783	0.5701
50.02	90.23	40.017	0.5801
60.15	87.05	41.167	0.5911
69.99	84.21	42.267	0.6000
80.17	81.49	43.367	0.6102
89.95	79.17	44.367	0.6193

TABLE XII.—ELEVENTH FUNDAMENTAL MIXTURE: 0% $C_6H_5CH_3$, 100% $C_2H_4Br_2$.

% CCl_4 .	Boiling point.	Refractive angle.	Specific volume.
0	130.23°	31.350°	0.4593
10.62	114.96	33.333	0.4765
20.27	104.97	34.183	0.4940
29.86	98.34	36.750	0.5101
39.85	93.25	38.300	0.5274
49.90	89.50	39.717	0.5445
60.02	86.35	41.033	0.5616
70.64	83.70	42.200	0.5787
80.02	81.04	43.367	0.5964
90.13	78.90	44.383	0.6187

crossed. It was suggested that the curves might appear better distributed if ethylene bromide were considered as the third component, and were, therefore, plotted as the abscissa. I therefore undertook to recalculate all the values so that each curve should correspond to a certain ratio of toluene to carbon tetrachloride. The calculation was carried out in the following manner: Let x = per cent. carbon tetrachloride, y = per cent. ethylene bromide, and z = per cent. toluene. In the present sets of curves we have $z/y = \%C_6H_5CH_3/\%C_2H_4Br_2$. Let this ratio be denoted by A . What is needed is the ratio $z/x = \%C_6H_5CH_3/\%CCl_4$. Let this ratio be denoted by B . Then $y = B/Ax$ and $z = Bx$. But $x + y + z = 100$. Therefore, $x = 100/(1 + B/A + B)$, $z = Bx$ and $y = z/A$. Let, for example, the problem be to calculate a set of data for the boiling-point curve of mixtures containing toluene and carbon tetrachloride in the ratio $B = 9 : 1$. We substitute, in the equation just given, this value for B , while for the ratio A we use consecutively the values $9 : 1$, $8 : 2$, $7 : 3$, $6 : 4$, $5 : 5$, $4 : 6$, $3 : 7$, $2 : 8$, and $1 : 9$, corresponding to the ratios of the curves that have been found experimentally. This will lead to a series of values for x and y . Now at the value of x found for a certain ratio A , say $9 : 1$, we read off the boiling point on the curve corresponding to this ratio. Evidently this boiling point must also correspond to the value y found for the same ratio. Hence we plot the boiling point as ordinate and y

as the abscissa. Thus, the boiling points for the whole series of x 's are read and re-plotted against the corresponding y 's. This will give us the curve where $B = z/x = \frac{\%C_6H_5CH_3}{\%CCl_4} = 90/10$. By thus assigning to B consecutively the values 8 : 2, 7 : 3, etc., we obtain the boiling points

TABLE XIII.—VALUES FOR THE BOILING-POINT CURVES.

$\frac{\% C_6H_5CH_3}{\% CCl_4}$	Percentages of $C_2H_4Br_2$ ("third component").										
	0%. °C.	10%. °C.	20%. °C.	30%. °C.	40%. °C.	50%. °C.	60%. °C.	70%. °C.	80%. °C.	90%. °C.	100%. °C.
100/0	110.11	110.81	111.62	112.65	113.77	115.05	116.69	118.56	121.00	124.43	130.23
90/10	106.98	107.80	108.79	109.95	111.28	112.78	114.60	116.85	119.83	123.81	..
80/20	103.87	104.77	105.88	107.25	108.63	110.28	112.39	114.98	118.51	123.15	..
70/30	100.74	101.70	102.84	104.25	105.99	107.80	110.11	113.02	116.97	122.40	..
60/40	97.50	98.58	99.85	101.45	103.18	105.20	107.79	111.06	115.54	121.57	..
50/50	94.21	95.39	96.77	98.47	100.26	102.44	105.28	108.96	113.69	120.59	..
40/60	90.82	92.18	93.70	95.50	97.57	99.87	102.70	106.68	112.02	119.57	..
30/70	87.48	88.98	90.65	92.53	94.71	97.32	100.48	104.61	110.30	118.62	..
20/80	84.00	85.65	87.50	89.51	91.85	94.67	98.10	102.46	108.60	117.50	..
10/90	80.50	82.26	84.33	86.58	89.05	92.01	95.63	100.40	107.03	116.34	..
0/100	76.87	78.81	81.06	83.61	86.35	89.46	93.18	98.10	105.21	115.00	..

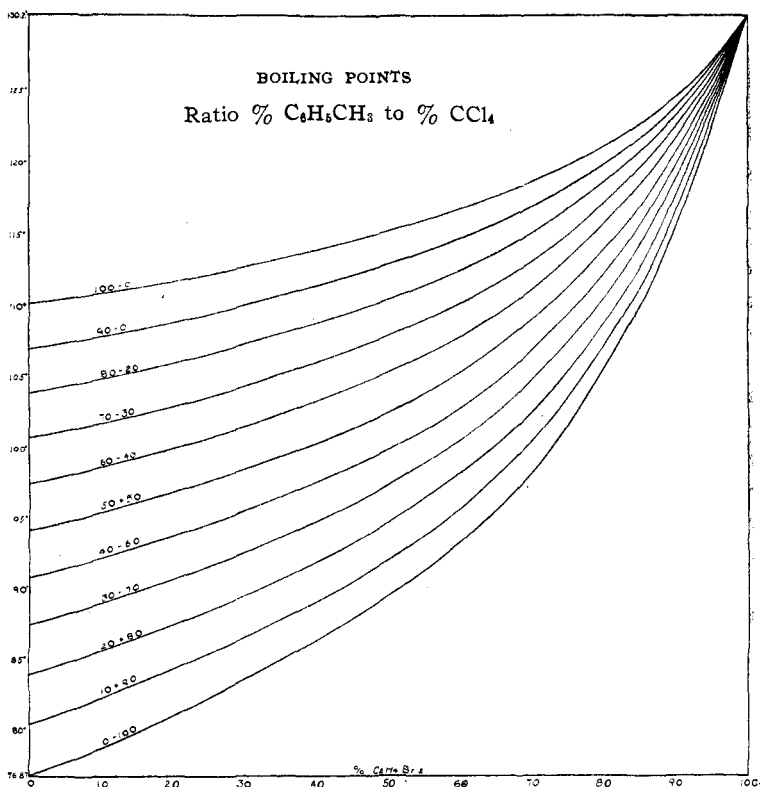


Fig. 3.

TABLE XIV.—VALUES FOR THE SPECIFIC VOLUMES.

Percentages of $C_2H_4Br_2$ ("third component").

$\frac{\% C_2H_4Br_2}{\% CCl_4}$	0%.	10%.	20%.	30%.	40%.	50%.	60%.	70%.	80%.	90%.	100%.
100/0	1.1593	1.0890	1.0190	0.9489	0.8790	0.8092	0.7395	0.6701	0.6002	0.5305	0.4596
90/10	1.1043	1.0405	0.9765	0.9124	0.8484	0.7844	0.7194	0.6545	0.5896	0.5244	..
80/20	1.0530	0.9940	0.9348	0.8755	0.8164	0.7572	0.6979	0.6381	0.5788	0.5190	..
70/30	1.0000	0.9463	0.8922	0.8382	0.7847	0.7309	0.6770	0.6222	0.5680	0.5139	..
60/40	0.9463	0.8977	0.8496	0.8012	0.7529	0.7043	0.6558	0.6065	0.5575	0.5086	..
50/50	0.8932	0.8502	0.8067	0.7638	0.7205	0.6772	0.6337	0.5903	0.5470	0.5031	..
40/60	0.8420	0.8035	0.7654	0.7278	0.6893	0.6510	0.6125	0.5740	0.5360	0.4980	..
30/70	0.7873	0.7550	0.7222	0.6897	0.6572	0.6246	0.5918	0.5585	0.5257	0.4923	..
20/80	0.7349	0.7072	0.6800	0.6527	0.6249	0.5971	0.5696	0.5421	0.5146	0.4870	..
10/90	0.6820	0.6599	0.6378	0.6155	0.5933	0.5711	0.5489	0.5262	0.5040	0.4816	..
0/100	0.6300	0.6130	0.5958	0.5789	0.5620	0.5450	0.5280	0.5109	0.4939	0.4768	0.4596

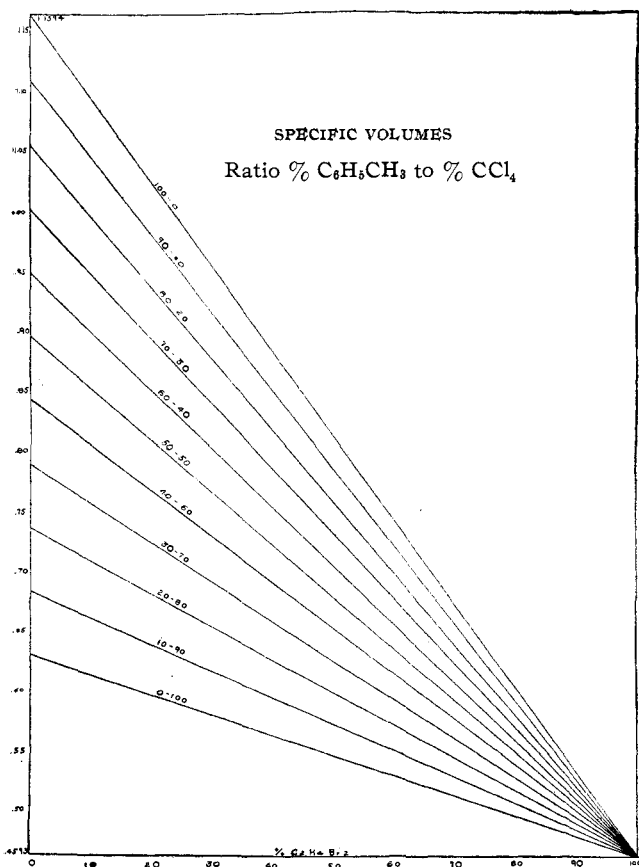


Fig. 4.

TABLE XV.—VALUES FOR THE REFRACTIVE ANGLES.

$\frac{\% \text{ CCl}_4}{\% \text{ C}_2\text{H}_4\text{Br}_2}$	Percentages of toluene ("third component").										
	0%.	10%.	20%.	30%.	40%.	50%.	60%.	70%.	80%.	90%.	100%.
100/0	45.37°	44.26°	43.30°	42.52°	41.86°	41.28°	40.78°	40.34°	39.98°	39.66°	39.37°
90/10	44.39	43.42	42.63	42.00	41.46	40.96	40.54	40.17	39.87	39.60	...
80/20	43.33	42.58	41.98	41.45	41.02	40.62	40.30	40.01	39.77	39.56	...
70/30	42.20	41.68	41.25	40.88	40.56	40.28	40.04	39.83	39.67	39.51	...
60/40	41.01	40.74	40.50	40.28	40.10	39.93	39.80	39.67	39.56	39.46	...
50/50	39.73	39.70	39.67	39.64	39.61	39.57	39.53	39.49	39.44	39.40	...
40/60	38.32	38.62	38.85	39.01	39.10	39.19	39.26	39.30	39.32	39.34	...
30/70	36.80	37.47	37.97	38.35	38.60	38.81	38.98	39.10	39.20	39.28	...
20/80	35.13	36.20	37.05	37.65	38.08	38.42	38.69	38.90	39.07	39.23	...
10/90	33.22	34.89	36.06	36.89	37.53	38.02	38.39	38.70	38.95	39.17	...
0/100	31.25	33.51	35.03	36.13	36.94	37.60	38.08	38.49	38.83	39.11	...

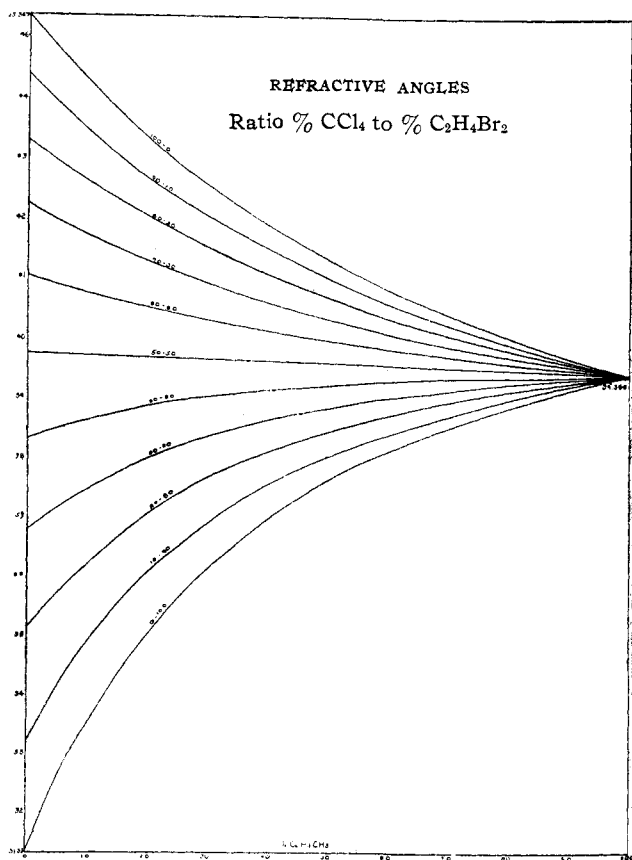


Fig. 5.

required for all the other curves in the new set, where ethylene bromide is regarded as the third component, that is, as the substance mixed with various binary mixtures of toluene and carbon tetrachloride. These boiling points are reproduced in Table XIII and graphically in Fig. 3.

Similarly recalculated values of the specific volumes are reproduced in Table XIV and Fig. 4. In the case of the refractive angles it was found necessary to recalculate the original results, using toluene as the "third component." The angles so obtained are reproduced in Table XV and Fig. 5.

In order to facilitate the reproduction of the curves, the values, calculated as just explained, were carefully plotted on a large scale, and the curves smoothed. The data tabulated below are those read off from the smoothed curves. In the tables, the percentage of the "third component" is given by the first horizontal line, while the first vertical column of figures gives the ratios of the "fundamental mixtures" corresponding to the several curves.

In order to test the availability of these data for analytical purposes, eight mixtures were prepared by carefully weighing the components, and then analyzed by the method outlined above. It was found that the curves representing respectively, mixtures of the same boiling point, the same specific volume, and the same refractive angle do not all intersect

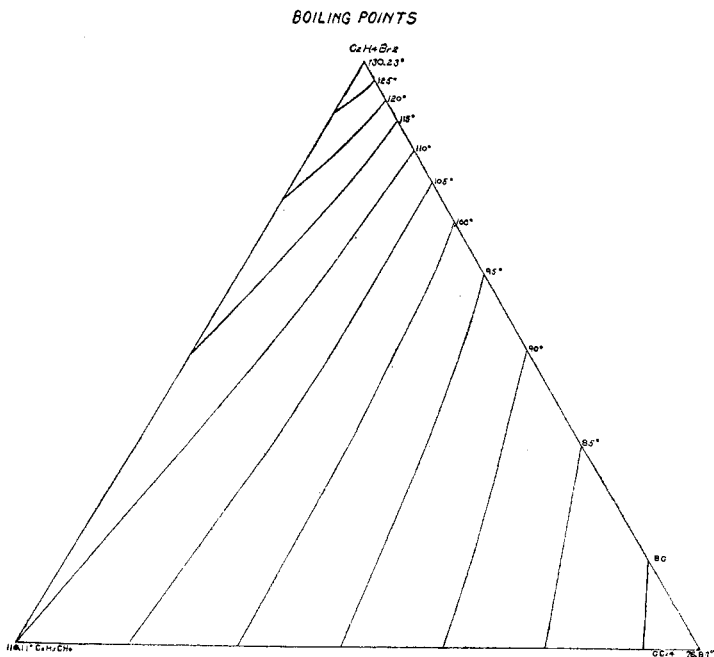


Fig. 6.

in exactly one point, as they should. This is obviously due to slight errors in the predetermined curves, or else to errors in observing the physical properties of the mixtures analyzed. However, the three points of intersection lie very close to one another. The point representing the true composition invariably falls on the specific-volume curve. This indicates that the pre-determined specific-volume curves are the most accurate, as might be expected. Consequently, the values for the mixtures were read in each case at the intersection of the specific-volume curve with the boiling-point curve on the one hand, and with the refractive-angle curve on the other hand. The mean if these two values was taken as the composition of the mixture.

The results of the eight consecutive analyses are reproduced below. In each case I give the boiling point, the refractive angle, and the specific volume as found for the mixture. The column under V + R represents the percentage of the components as shown by the intersection of the specific-volume curve with the refractive-angle curve, while the column under V + T represents the values for the intersection of the specific-volume curve with the boiling-temperature curve.

TABLE XVI.—MIXTURE 1.

Boiling point under 749 mm.....				80.55°	
Refractive angle at 25°.....				43.84°	
Specific volume at 25°.....				0.6325	
	V + R.	V + T.	Found. Mean.	True com- position.	Diff. %
% CCl ₄	85.20	84.80	85.00	84.93	+0.07
% C ₂ H ₄ Br ₂	10.80	11.05	10.92	10.93	-0.01
% C ₇ H ₈	4.00	4.15	4.08	4.14	-0.06

TABLE XVII.—MIXTURE 2.

Boiling point under 749 mm.....				86.73°	
Refractive angle at 25°.....				42.117°	
Specific volume at 25°.....				0.6800	
	V + R.	V + T.	Found. Mean.	True com- position.	Diff. %
% CCl ₄	66.35	66.55	66.45	66.38	+0.07
% C ₂ H ₄ Br ₂	18.25	18.15	18.20	18.13	+0.07
% C ₇ H ₈	15.40	15.30	15.35	15.49	-0.14

TABLE XVIII.—MIXTURE 3.

Boiling point at 749 mm.....				97.38°	
Refractive angle at 25°.....				39.93°	
Specific volume at 25°.....				0.7593	
	V + R.	V + T.	Found. Mean.	True com- position.	Diff. %
% CCl ₄	36.45	37.50	36.98	37.04	-0.06
% C ₂ H ₄ Br ₂	29.55	28.75	29.15	29.14	+0.01
% C ₇ H ₈	34.00	33.75	33.87	33.82	+0.05

TABLE XIX.—MIXTURE 4.

Boiling point at 749 mm.....					103.5°
Refractive angle at 25°.....					37.77°
Specific volume at 25°.....					0.6356
	V + R.	V + T.	Found. Mean.	True com- position.	Diff. %.
% CCl ₄	22.50	23.00	22.75	22.88	-0.13
% C ₂ H ₄ Br ₂	57.80	57.50	57.65	57.54	+0.11
% C ₇ H ₈	19.70	19.50	19.60	19.58	+0.02

TABLE XX.—MIXTURE 5.

Boiling point at 749 mm.....					109.85°
Refractive angle at 25°.....					39.330
Specific volume at 25°.....					0.8941
	V + R.	V + T.	Found. Mean.	True com- position.	Diff. %.
% CCl ₄	2.20	1.65	1.925	1.89	+0.035
% C ₂ H ₄ Br ₂	4.20	4.55	4.375	4.47	-0.095
% C ₇ H ₈	93.60	93.80	93.700	93.64	+0.060

TABLE XXI.—MIXTURE 6.

Boiling point at 749 mm.....					111.21°
Refractive angle at 25°.....					35.125°
Specific volume at 25°.....					0.5374
	V + R.	V + T.	Found. Mean.	True com- position.	Diff. %.
% CCl ₄	8.15	8.10	8.12	8.13	+0.01
% C ₂ H ₄ Br ₂	79.55	79.10	79.33	79.59	+0.26
% C ₇ H ₈	12.30	12.80	12.55	12.28	-0.27

TABLE XXII.—MIXTURE 7.

Boiling point at 749 mm.....					112.5°
Refractive angle at 25°.....					34.64°
Specific volume at 25°.....					0.5202
	V + R.	V + T.	Found. Mean.	True com- position.	Diff. %.
% CCl ₄	11.60	11.75	11.675	11.15	+0.52
% C ₂ H ₄ Br ₂	82.60	82.50	82.55	82.90	-0.35
% C ₇ H ₈	5.80	5.75	5.775	5.95	-0.17

TABLE XXIII.—MIXTURE 8.

Boiling point at 749 mm.....					122.23°
Refractive angle at 25°.....					33.10°
Specific volume at 25°.....					0.4980
	V + R.	V + T.	Found. Mean.	True com- position.	Diff. %.
% CCl ₄	4.10	3.90	4.00	3.49	-0.51
% C ₂ H ₄ Br ₂	91.60	91.80	91.70	91.85	+0.15
% C ₇ H ₈	4.30	4.30	4.30	4.66	+0.36

These results show that the method is quite accurate. The largest error occurs when the percentage of ethylene bromide is very great.

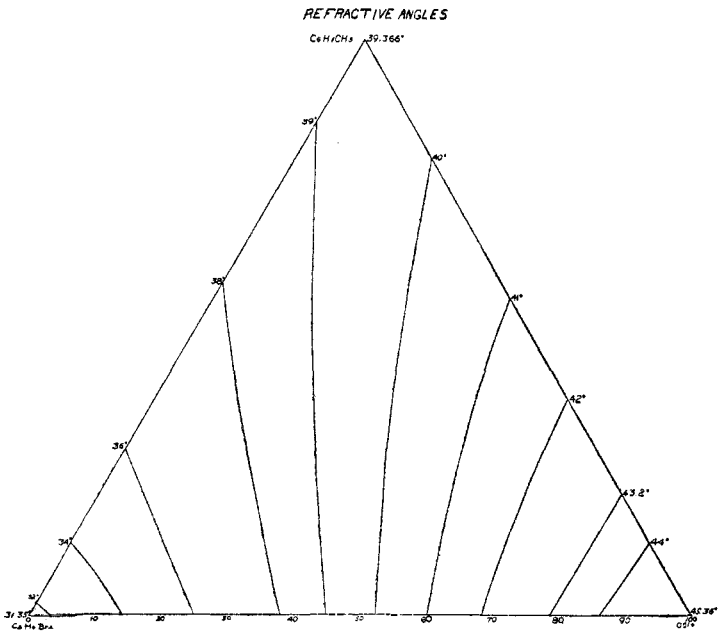


Fig. 7.

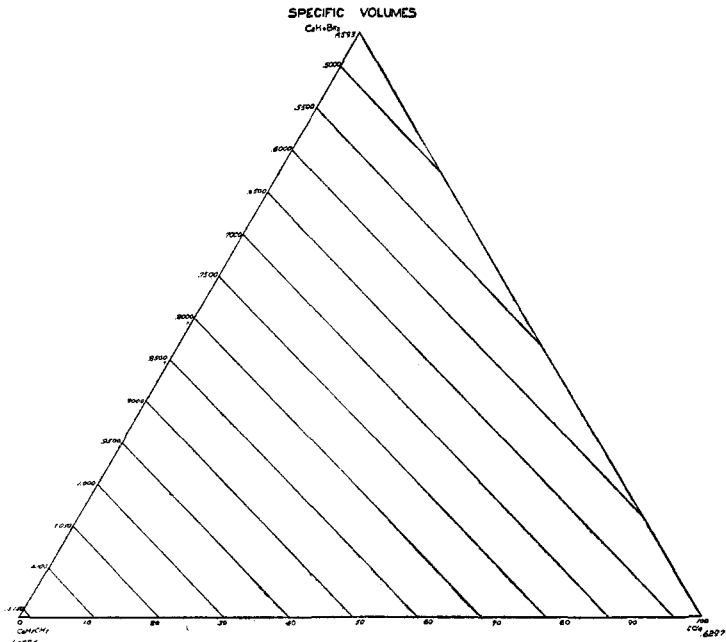


Fig. 8.

Evidently the curves are not very accurate in this region. The inaccuracy may be due to the fact that ethylene bromide takes up moisture from the atmosphere with extreme rapidity. This, of course, would affect the physical properties of the mixtures rich in this component to a considerable extent. But, as the analyses show, the errors even in that region do not exceed half a per cent. Since the completion of the work I have further used the method in a large number of cases, with similarly satisfactory results.

It seemed desirable to see how the curves would appear if drawn according to the Roozeboom method of representation, in equilateral triangles. Figs. 6, 7, and 8 represent, respectively, curves of equal boiling points, of equal refractive angles, and of equal specific volumes.

In conclusion, I wish to express my most sincere gratitude to Professor M. A. Rosanoff, at whose suggestion and under whose guidance this work was carried out. My thanks are also due to my friend, H. M. Potter, Assistant Professor of the Oklahoma Agricultural and Mechanical College, for a great deal of assistance in the experimental work.

WORCESTER, MASS.

NOTE.

An Efficient Boiling Rod.—We have found the following forms of boiling rods very effective and having several advantages over the boiling capillaries and other means usually employed to prevent bumping. Crush a small piece of an alundum crucible or of a porous porcelain plate in a mortar to small particles about one-half millimeter in diameter. The material should not, however, be finely powdered. Place this coarse powder in a small porcelain crucible and heat it red hot over the blast lamp. Heat one end of a small glass rod 10–12 centimeters in length until it softens and dip it into the alundum particles, which will adhere to the rod. Heat the rod again and repeat two or three times until a suitable amount of alundum particles have gathered on the end of the rod. Finally heat the rod in the lamp until the particles adhere to the glass. Cool slowly and rub off any loose particles by rubbing the porous end through the fingers in a cloth or towel.

Another form of rod can be prepared by fusing one end of a narrow rectangular or triangular piece of alundum or porous porcelain into the end of a glass rod and bending the end of the rod in such a manner at the joint that the piece of alundum will lie on the bottom of the beaker or flask. The size of the plate can be varied and for some purposes larger plates may be used but for quantitative work it is best to have the piece as small as possible, because porcelain plates or alundum absorb acids and generally require repeated washings with hot water before they become neutral