CORRECTION.

In the article on "Leakage Prevention by Shielding, Especially in Potentiometer Systems," by Walter P. White, which appeared in the October number of this year, on page 2018, 7th line from the bottom of the page, instead of: "arrangement described in connection with Fig. 7 of the previous paper on potentiometers," it should read: "arrangement described in connection with Section 4, (a) of the previous paper on potentiometers, page 1875."

THE PARTIAL VAPOR PRESSURES OF TERNARY MIXTURES OF TOLUENE, CARBON TETRACHLORIDE AND ETHYLENE BROMIDE.

By M. A. Rosanoff, John F. W. Schulze and R. A. Dunphy.

Received August 17, 1914.

The measurements reported in this paper were carried out in connection with a study of fractional distillation with regulated stillheads. In the case of binary mixtures, F. D. Brown[1] has shown that, if a saturated

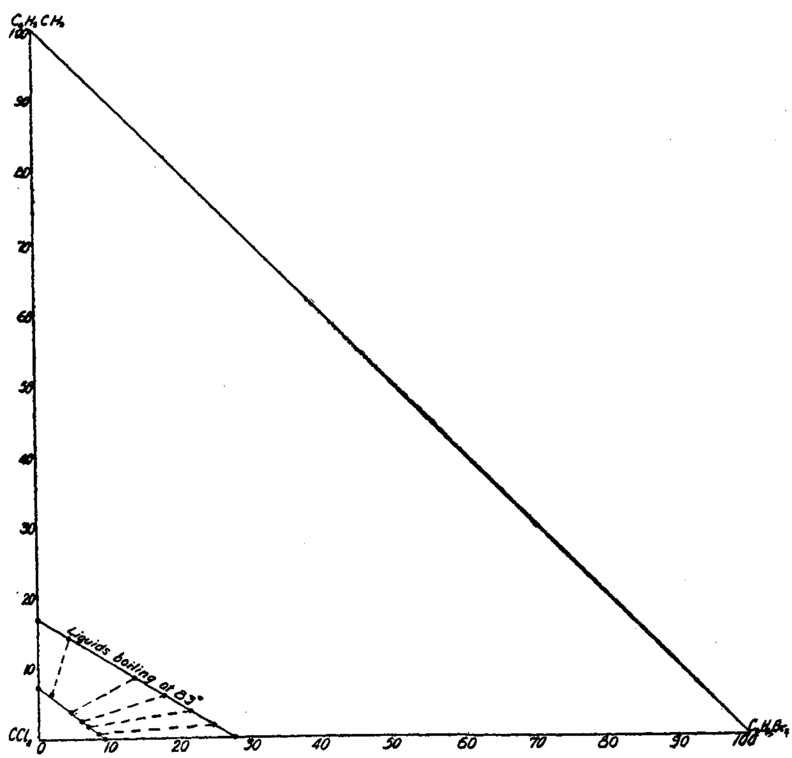

Fig 1.

[1] F. D. Brown, *Trans. Chem. Soc.*, 37, 49 (1880) and especially *Ibid.*, 39, 517 (1881).

vapor is partially condensed in a stillhead maintained at a constant temperature, the residual vapor escaping from the stillhead has a *constant composition, viz.*, the composition of the vapor given off by that liquid mixture which boils at the temperature of the stillhead. The effect of the regulated stillhead on vapors containing more than two components has never been investigated, and before such an investigation could be undertaken it was necessary to take two preliminary steps: (1) to work out a method by which consecutive fractions of a ternary distillate could be rapidly and accurately analyzed; (2) with a view to discovering the law involved, to determine the partial pressures of the ternary mixtures of a suitable set of three substances, at the boiling points of the mixtures under ordinary atmospheric pressure.

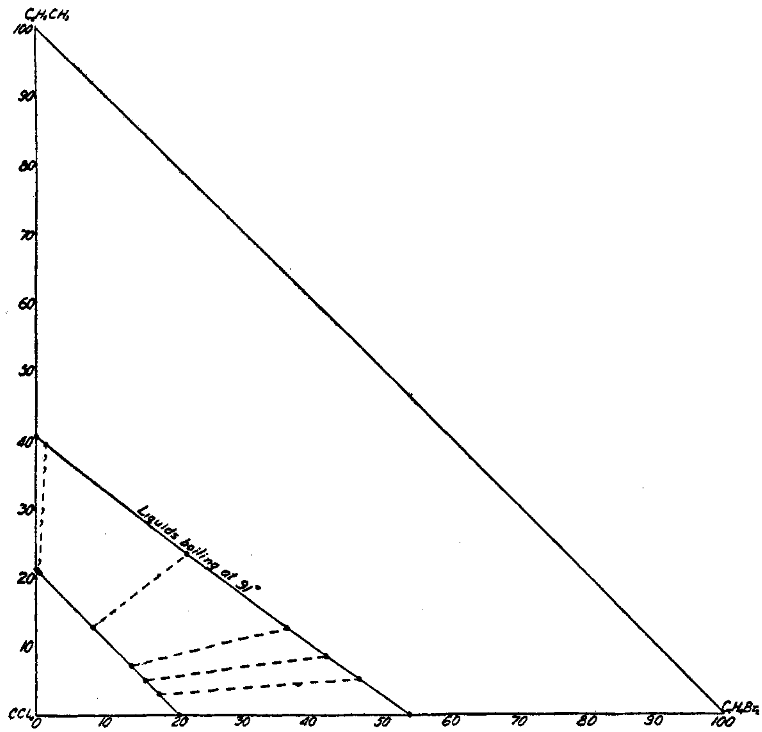

Fig 2.

Toluene, carbon tetrachloride, and ethylene bromide were chosen, because, on the one hand, their ternary boiling point surface is not complicated by either a maximum or a minimum; and because, on the other hand, they differ widely in their physical properties, so that their mixtures could be accurately analyzed by a physico-chemical method. The needed analytical method was worked out by one of us and fully described in a separate communication.[1] We next undertook to determine the required partial pressures or, what is the same, the composition of the vapors in equilibrium with various mixtures of our three substances.

As to the method to be employed, there could be no hesitation. Von Zawidzki's[2] method, in which 1 cc. is distilled off from about 125 cc. of mixture, could not be used; our analytical procedure called for about 10 cc. of the liquid to be analyzed, and to obtain such a quantity of distillate without greatly affecting the composition of the original mixture, we should have had to use, in each single run, as much as 1 to 1.5 liters of mixture;

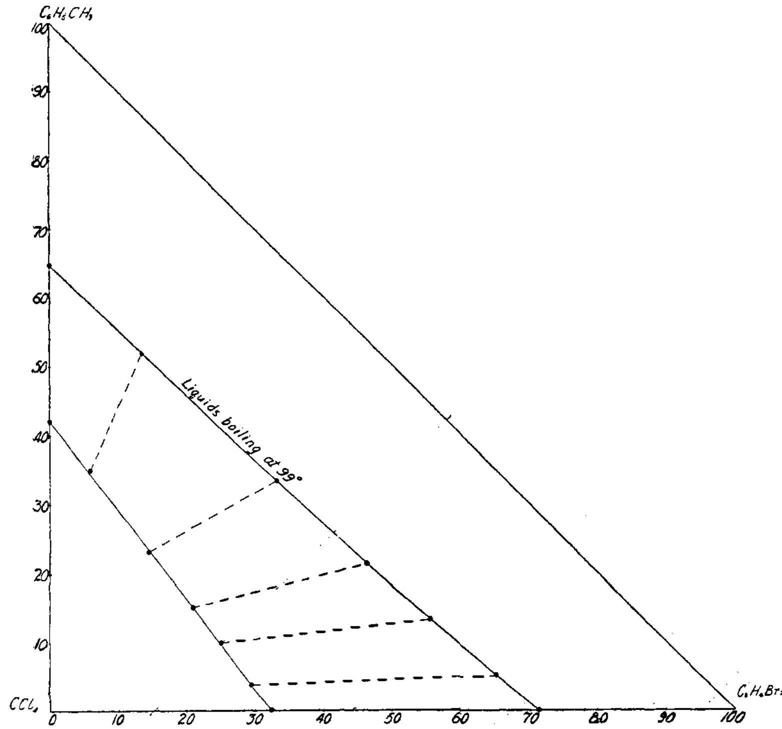

Fig. 3.

which was impracticable. The method of Rosanoff, Lamb, and Breithut[3] could not be used as it would have been exceedingly difficult to produce a ternary saturated vapor of constant composition. There remained the method described by Rosanoff, Bacon and White,[4] and this we found to work as well with ternary as it does with binary mixtures.

[1] Schulze, This Journal, **36**, 498 (1914).

[2] Von Zawidzki, *Z. physik. Chem.*, **35**, 129 (1900).

[3] Rosanoff, Lamb and Breithut, This Journal, **31**, 448 (1909); *Z. physik. Chem.*, **66**, 349 (1909).

[4] Rosanoff, Bacon and White, This Journal, **36**, 1803 (1914).

As in the case of binary mixtures, the method consisted simply in preparing a set of different mixtures of exactly known composition, subjecting each to distillation without reflux condensation, and analyzing consecutive fractions of the distillates. The amount of mixture employed each time was only 100 cc. The analyses were made by determining both the index of refraction and the density of each separate distillate. The treatment of the results was more laborious than with binary mixtures, owing to the fact that three-dimensional coördinates could not be conveniently employed. The method involves, namely, plotting the com-

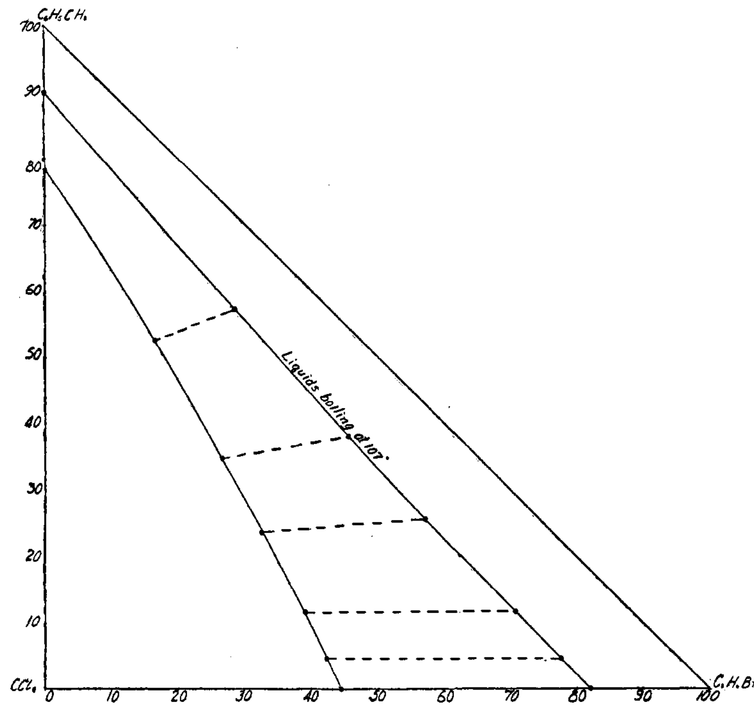

Fig. 4.

position of the first fraction against the weight of that fraction, the composition that would result by mixing the first and second fractions, against the combined weight of those two fractions, then the combined composition of Fractions 1 + 2 + 3 against the combined weight of the three fractions, etc., and extending the resulting curve to where the weight of distillate is zero. The point thus attained by the curve would indicate the composition of the first infinitesimal amount of vapor evolved by the given mixture. In the case of ternary mixtures the composition would require two coördinate axes for its representation, while the corresponding weights require a third axis. To obtain the desired result with the aid or ordinary cross-section paper, we had to resort to an indirect procedure, and it is this that involved some additional labor. We proceeded as follows: Having calculated the combined composition of Fractions 1 + 2, Fractions 1 + 2 + 3, etc., we ascertained, from Schulze's curves, the indices of refraction and the densities that these combined distillates would have. The indices and the densities were *separately* plotted against the weights. In this manner two separate plane curves were obtained, which, extended to where weight equals zero, indicated respectively, the refractive index and the density of the first infinitesimal quantity of distillate. The two physical properties revealed *the composition of that first infinitesimal distillate or, what is the same, of the vapor in equilibrium with the given ternary mixture.*

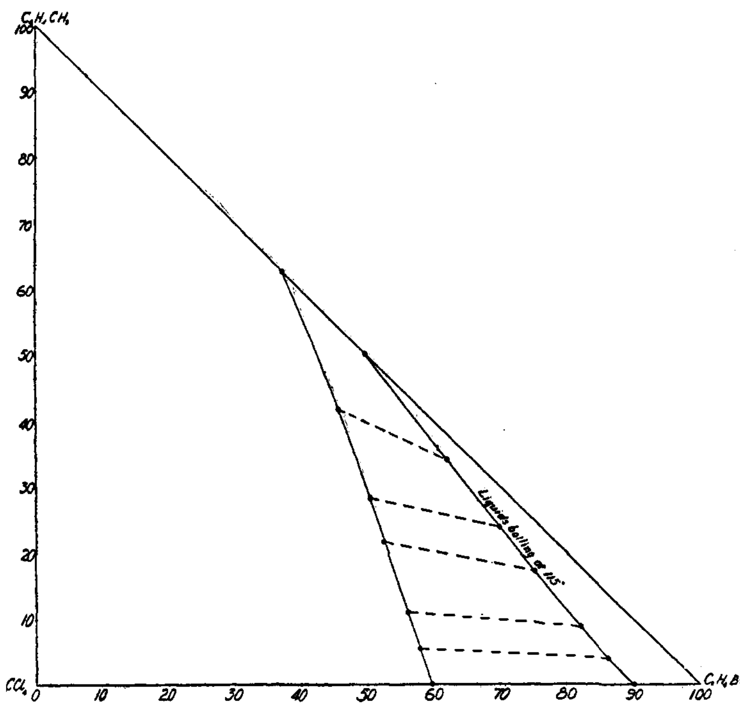

Fig. 5.

The measurements, as already stated, were undertaken as preliminary to a study of the regulated stillhead. For the purposes of that study it was necessary to learn what vapors are in equilibrium with the various ternary liquids boiling at least at some one temperature. We did this for five different temperatures, *viz.*, for 83°, 91°, 99°, 107°, and 115°. And for each of these temperatures we studied five different ternary mixtures and the two binary mixtures, all boiling at that temperature. The results, tabulated below, are graphically reproduced in Figs. 1 to 5. The system of coördinates used is an isosceles right-angled triangle, which is by far the most convenient for practical purposes. The length of each of the equal sides is 100. Each vertex represents one of the components in the pure state. Every point on a side represents a binary mixture. Any point within the triangle represents a ternary mixture: its perpendicular distance from each of the two equal sides measures the percentage of the component represented by the vertex opposite to that side; its distance from the hypothenuse, measured alone a line parallel to either of the two equal sides, represents the percentage of the third component. In each of our figures, the heavier curve is an isothermal, showing the compositions of the various mixtures boiling at the stated temperature; the lighter curve represents the composition of the vapors in equilibrium with those various liquids, the point for each liquid studied being connected by a tie-line with that representing the corresponding vapor.

The very same substances were used again that had been prepared and purified in working out the analytical method.[1]

In the tables below all percentages are *by weight.*

Numerical Results.

TABLE I.—FIRST MIXTURE OF BOILING POINT 83°. COMPOSITION OF THE MIXTURE: 83.00% CCl_4 + 17.00% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	22.745	0.6693	44.442	92.35	7.65	0
2.......	22.647	0.6740	44.358	91.45	8.55	0
3.......	21.283	0.6827	44.192	89.8	10.2	0
4.......	21.367	0.6948	43.958	87.5	12.5	0
5.......	20.345	0.7171	43.567	83.3	16.7	0

Hence, composition of first infinitesimal amount of distillate: 92.7% CCl_4 + 7.3% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$.

TABLE II.—SECOND MIXTURE OF BOILING POINT 83°. COMPOSITION OF THE MIXTURE: 81.26% CCl_4 + 14.34% $C_6H_5CH_3$ + 4.40% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	21.498	0.6610	44.417	91.25	6.75	2.0
2.......	24.456	0.6644	44.342	90.45	7.4	2.15
3.......	23.146	0.6713	44.158	88.7	8.8	2.5
4.......	23.951	0.6815	43.900	86.1	10.85	3.05
5.......	20.611	0.7006	43.433	81.3	14.8	3.9

Hence, composition of first infinitesimal amount of distillate: 91.8% CCl_4 + 6.3% $C_6H_5CH_3$ + 1.9% $C_2H_4Br_2$.

[1] Schulze, *loc. cit.*

TABLE III.—THIRD MIXTURE OF BOILING POINT 83°. COMPOSITION OF THE MIXTURE: 77.76% CCl_4 + 8.64% $C_6H_5CH_3$ + 13.60% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	22.152	0.6423	44.433	91.3	3.95	4.75
2.......	21.829	0.6437	44.367	90.65	4.35	5.0
3.......	20.959	0.6457	44.200	88.9	5.1	6.0
4.......	22.748	0.6487	43.967	86.5	6.1	7.4
5.......	21.876	0.6545	43.577	82.45	7.85	9.7

Hence, composition of first infinitesimal amount of distillate: 91.8% CCl_4 +3.75% $C_6H_5CH_3$ + 4.45% $C_2H_4Br_2$.

TABLE IV.—FOURTH MIXTURE OF BOILING POINT 83°. COMPOSITION OF THE MIXTURE: 76.04% CCl_4 + 6.16% $C_6H_5CH_3$ + 17.80% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	24.000	0.6342	44.425	91.0	2.8	6.2
2.......	23.463	0.6345	44.350	90.2	3.1	6.7
3.......	23.548	0.6352	44.150	88.3	3.6	8.1
4.......	23.516	0.6366	43.867	85.5	4.5	10.0
5.......	23.181	0.6385	43.350	80.1	6.1	13.8

Hence, composition of first infinitesimal amount of distillate: 91.4% CCl_4 + 2.6% $C_6H_5CH_3$ + 6.0% $C_2H_4Br_2$.

TABLE V.—FIFTH MIXTURE OF BOILING POINT 83°. COMPOSITION OF THE MIXTURE: 74.67% CCl_4 + 3.93% $C_6H_5CH_3$ + 21.40% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive. angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	25.734	0.6268	44.450	91.1	1.8	7.1
2.......	25.779	0.6265	44.350	90.0	2.0	8.0
3.......	24.891	0.6255	44.117	87.8	2.5	9.7
4.......	27.162	0.6241	43.750	84.1	3.1	12.8
5.......	23.929	0.6210	42.958	76.3	4.5	19.2

Hence, composition of first infinitesimal amount of distillate: 91.4% CCl_4 + 1.8% $C_6H_5CH_3$ + 6.8% $C_2H_4Br_2$.

TABLE VI.—SIXTH MIXTURE OF BOILING POINT 83°. COMPOSITION OF THE MIXTURE: 73.42% CCl_4 + 1.88% $C_6H_5CH_3$ + 24.70% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	23.056	0.6198	44.417	90.5	0.8	8.7
2.......	24.124	0.6190	44.350	89.8	1.0	9.2
3.......	24.481	0.6169	44.150	87.9	1.1	11.0
4.......	24.350	0.6137	43.850	85.1	1.3	13.6
5.......	24.129	0.6079	43.283	79.4	1.9	18.7

Hence, composition of first infinitesimal amount of distillate: 90.8% CCl_4 + 0.8% $C_6H_5CH_3$ + 8.4% $C_2H_4Br_2$.

TABLE VII.—SEVENTH MIXTURE OF BOILING POINT 83°. COMPOSITION OF THE MIXTURE: 72.30% CCl_4 + 0% $C_6H_5CH_3$ + 27.70% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	24.046	0.6136	44.425	90.4	0	9.6
2.......	24.461	0.6120	44.358	89.8	0	10.2
3.......	24.109	0.6087	44.150	87.7	0	12.3
4.......	24.539	0.6037	43.858	84.8	0	15.2
5.......	24.389	0.5941	43.250	79.2	0	20.8

Hence, composition of first infinitesimal amount of distillate: 90.7% CCl_4 + 0% $C_6H_5CH_3$ + 9.3% $C_2H_4Br_2$.

TABLE VIII.—FIRST MIXTURE OF BOILING POINT 91°. COMPOSITION OF THE MIXTURE: 59.40% CCl_4 + 40.60% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	20.514	0.7473	43.083	77.6	22.4	0
2.......	20.846	0.7632	42.841	74.6	25.4	0
3.......	18.603	0.7895	42.467	69.6	30.4	0
4.......	19.676	0.8276	42.000	62.2	37.8	0
5.......	16.854	0.8931	41.283	50.0	50.0	0

Hence, composition of first infinitesimal amount of distillate: 78.6% CCl_4 + 21.4% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$.

TABLE IX.—SECOND MIXTURE OF BOILING POINT 91°. COMPOSITION OF THE MIXTURE: 59.16% CCl_4 + 39.44% $C_6H_5CH_3$ + 1.40% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	20.816	0.7431	43.100	77.5	21.9	0.6
2.......	20.026	0.7582	42.867	74.6	24.8	0.6
3.......	18.790	0.7862	42.483	69.3	30.0	0.7
4.......	17.957	0.8175	42.067	63.3	36.0	0.7
5.......	16.585	0.8727	41.383	51.9	46.7	1.4

Hence, composition of first infinitesimal amount of distillate: 78.7% CCl_4 + 20.8% $C_6H_5CH_3$ + 0.5% $C_2H_4Br_2$.

TABLE X.—THIRD MIXTURE OF BOILING POINT 91°. COMPOSITION OF THE MIXTURE: 54.67% CCl_4 + 23.43% $C_6H_5CH_3$ + 21.90% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	21.867	0.6855	43.150	78.2	13.5	8.3
2.......	21.606	0.6926	42.900	75.4	15.1	9.5
3.......	21.513	0.7048	42.433	69.5	18.2	12.3
4.......	20.527	0.7218	41.800	61.6	22.5	15.9
5.......	19.911	0.7475	40.650	46.3	29.8	23.9

Hence, composition of first infinitesimal amount of distillate: 79.1% CCl_4 + 12.8% $C_6H_5CH_3$ + 8.1% $C_2H_4Br_2$.

TABLE XI.—FOURTH MIXTURE OF BOILING POINT 91°. COMPOSITION OF THE MIXTURE: 50.88% CCl_4 + 12.72% $C_6H_5CH_3$ + 36.40% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	22.860	0.6448	43.150	78.25	7.5	14.25
2.......	23.822	0.6467	42.883	75.5	8.4	16.1
3.......	23.250	0.6494	42.275	68.9	10.5	20.6
4.......	23.362	0.6528	41.392	59.3	13.2	27.5
5.......	21.540	0.6541	39.783	41.9	17.6	40.5

Hence, composition of first infinitesimal amount of distillate: 79.0% CCl_4 + 7.2% $C_6H_5CH_3$ + 13.8% $C_2H_4Br_2$.

TABLE XII.—FIFTH MIXTURE OF BOILING POINT 91°. COMPOSITION OF THE MIXTURE: 49.22% CCl_4 + 8.68% $C_6H_5CH_3$ + 42.10% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	24.234	0.6289	43.117	77.8	5.3	16.9
2.......	24.755	0.6287	42.825	74.8	6.1	19.1
3.......	23.758	0.6274	42.183	68.5	7.4	24.1
4.......	23.339	0.6245	41.217	58.9	9.4	31.7
5.......	23.739	0.6150	39.300	40.4	12.4	47.2

Hence, composition of first infinitesimal amount of distillate: 79.0% CCl_4 + 5.1% $C_6H_5CH_3$ + 15.9% $C_2H_4Br_2$.

TABLE XIII.—SIXTH MIXTURE OF BOILING POINT 91°. COMPOSITION OF THE MIXTURE: 47.88% CCl_4 + 5.32% $C_6H_5CH_3$ + 46.80% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	24.777	0.6155	43.150	78.3	3.3	18.4
2.......	24.602	0.6138	42.850	75.3	3.7	21.0
3.......	24.453	0.6092	42.200	69.1	4.6	26.3
4.......	24.320	0.6011	41.133	59.1	5.8	35.1
5.......	24.511	0.5814	38.842	39.0	8.0	53.0

Hence, composition of first infinitesimal amount of distillate: 79.4% CCl_4 + 3.0% $C_6H_5CH_3$ + 17.6% $C_2H_4Br_2$.

TABLE XIV.—SEVENTH MIXTURE OF BOILING POINT 91°. COMPOSITION OF THE MIXTURE: 45.80% CCl_4 + 0% $C_6H_5CH_3$ + 54.20% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	28.555	0.5933	43.200	78.5	0	21.5
2.......	25.441	0.5878	42.833	75.2	0	24.8
3.......	25.965	0.5759	42.033	68.3	0	31.7
4.......	26.374	0.5551	40.517	56.0	0	44.0
5.......	28.389	0.5109	36.800	30.1	0	69.9

Hence, composition of first infinitesimal amount of distillate: 79.7% CCl_4 + 0% $C_6H_5CH_3$ + 20.3% $C_2H_4Br_2$.

TABLE XV.—FIRST MIXTURE OF BOILING POINT 99°. COMPOSITION OF THE MIXTURE: 35.40% CCl_4 + 64.60% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	17.197	0.8610	41.600	56.0	44.0	0
2.......	16.973	0.8852	41.367	51.5	48.5	0
3.......	16.153	0.9281	40.967	43.5	56.5	0
4.......	16.029	0.9796	40.533	33.8	66.2	0
5.......	14.152	1.0410	40.067	22.3	77.7	0

Hence, composition of first infinitesimal amount of distillate: 57.7% CCl_4 + 42.3% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$.

TABLE XVI.—SECOND MIXTURE OF BOILING POINT 99°. COMPOSITION OF THE MIXTURE: 34.64% CCl_4 + 51.96% $C_6H_5CH_3$ + 13.40% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	18.596	0.8125	41.617	57.2	36.5	6.3
2.......	18.019	0.8333	41.300	51.8	40.8	7.4
3.......	17.841	0.8636	40.850	44.1	47.0	8.9
4.......	17.161	0.8994	40.333	34.0	54.8	11.2
5.......	16.080	0.9385	39.750	22.1	63.1	14.8

Hence, composition of first infinitesimal amount of distillate: 59.1% CCl_4 + 35.0% $C_6H_5CH_3$ + 5.9% $C_2H_4Br_2$.

TABLE XVII.—THIRD MIXTURE OF BOILING POINT 99°. COMPOSITION OF THE MIXTURE: 33.50% CCl_4 + 33.50% $C_6H_5CH_3$ + 33.00% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	19.716	0.7313	41.683	59.9	24.3	15.8
2.......	20.311	0.7443	41.275	54.4	27.5	18.1
3.......	18.853	0.7606	40.675	46.1	31.9	22.0
4.......	18.791	0.7778	39.950	35.3	36.9	27.8
5.......	18.188	0.7907	39.033	22.0	42.0	36.0

Hence, composition of first infinitesimal amount of distillate: 62.5% CCl_4 + 23.2% $C_6H_5CH_3$ + 14.3% $C_2H_4Br_2$.

TABLE XVIII.—FOURTH MIXTURE OF BOILING POINT 99°. COMPOSITION OF THE MIXTURE: 32.16% CCl_4 + 21.44% $C_6H_5CH_3$ + 46.40% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	21.482	0.6776	41.675	61.5	16.2	22.3
2.......	22.122	0.6832	41.200	55.9	18.4	25.7
3.......	21.453	0.6892	40.367	46.1	21.6	32.3
4.......	21.343	0.6932	39.333	34.0	25.0	41.0
5.......	21.138	0.6860	37.875	17.9	27.8	54.3

Hence, composition of first infinitesimal amount of distillate: 64.1% CCl_4 + 15.1% $C_6H_5CH_3$ + 20.8% $C_2H_4Br_2$.

TABLE XIX.—FIFTH MIXTURE OF BOILING POINT 99°. COMPOSITION OF THE MIXTURE: 31.15% CCl_4 + 13.35% $C_6H_5CH_3$ + 55.50% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	23.196	0.6398	41.692	63.0	10.5	26.5
2.......	23.519	0.6399	41.083	56.7	12.0	31.3
3.......	23.195	0.6388	40.142	47.0	14.0	39.0
4.......	23.467	0.6303	38.600	31.8	16.6	51.6
5.......	24.275	0.6108	36.683	14.8	17.9	67.3

Hence, composition of first infinitesimal amount of distillate: 65.0% CCl_4 + 10.0% $C_6H_5CH_3$ + 25.0% $C_2H_4Br_2$.

TABLE XX.—SIXTH MIXTURE OF BOILING POINT 99°. COMPOSITION OF THE MIXTURE: 29.67% CCl_4 + 5.23% $C_6H_5CH_3$ + 65.10% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	25.059	0.5987	41.650	64.3	4.3	31.4
2.......	26.007	0.5920	40.875	57.2	5.0	37.8
3.......	26.686	0.5792	39.517	45.6	6.0	48.4
4.......	26.811	0.5559	37.200	27.1	7.3	65.6
5.......	26.210	0.5265	34.617	10.2	7.1	82.7

Hence, composition of first infinitesimal amount of distillate: 66.7% CCl_4 + 4.0% $C_6H_5CH_3$ + 29.3% $C_2H_4Br_2$.

TABLE XXI.—SEVENTH MIXTURE OF BOILING POINT 99°. COMPOSITION OF THE MIXTURE: 28.55% CCl_4 + 0% $C_6H_5CH_3$ + 71.45% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	26.418	0.5709	41.650	65.3	0	34.7
2.......	26.960	0.5571	40.650	57.2	0	42.8
3.......	28.091	0.5350	38.900	44.1	0	55.9
4.......	28.907	0.5006	35.817	23.9	0	76.1
5.......	31.107	0.4707	32.667	6.7	0	93.3

Hence, composition of first infinitesimal amount of distillate: 67.6% CCl_4 + 0% $C_6H_5CH_3$ + 32.4% $C_2H_4Br_2$.

TABLE XXII.—FIRST MIXTURE OF BOILING POINT 107°. COMPOSITION OF THE MIXTURE: 9.90% CCl_4 + 90.10% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	14.330	1.0549	39.967	19.6	80.4	0
2.......	13.999	1.0760	39.850	15.7	84.3	0
3.......	14.195	1.0941	39.733	12.3	87.7	0
4.......	14.029	1.1144	39.600	8.5	91.5	0
5.......	14.762	1.1368	39.483	4.2	95.8	0

Hence, composition of first infinitesimal amount of distillate: 21.5% CCl_4 + 78.5% $C_6H_5CH_3$ + 0% $C_2H_4Br_2$.

TABLE XXIII.—SECOND MIXTURE OF BOILING POINT 107°. COMPOSITION OF THE MIXTURE: 14.32% CCl_4 + 57.28% $C_6H_5CH_3$ + 28.40% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	16.873	0.8820	40.017	30.0	53.2	16.8
2.......	17.085	0.8964	39.742	24.7	56.5	18.8
3.......	16.437	0.9099	39.400	18.2	59.9	21.9
4.......	16.921	0.9175	39.050	12.0	62.5	25.5
5.......	15.999	0.9126	38.633	5.5	63.4	31.1

Hence, composition of first infinitesimal amount of distillate: 32.1% CCl_4 + 51.5% $C_6H_5CH_3$ + 16.4% $C_2H_4Br_2$.

TABLE XXIV.—THIRD MIXTURE OF BOILING POINT 107°. COMPOSITION OF THE MIXTURE: 16.32% CCl_4 + 38.08% $C_6H_5CH_3$ + 45.60% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	19.324	0.7752	40.017	36.4	36.2	27.4
2.......	19.358	0.7841	39.583	30.5	39.0	30.5
3.......	19.413	0.7904	39.017	22.0	41.9	36.1
4.......	19.227	0.7874	38.350	13.0	43.5	43.5
5.......	19.264	0.7698	37.683	5.8	42.8	51.4

Hence, composition of first infinitesimal amount of distillate: 38.6% CCl_4 + 34.8% $C_6H_5CH_3$ + 26.6% $C_2H_4Br_2$.

TABLE XXV.—FOURTH MIXTURE OF BOILING POINT 107°. COMPOSITION OF THE MIXTURE: 17.12% CCl_4 + 25.68% $C_6H_5CH_3$ + 57.20% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	21.184	0.7042	39.967	40.6	25.0	34.4
2.......	20.802	0.7079	39.358	33.1	27.3	39.6
3.......	21.126	0.7067	38.592	24.0	29.3	46.7
4.......	21.185	0.6994	37.700	15.1	30.5	54.4
5.......	21.820	0.6780	36.750	5.9	29.7	64.4

Hence, composition of first infinitesimal amount of distillate: 43.9% CCl_4 + 23.7% $C_6H_5CH_3$ + 32.4% $C_2H_4Br_2$.

TABLE XXVI.—FIFTH MIXTURE OF BOILING POINT 107°. COMPOSITION OF THE MIXTURE: 17.58% CCl_4 + 11.72% $C_6H_5CH_3$ + 70.75% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	24.002	0.6211	39.850	45.2	12.2	42.6
2.......	24.133	0.6153	38.858	35.9	13.5	50.6
3.......	24.510	0.6039	37.600	24.7	14.6	60.7
4.......	24.710	0.5860	36.117	12.9	14.9	72.2
5.......	25.360	0.5607	34.733	4.6	13.3	82.1

Hence, composition of first infinitesimal amount of distillate: 49.3% CCl_4 + 11.6% $C_6H_5CH_3$ + 39.1% $C_2H_4Br_2$.

TABLE XXVII.—SIXTH MIXTURE OF BOILING POINT 107°. COMPOSITION OF THE MIXTURE: 17.84% CCl_4 + 4.46% $C_6H_5CH_3$ + 77.70% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	26.187	0.5756	39.817	48.5	4.8	46.7
2.......	25.844	0.5622	38.500	38.0	5.4	56.6
3.......	27.001	0.5433	36.708	24.7	6.0	69.3
4.......	28.328	0.5201	34.650	11.5	5.9	82.6
5.......	29.894	0.4986	33.067	3.3	4.8	91.9

Hence, composition of first infinitesimal amount of distillate: 53.1% CCl_4 + 4.6% $C_6H_5CH_3$ + 42.3% $C_2H_4Br_2$.

TABLE XXVIII.—SEVENTH MIXTURE OF BOILING POINT 107°. COMPOSITION OF THE MIXTURE: 18.00% CCl_4 + 0% $C_6H_5CH_3$ + 82.00% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	28.039	0.5459	39.750	50.5	0	49.5
2.......	26.919	0.5256	38.083	38.7	0	61.3
3.......	28.723	0.5007	35.817	24.0	0	76.0
4.......	29.234	0.4769	33.375	10.1	0	89.9
5.......	31.172	0.4637	31.850	2.4	0	97.6

Hence, composition of first infinitesimal amount of distillate: 55.5% CCl_4 + 0% $C_6H_5CH_3$ + 44.5% $C_2H_4Br_2$.

TABLE XXIX.—FIRST MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE MIXTURE: 0% CCl_4 + 50.40% $C_6H_5CH_3$ + 49 60% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	17.144	0.8920	38.175	0	61.9	38.1
2.......	18.419	0.8763	38.083	0	59.6	40.4
3.......	17.651	0.8587	37.950	0	57.1	42.9
4.......	23.047	0.8307	37.750	0	53.1	46.9
5.......	18.346	0.7881	37.392	0	47.0	53.0

Hence, composition of first infinitesimal amount of distillate: 0% CCl_4 + 62.9% $C_6H_5CH_3$ + 37.1% $C_2H_4Br_2$.

TABLE XXX.—SECOND MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE MIXTURE: 3.81% CCl_4 + 34.29% $C_6H_5CH_3$ + 61.90% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	18.090	0.7744	38.083	10.6	42.3	47.1
2.......	19.274	0.7667	37.792	7.6	41.9	50.5
3.......	18.998	0.7540	37.467	5.0	40.6	54.4
4.......	21.530	0.7340	37.100	3.0	38.3	58.7
5.......	21.960	0.7016	36.600	1.0	34.2	64.8

Hence, composition of first infinitesimal amount of distillate: 12.3% CCl_4 + 42.1% $C_6H_5CH_3$ + 45.6% $C_2H_4Br_2$.

TABLE XXXI.—THIRD MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE MIXTURE: 6.00% CCl_4 + 24.00% $C_6H_5CH_3$ + 70.00% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	21.171	0.6995	37.983	17.5	29.9	52.6
2.......	21.543	0.6921	37.450	11.1	31.5	57.4
3.......	21.509	0.6792	36.908	7.6	29.4	63.0
4.......	21.668	0.6599	36.333	3.9	27.6	68.5
5.......	23.061	0.6315	35.683	1.4	24.1	74.5

Hence, composition of first infinitesimal amount of distillate: 21.2% CCl_4 + 28.5% $C_6H_5CH_3$ + 50.3% $C_2H_4Br_2$.

TABLE XXXII.—FOURTH MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE MIXTURE: 7.44% CCl_4 + 17.36% $C_6H_5CH_3$ + 75.20% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CC_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	20.857	0.6530	37.983	22.8	22.0	55.2
2.......	21.763	0.6437	37.233	15.8	22.4	61.8
3.......	22.558	0.6316	36.517	10.1	22.0	67.9
4.......	22.841	0.6134	35.758	5.0	20.7	74.3
5.......	23.669	0.5887	35.017	2.0	17.9	80.1

Hence, composition of first infinitesimal amount of distillate: 25.7% CCl_4 + 21.8% $C_6H_5CH_3$ + 52.5% $C_2H_4Br_2$.

TABLE XXXIII.—FIFTH MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE MIXTURE: 8.88% CCl_4 + 8.87% $C_6H_5CH_3$ + 82.25% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	24.412	0.5880	37.750	28.1	11.5	60.4
2.......	25.717	0.5756	36.600	19.1	11.9	69.0
3.......	25.136	0.5601	35.425	11.0	11.6	77.4
4.......	26.253	0.5422	34.367	4.9	10.6	84.5
5.......	27.417	0.5219	33.467	1.4	8.5	90.1

Hence, composition of first infinitesimal amount of distillate: 32.7% CCl_4 + 11.2% $C_6H_5CH_3$ + 56.1% $C_2H_4Br_2$.

TABLE XXXIV.—SIXTH MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE MIXTURE: 9.66% CCl_4 + 4.14% $C_6H_5CH_3$ + 86.20% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	26.402	0.5517	37.567	30.9	5.6	63.5
2.......	27.329	0.5351	36.067	20.5	5.8	73.7
3.......	28.942	0.5171	34.525	11.4	5.4	83.2
4.......	28.855	0.5006	33.250	4.5	4.7	90.8
5.......	30.973	0.4870	32.450	0.8	3.7	95.5

Hence, composition of first infinitesimal amount of distillate: 36.5% CCl_4 + 5.5% $C_6H_5CH_3$ + 58.0% $C_2H_4Br_2$.

TABLE XXXV.—SEVENTH MIXTURE OF BOILING POINT 115°. COMPOSITION OF THE MIXTURE: 10.00% CCl_4 + 0% $C_6H_5CH_3$ + 90.00% $C_2H_4Br_2$.

Distillate No.	Weight of distillate.	Spec. vol.	Refractive angle.	% CCl_4.	% $C_6H_5CH_3$.	% $C_2H_4Br_2$.
1.......	28.588	0.5160	37.233	32.7	0	67.3
2.......	29.331	0.4956	35.333	21.1	0	78.9
3.......	29.414	0.4780	33.508	11.5	0	88.5
4.......	31.646	0.4665	32.200	4.6	0	95.4
5.......	31.456	0.4611	31.583	1.3	0	98.7

Hence, composition of first infinitesimal amount of distillate: 40.0% CCl_4 + 0% $C_6H_5CH_3$ + 60.0% $C_2H_4Br_2$.

TABLE XXXVI.—SUMMARY.

		Composition of liquid.			Composition of vapor.		
Temp.	Mixture.	% CCl_4.	% C_7H_8.	% $C_2H_4Br_2$.	% CCl_4.	% C_7H_8.	% $C_2H_4Br_2$.
83°	1	83.00	17.00	0	92.7	7.3	0
83°	2	81.26	14.34	4.40	91.8	6.3	1.9
83°	3	77.76	8.64	13.60	91.8	3.75	4.45
83°	4	76.04	6.16	17.800	91.4	2.6	6.0
83°	5	74.67	3.93	21.40	91.4	1.8	6.8
83°	6	73.42	1.88	24.70	90.8	0.8	8.4
83°	7	72.30	0	27.70	90.7	0	9.3
91°	1	59.40	40.60	0	78.6	21.4	0
91°	2	59.16	39.44	1.4	78.7	20.8	0.5
91°	3	54.67	23.43	21.90	79.1	12.8	8.1
91°	4	50.88	12.72	36.40	79.0	7.2	13.8
91°	5	49.22	8.68	42.10	79.0	5.1	15.9
91°	6	47.88	5.32	46.80	79.4	3.0	17.6
91°	7	45.80	0	54.2	79.7	0	20.3
99°	1	35.40	64.60	0	57.7	42.3	0
99°	2	34.64	51.96	13.40	59.1	35.0	5.9
99°	3	33.50	33.50	33.00	62.5	23.2	14.3
99°	4	32.16	21.44	46.40	64.1	15.1	20.8
99°	5	31.15	13.35	55.50	65.0	10.0	25.0
99°	6	29.67	5.23	65.10	66.7	4.0	29.3
99°	7	28.55	0	71.45	67.6	0	32.4
107°	1	9.90	90.10	0	21.5	78.5	0
107°	2	14.32	57.28	28.40	32.1	51.5	16.4
107°	3	16.32	38.08	45.60	38.6	34.8	26.6
107°	4	17.12	25.68	57.20	43.9	23.7	32.4
107°	5	17.58	11.72	70.75	49.3	11.6	39.1
107°	6	17.84	4.46	77.70	53.1	4.6	42.3
107°	7	18.00	0	82.0	55.5	0	44.5
115°	1	0	50.40	49.60	0	62.9	37.1
115°	2	3.81	34.29	61.90	12.3	42.1	45.6
115°	3	6.00	24.00	70.00	21.2	28.5	50.3
115°	4	7.44	17.36	75.20	25.7	21.8	52.5
115°	5	8.88	8.87	82.25	32.7	11.2	56.1
115°	6	9.66	4.14	86.20	36.5	5.5	58.0
115°	7	10.00	0	90.00	40.0	0	60.0

In conclusion, it is a duty to state that the cost of this investigation has been defrayed out of a grant from the Rumford Fund of the American Academy, for which we express our thanks to the Rumford Committee.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH,
UNIVERSITY OF PITTSBURGH.

SUBSTITUTION IN THE BENZENE NUCLEUS.

BY A. F. HOLLEMAN.

Received September 23, 1914.

A few years ago, I showed[1] that none of the hypotheses proposed to explain the phenomena of substitution in benzene nucleus are able to give a satisfactory explanation of the facts. Since then, H. S. Fry, in a series of papers,[2] published a new hypothesis and was able to explain some of the phenomena observed by means of it, *e. g.*, the fact that, in the rearrangement of phenyl acetyl nitrogen chloride $C_6H_5NCl.COCH_3$ and similar compounds, the halogen enters only in positions ortho or para to the nitrogen atom.

However, on studying this hypothesis more closely it seems to me that there are so many objections against it, that it cannot be accepted. I venture to present the most important ones in the following lines:

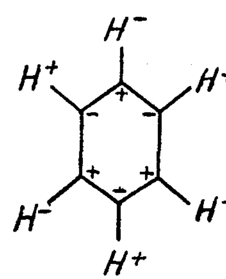

Fig. 1.

1. Fry admits that benzene has the structure of Fig. 1, based on Thomson's electronic theory of linking of the atoms. As he observes, this formula indicates the possibility of two isomeric compounds C_6H_5X, whereas no such isomers have been found thus far. In order to explain this, he assumes either that one of the two isomers ("electromers"), *e. g.*, of chlorobenzene is unstable under ordinary physical conditions, or that monochlorobenzene is an equilibrium mixture of two tautomeric electromers. It seems to me that serious objections may be made against both of these auxiliary hypotheses. With regard to the first one; admitting $C_6H_5\overset{-}{Cl}$ to be stable, $C_6H_5\overset{+}{Cl}$ would be unstable. But in o-$C_6H_4Cl_2$ and p-$C_6H_4Cl_2$, where one Cl-atom is negative and the other positive, we have perfectly stable compounds. On the other hand, if monochlorobenzene is a mixture of $C_6H_5\overset{-}{Cl}$ and $C_6H_5\overset{+}{Cl}$, the nitration of such a mixture ought to give a mixture of *o*- and *p*-chloronitrobenzene (derived from $C_6H_5\overset{-}{Cl}$) and of *m*-chloronitrobenzene (derived from $C_6H_5\overset{+}{Cl}$), since—according to Fry—"substituents of the same sign occupy positions which

[1] "Die direkte Einführung von Substituenten in den Benzolkern," p. 203.

[2] THIS JOURNAL, 34, 664 (1912); 36, 248, 262 (1914); see also *Z. physik. Chem.*, 76, 385 (1910).