A METHOD OF ANALYSIS FOR THE SYSTEM BENZENE-ETHYL ALCOHOL-CARBON TETRACHLORIDE

by

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To DR. A. N. CAMPBELL

for his invaluable direction and encouragement during this research, the thanks of the writer are sincerely offered.

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INTRODUCTION

(a) Origins of the Problem

Comparatively speaking ternary liquid systems have been incompletely investigated experimentally. Not only does this contrast with the mass of information available on binary systems, but it also reveals an obvious lag of experimental behind theoretical aspects of the problem. For the ternary system of the three common substances, benzene, alcohol and carbon tetrachloride, this is sharply in evidence. While the constituent binaries have been repeatedly and variously investigated, the ternary has only once been intensively studied.

F. A. H. Schreinemakers[1,2] determined by a dynamic method the boiling temperatures at different pressures of ternary mixtures of the system benzene-alcohol-carbon tetrachloride. Graphically his pressure-temperature (P-T) curves allowed him to deduce pressure-concentration (P-x) and temperature-concentration (T-X) relations. Figure 1 is a typical vapor pressure surface of ternary liquid at constant temperature; Figure 2 is the surface projected, numbers on the composition triangle indicating the pressure on the isobars. Similarly Figure 3 is the boiling surface of ternary liquid at constant pressure; Figure 4 is its projection, numbers in the triangle giving the temperature of the isotherms.

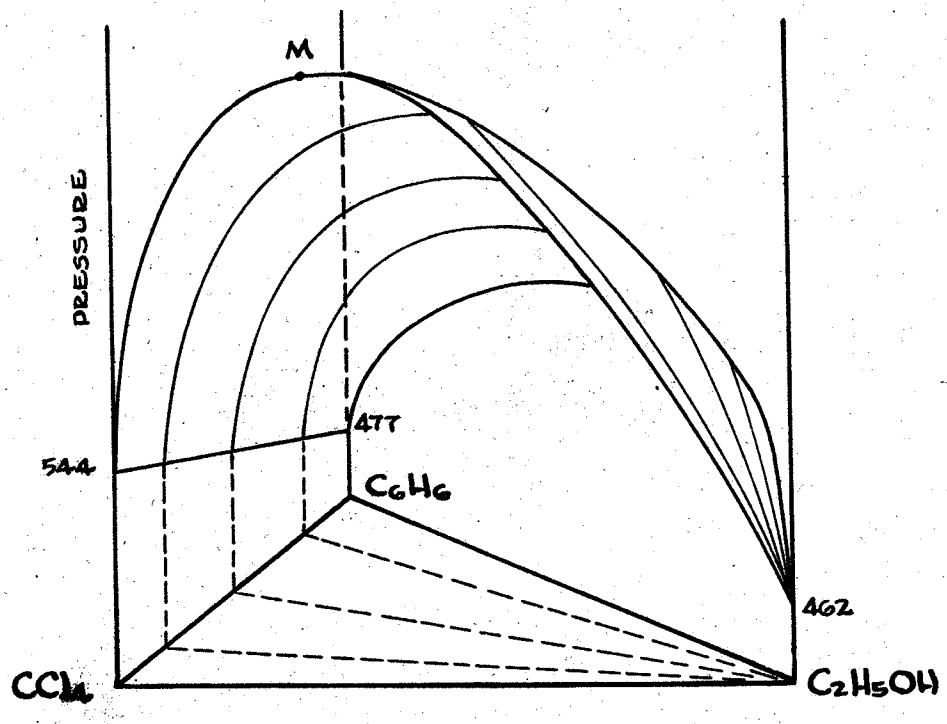


FIGURE 1.

VAPOR PRESSURES OF THE SYSTEM C_6H_6 - C_2H_5OH - CCl_4 AT TEMP. 66° C.

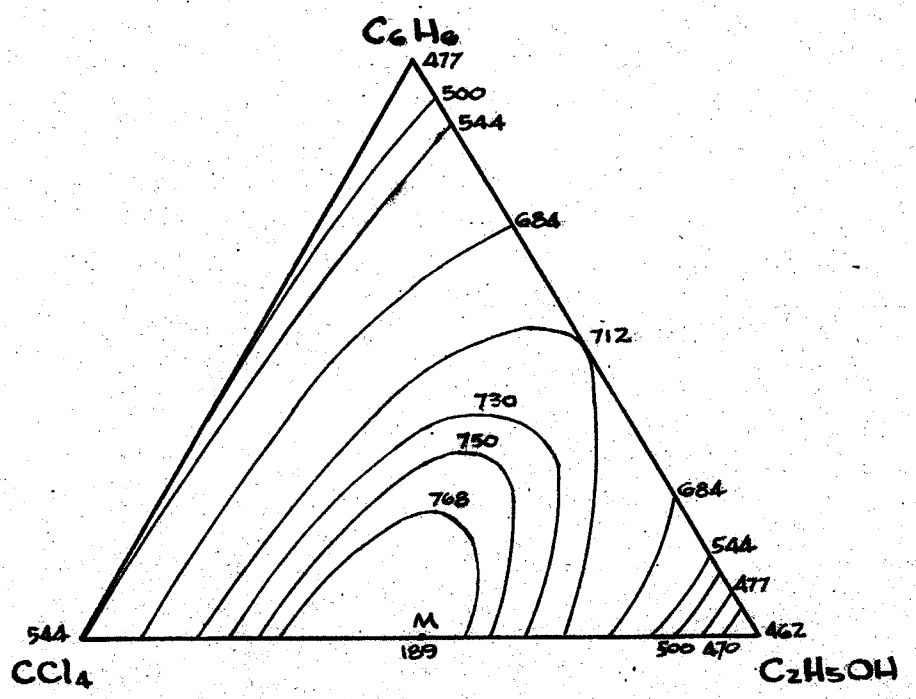


FIGURE 2.

ISOBARS AT 66° C.

Schreinemakers' results emphasize the "totality of the phenomenon," the rather complete P-T-X relations of ternary liquid mixtures. He points out, however, that improvements in his method would probably increase his accuracy. Although Schreinemakers' treatment of the vapor pressures of ternary liquids is adequate, liquid-vapor equilibrium data are lacking, and the vapor-composition surface corresponding to the liquidus surface does not appear in his diagrams. Indeed, the limitations of his method precluded such data - the simultaneous analysis of liquid and vapor was actually impracticable.

To complete Schreinemakers' work, liquid-vapor equilibria on isobaric or isothermal distillation would have to be studied, the azeotropic mixtures verified, and the vapor surface added to Figures 1 and 3. Clearly this involved finding a suitable distillation apparatus, the construction of a barostat, and the development of a method of analysis.

A barostat operating at 760 mm. whose design was largely suggested by Matthews and Faville[3], and Leroy[4] has been constructed by W. J. Dulmage.[30]

In a distillation problem of this kind, the attainment of equilibrium between liquid and vapor, and the analysis of these phases, have in the past presented practical difficulties. Sydney Young[5] treats the problem

historically, reviewing the results obtained by different workers using a variety of distillation methods. Relevant here is the improvement in technique devised by Rosanoff[6] who passed saturated mixed vapor of constant composition through a liquid of the same substances until equilibrium was reached.

A further fundamental advance was made when Sameshima[7] introduced a condensation trap in his distillation apparatus, from which condensed vapor was circulated back to the liquid mixture until equilibrium was attained. The evolution of an equilibrium still has continued, the one to be used being essentially that of Scatchard[8] (Figure 5). Traditional difficulties such as superheating of liquid, reflux condensation and entrainment of vapor, and lack of equilibrium, tend to be eliminated by the use of a Cottrell-type pump (H), a double boiler (E,F), and a hold up trap (C).

This still makes simple the removal of liquid and condensed vapor samples from the inner boiler and the condensate trap respectively. The analytic procedure involved in finding the composition of these samples is, properly speaking, the core of this work. Such a procedure has been developed - the analysis of ternary mixtures is now possible with an accuracy of 0.3 percent.

(b) Statement of the Problem

Had the system benzene-alcohol-carbon tetrachloride consisted of materials readily analyzable by usual methods, no great interest would be attached to the analytic procedure. All three are volatile organic compounds, infinitely miscible in one another. There is no alternative but to use physical methods in their analysis. Just as one specific property is usually sufficient to fix the composition of a binary mixture, so two will generally suffice to identify compositions of a ternary. (At least one exception is afforded by the system carbon tetrachloride-alcohol-water studied by Curtis and Titus[9]).

Before any unknown mixture can be analyzed, calibration data must be drawn up from known mixtures. Properties such as refractive index, density, viscosity, melting point, etc., afforded a choice. Of these refractive index and density measurements were chosen. Not only did these properties prove satisfactory in effecting a separation between mixtures of similar composition, but they were also experimentally accessible. Finally, small quantities (10 c.c.) could be used in analysis, a factor especially important in the analysis of a condensed vapor.

A brief reference to the analysis of other ternary systems will indicate the nature of this problem.

For the ternary system aniline-phenol-water A. N. Campbell[10] found conductimetric titration of the aniline and phenol both convenient and satisfactory to 0.5 percent accuracy. In the system acetic acid-benzene-carbon tetrachloride McMillan and McDonald[11] easily obtained by titration the percentage of one component, the acetic acid. The refractive index of the benzene-carbon tetrachloride layer was compared with indices on a calibration curve, both properties yielding an analysis of 1.0 percent accuracy. Barbaudy[12] used density and refractive index data to analyze the ternary system benzene-alcohol-water with an accuracy of 0.25 percent.

The analytic procedure for this system compares favorably with those mentioned - the degree of accuracy is generally within 0.2 percent.

PREVIOUS INVESTIGATIONS

THE BINARY SYSTEMS - PREVIOUS INVESTIGATIONS - d_4^{25}

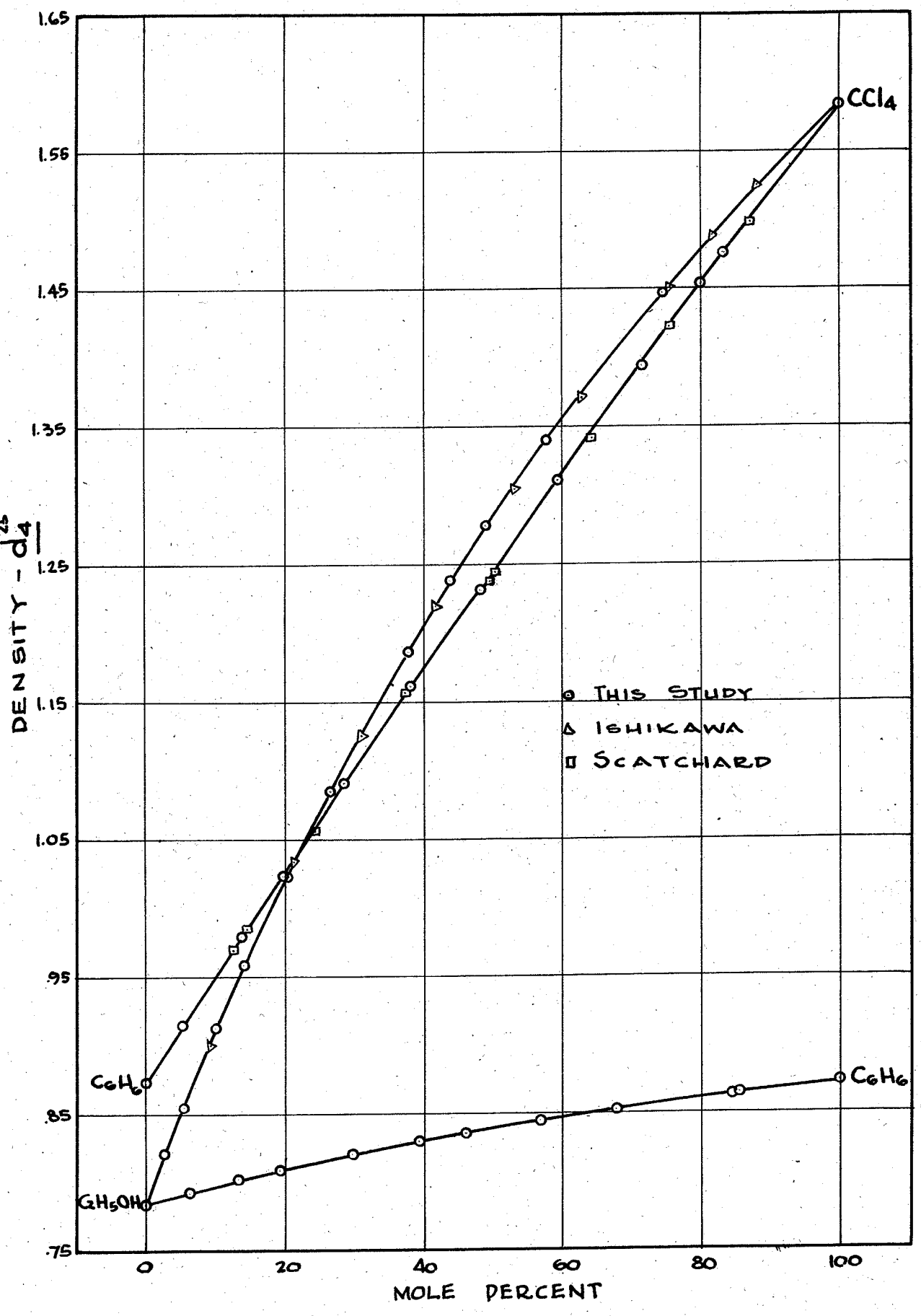


FIGURE 6.

Previous Investigations

(a) Benzene-Alcohol (C_6H_6 - C_2H_5OH)

Barbaudy[12], studying the ternary system benzene-alcohol-water, determined densities and refractive indices (N_D) of ternary mixtures at 25°. From his data he calculated specific volumes and refractivities. Other workers[13,26,27], whose results were not available, have supplied similar data of varying reliability at other temperatures.

The majority of Barbaudy's density values coincide with the experimental curve of this study given in Figure 6. His figures for refractive index (N_D) generally parallel those for (N_C) given in this study (Figure 7).

(b) Carbon Tetrachloride-Alcohol (CCl_4 - C_2H_5OH)

King and Smedley[14], in a vapor pressure study, determined densities for this binary at 20° very crudely.

Ishikawa and Yamaguchi[15], studying isothermal distillation of this system, used densities at 25° for analysis. The density of their alcohol indicates a small water content of 0.3 percent while their carbon tetrachloride also differs slightly from the material used in this study. Nevertheless Figure 6 shows that these small deviations affect but little a comparison between their work and this.

THE BINARY SYSTEMS - PREVIOUS INVESTIGATIONS N_C^{25}

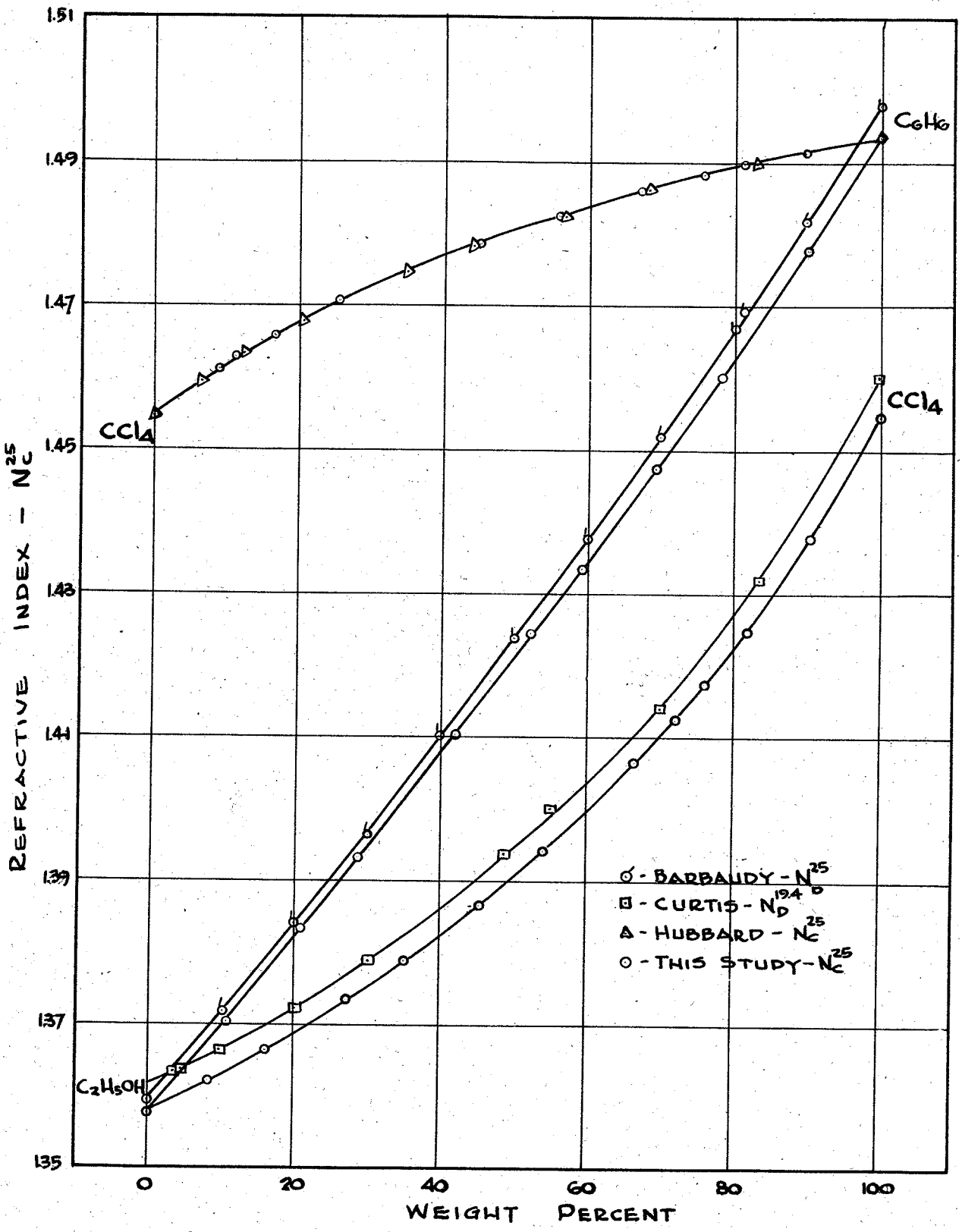


FIGURE 7

THE BINARY SYSTEMS - N_C^{25} VS. MOLE PERCENT.

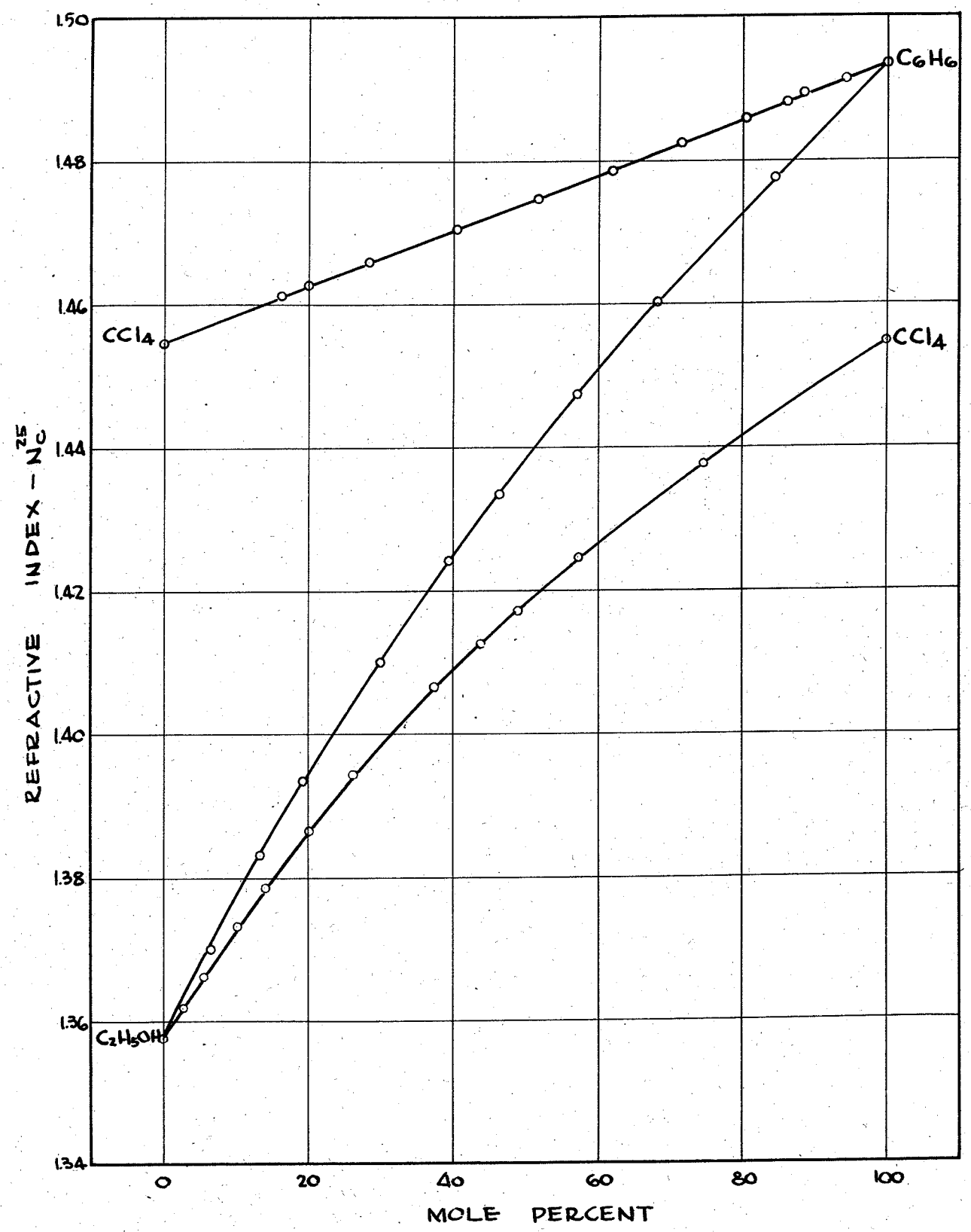


FIGURE 8

Curtis and Titus[9], studying the ternary system carbon tetrachloride-alcohol-water, determined densities and refractive indices (N_D) at 19.4°. Their refractive index curve parallels the N_C - curve of this study in Figure 7 .

(c) Benzene-Carbon Tetrachloride (C_6H_6 - CCl_4)

Brown[16], studying volumes and volume changes of mixtures, found densities for this binary at 20°. In a similar study, Wood and Brusie[17] evaluated thermodynamic functions from density-composition results at 30°.

In connection with vapor pressure studies, Rosanoff[18] and Zawidzki[19] determined refractive indices at 25.2° for analysis.

McMillan and McDonald[11], developing an analytic method for the analysis of ternary mixtures of acetic acid, benzene and carbon tetrachloride, found densities at 27° and refractive indices (N_D) at 25°. They do not claim more than 1.0 percent precision; moreover the properties of their materials indicate substantial impurities.

For a study of vapor-liquid equilibrium Scatchard, Wood and Mochel[20] determined densities at 25°. Their values are compared with results of this study in Figure 6.

Hubbard's[21] results for densities and refractive indices (N_D, N_C, etc.) of various binaries including this are quoted in the International Critical Tables. His N_Q data is compared with the experimental curve of this study in Figure 7.

EXPERIMENTAL

(a) Purification of Materials

In preliminary work, materials at hand required substantial purification. The following gives full details of methods used when the starting materials were impure. In this study, however, only the alcohol was extensively purified while the benzene and carbon tetrachloride, the best obtainable, required a minimum of purification operations.

All purifications were carried out in dry apparatus. Portions collected were protected from the atmosphere by drying tubes. Materials were kept in closed, glass-stoppered bottles. When liquid was removed, a syphon arrangement allowed dry air to drive over liquid.

Benzene

Commercial "Practical" benzene was shaken with concentrated sulphuric acid for several days. The benzene layer was separated, shaken with fresh acid, washed and dehydrated over calcium chloride. It was left over sodium for several days more, refluxed and then rectified. The density of this benzene was still unsatisfactory.

For the actual calibration very pure "Analar" benzene was used directly as a starting material.

Carbon Tetrachloride

One litre "Eastman Practical" carbon tetrachloride was shaken with 10 percent sodium hydroxide and 10 percent potassium permanganate for two days, then refluxed for one day. It was distilled, dried over calcium chloride, and fractionated from phosphorus pentoxide.

In this study "Analar" carbon tetrachloride, fractionated from phosphorus pentoxide and collected in a 0.2° range, was used as a starting material.

Ethyl Alcohol

Stock alcohol (6 percent water) was refluxed with 25 c.c. 12 N sulfuric acid and distilled. The middle distillate was treated with 20 grams sodium hydroxide and 10 grams silver nitrate, refluxed, and distilled. Again only the middle distillate was collected. This was further treated with several portions of lime calcined at 1000°C. After several days this alcohol was filtered, refluxed over fresh lime, and fractionated. First and last fractions were rejected; the alcohol was collected over a 0.2° range.

This alcohol, having a water content of less than 0.07 percent, was used as a starting material.

Published properties of the "pure" materials differ, showing their purity is variable. Only the density figure for alcohol determined at the Bureau of Standards by

Osborne, McKelvey and Bearce[22] is generally accepted. Table I reveals the differences in the properties of materials used by various workers. It also will explain why the binary systems had to be repeated for the materials available.

(b) Procedure

Temperature Control

It is well known that density and refractive index vary with temperature. The maximum change in either value for a 0.1° variation is less than .0001 units for all the components. To ensure standard conditions of calibration reproducible for the analysis, a thermostat at 25.00° (indicated by a standard thermometer) was used. A Beckman in the thermostat showed a total fluctuation of 0.033°, - far beyond the precision required for density. Thermostat water at 25° was circulated through the prism of a Pulfrich refractometer. Here temperature control was better than 0.05° giving N_D with required accuracy.

Preparation of Mixtures

Mixtures were made up by weighing in 100 cc. long-necked, glass-stoppered flasks. Each flask was paired with a counterpoise which was treated identically in all operations. The stoppered flask and contents were left in the thermostat for at least half an hour and were

TABLE I

Purity of Materials

	C_6H_6			C_2H_5OH			CCl_4		
	d_4^{25}	n_C^{25}	n_D^{25}	d_4^{25}	n_C^{25}	n_D^{25}	d_4^{25}	n_C^{25}	n_D^{25}
This Study	.87376	1.49331	1.49797	.78524	1.35767		1.58455	1.45478	
Ishikawa[15]				.7860			1.5842		
Barbaudy[12]	.87363		1.49795	.78506		1.3592			
Scatchard[20]	.87370						1.58426		
McMillan[11]	.8734[27°]		1.4985				1.5866[27°]		1.4549
Osborne[22]				.78506					
Martin[23]	.87286	1.49312							
Hubbard[21]	.87372	1.49330	1.49794				1.58456	1.45464	1.45732
Vartoressian[24]	.8727		1.4976	.7852		1.3598			

(11)

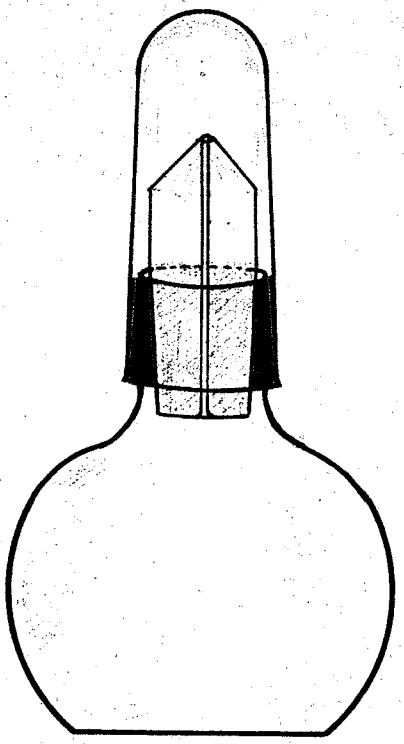
shaken occasionally. The density and refractive index was then obtained at the same time from any one mixture.

Weighings to six, sometimes five, significant figures were usual. Percentages for composition will be listed to four figures, although three are sufficient in this study. The fourth figure may be doubtful for the following reasons: (1) omission of buoyancy corrections, (2) leakage at the stoppers, (3) evaporation on opening flasks or transferring liquids. These errors are to some extent compensatory. In any case composition figures are certainly much more accurate than 0.1 percent.

Refractive Index Measurements

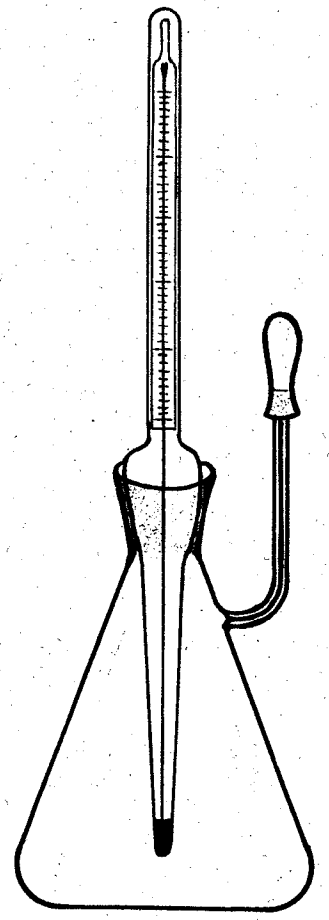
The ternary mixture at 25° was tested in a Pulfrich refractometer until a constant reading was obtained. The refractometer required a correction of + 41 minutes. A hydrogen discharge tube was the monochomatic source, the indices N_C therefore being for the hydrogen red line H_α

Slow leakage, hence fractionation and change in composition, tended to alter readings over a prolonged period. But the liquid mixture and the prism were always brought to 25° beforehand so that readings could be made rapidly. The refractometer gave the value of the angle of refraction to one minute, allowing a variability of .00010 in the refractive index.



WELD S.G. BOTTLE

FIGURE 9.



LEACH S.G. BOTTLE

FIGURE 10.

Density Determinations

Densities were obtained in the ordinary manner using a Leach pycnometer (50 c.c.) and a Weld specific gravity bottle (25 c.c.). The volume of both bottles was accurately determined at 25° from the weight of pure distilled water they contained.

Since the specific gravity bottles containing a volatile mixture lost weight very gradually due to leakage, the actual procedure was as follows. The ternary mixture at 25° was poured into the pycnometer which was then placed in the thermostat. When the excess liquid evaporated rapidly from the tip (a minimum of fractionation) the pycnometer was immediately capped, carefully wiped, placed in the balance case for a few minutes, and weighed. A counterpoise for each pycnometer was treated identically. Reproducability in densities, calculated to six figures, was better than .0001.

(c) Calculations

Liquids are sometimes characterised by a relative density given by $d^t_t = \frac{W^l}{W}$

where W^l is the weight of liquid and W the weight of water at the same temperature t. Where the specific gravity of the liquid at temperature t° is required the weight of

liquid at t^o must be compared with the same volume of water at 4^oC. This is given by the expression $d_4^t = \frac{W^l}{W} D$ where D is the density of water at t^o.

In this study, since the density results were to be used directly in analysis, the weights W^l and W were not corrected for buoyancy of air. Since the density bottles were counterpoised, variations in buoyancy posed no problem. All the experimental densities in this study are therefore not corrected to vacuum. But wherever a comparison between the results in this study with those of other workers is made, all densities should be assumed corrected, for example, Figure 6. The symbol will be $\underline{d}_4^t$ for the corrected density, contrasted with d_4^t for the uncorrected.

To make the experimental densities of Table 2 publishable, Table 3 supplies the corrections which will readily correct any density figure.

RESULTS

TABLE 2.

Experimental Results

% CCl_4	% C_6H_6	% C_2H_5OH	d_4^{25}	n_C^{25}
100	0	-	1.5852	1.45478
90.92	9.08		1.4760	1.46118
88.81	11.19		1.4537	1.46295
83.18	16.82		1.3940	1.46592
74.25	25.75		1.3102	1.47055
64.75	35.25		1.2313	1.47487
54.71	45.29		1.1615	1.47866
43.98	56.02		1.0910	1.48244
32.66	67.34		1.0235	1.48598
24.06	75.94		.9793	1.48819
18.57	81.43		.9530	1.48943
10.02	89.98		.9148	1.49132
0	100		.8736	1.49331
0	-	100	.7850	1.35767
8.76		91.24	.8216	1.36199
16.45		83.55	.8567	1.36628
27.32		72.68	.9116	1.37316
35.57		64.33	.9581	1.37882
45.61		54.19	1.0227	1.38658
54.44		45.56	1.0841	1.39414
66.90		33.10	1.1865	1.40628
72.36		27.64	1.2380	1.41259
76.27		23.73	1.2771	1.41732
82.09		17.91	1.3406	1.42478
90.73		9.27	1.4476	1.43781

TABLE 2 (Continued)

% CCl_4	% C_6H_6	% C_2H_5OH	d_4^{25}	n_C^{25}
-	10.69	89.31	.7939	1.37042
	21.01	79.99	.8026	1.38318
	28.94	71.06	.8092	1.39327
	42.05	57.95	.8203	1.41018
	52.55	47.45	.8292	1.42418
	59.26	40.74	.8351	1.43326
	69.30	30.70	.8438	1.44738
	78.38	21.62	.8520	1.46027
	90.28	9.72	.8632	1.47789
	90.94	9.06	.8638	
66.90	0	33.10	1.1865	1.40628
59.21	11.49	29.30	1.1387	1.41903
50.46	24.56	24.98	1.0891	1.43256
44.46	33.54	22.00	1.0576	1.44103
37.09	44.70	18.30	1.0210	1.45109
29.63	55.71	14.66	.9873	1.46037
24.74	63.02	12.24	.9663	1.46631
16.71	75.02	8.27	.9340	1.47555
8.36	87.51	4.13	.9027	1.48445
2.50	96.27	1.23	.8820	1.49084

TABLE 2 (Continued)

% CCl_4	% C_6H_6	% C_2H_5OH	d_4^{25}	n_C^{25}
72.36	0	27.64	1.2380	1.41259
65.90	8.93	25.17	1.1927	1.42216
58.07	19.75	22.18	1.1425	1.43296
50.59	30.08	19.33	1.0965	1.44255
43.30	40.16	16.54	1.0587	1.45126
36.07	50.15	13.78	1.0222	1.45937
27.39	62.15	10.46	.9816	1.46848
19.93	72.46	7.61	.9495	1.47574
13.34	81.57	5.09	.9228	1.48166
6.64	90.83	2.53	.8974	1.48771
16.46	0	83.55	.8567	1.36628
14.97	9.01	76.02	.8581	1.37728
13.62	17.19	69.19	.8594	1.38736
11.59	29.55	58.86	.8613	1.40248
9.81	40.36	49.83	.8629	1.41561
7.91	51.94	40.15	.8646	1.43034
5.48	66.70	27.82	.8669	1.44918
4.88	70.33	24.79	.8678	1.45309
2.46	85.04	12.50	.8705	1.47277
1.33	91.89	6.76	.8713	1.48244

TABLE 2 (Continued)

% CCl_4	% C_6H_6	% C_2H_5OH	d_4^{25}	n_C^{25}
8.757	0	91.24	.8216	1.36199
8.05	6.03	83.91	.8256	1.37165
6.94	20.76	72.30	.8320	1.38755
6.13	29.97	63.90	.8366	1.39910
5.25	40.00	54.75	.8416	1.41179
4.38	49.95	45.67	.8465	
3.80	56.58	39.62	.8498	1.43336
3.05	65.22	31.73	.8540	1.44455
2.21	74.82	22.97	.8591	1.45748
1.54	82.47	15.99	.8631	1.46800
.61	93.02	6.37	.8690	1.48282
27.32	0	72.68	.9116	1.37316
24.73	9.50	65.88	.9074	1.38454
22.30	18.39	59.31	.9036	1.39524
18.87	30.92	50.21	.8983	1.41028
14.84	45.65	39.50	.8924	1.42791
10.98	59.80	29.22	.8877	1.44516
8.48	70.54	21.41	.8834	1.45799
5.86	78.56	15.58	.8805	1.46731
4.68	82.87	12.45	.8791	1.47124
1.95	92.86	5.19	.8754	1.48436

TABLE 2 (Continued)

% CCl_4	% C_6H_6	% C_2H_5OH	d_4^{25}	n_C^{25}
45.81	0	54.19	1.0227	1.38658
40.48	11.64	47.88	1.0017	1.40039
36.72	19.83	43.44	.9879	1.40998
32.11	29.91	37.98	.9714	1.42146
27.30	40.41	32.29	.9550	1.43301
20.71	54.79	24.50	.9324	1.44888
18.77	59.02	22.21	.9278	1.45268
15.25	66.71	18.04	.9168	1.46047
7.43	73.78	8.79	.9063	1.46799
54.44	0	45.56	1.0841	1.39414
49.98	8.80	41.82	1.0691	1.40517
44.23	18.76	37.01	1.0345	1.41622
38.37	29.52	32.11	1.0093	1.42786
32.50	40.31	27.19	.9884	1.43751
27.58	49.33	23.09	.9688	1.44657
23.27	57.25	19.48	.9522	1.45448
22.49	58.68	18.83	.9485	1.45629
17.77	67.36	14.87	.9314	1.46464
11.32	79.20	9.48	.9093	1.47516
6.05	88.89	5.06	.8920	1.48378

TABLE 2 (Continued)

% CCl_4	% C_6H_6	% C_2H_5OH	d_4^{25}	n_C^{25}
35.57	0	64.43	.9581	1.37882
31.70	10.89	57.41	.9474	1.39192
28.19	20.74	51.07	.9383	1.40368
24.30	31.68	44.02	.9284	1.41652
20.08	43.56	36.36	.9179	1.43013
17.06	52.08	30.89	.9107	1.43982
13.18	62.94	23.88	.9020	1.45188
11.88	66.61	21.51	.8985	1.45629
8.92	74.92	16.16	.8922	1.46552
5.61	83.87	10.52	.8850	1.47555
2.52	92.91	4.57	.8782	1.48550
82.09	0	17.91	1.3406	1.42478
74.09	9.74	16.17	1.2733	1.43468
65.15	20.64	14.21	1.2061	1.44435
55.76	32.08	12.16	1.1429	1.45359
32.50	60.41	7.09	1.0123	1.47282
31.14	62.07	6.79	1.0055	1.47398
25.10	69.42	5.48	.9768	1.47779
16.11	80.38	3.51	.9369	1.48376
6.66	91.86	1.46	.8988	1.48960

TABLE 2 (Continued)

% CCl_4	% C_6H_6	% C_2H_5OH	d_4^{25}	n_D^{25}
90.73	0	9.27	1.4476	1.43761
82.14	9.47	8.39	1.3623	1.44626
67.14	26.00	6.86	1.2356	1.45828
53.41	41.13	5.46	1.1309	1.46799
39.01	56.11	3.88	1.0471	1.47691
26.65	70.63	2.72	.9882	1.48244
15.91	82.46	1.63	.9386	1.48714
6.15	93.22	0.63	.8976	1.49160
0	28.94	71.06	.8092	1.39327
11.04	25.57	62.79	.8582	1.39711
20.61	22.92	56.27	.9010	1.40059
32.63	19.50	47.87	.9629	1.40547
45.28	16.41	40.31	1.0263	1.41058
55.52	12.87	31.61	1.1105	1.41722
59.56	11.70	28.74	1.1422	1.41994
69.10	8.94	21.96	1.2224	1.42610
78.16	6.32	15.52	1.3098	1.43266
89.03	3.17	7.80	1.4323	1.44324

TABLE 2 (Continued

% CCl_4	% C_6H_6	% C_2H_5OH	d_4^{25}	n_C^{25}
10.08	70.48	19.44	.8936	1.46007
21.14	61.81	17.05	.9442	1.45987
30.02	54.85	15.13	.9892	1.45967
38.01	48.59	13.40	1.0355	1.45927
52.68	37.09	10.23	1.1263	1.45878
60.21	31.19	8.60	1.1800	1.45838
70.41	23.19	5.40	1.2627	1.45778
78.93	16.51	4.56	1.3409	1.45689
89.78	8.01	2.21	1.4563	1.45608
0	78.38	21.62	.8520	1.46027
0	21.01	78.99	.8026	1.38318
10.52	18.80	70.68	.8466	1.38726
24.06	15.95	59.97	.9111	1.39326
31.44	14.40	54.16	.9502	1.39692
40.22	12.56	47.22	1.0014	1.40179
48.41	10.84	40.75	1.0545	1.40638
60.76	8.24	30.98	1.1466	1.41490
70.84	6.13	23.03	1.2335	1.42276
81.00	4.00	15.00	1.3361	1.43195

TABLE 2 (Continued

% CCl_4	% C_6H_6	% C_2H_5OH	d_4^{25}	n_C^{25}
0	90.28	9.72	.8632	1.47789
11.90	79.54	8.56	.9127	1.47642
22.43	70.03	7.54	.9614	1.47516
36.59	57.25	6.16	1.0357	1.47291
47.02	47.83	5.15	1.0983	1.47104
59.62	36.46	3.92	1.1846	1.46819
68.14	28.76	3.10	1.2511	1.46641
74.03	23.45	2.52	1.3020	1.46464
81.72	16.60	1.78	1.3745	1.46206
93.00	6.32	0.68	1.4971	1.45778
0	59.26	40.74	.8351	1.43326
14.02	50.95	35.03	.8943	1.43549
22.25	46.07	31.68	.9332	1.43640
32.12	40.23	27.65	.9844	1.43791
40.66	35.16	24.18	1.0335	1.43932
48.82	30.33	20.85	1.0851	1.44083
60.29	23.53	16.18	1.1676	1.44325
69.37	18.15	12.48	1.2421	1.44546
81.98	10.66	7 .34	1.3630	1.44848
95.43	2.71	1.86	1.5215	1.45288

TABLE 2 (Continued)

% CCl_4	% C_6H_6	% C_2H_5OH	d_4^{25}	n_C^{25}
0	52.55	47.45	.8292	1.42418
15.33	44.49	40.18	.8945	1.42690
21.75	41.12	37.13	.9259	1.42821
32.22	35.62	32.10		
42.36	30.29	27.35		1.43326
51.40	25.54	23.06		1.43569
62.81	19.54	17.65	1.1851	1.43892
76.61	12.34	11.15	1.3044	1.44365
83.72	8.56	7.72	1.3758	1.44637
92.23	4.08	3.69	1.4774	1.45039
0	42.05	57.95	.8203	1.41018
9.46	38.07	52.47	.8595	1.41269
20.22	33.54	46.23	.9089	1.41560
28.91	29.89	41.20	.9531	1.41813
39.77	25.33	34.90	1.0147	1.42196
51.16	20.54	28.30	1.0856	1.42600
58.96	17.26	23.78	1.1460	1.42973
70.78	12.29	16.93	1.2446	1.43530
81.33	7.65	10.82	1.3451	1.44088
91.18	3.71	5.11	1.4598	1.44728

TABLE 2 (Continued)

% CCl_4	% C_6H_6	% C_2H_5OH	d_4^{25}	n_C^{25}
0	69.30	30.70	.8438	1.44736
8.70	63.27	28.03	.8796	1.44788
18.51	56.47	25.02	.9237	1.44618
28.12	49.81	22.07	.9714	1.44998
37.43	43.36	19.21	1.0225	1.44968
45.62	37.69	16.69	1.0722	1.44999
54.08	31.82	14.10	1.1290	1.45059
64.30	24.74	10.96	1.2058	1.45148
73.69	18.09	8.02	1.2865	1.44228
87.38	8.75	3.87	1.4261	1.45349
92.20	5.41	2.39	1.4829	1.45379
0	10.69	89.31	.7959	1.37042
10.18	9.60	80.22	.8369	1.37517
20.12	8.54	71.34	.8830	1.37998
31.16	7.36	61.48	.9340	1.38561
37.92	6.64	55.44	.9732	1.38951
48.66	5.49	45.85	1.0425	1.39701

TABLE 3

Corrections for Analytic Densities d_4^{25} to Vacuo g_4^{25}

over 1.55	+ .0007
1.45 - 1.55	+ .0006
1.36 - 1.45	+ .0005
1.29 - 1.36	+ .0004
1.25 - 1.29	+ .0003
1.12 - 1.25	+ .0002
1.04 - 1.12	+ .0001
.955 - 1.04	.0000
.870 - .955	∓ .0001
.785 - .870	∓ .0002

TABLE 4 (a)

Derived Isodensity Data

CCl_4 / C_2H_5OH	0 / 100	8.76 / 91.24	16.45 / 83.55	27.32 / 72.68	35.57 / 64.43	45.81 / 54.19	54.44 / 45.56	66.9 / 33.1	72.36 / 27.64	82.09 / 17.91	90.73 / 9.27	100 / 0
d_4^{25}	Percent C_6H_6 in Ternary											
.800	18.00											
.820	41.72											
.840	64.70	36.80										
.860	87.04	76.90	24.10									
.880				80.30	90.90	94.36	95.78	97.12	97.50	97.98	98.04	98.38
.900				27.40	64.16	78.87	84.22	88.48	89.77	91.44	92.46	93.37
.920					40.90	64.18	73.17	80.34	82.42	85.30	87.12	88.73
.940					19.00	50.22	62.92	72.53	75.46	79.42	82.00	84.17
.960						36.98	52.98	65.08	68.83	73.81	77.08	79.77
.980						24.33	43.20	58.00	62.46	68.44	72.40	75.62
1.000						12.20	33.68	51.23	56.48	63.36	67.86	71.68
1.020						1.16	24.62	44.80	50.70	58.42	63.52	67.93
1.040							16.23	38.68	45.13	53.67	59.37	64.36
1.060							8.23	32.78	39.74	49.14	55.37	60.98
1.080							1.28	27.00	34.58	44.78	51.53	52.68
1.100								21.44	29.60	40.57	47.82	54.53
1.120								16.10	24.80	36.56	44.27	51.42
1.140								11.02	20.19	32.63	40.90	48.38
1.160								6.23	15.78	28.79	37.61	45.46
1.180								1.47	11.46	25.13	34.43	42.42
1.200									7.40	21.60	31.37	39.56
1.220									3.37	18.23	28.30	36.77

TABLE 4 (b)

Derived Isodensity Data

C_6H_6 / C_2H_5OH	0 / 100	10.69 / 89.31	21.01 / 78.99	28.94 / 71.06	42.05 / 57.95	52.55 / 47.45	59.26 / 40.74	69.30 / 30.70	78.38 / 21.62	90.28 / 9.72
	Percent CCl_4 in Ternary									
	3.54	1.47								
	8.24	6.23	4.16	2.53						
	12.79	10.88	8.92	7.32	4.66	2.53	1.13			
	17.14	15.40	13.53	12.00	9.40	7.24	5.92	3.99	1.97	
	21.21	19.63	17.93	16.45	14.00	11.93	10.60	8.78	6.77	4.07
	25.12	23.42	22.01	20.58	18.38	16.44	15.22	13.40	11.57	8.93
	28.94	27.18	25.97	24.46	22.57	20.79	19.53	17.78	16.06	13.60
	32.53	30.79	29.73	28.28	26.50	24.58	23.66	21.90	20.30	18.03
	35.96	34.33	33.33	32.00	30.27	28.30	27.56	25.87	24.38	22.24
	39.27	37.66	36.77	35.62	33.87	31.99	31.30	29.64	28.33	26.14
	42.42	40.69	40.02	39.03	37.34	35.52	34.96	33.37	32.06	30.00
	45.42	43.70	43.12	42.30	40.63	38.98	38.37	36.98	35.67	33.70
	48.27	46.66	46.20	45.46	43.82	42.25	41.66	40.46	39.11	37.34
	51.10	49.57	49.21	48.48	46.88	45.46	44.86	43.78	42.38	40.74
	53.86	52.41	51.97	51.37	49.93	48.56	47.97	46.87	45.62	44.06
	56.54	55.18	54.66	54.13	52.75	51.47	50.96	49.90	48.75	47.24
	59.13	57.80	57.26	56.61	55.54	54.38	53.78	52.80	51.76	50.36
	61.56	60.32	59.81	59.17	58.21	57.12	56.38	55.64	54.67	53.37
	63.94	62.68	62.24	61.64	60.80	59.80	59.30	58.42	57.53	56.23
	66.23	65.03	64.64	64.12	63.24	62.40	61.76	61.03	60.20	58.47
	68.43	67.33	66.98	66.55	65.67	64.82	64.23	63.56	62.60	61.68
	70.58	69.58	69.24	68.82	68.00	67.19	66.68	66.06	65.82	64.24
	72.63	71.70	71.44	71.03	70.23	69.52	69.08	68.43	67.43	66.88

			62.46	68.44	72.40	75.62	
1.020	12.20	33.68	51.23	56.48	63.36	67.86	71.68
1.040	1.16	24.62	44.80	50.70	58.42	63.52	67.93
1.060		16.23	38.68	45.13	53.67	59.37	64.36
1.080		8.23	32.78	39.74	49.14	55.37	60.98
1.100		1.28	27.00	34.58	44.78	51.53	52.68
1.120			21.44	29.60	40.57	47.82	54.53
1.140			16.10	24.80	36.56	44.27	51.42
1.160			11.02	20.19	32.63	40.90	48.38
1.180			6.23	15.78	28.79	37.61	45.46
1.200			1.47	11.46	25.13	34.43	42.42
1.220				7.40	21.60	31.37	39.56
1.240				3.37	18.23	28.30	36.77
1.260					14.98	25.32	34.12
1.280					11.74	22.44	31.60
1.300					8.62	19.94	29.21
1.320					5.73	17.66	26.87
1.340					2.86	14.47	24.62
1.360					0.03	12.03	22.42
1.380						9.63	20.33
1.400						7.36	18.22
1.420						5.12	16.22
1.440						2.93	14.30
1.460						0.76	12.42
1.480							10.52
1.500							8.73
1.520							6.98
1.540							5.29
1.560							3.63
1.580							2.04
							0.42

39.27	37.66	36.77	35.62	33.87	31.99	31.30	29.[illegible]		
42.42	40.69	40.02	39.03	37.34	35.52	34.96	33.37	32.[illegible]	30.00
45.42	43.70	43.12	42.30	40.63	38.98	38.37	36.98	35.67	33.70
48.27	46.66	46.20	45.46	43.82	42.25	41.66	40.46	39.11	37.34
51.10	49.57	49.21	48.48	46.88	45.46	44.86	43.78	42.38	40.74
53.86	52.41	51.97	51.37	49.93	48.56	47.97	46.87	45.62	44.06
56.54	55.18	54.66	54.13	52.75	51.47	50.96	49.90	48.75	47.24
59.13	57.80	57.26	56.61	55.54	54.38	53.78	52.80	51.76	50.36
61.56	60.32	59.81	59.17	58.21	57.12	56.38	55.64	54.67	53.37
63.94	62.68	62.24	61.64	60.80	59.80	59.30	58.42	57.53	56.23
66.23	65.03	64.64	64.12	63.24	62.40	61.76	61.03	60.20	58.47
68.43	67.33	66.98	66.55	65.67	64.82	64.23	63.56	62.60	61.68
70.58	69.58	69.24	68.82	68.00	67.19	66.68	66.06	65.82	64.24
72.63	71.70	71.44	71.03	70.23	69.52	69.08	68.43	67.43	66.78
74.64	73.74	73.53	73.20	72.42	71.78	71.38	70.71	69.74	69.21
76.59	75.75	75.54	75.27	74.58	73.99	73.57	72.98	72.06	71.54
78.46	77.68	77.56	77.27	76.62	76.08	75.67	75.06	74.36	73.78
80.36	79.59	79.43	79.18	78.66	78.17	77.78	77.13	76.54	75.99
82.10	81.40	81.32	81.07	80.63	80.17	79.77	79.17	78.64	78.17
83.83	83.20	83.15	82.90	82.51	82.12	81.67	81.18	80.73	80.22
85.53	84.95	84.91	84.67	84.33	84.00	83.58	83.09	82.73	82.25
87.16	86.67	86.58	86.42	86.06	85.79	85.46	85.00	84.63	84.21
88.72	88.37	88.24	88.03	87.80	87.50	87.23	86.80	86.54	86.13
90.22	89.99	89.83	89.70	89.52	89.21	88.98	88.62	88.31	87.99
91.70	91.57	91.37	91.26	91.20	90.86	90.63	90.36	90.20	89.78
93.15	93.01	92.87	92.77	92.71	92.46	92.26	92.00	91.89	91.54
94.54	94.44	94.34	94.23	94.19	94.02	93.83	93.61	93.56	93.25
95.86	95.83	95.73	95.66	95.64	95.55	95.35	95.20	95.14	94.88
97.18	97.17	97.07	97.04	97.02	96.97	96.81	96.73	96.66	96.47
98.42	98.43	98.37	98.37	98.37	98.36	98.29	98.20	98.15	98.04
99.62									99.54

TABLE 5 (a)

Derived Isofract Data

CCl_4 / C_2H_5OH	0 / 100	8.76 / 91.24	16.45 / 83.55	27.32 / 72.68	35.57 / 64.43	45.81 / 54.19	54.44 / 45.56	66.9 / 33.1	72.36 / 27.64	82.09 / 17.91	90.73 / 9.27	100 / 0
N_C^{25}	Percent C_6H_6 in Ternary											
1.360	1.93											
1.365	6.17	2.54										
1.370	10.34	6.66	3.06									
1.375	14.38	10.73	7.14	1.49								
1.380	18.42	14.83	11.22	5.66	0.94							
1.385	22.43	18.83	15.26	9.82	5.03							
1.390	26.38	22.82	19.39	13.99	9.22	2.84						
1.395	30.25	26.77	23.57	18.16	13.51	7.01	0.65					
1.400	34.18	30.62	27.79	22.21	17.66	11.30	4.67					
1.405	38.07	34.64	31.76	26.35	21.94	15.60	8.66					
1.410	41.90	38.57	35.78	30.56	26.14	19.92	13.16	3.32				
1.415	45.67	42.52	39.73	34.76	30.40	24.22	17.68	7.80	2.23			
1.420	49.42	46.42	43.76	38.94	34.73	28.60	22.24	12.40	6.88			
1.425	53.14	50.26	47.78	43.15	39.08	33.13	26.82	17.16	11.63	0.23		
1.430	56.83	54.05	51.78	47.32	43.48	37.70	31.66	22.02	16.68	5.03		
1.435	60.48	57.83	55.72	51.42	47.80	42.41	37.74	27.08	21.88	10.16		
1.440	64.10	61.70	59.62	55.53	52.17	47.07	41.81	32.46	27.26	15.62	2.52	
1.445	67.63	65.47	63.48	59.66	56.53	51.82	46.90	37.95	32.83	21.40	8.06	
1.450	71.17	69.24	67.23	63.82	60.90	56.62	52.08	43.50	38.62	27.60	14.16	
1.455	74.67	72.96	71.18	67.98	65.33	61.50	57.28	49.37	44.63	34.02	20.98	0.28
1.460	78.16	76.60	75.07	72.18	69.88	66.33	62.47	55.24	51.00	40.79	28.48	7.18
1.465	81.56	80.26	78.97	76.55	74.37	71.21	67.73	61.40	57.48	48.00	36.30	15.13
1.470	84.96	83.80	82.77	80.83	78.93	76.13	73.20	67.63	64.24	55.67	44.84	24.73
1.475	88.34	87.46	86.53	85.01	83.42	81.12	78.77	74.18	71.41	64.73	54.28	35.58

(29)

TABLE 5 (b)

Derived Isofract Data

C_6H_6 / C_2H_5OH	0 / 100	10.69 / 89.31	21.01 / 78.99	28.94 / 71.06	42.05 / 57.95	52.55 / 47.45	59.26 / 40.74	69.30 / 30.70	78.38 / 21.62	90.28 / 9.72
Percent CCl_4 in Ternary										
4.81										
14.18										
22.47										
30.10	9.81									
37.18	20.07									
43.77	29.84	4.91								
49.83	38.60	16.87								
55.42	45.87	27.58	5.54							
60.66	52.48	37.20	19.39							
65.63	58.54	46.00	31.58							
70.22	64.16	53.88	42.23							
74.43	69.36	60.88	51.48	18.28						
78.46	74.18	67.53	59.83	34.38						
82.20	78.68	73.48	67.44	48.58	5.00					
85.68	82.88	79.01	74.56	59.99	29.40					
89.00	86.83	83.96	80.92	70.08	48.90	12.60				
92.02	90.47	88.48	86.56	79.61	66.24	44.38				
94.83	93.86	92.70	91.63	87.77	80.06	67.84				
97.47	97.03	96.58	96.12	94.48	91.48	87.33	45.90			
								98.40	99.47	
								17.70	87.17	
									72.66	
									51.84	

C_2H_5OH	100	91.24	83.55	72.68	64.43	54.19	45.56	33.1	27.64	17.91	9.27	0.

n_C^{25}	Percent C_6H_6 in Ternary										
1.360	1.93										
1.365	6.17	2.54									
1.370	10.34	6.66	3.06								
1.375	14.38	10.73	7.14	1.49							
1.380	18.42	14.83	11.22	5.66	0.94						
1.385	22.43	18.83	15.26	9.82	5.03						
1.390	26.38	22.82	19.39	13.99	9.22	2.84					
1.395	30.25	26.77	23.57	18.16	13.51	7.01	0.65				
1.400	34.18	30.62	27.79	22.21	17.66	11.30	4.67				
1.405	38.07	34.64	31.76	26.35	21.94	15.60	8.66				
1.410	41.90	38.57	35.78	30.56	26.14	19.92	13.16	3.32			
1.415	45.67	42.52	39.73	34.76	30.40	24.22	17.68	7.80	2.23		
1.420	49.42	46.42	43.76	38.94	34.73	28.60	22.24	12.40	6.88		
1.425	53.14	50.26	47.78	43.15	39.08	33.13	26.82	17.16	11.63	0.23	
1.430	56.83	54.05	51.78	47.32	43.48	37.70	31.66	22.02	16.68	5.03	
1.435	60.48	57.83	55.72	51.42	47.80	42.41	37.74	27.08	21.88	10.16	
1.440	64.10	61.70	59.62	55.53	52.17	47.07	41.81	32.46	27.26	15.62	2.52
1.445	67.63	65.47	63.48	59.66	56.53	51.82	46.90	37.95	32.83	21.40	8.06
1.450	71.17	69.24	67.23	63.82	60.90	56.62	52.08	43.50	38.62	27.60	14.16
1.455	74.67	72.96	71.18	67.98	65.33	61.50	57.28	49.37	44.63	34.02	20.98	0.28
1.460	78.16	76.60	75.07	72.18	69.88	66.33	62.47	55.24	51.00	40.79	28.48	7.18
1.465	81.56	80.26	78.97	76.55	74.37	71.21	67.73	61.40	57.48	48.00	36.30	15.13
1.470	84.96	83.80	82.77	80.83	78.93	76.13	73.20	67.63	64.24	55.67	44.84	24.73
1.475	88.34	87.46	86.53	85.01	83.42	81.12	78.77	74.18	71.41	64.73	54.28	35.58
1.480	91.62	91.01	90.06	89.14	87.96	86.22	84.43	81.01	78.96	73.50	64.82	49.13
1. 485	94.76	94.40	93.96	93.24	92.43	91.36	90.18	88.03	86.69	82.94	76.98	64.19
1.490	97.83	97.74	97.58	97.27	96.88	96.54	96.00	95.20	94.63	91.98	89.77	83.52

C_2H_5OH	100	89.31	78.99	71.06	57.95	47.45	40.74	30.70	21.62	9

Percent CCl_4 in Ternary											
4.81											
14.18											
22.47											
30.10	9.81										
37.18	20.07										
43.77	29.84	4.91									
49.83	38.60	16.87									
55.42	45.87	27.58	5.54								
60.66	52.48	37.20	19.39								
65.63	58.54	46.00	31.58								
70.22	64.16	53.88	42.23								
74.43	69.36	60.88	51.48	18.28							
78.46	74.18	67.53	59.83	34.38							
82.20	78.68	73.48	67.44	48.58	5.00						
85.68	82.88	79.01	74.56	59.99	29.40						
89.00	86.83	83.96	80.92	70.08	48.90	12.60					
92.02	90.47	88.48	86.56	79.61	66.24	44.38					
94.83	93.86	92.70	91.63	87.77	80.06	67.84					
97.47	97.03	96.58	96.12	94.48	91.48	87.33	45.90				
								98.40	99.		
								17.70	87.		
									72.		
									51,		
									23.		

DISCUSSION OF RESULTS

(a) EXPERIMENTAL CURVES d_4^{25}

FIGURE 11.

(a.) EXPERIMENTAL CURVES N_c^{25}

FIGURE 12

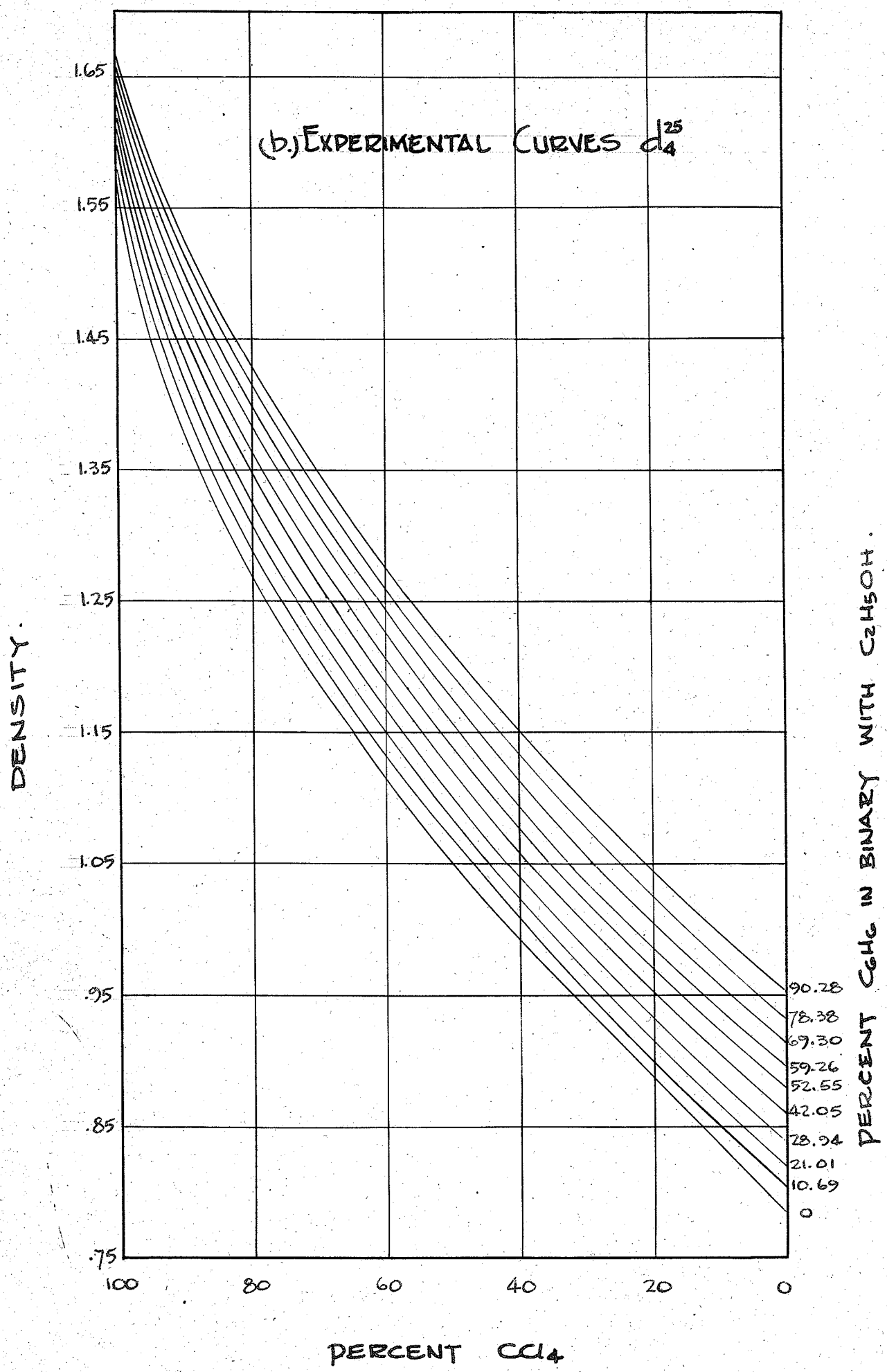

(b.) EXPERIMENTAL CURVES d_4^{25}
DENSITY.
1.65
1.55
1.45
1.35
1.25
1.15
1.05
.95
.85
.75
100
80
60
40
20
0
PERCENT CCl_4
PERCENT C_6H_6 IN BINARY WITH C_2H_5OH.
90.28
78.38
69.30
59.26
52.55
42.05
28.94
21.01
10.69
0

FIGURE 13.

(b.) EXPERIMENTAL CURVES N_c^{25}

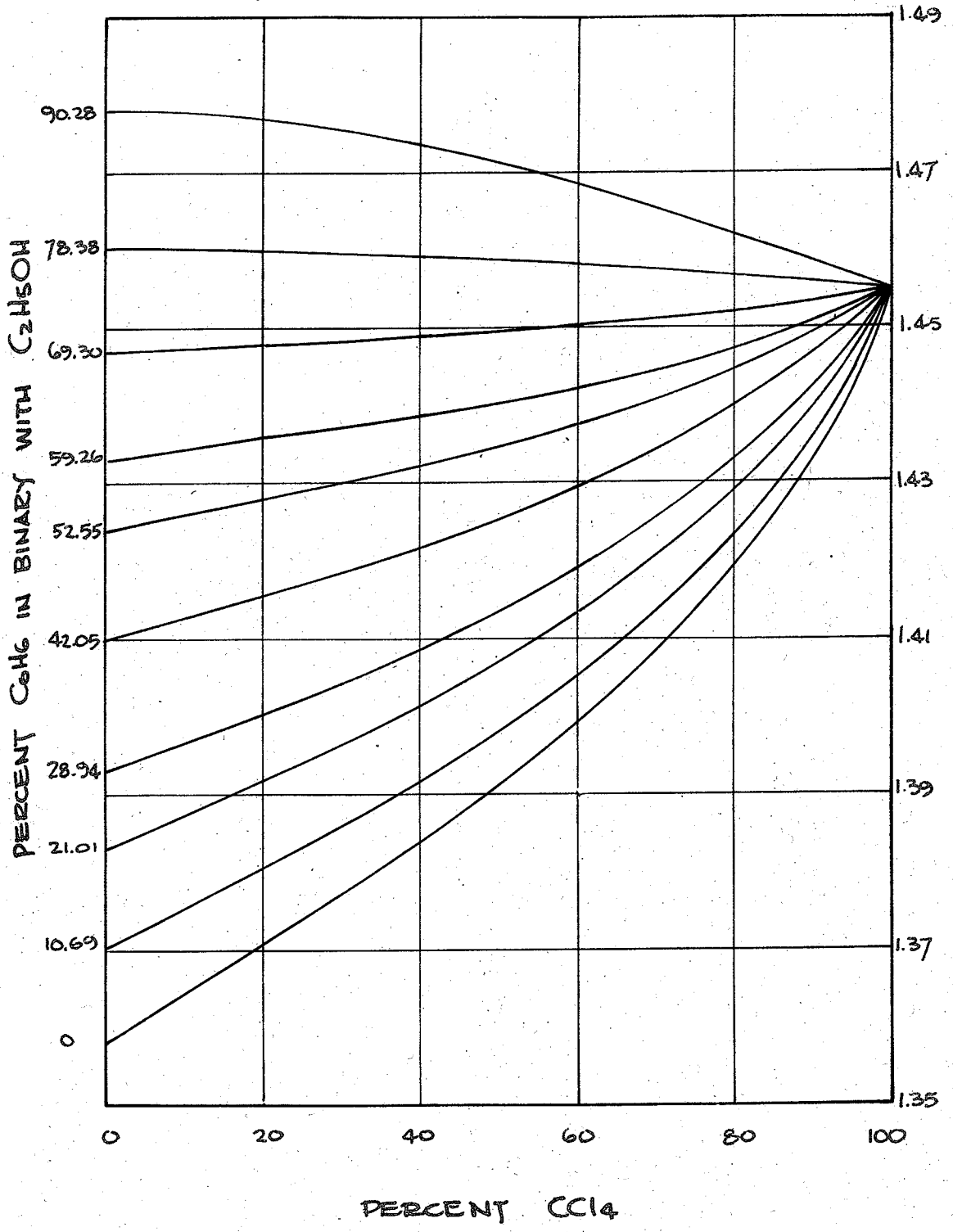


FIGURE 14.

(a) Experimental Curves

An orderly method of obtaining and assembling data in ternary systems is afforded by the use of pseudo-binary curves. Schreinemakers, for example, used it in tabulating his vapor pressure data. It consists simply in adding to a fixed binary mixture varying amounts of the third component. Now, treating the binary as one component, it is possible to plot any property against composition on a rectilinear diagram. Figures 11-14 scaled down four times summarize the experimental results of Table 2.

Here ternary mixtures were made up of binaries of benzene-alcohol or carbon tetrachloride-alcohol to which carbon tetrachloride or benzene respectively were added. In Figure 11, for example, the figures on the left represent the percentage of benzene in the binary benzene - alcohol. To each of these carbon tetrachloride was added giving rise to the isothermal density-composition curves, all of which must inevitably end at the density of carbon tetrachloride. Similarly Figure 12 gives curves of refractive index for these same mixtures. Figures 13 and 14 are analogous, but carbon tetrachloride is in the initial binary with alcohol. (In Figure 13, to facilitate reading, each curve has the indicated scale

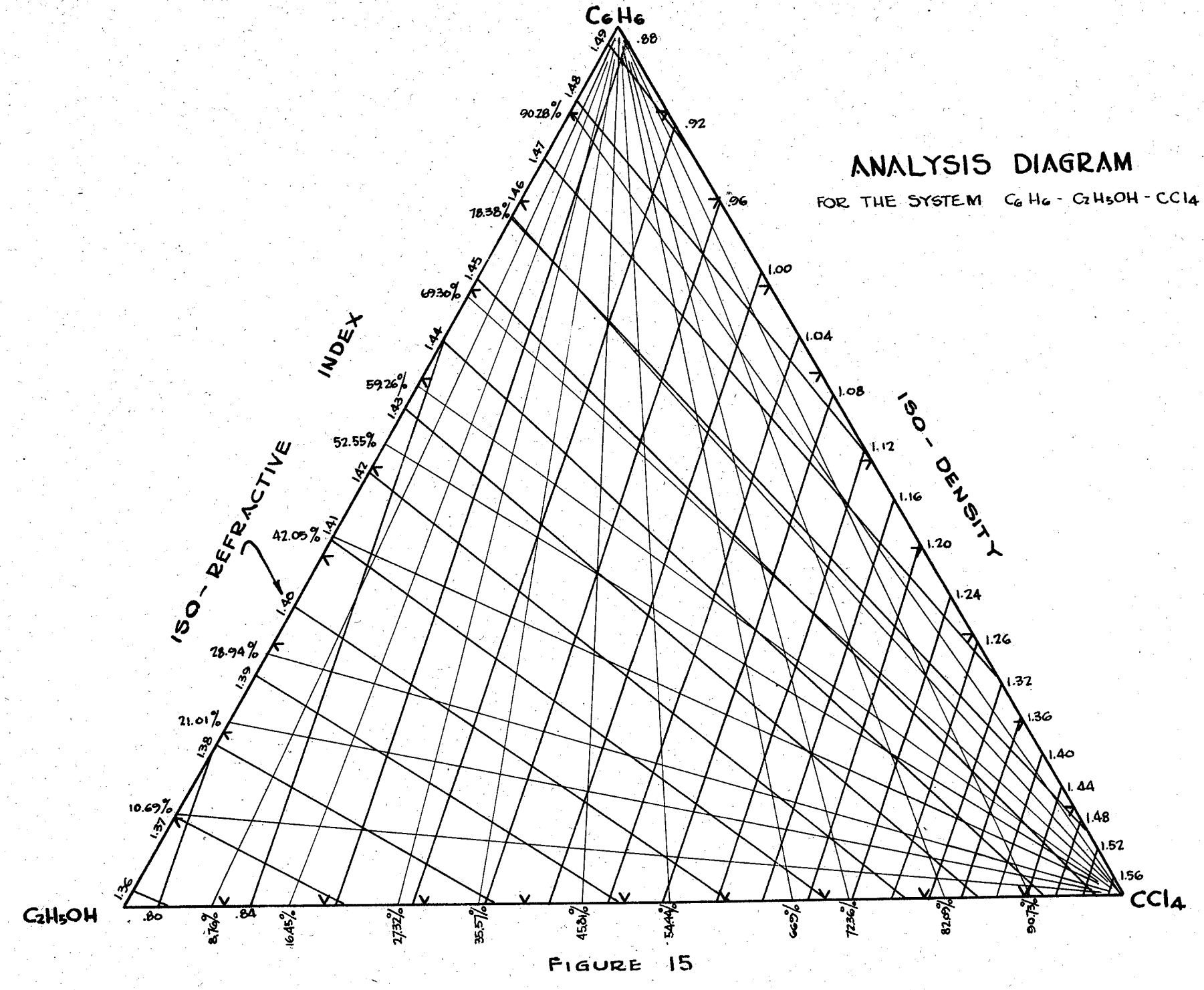

C6H6
C2H5OH
CCl4
ANALYSIS DIAGRAM
FOR THE SYSTEM C6H6 - C2H5OH - CCl4
ISO-REFRACTIVE INDEX
ISO-DENSITY
1.49
1.48
1.47
1.46
1.45
1.44
1.43
1.42
1.41
1.40
1.39
1.38
1.37
1.36
.88
.92
.96
1.00
1.04
1.08
1.12
1.16
1.20
1.24
1.26
1.32
1.36
1.40
1.44
1.48
1.52
1.56
90.28%
78.38%
69.30%
59.26%
52.55%
42.05%
28.94%
21.01%
10.69%
.80
.84
8.76%
16.45%
27.32%
35.57%
45.81%
54.44%
66.5%
72.36%
82.09%
90.73%

FIGURE 15

moved vertically by a multiple of .0100 density units - all points at 100 percent are identical with the density of carbon tetrachloride.)

Theoretically one binary starting material should have been sufficient. Although considerable overlapping occurs in the central portions of Figures 12 and 14, one binary set tends to supplement the other in regions where data is scanty. This will become more obvious when Figure 15 is discussed.

(b) Calibration Diagram

Figure 15, scaled down four times from the actual calibration diagram used, is based on points taken from the experimental curves. Lines running from the base upward are lines of constant density, isodensity lines; lines sloping generally from the right side to the base are lines of constant refractive index, isofracts (term by Bowen[25]). Horizontals cutting the rectangular experimental curves in Figure 11-14 gave sets of composition data corresponding to constant densities (Table 4) and refractive indices (Table 5). Any sequence obtained for a constant density from Figures 11 and 13 gave an isodensity line in Figure 15; any sequence obtained from Figures 12 and 14 for a constant refractive index gave an isofract in Figure 15.

Each of the experimental curves in Figures 11-14 had two components in a fixed weight ratio. These fixed ratios of composition are represented by the fainter lines originating from the benzene and carbon tetrachloride corners in Figure 15. Naturally all derived data must fall on these lines. Indeed, the drawing up of the triangular calibration diagram is greatly simplified if these lines are drawn in first.

The angle of intersection of the two sets of iso-lines averages about 60 degrees. Had this angle been close to a right angle, the maximum precision of analysis would have been possible. Had this angle been close to, or at 0 degrees (parallel lines), or had a double intersection occurred (excessive curvature in one set), the analysis would have been impossible. As it is, the triangle in use with sides almost three feet in length, and with a criss-cross grid of iso-lines, has proven satisfactory.

The use of this calibration diagram is simple. Any ternary mixture will have a refractive index and a density lying on the diagram between two isofracts and two isodensity lines. These known properties, lying on interpolated lines, will "intersect" at a unique point giving the composition of unknown mixture.

Although no more than 0.3 percent accuracy will be claimed, the analysis is usually better than 0.2 percent of the total for each of the components. The following mixtures prepared at random weighed compositions were used to test the accuracy of Figure 15. Compositions derived from the diagram, that is from the physical properties, shall be named "derived," as contrasted with the actual "weighed" figures.

TABLE 6

Accuracy of the Analytic Diagram

No.		d_4^{25}	N_C	% C_6H_6	% C_2H_5OH	% CCl_4	Maximum Deviations %
1	Weighed		1.45088	71.83	28.17	0	
	Derived			71.85	28.15		.02
2	Weighed	1.41033		15.20	0	84.80	
	Derived			15.15		84.85	.05
3	Weighed	1.0610	1.43074	26.32	27.39	46.29	
	Derived			26.3	27.3	46.4	.11
4	Weighed	.9124	1.45548	63.77	21.24	14.99	
	Derived			63.6	21.1	15.1	.15
5	Weighed	.8824	1.47643	85.07	9.99	4.94	
	Derived			85.1	9.95	4.95	.05
6	Weighed	1.4425	1.44606	4.37	6.13	89.50	
	Derived			4.2	6.3	89.5	.17
7	Weighed	1.1859	1.44103	20.50	16.55	62.95	
	Derived			20.70	16.35	62.95	.20
8	Weighed	.8413	1.37174	6.03	82.10	11.88	
	Derived			6.2	82.0	11.8	.17
9	Weighed	.8108	1.36779	6.08	88.92	5.00	
	Derived			6.3	88.9	4.8	.22

It should be noted that where the isodensity lines and the isofracts are close together the analysis will probably be most accurate. In general, however, where the isodensity lines are widely spread, the isofracts are close together, and vice versa. The alcohol corner is the least covered, and therefore the least accurate. Analyses there will be decidedly altered by errors of .00010 for either property.

(c) Applications

Analysis of Commercial Materials

The use of the analysis diagram for so-called "practical" or "stock" materials of industry deserves brief discussion. Table 7, following, lists the properties of commercial materials together with their deviation from the pure materials of this study, while Table 8 compares weighed with derived compositions. The densities and indices of ternary mixtures were corrected approximately by the "mixture rule" in which the weight given each component was taken from the crude analysis deduced from the uncorrected properties.

TABLE 7

Properties of Commercial Materials

	d_4^{25}	deviation	N_C^{25}	deviation
B.D.H. Technical Benzene	.8732	± .0004	1.49300	± .00031
Eastman's Practical Carbon Tetrachloride	1.5848	± .0004	1.45458	± .00020
Alcohol (1.7% Water)	.7902	± .0052	1.35847	± .00080

TABLE 8

Analysis of a Commercial Mixture

	d_4^{25}	d_4^{25}(corr)	N_C^{25}	N_C(corr)	% C_6H_6	% C_2H_5OH	% CCl_4
Weighed	1.0061		1.45009		45.7	19.9	34.4
Derived		1.0053		1.45046	46.4	19.3	34.3

The maximum error in the above analysis was 0.7 percent. Any error will naturally depend on the purity of the starting materials. Although a thorough survey of every region of the diagram was not made, it is probable that the above materials in ternary mixtures could be analyzed to well within 2.0 percent. This is fair accuracy and industrial application is at least practicable.

Deviations from Ideality

"An ideal solution obeys Raoult's law at all temperatures and pressures ..... the formation of such a solution will take place from its component liquids without any heat of mixing and without any change in volume."[28]

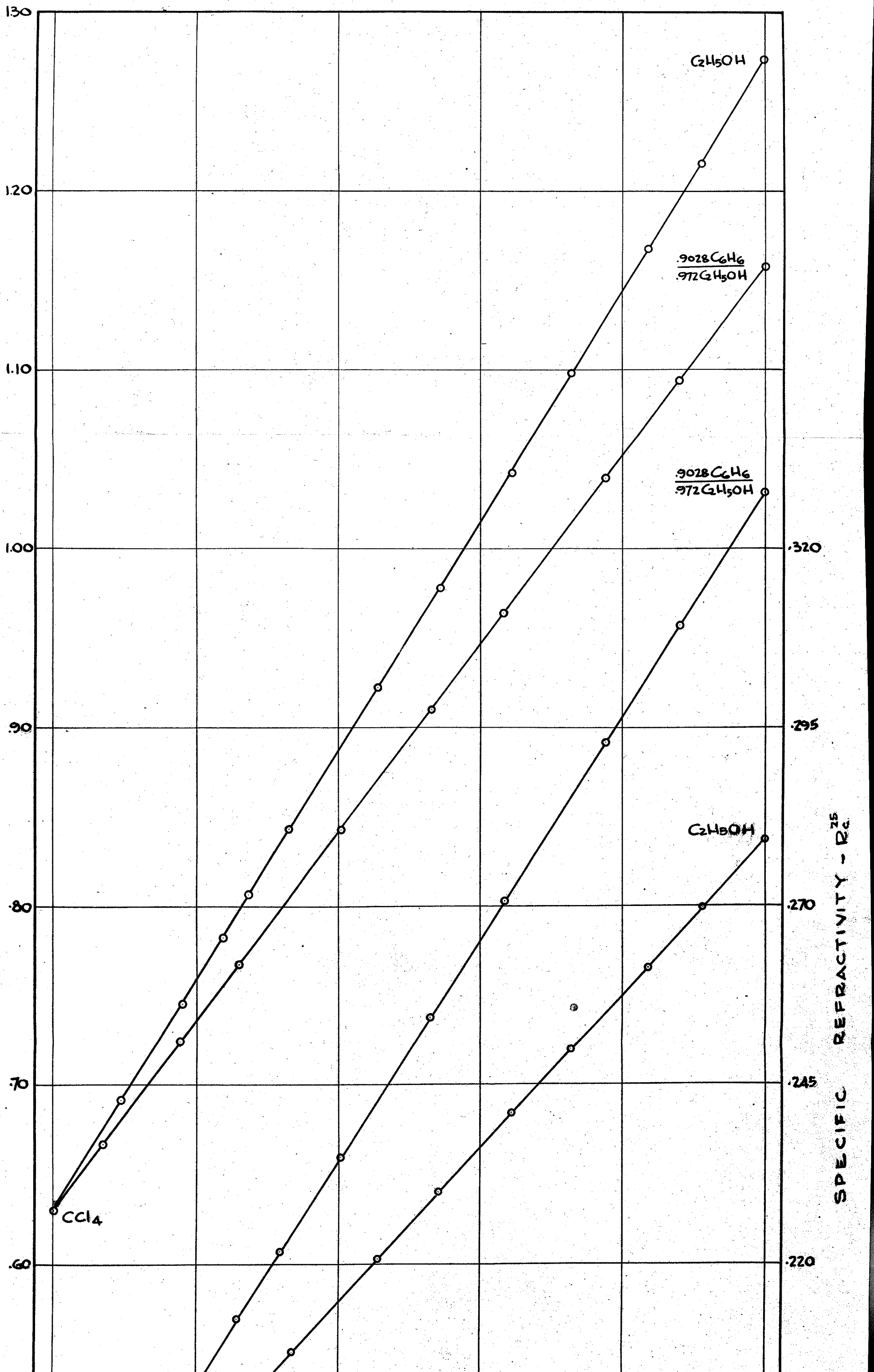
It is not proposed to digress at this point too deeply into the ideality of these solutions. Preceding experimental curves (Figures 11-14) throw no light on this question, although the maximum hump in Schreinemakers' vapor surface (Figure 1) implies departures from ideality in most pseudo-binary mixtures. From the results of this study it is possible to calculate approximate changes in specific volume and refractivity on mixing the components. (The specific refractivity R_C^{25}, given by the Lorenz equation, is $R_C^{25} = \frac{n^2 - 1}{n^2 + 2} \frac{1}{d}$.) Such calculations have already been made for the binary systems by Hubbard[21], Barbaudy[12], and Hildebrand[28], to mention only a few. Also, figures for partial vapor pressures and temperature changes on mixing are at least equally important in a discussion of non-ideality. Therefore, only the binary alcohol-carbon tetrachloride, and one ternary were chosen for a few calculations and explanatory remarks.

TABLE 9

Derived Properties

% CCl_4	% C_6H_6	% C_2H_5OH	d_4^{25}	n_C^{25}	Specific Volume	Specific Refractivity	Molar Volume
0	-	100	.7852	1.35767	1.2736	.2794	58.69
8.76		91.24	.8218	1.36199	1.2168	.2699	59.72
16.45		83.55	.8569	1.36628	1.1670	.2616	60.76
27.32		72.68	.9117	1.37316	1.0969	.2500	62.49
35.57		64.33	.9561	1.37862	1.0437	.2411	64.12
45.61		54.19	1.0227	1.38656	.9778	.2300	66.23
54.44		45.56	1.0842	1.39414	.9223	.2207	68.68
66.90		33.10	1.11867	1.40628	.8427	.2071	73.06
72.36		27.64	1.2382	1.41259	.8076	.2012	75.45
76.27		23.73	1.2768	1.41732	.7832	.1971	77.48
82.09		17.91	1.3402	1.42478	.7462	.1907	80.90
90.73		9.27	1.4471	1.43781	.6910	.1813	87.36
100		0	1.5846	1.45478	.6311	.1712	97.09
0	90.28	9.72	.8634	1.47769	1.1582	.3278	84.74
11.90	79.54	8.56	.9128	1.47642	1.0955	.3092	85.49
22.43	70.03	7.54	.9614	1.47516	1.0401	.2929	86.24
36.59	57.25	6.16	1.0357	1.47291	.9655	.2708	87.42
47.02	47.83	5.15	1.0982	1.47104	.9106	.2545	88.43
59.62	36.46	3.92	1.1846	1.46819	.8442	.2348	89.87
68.14	28.76	3.10	1.2508	1.46641	.7995	.2216	91.02
74.03	23.43	2.52	1.3016	1.46464	.7683	.2123	91.89
81.72	16.50	1.78	1.3740	1.46206	.7278	.2001	93.19
93.00	6.32	0.68	1.4965	1.45778	.6682	.1823	95.43
100	0	0	1.5846	1.45478	.6311	.1712	97.09

SPECIFIC VOLUME AND SPECIFIC REFRACTIVITY :
DETERMINATION OF THE IDEALITY
OF THE SYSTEM C_6H_6-C_2H_5OH-CCl_4



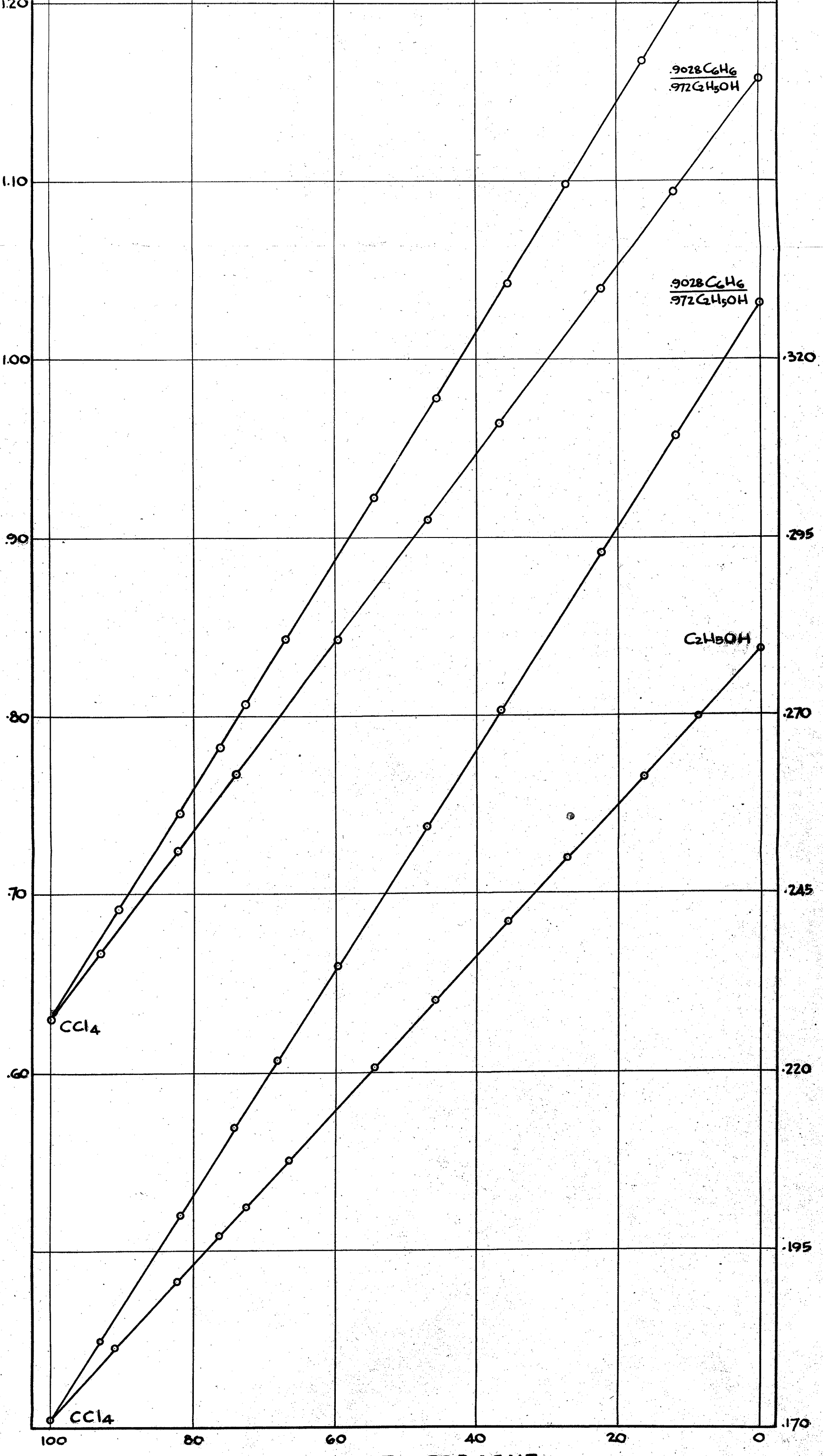

SPECIFIC VOLUME
1.20
1.10
1.00
.90
.80
.70
.60
.9028 C6H6 / .972 C2H5OH
.9028 C6H6 / .972 C2H5OH
C2H5OH
CCl4
CCl4
.320
.295
.270
.245
.220
.195
.170
SPECIFIC REFRACTIVITY - Rd25
100
80
60
40
20
0
WEIGHT PERCENT

FIGURE 16

Molar volumes plotted against mole percent gave practically straight lines for both binary and ternary. These curves are omitted. Similarly the specific volume and specific refractivity plotted against weight percent (Figure 16) yielded linear curves for all but the binary alcohol-carbon tetrachloride. Here a contraction in volume , about 0.2 percent, was clearly apparent. Hildebrand[28] calculated the deviations in benzene-alcohol, finding a change of +.01 percent. In the benzene-carbon tetrachloride Hubbard[21] found a change of about +.03 percent. Of the true binary systems the alcohol-carbon tetrachloride has the greatest spread in specific volume - perhaps the order of all these deviations at this temperature could have been expected.

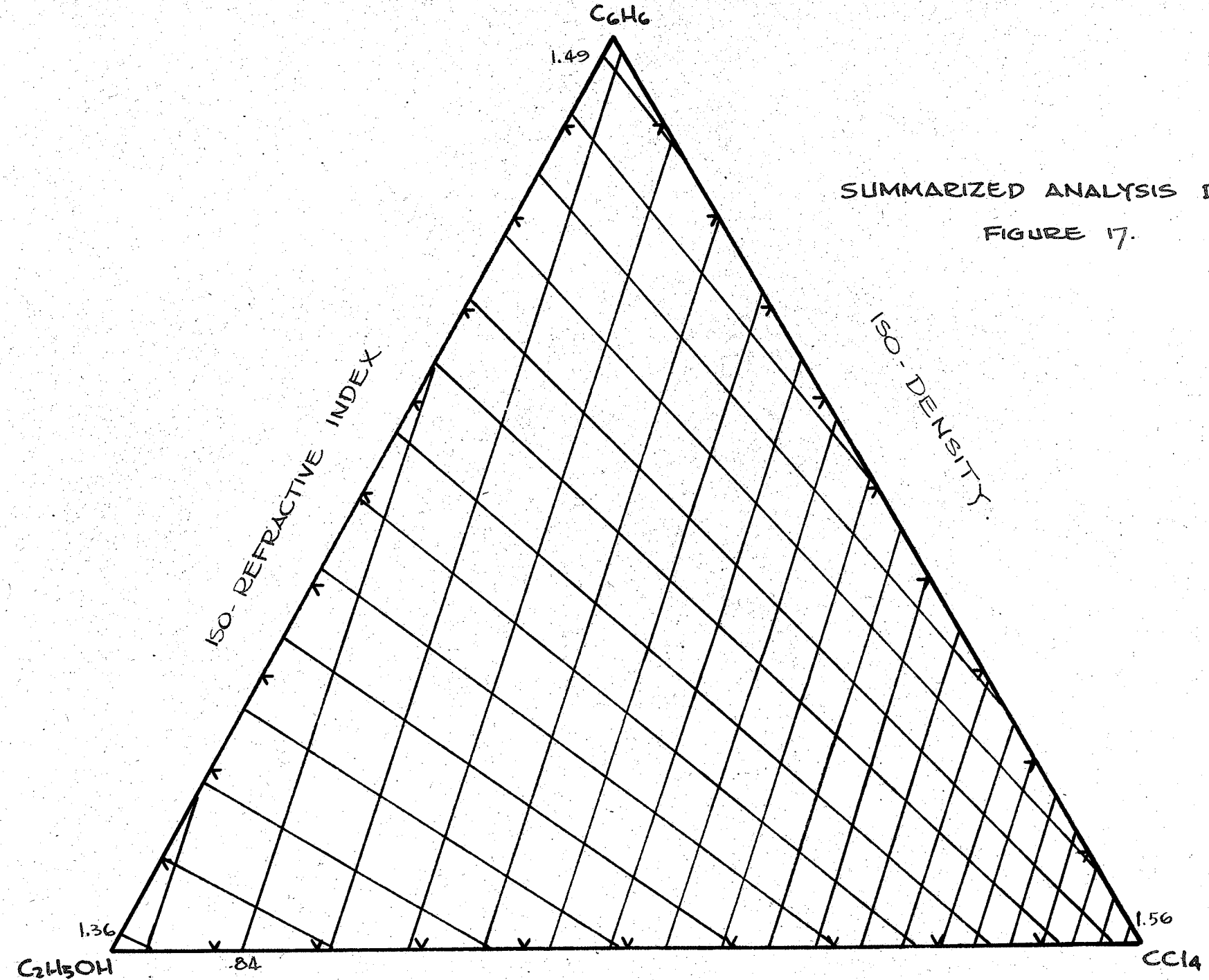
The volume changes in the binary considered here imply non-ideality. This conflicts with the linear nature of the refractivity curve; but calculations do reveal a negative deviation in the refractivity of less than .01 percent. Taken alone these facts are inconclusive; but when the positive departures from Raoult's law found by Ishikawa and Yamaguchi[15] at 25° are taken into account, this binary would be classed as non-ideal.

The linear "specific" curves for the ternary imply ideality. Again, calculations show that the graphical

method conceals a positive deviation in the specific volume and a negative deviation in the specific refractivity, both less than 0.01 percent. Since the limiting binary systems show opposite volume changes this intermediate ternary could conceivably be ideal. The lack of accurate ternary data on both partial pressures and temperature changes on mixing rule out categorical conclusions, especially since the maximum in Schreinemakers' vapor surface implies non-ideality for most solutions.

Partial molar quantities derived in various ways (see Lewis and Randall[29]) could logically follow at this stage, but they would merely prove to be a variation of the preceding discussion. Without further data then, the significance of the deviations, measurably small as they seem, and their relation to the ideality of the system, cannot be completely evaluated.

CONCLUSIONS



SUMMARIZED ANALYSIS DIAGRAM

FIGURE 17.

1. Densities and refractive indices (N_D) have been determined for the ternary system at 25°C.

2. A method for the analysis of ternary liquid mixtures of the system benzene-ethyl alcohol-carbon tetrachloride has been developed.

3. The limit of accuracy for the analysis of ternary mixtures is 0.3 percent.

4. Application to commercial materials is possible within an accuracy of 2.0 percent.

BIBLIOGRAPHY

1. F.A.H. Schreinemakers, Z.Phys.Chem., 47, 445 (1903).

2. F.A.H. Schreinemakers, Z.Phys.Chem., 48, 257 (1904).

3. J.H. Matthews and K.E. Faville, J.Phys.Chem. 22, 3 (1918).

4. D.J. Leroy, Ind.Eng.Chem., 17, 652 (1945).

5. S. Young, "Distillation Principles and Processes," p.62 ff, (1922).

6. M.A. Rosanoff, A.B. Lamb, F.E. Breithut, J.A.C.S. 31, 448 (1909).

7. J. Sameshima, J.A.C.S., 40, 1483 (1918).

8. G. Scatchard, C.L. Raymond, H.H. Gilman, J.A.C.S., 60, 1275 (1938).

9. H.A. Curtis and E.Y. Titus, J.Phys.Chem., 19, 739 (1915).

10. A.N. Campbell, J.A.C.S., 67, 981 (1945).

11. W.R. McMillan and J.H. McDonald, Ind.Eng.Chem., Anal.Ed., 15, 114 (1943).

12. M.J. Barbaudy, Bull.Soc.Chim.de France, 39, 371 (1926).

13. Schreder, Journ.Soc.Chim.Russe, 49, 647 (1917).

14. King and Smedley, J.Phys.Chem., 28, 1268 (1924).

15. F.Ishikawa and T.Yamaguchi, Bull.of Inst.of Phys.Chem.Res.17,246 (1938).

16. F.D. Brown, J.Chem.Soc., 39, 207,304 (1881).

17. S.E. Wood and J.P. Brusie, J.A.C.S., 65, 1891 (1945).

18. M.A. Rosanoff and C.E. Easley, J.A.C.S., 31, 969 (1909).

19. J.V. Zawidzki, Z.Phys.Chem., 35, 145 (1900).

20. G. Scatchard, S.E. Wood, J.M. Mochel, J.A.C.S.62,712 (1940).

21. J.C. Hubbard, Phys. Rev., 30, 740 (1910).
Z.Phys.Chem., 74, 207 (1910).

22. N.S. Osborne, C.C. McKelvey, A.W. Bearce, Bureau of Standards Bulletin, 9, 327 (1913).

23. A.R. Martin and B. Collie, J.Chem.Soc., 2662, Vol.1 (1932).

24. K.A. Varteressian and M.R. Fenske, Ind.Eng.Chem., 28, 928 (1936)

25. N.L. Bowen, Amer.Jour.Sci., 40, 176 (1915).

26. Kowalski and Modzelewski, C.R., 133, 33 (1901)

27. J.H. Rakshit, Zeit.f.Electroch., 31, 320 (1925).

28. J.H. Hildebrand, "Solubility" Chapt.V (1924).

29. G.N. Lewis and M. Randall, "Thermodynamics." pp.38-40.(1923).

30. W.J. Dulmage, Research Student at the University of Manitoba.