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Purification, Purity, and Freezing Points of 7 Heptanes, 16 Octanes, 6 Pentenes, Cyclopentene, and 7 C_9H_{12} Alkylbenzenes of the API-Standard and API-NBS Series[1]*

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This report describes the purification and determination of freezing points and purity of 37 hydrocarbons of the API-Standard and API-NBS series, including 7 heptanes, 16 octanes, 6 pentenes, cyclopentene, and 7 C_9H_{12} alkylbenzenes.

I. Introduction

A recent report from this laboratory described the purification and determination of freezing points and purity of the first 31 compounds of the API-NBS series of hydrocarbons [1].** Beginning July 1, 1944, the preparation of hydrocarbons of the API-NBS series was greatly accelerated by the cooperative program on standard samples of hydrocarbons operated by the American Petroleum Institute and the National Bureau of Standards.[3]

Under the cooperative program, the target for the final product was 1 liter of API-Standard material with a purity of 99.8 mole percent to be used for standard samples, plus 0.2 liter of material of higher purity for the API-NBS samples, to be made available on loan to qualified investigators for the measurement of needed properties.[4]

*Presented before the Division of Petroleum Chemistry of the American Chemical Society, Chicago, Ill., September 1946.

**Figures in brackets indicate the literature references at the end of this paper.

[1] This investigation was performed at the National Bureau of Standards as part of the work of the American Petroleum Institute Research Project 6 on the Analysis, Purification, and Properties of Hydrocarbons.

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[3] This cooperative program on standard samples of hydrocarbons was organized by the then newly formed API Research Project 46 Committee on Hydrocarbons for Spectrometer Calibration (W. J. Sweeney, chairman, L. C. Beard, Jr., T. G. Delbridge, F. E. Frey, H. Gershinowitz, H. Levin, and R. F. Marschner, with H. J. Hall as secretary, and C. E. Boord, M. R. Fenske, F. D. Rossini, and F. C. Whitmore as consultants). This committee was set up by the API Advisory Committee on Fundamental Research on the Composition and Properties of Petroleum (J. Bennett Hill, then chairman) to effect a cooperative program with the National Bureau of Standards whereby there could be brought to bear on the problem of preparing standard samples of hydrocarbons all the facilities of the existing research projects of the Institute so that the provision of finished hydrocarbon standards could be materially speeded up. See references [2 and 3] for further details.

[4] The allocation of these samples is handled by the Advisory Committee for the API Research Project 44 on the "Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons" (W. E. Kuhn, chairman, Otto Beeck, Gustav Egloff, and S. S. Kurtz, Jr., with F. D. Rossini as supervisor of the project).

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II. Materials

The starting materials were supplied as follows: [5]

By the API Research Project 45 on the "Synthesis and Properties of Hydrocarbons of Low-Molecular Weight" at the Ohio State University, Columbus, Ohio, under the supervision of C.. E Boord: 3-Ethylpentane, 2-methylheptane, 3-methylheptane, 4-methylheptane, 3-ethylhexane, 2,2-dimethylhexane, 2,3-dimethylhexane, 3,3-dimethylhexane, 3,4-dimethylhexane, 2-methyl-3-ethyl-

[5] A letter (*B*) following the name of a compound indicates that, for the API-NBS series, it is a second (and usually slightly purer) sample of the given compound, the first sample of which is labeled (*A*). (See reference [1].)

TABLE 1.—*Information on the purification of 37 API–Standard and API–NBS hydrocarbons*

Compound [a]	Laboratory [b] providing starting material	Hydrocarbon charged for distillation		Distillation [f]								Volume of selected sample	
		Volume	Purity	Kind [c]	Azeotrope-forming substance [d]	Amount of hydrocarbon in the azeotropic distillate [e]	Distilling column number [f]	Number of theoretical plates [f] (approx.)	Reflux ratio [f] (approx.)	Rate of collection of distillate	Results plotted in figure	API-Standard	API-NBS
PARAFFINS													
		Liters	*Mole %*			*% by volume*				*ml/hr*		*ml*	*ml*
2-Methylhexane	Ethyl	0.70		Azeo	Methanol	60	11	([s])	290/1	2.5	3		
		.44 [g] 1.75		do	Ethanol	64	10	135	145/1	5.0	4	1340	300
3-Methylhexane	do	.81		do	Methanol	60	11	([s])	290/1	2.5	5		
		.65 [h] 2.38		do	Ethanol	64	7	130	145/1	8.5	6	1160	325
3-Ethylpentane	APIRP45	2.87		do	do	65	10	135	145/1	5.0	7	1820	260
2,2-Dimethylpentane	Socony-Vacuum	3.70	97.94	do	do	74	7	130	145/1	8.5	8	2110	275
2,3-Dimethylpentane	General Motors	3.87		do	do	64	8	130	145/1	8.5	9	1215	291
2,4-Dimethylpentane	APIRP6 [t]	2.00	99.35	do	do	71	4	200	145/1	5.0	10	1200	250
3,3-Dimethylpentane	Ethyl	1.87		do	do	68	9	135	145/1	5.0	11	1020	
Do	APIRP45	3.15		do	do	68	7	130	155/1	8.0	12		465
n-Octane	APRIP6 [u]	6.38	98.78	Reg			13	130	155/1	8.0	13		
		2.48	99.75	Azeo	Cell	72	15	125	110/1	14.0	14	1620	325
2-Methylheptane	APIRP45	2.01	96.71	do	Ethanol	41	7	130	145/1	8.5	15	930	144
3-Methylheptane	do	5.87		Reg			14	125	110/1	14.0	16		
		2.99		do			4	200	160/1	4.5	17		
		[v] 1.80		Azeo	Ethanol	39	8	130	145/1	8.5	18		
		1.53	99.46	Reg			4	200	160/1	4.5	19	970	185
4-Methylheptane	do	2.38	99.73	do			12	135	185/1	4.0	20		
		1.85		Azeo	Ethanol	39	14	125	125/1	12.5	21	1060	230
3-Ethylhexane	do	5.15		Reg			7	130	145/1	8.5	22		
		3.27		do			10	135	165/1	4.5	23	1150	286
2,2-Dimethylhexane	do	3.75	[i] 98.25	do			15	125	110/1	14.0	24		
		2.70	99.19	Azeo	Ethanol	54	13	130	155/1	8.0	25	920	192
2,3-Dimethylhexane	APIRP45	2.64		Reg			12	135	165/1	4.5	26		
		1.65		Azeo	Ethanol	45	8	130	155/1	8.0	27	945	205
2,4-Dimethylhexane	Penn State	3.70		Reg			9	135	145/1	5.0	28		
		3.20		Azeo	Me. Cell	75	7	130	145/1	8.5	29	1206	365
2,5-Dimethlyhexane	do	3.10	99.30	do	Cell	84	14	125	110/1	14.0	30	1216	355
3,3-Dimethylhexane	APIRP45	3.40		do	do	83	14	125	110/1	14.0	31		
		2.00		Reg			12	135	185/1	4.0	32	1000	250
3,4-Dimethylhexane	do	2.40		do			12	135	145/1	5.0	33		
		1.86		Azeo	Ethanol	40	8	130	155/1	8.0	34	880	151
2-Methyl-3-ethylpentane	do	2.63		Reg			12	135	145/1	5.0	35		
		1.85		do			4	200	160/1	4.5	36	1000	218
3-Methyl-3-ethylpentane	APIRP45	3.70		Azeo	Cell	76	14	125	110/1	14.0	37		
		3.13		Reg			9	135	165/1	4.5	38	1135	235
2,2,3-Trimethylpentane	General Motors	12.25	91.4	do			6	125	110/1	14.0	39		
		2.52	99.05	Azeo	Ethanol	47	15	125	125/1	12.5	40		
		1.82	99.40	Reg			4	200	160/1	4.5	41	[k] 470	330
		[j] 3.30		Azeo	Me. Cell	76	15	125	125/1	12.5	42	[k] 1080	
2,3,3-Trimethylpentane	Penn State	3.00	94.2	Reg			9	135	145/1	5.0	43		
		2.23		Azeo	Ethanol	43	8	130	155/1	8.0	44	990	250
2,3,4-Trimethylpentane	APIRP45	4.17		Reg			7	130	145/1	8.5	45		
		2.58		Azeo	Ethanol	43	14	125	125/1	12.5	46	1370	380

See footnotes at end of table.

TABLE 1.—*Information on the purification of 37 API–Standard and API–NBS hydrocarbons*—Continued

Compound [a]	Laboratory [b] providing starting material	Hydrocarbon charged for distillation: Volume	Hydrocarbon charged for distillation: Purity	Distillation [f]: Kind [c]	Azeotrope-forming substance [d]	Amount of hydrocarbon in the azeotropic distillate [e]	Distilling column number [f]	Number of theoretical plates [f] (approx.)	Reflux ratio [f] (approx.)	Rate of collection of distillate	Results plotted in figure	Volume of selected sample: API-Standard	Volume of selected sample: API-NBS
ALKYLBENZENES													
		Liters	*Mole %*			*% by volume*				*ml/hr*		*ml*	*ml*
n-Propylbenzene (*B*)	APIRP6 [v]	[l] 5.50		Reg			8	130	125/1	10.0	47		
		[m] 5.15		Azeo	Cell	23	5	125	110/1	14.0	48		
		2.12	99.42	Reg			13	130	200/1	6.0	49	1310	340
1-Methyl-2-ethylbenzene	APIRP45	2.54		do			7	130	145/1	8.5	50		
		1.91		Azeo	Cell. [n]	8	4	200	145/1	5.0	51	988	250
					Me. Carb.	84							
1-Methyl-3-ethylbenzene	do	2.50		Reg			8	130	145/1	8.5	52		
		1.20		Azeo	Me. Carb.	92	8	130	145/1	8.5	53		
		1.00	93.5	do	do	92	9	135	145/1	5.0	54		
		[o] 2.30	93.0										
		1.19	97.26				(p)				55	685	45
1-Methyl-4-ethylbenzene	NACA	2.03	99.60	Azeo	Me. Carb.	91	12	135	145/1	5.0	56	1145	275
1,2,3-Trimethylbenzene (*B*)	APIRP45	2.03	99.75	do	do	74	10	135	165/1	4.5	57	1025	153
1,2,4-Trimethylbenzene (*B*)	NACA	3.41	99.59	do	do	85	4	200	145/1	5.0	58	1215	280
1,3,5-Trimethylbenzene	APIRP45	1.62		Reg			8	130	155/1	8.0	59		
		1.20		Azeo	Me. Carb.	88	8	130	155/1	8.0	60		[r] 260
		[q] 0.83		do	do	80	8	130	155/1	8.0	61	2260	
		[q] 2.16											
MONOOLEFINS													
1-Pentene	Phillips	3.40	95.0	Reg			4	200	160/1	4.5	62	1050	195
cis-2-Pentene	APIRP45	4.34		Azeo	Methanol	90	4	200	180/1	4.0	63	408	82
trans-2-Pentene	do	2.10	99.90	Reg			1	150	130/1	2.3	64	1425	367
2-Methyl-1-butene	General Motors	8.32		do			5	125	125/1	12.5	65		
		3.45	99.71	do			13	130	200/1	6.0	66	1405	450
3-Methyl-1-butene	Houdry Process	1.26	99.54	do			1	150	130/1	2.5	67	778	88
2-Methyl-2-butene	General Motors	15.0		do			6	125	125/1	12.5	68		
		5.46	99.81	do			8	130	155/1	8.0	69	2070	530
Cyclopentene	Atlantic	1.40		do			12	135	185/1	4.0	70	1030	240
	APIRP45	0.70											

[a] *(B)* following the name of a compound indicates that for the API–NBS series, it is a second (and usually slightly purer) sample of the given compound, the first sample of which is labeled *(A)*. (See reference [1]).

[b] The abbreviations represent the following laboratories: APIRP45; American Petroleum Institute Research Project 45 (formerly the American Petroleum Institute Hydrocarbon Research Project) at the Ohio State University, Columbus, Ohio. Penn State: Hydrocarbon Laboratory at the Pennsylvania State College, State College, Pa. General Motors: General Motors Corporation, Detroit, Mich. Ethyl: Ethyl Corporation, Detroit, Mich. NACA: National Advisory Committee for Aeronautics, Aeronautical Engine Research Laboratory, Cleveland, Ohio. Atlantic: Atlantic Refining Co., Philadelphia, Pa. Houdry Process: Houdry Process Corporation, Marcus Hook, Pa. Phillips: Phillips Petroleum Company, Bartlesville, Okla. Socony-Vacuum: Socony-Vacuum Laboratories, Paulsboro, N. J. APIRP6: American Petroleum Institute Research Project 6 at the National Bureau of Standards, Washington, D. C.

[c] The abbreviations are: Azeo., azeotropic; Reg., regular.

[d] The abbreviations are: Cell., Cellosolve (ethylene glycol monoethyl ether); Me. Cell., methyl Cellosolve (ethylene glycol monomethyl ether); Me. Carb., methyl Carbitol (diethylene glycol monomethyl ether).

[e] Approximate value obtained from the actual volume of hydrocarbon recovered by extracting the azeotrope-forming substance with water in separatory funnels.

[f] See reference [4] for further details.

[g] This is a second lot of 2-methylhexane supplied by the Ethyl Corporation.

[h] This is a second lot of 3-methylhexane supplied by the Ethyl Corporation.

[i] Calculated from the measured freezing points of three separate lots which were blended together for this charge.

[j] This charge consisted of fractions 154 to 213 from column 6 (see fig. 39).

[k] The total volume of the API–Standard sample was 1,550 ml.

[l] One of two similar charges.

[m] This charge consisted of material, having substantially the same composition, from each of the two previous distillations (see footnote 1).

[n] The distillation was begun with Cellosolve as the azeotrope-forming substance, but because of the small percentage of hydrocarbon in the azeotropic distillate, methyl Carbitol was added to complete the distillation.

[o] This is a second lot of 1-methyl-3-ethylbenzene supplied by the API Research Project 45.

[p] This material was given its final purification by B. J. Mair by the method of sulfonation and hydrolysis previously used to purify *m*-xylene. See reference [6].

[q] The 0.83 liter for this charge consisted of 0.39 liter (fractions 1 to 3, 57) from the first distillation in column 8 (see fig. 59), and 0.44 liter from the second distillation in column 8 (see fig. 60). The 2.16 liters is a second lot of 1,3,5-trimethylbenzene supplied by the API Research Project 45.

[r] Previously reported. See reference [1].

[s] The number of theoretical plates for this column was not determined.

[t] This starting material was obtained by distillation from a commercial "propylene" alkylate (propylene+isobutane).

[u] Obtained by purchase of commercially available material from the Connecticut Hard Rubber Company, New Haven, Conn.

[v] Obtained by purchase of commercially available material from the Dow Chemical Co., Midland, Mich.

[w] This charge consisted of 0.19 liter (fractions 130 to 134) from the distillation in column 14 (see fig. 16) and 1.61 liters from the distillation in column 4 (see fig. 17).

pentane, 3-methyl-3-ethylpentane, 2,3,4-trimethylpentane, 1-methyl-2-ethylbenzene, 1-methyl-3-ethylbenzene, 1,2,3-trimethylbenzene (*B*), 1,3,5-trimethylbenzene, *cis*-2-pentene, *trans*-2-pentene, and cyclopentene (one-third).

By the Hydrocarbon Laboratory at the Pennsylvania State College, State College, Pa., under the supervision of F. C. Whitmore: 2,4-Dimethylhexane, 2,5-dimethylhexane, and 2,3,3-trimethylpentane.

By the General Motors Corporation Research Laboratories, Detroit, Mich., through T. A. Boyd and W. G. Lovell: 2,3-Dimethylpentane, 2-methyl-1-butene, 2,2,3-trimethylpentane, 2-methyl-2-butene.

By the Ethyl Corporation, Detroit, Mich., through George Calingaert: 2-Methylhexane, 3-methylhexane, and 3,3-dimethylpentane.

By the National Advisory Committee for Aeronautics, through its Aeronautical Engine Research Laboratory at Cleveland, Ohio: 1-Methyl-4-ethylbenzene, 1,2,4-trimethylbenzene (*B*).

By the Atlantic Refining Co., Philadelphia, Pa., through T. G. Delbridge: Cyclopentene (two-thirds).

By the Houdry Process Corporation, Marcus Hook, Pa., through E. A. Smith: 3-Methyl-1-butene.

By the Phillips Petroleum Co., Bartlesville, Okla., through F. E. Frey: 1-Pentene.

By the Socony-Vacuum Laboratories, Paulsboro, N. J., through L. C. Beard, Jr.: 2,2-Dimethylpentane.

By the API Research Project 6 at the National Bureau of Standards, under the supervision of F. D. Rossini: 2,4-Dimethylpentane, *n*-octane, and *n*-propylbenzene (B).

Table 1 summarizes the amounts of the starting materials, and gives some additional information as to the source and purity.

III. Purification

The procedure followed in the process of purification and determination of purity can be illustrated by considering a given compound, as follows:

The starting material for 2-methyl-1-butene was 8.3 liters of hydrocarbon, supplied by the Research Laboratories of the General Motors Corporation and estimated by them to be about 90 per cent pure. The 8.3 liters of starting material was put into column 5 (having approximately 125 theoretical plates at total reflux) on December 8, 1944, and the distillation, running 24 hours a day, 7 days a week, at a reflux ratio of 125/1 and with a rate of collection of distillate of 12.5 ml/hr, was concluded on January 12, 1945. The distillation time was 840 hours, with about 30 hours to reach equilibrium at the start. The details of the assembly, testing, and operation of the distilling columns used in this work are given in reference [4]. The records from the distillation yielded accurate values of the boiling point, to the nearest 0.01° C at the given controlled pressure of 724.5 mm Hg, of the distillate as a function of its volume [4]. The refractive index, n_D at 25° C, of each of the fractions of distillate was measured to ±0.0001, using NBS Standard Samples of 2,2,4-trimethylpentane, methylcyclohexane, and toluene as reference substances, on Valentine refractometers, Abbe-type, graduated directly to 0.0001. The purity of four selected fractions was determined by measuring freezing points, using the apparatus and procedure already described [5]. From the freezing points of these four fractions, the upper curve of figure 65 was constructed, giving the freezing point of the distillate and its purity (scale at upper right) as a function of its volume over the range of higher purity. Figure 65 also shows the refractive index (n_D at 25° C) and the boiling point (in ° C at 724.5 mm Hg) of the distillate as a function of its volume. Figure 1 gives a view of the freezing-point apparatus in operation. A typical time-temperature melt-curve is shown in figure 2.

From the first distillation, it is seen that 3.45 liters of material of 99.7 mole percent purity, marked X in figure 65, was available for the second distillation. This material was put into Column 13 (having approximately 130 theoretical plates at total reflux) on February 7, 1945, and the distillation, running 24 hours a day, 7 days a week, at a reflux ratio of 200/1 and with a rate of collection of distillate of 6.0 ml/hr, was concluded on March 5, 1945. The distillation time was 624 hours, with about 30 hours to reach equilibrium

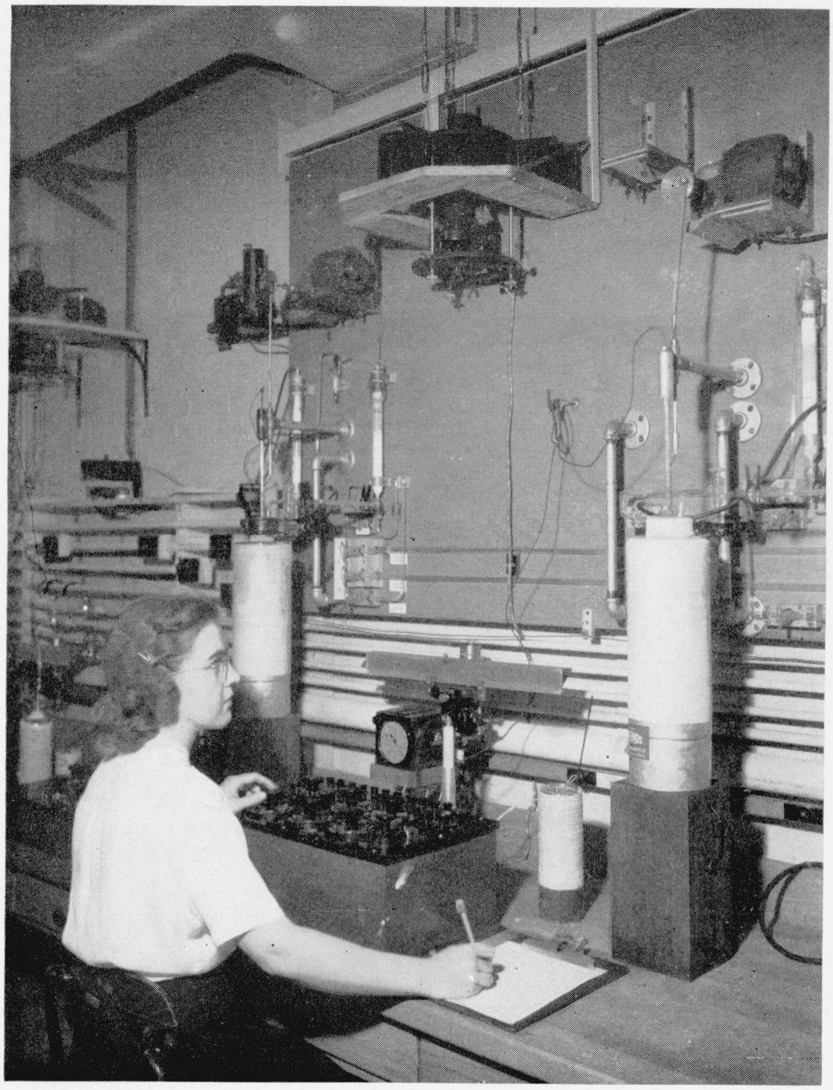

FIGURE 1.—*Freezing-point apparatus for determining the purity of hydrocarbons.*

at the start. As before, measurements and plots were made of refractive index, boiling point, freezing point, and purity, with the results shown in figure 66. The part marked Z was taken as the API–NBS sample and the parts marked Y were taken as the material for the standard sample. The material marked W in figures 65 and 66 was returned to the supplier. The final products for this compound consisted of an API–NBS sample having a volume of 0.45 liter and a purity of 99.89 $\pm$0.08 mole percent and an API-Standard sample having a volume of 1.41 liters and a purity of 99.86 $\pm$0.08 mole percent.

In addition to the name of the laboratory supplying the starting materials, table 1 and its footnotes, give complete information for each distillation for each of the compounds.

Figures 3 to 70, inclusive, show graphically the results of the distillations listed in table 1. These figures give, as a function of the volume of hydrocarbon distillate, the refractive index (n_D at 25° C to $\pm$0.0001 deg C), the boiling point of the distillate (at the controlled pressure of 724.5 mm Hg, to $\pm$0.01 deg C), the freezing point of selected fractions of hydrocarbon distillate (in air at 1 atm, usually with a precision near $\pm$0.003 deg C), and the purity of the hydrocarbon distillate. W, X, Y, and Z indicate the disposition of the material, as follows: W, returned to the laboratory supplying the material; X, blended for redistillation; Y, used for the API-Standard material; Z, used for the API-NBS material.

In connection with the purification of hydrocarbons, the following points are to be noted: (a) A logical, simple purification following the original synthesis or other preparation of a given hydrocarbon concentrate will usually remove all impurities except more-or-less close-boiling isomers, (b) an impurity of several percent of close-boiling isomers will have relatively little effect on the boiling point, refractive index, or density, but will normally affect the freezing point appreciably, (c) in a series of fractions obtained from a distillation at high efficiency of a hydrocarbon containing close-boiling isomers as impurity, the fractions of highest purity will be beyond or ahead of the middle portion of the distillate as frequently as in the middle portion, (d) for producing material of highest purity, the blending of the fractions of distillate can be done safely only on the basis of the freezing points of selected fractions. An example of a case where the purest material is near the beginning of a distillation is shown in figure 25, for 2,2-dimethylhexane, and an example of a case where the purest material is at the very end of the distillation is shown in figure 63, for *cis*-2-pentene.

IV. Freezing Points, Cryoscopic Constants, and Purity

Table 2 gives the following information for each of the compounds (except as otherwise indicated): The kind of time-temperature curves; whether freezing or melting, used to determine the freezing point [5]; the freezing point of the actual sample, in air at 1 atm [5], for both the API-Standard and the API-NBS lots; the calculated value of the freezing point for zero impurity [5]; the value of the cryoscopic constant determined from the lowering of the freezing point on the addition of a known amount of an appropriate impurity [5]; and the resulting calculated amount of impurity in the API-Standard and the API-NBS material.

Grateful acknowledgment is made to the organizations and individuals listed in section II of this report for their contributions of materials for use in this work.

Table 2.—*Freezing points and purity of 37 API-Standard and API-NBS hydrocarbons*

Compound [a]	Kind of time temperature observations used to determine the freezing point [b]	Freezing point of the actual selected sample, in air at 1 atm [c]		Freezing point for zero impurity in air at 1 atm [c]	Cryoscopic constant [b] *A*	Calculated amount of impurity in the actual selected sample [d]	
		API-Standard	API-NBS			API-Standard	API-NBS
PARAFFINS							
		°C	°C	°C	deg⁻¹	Mole %	Mole %
2-Methylhexane	M	−118.321	−118.311	−118.270±0.015	[e] (0.0445)	0.23±0.07	0.18±0.07
3-Methylhexane						[f] (.25±0.15)	[f] (.20±0.15)
3-Ethylpentane	M	−118.620	−118.605	−118.593±0.010	[e] (.0476)	.13±0.03	.06±0.03
2,2-Dimethylpentane	F and M	−123.858	−123.852	−123.790±0.020	[e] (.0316)	.21±0.06	.19±0.06
2,3-Dimethylpentane						[f] (.25±0.15)	[f] (.20±0.15)
2,4-Dimethylpentane	F and M	−119.280	−119.265	−119.230±0.015	[e] (.0340)	.17±0.05	.12±0.05
3,3-Dimethylpentane	M	−134.51(I)	−134.51(I)	−134.46 ±0.04(I)	[e] (.0442) (I)	.22±0.18	.22±0.18
				−134.95 ±0.05(II)(u)			
				−135.36 ±0.05(III)(u)			
n-Octane	F	−56.810	−56.807	−56.798±0.008	[e] (.0530)	.06±0.04	.05±0.04
2-Methylheptane	M	−109.129	−109.114	−109.04 ±0.04	.0458	.41±0.18	.34±0.18
3-Methylheptane	M	−120.585	−120.565	−120.50 ±0.04	.0587	.50±0.23	.38±0.23
4-Methylheptane	M	−120.977	−120.975	−120.955±0.012	.0563	.12±0.07	.11±0.07
3-Ethylhexane						[f] (.30±0.20)	[f] (.25±0.20)
2,2-Dimethylhexane	M	−121.261	−121.246	−121.18 ±0.03	.0354	.29±0.11	.23±0.11
2,3-Dimethylhexane						[f] (.30±0.20)	[f] (.25±0.20)
2,4-Dimethylhexane						[f] (.30±0.20)	[f] (.25±0.20)
2,5-Dimethylhexane	F and M	−91.265	−91.258	−91.200±0.015	.0467	.30±0.09	.27±0.09
3,3-Dimethylhexane	M	[g] −126.18	[g] −126.16	[e](−126.10 ±0.05)	[e] (.04)	.30±0.20	.25±0.20
3,4-Dimethylhexane						[f] (.30±0.20)	[f] (.25±0.20)
2-Methyl-3-ethylpentane	M	−115.002	−115.001	−114.960±0.020	.0544	.23±0.11	.22±0.11
3-Methyl-3-ethylpentane	F and M	−90.890	−90.888	−90.870±0.010	.0392	.08±0.04	.07±0.04
2,2,3-Trimethylpentane	M	−112.375	−112.350	−112.27 ±0.05	.0401	.42±0.20	.32±0.20
2,3,3-Trimethylpentane	F	−101.341	−101.034	−100.70 ±0.10	.0062	.40±0.08	.21±0.08
2,3,4-Trimethylpentane	M	−109.257	−109.252	−109.210±0.015	[e] (.04122)	.19±0.06	.17±0.06
ALKYLBENZENES							
n-Propylbenzene (*B*)	M	−99.574(I)	−99.560(I)	−99.500±0.024(I)	[h] 0.034(I)	0.25 ±0.08	0.20±0.08
	M			−101.55 ±0.03(II)(u)	.032(II)		
1-Methyl-2-ethylbenzene	M	−80.917(I)	−80.909(I)	−80.833±0.020(I)	.0346(I)	.27 ±0.07	.24±0.07
	M			−86.556±0.020(II)(u)	[h] .033(II)		
1-Methyl-3-ethylbenzene	M	−95.66(I)	−95.63(I)	−95.55 ±0.05(I)	.029(I)	.32 ±0.15	.23±0.15
	M			−96.96 ±0.05(II)(u)	[h] .029(II)		
1-Methyl-4-ethylbenzene	M	−62.400	−62.367	−62.350±0.010	.0344	.17 ±0.03	.06±0.03
1,2,3-Trimethylbenzene(*B*)	M	−25.386	−25.381	−25.375±0.006	.0164	.018±0.012	.010±0.009
1,2,4-Trimethylbenzene(*B*)	M	−43.912(I)	−43.907(I)	−43.80 ±0.07(I)	.0282(I)	.32 ±0.20	.30±0.20
				−49.00 ±0.07(II)(u)			
1,3,5-Trimethylbenzene	M	−44.741(I)		−44.720±0.010(I)	[e](.022) (I)	.05 ±0.02	
				−49.790±0.020(II)(u)			
				−51.680±0.020(III)(u)			
MONOOLEFINS							
1-Pentene	M	−165.40	−165.37	−165.27 ±0.08	0.051	0.66 ±0.40	0.51 ±0.40
cis-2-Pentene	M	−151.443	−151.403	−151.370±0.025	.062	.45 ±0.15	.20 ±0.15
trans-2-Pentene	F and M	−140.252	−140.248	−140.235±0.010	.0530	.09 ±0.05	.07 ±0.05
2-Methyl-1-butene	F and M	−137.587	−137.582	−137.560±0.015	.0516	.14 ±0.08	.11 ±0.08
3-Methyl-1-butene	F and M	−168.541	−168.538	−168.500±0.020	.0580	.24 ±0.12	.22 ±0.12
2-Methyl-2-butene	F and M	−133.793	−133.792	−133.780±0.010	[e] (.0462)	.06 ±0.05	.055±0.046
Cyclopentene	F and M	−135.086	−135.082	−135.070±0.010	.0212	.034±0.021	.025±0.021

[a] A letter (*B*) following the name of a compound indicates that, for the API–NBS series, it is a second (and usually slightly purer) sample of the given compound, the first sample of which is labeled (*A*). (See reference [1].)

[b] *F* indicates freezing and *M* indicates melting. See reference [5] for experimental details and the definition of the cryoscopic constant.

[c] When a given hydrocarbon has more than one crystalline form, the several forms will be labeled I, II, and III, in order of decreasing temperature of fusion (or freezing point). Forms other than I will be, at their respective freezing points, in metastable equilibrium with the under-cooled liquid, but will be unstable with respect to transition to some other solid form at the same temperature and pressure (one atmosphere). This is indicated by a letter *u* in parentheses following the Roman numeral.

[d] The values in this column, except as otherwise indicated, were calculated as described in reference [5], using the values of the cryoscopic constants and freezing points for zero impurity given in the preceding columns.

[e] Not determined in this investigation. From the "*z*" tables of the American Petroleum Institute Research Project 44 [7].

[f] Estimated by analogy with isomers subjected to similar purification.

[g] The uncertainty in this value may be several hundredths of a degree.

[h] Estimated from the measured value of the cryoscopic constant.

V. References

[1] A. R. Glasgow, Jr., E. T. Murphy, C. B. Willingham, and F. D. Rossini, J. Research NBS **37,** 141 (1946) RP1734.

[2] R. L. Demmerle, Chem. Eng. News **24,** No. 15, 2020 (1946).

[3] Tech. News Bul. NBS 350 (June 1946).

[4] C. B. Willingham and F. D. Rossini, J. Research NBS **37,** 15 (1946) RP1724.

[5] A. R. Glasgow, Jr., A. J. Streiff, and F. D. Rossini, J. Research NBS **35,** 355 (1945) RP1676.

[6] B. J. Mair, D. J. Termini, C. B. Willingham, and F. D. Rossini, J. Research NBS **37,** 229 (1946) RP1744.

[7] American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Heat and Entropy of Fusion, Freezing Points, and Cryoscopic Constants. Tables 1z, 2z, 3z, 5z, and 6z.

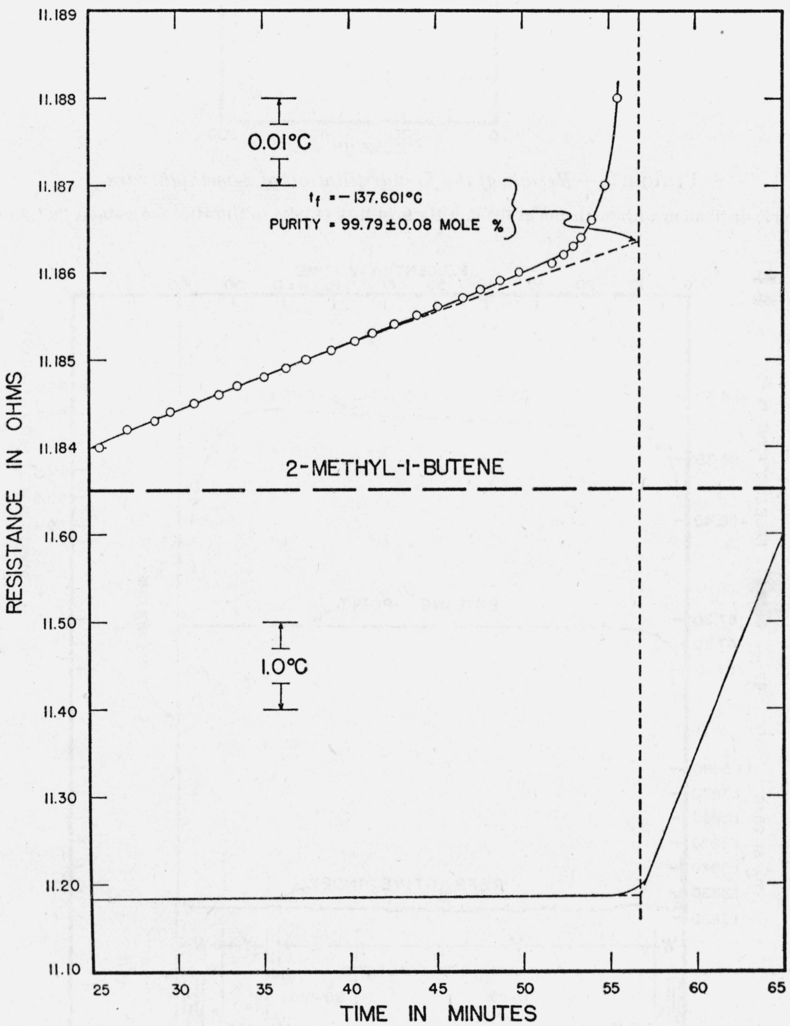

FIGURE 2.—*Time-temperature warming curves for determining the freezing point of a sample of 2-methyl-1-butene.*

The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer (0.1 ohm is approximately 1.0° C). The scale of abscissas gives the time in minutes. The same data are used for both curves, but the scale of temperature (or resistance) for the upper curve is magnified one hundred times that for the lower curve.

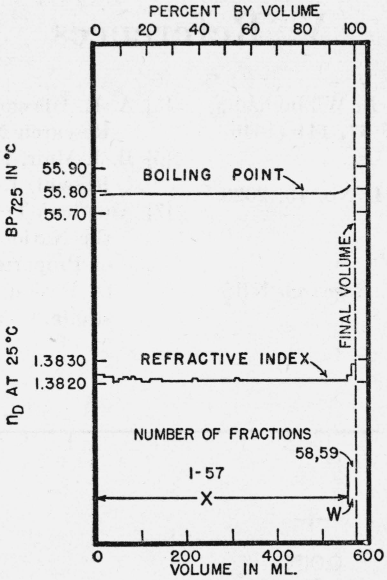

FIGURE 3.—*Results of the first distillation of 2-methylhexane.*

Azeotropic distillation with methanol at 725 mm Hg in still 11 (4/18/44 to 5/10/44). See footnote "g" of table 1.

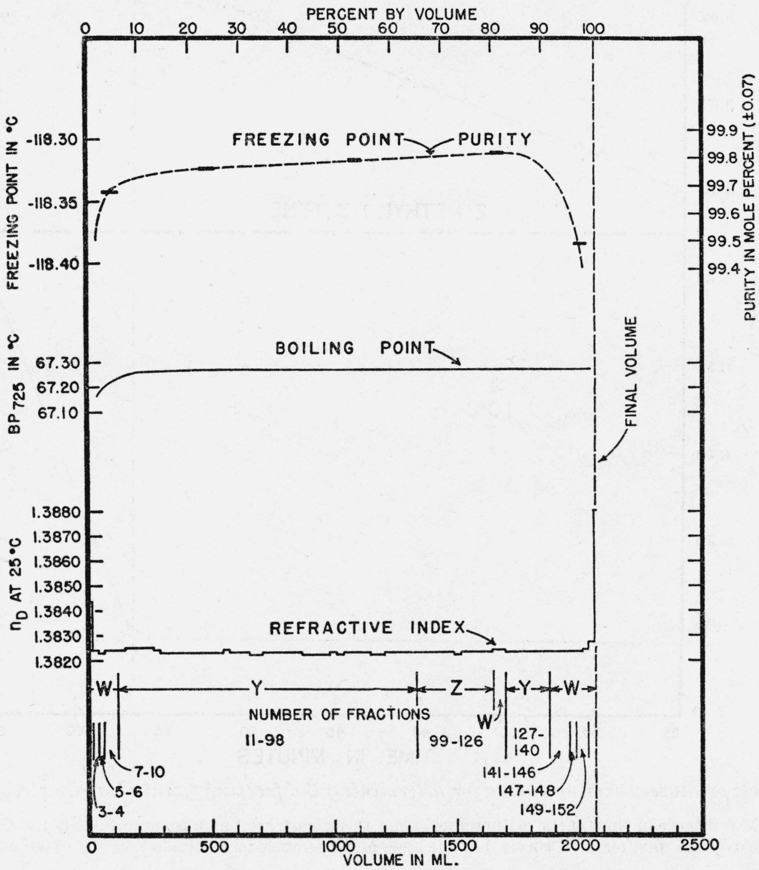

FIGURE 4.—*Results of the second and final distillation of 2-methylhexane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 10 (10/11/44 to 11/9/44). 50 ml of fractions 99 to 126 (marked "*W*") was returned to the supplier as a "best" sample.

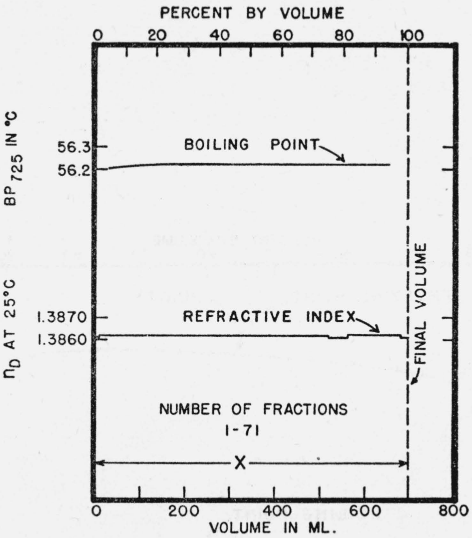

FIGURE 5.—*Results of the first distillation of 3-methylhexane.*

Azeotropic distillation with methanol at 725 mm Hg in still 11 (5/10/44 to 6/3/44).

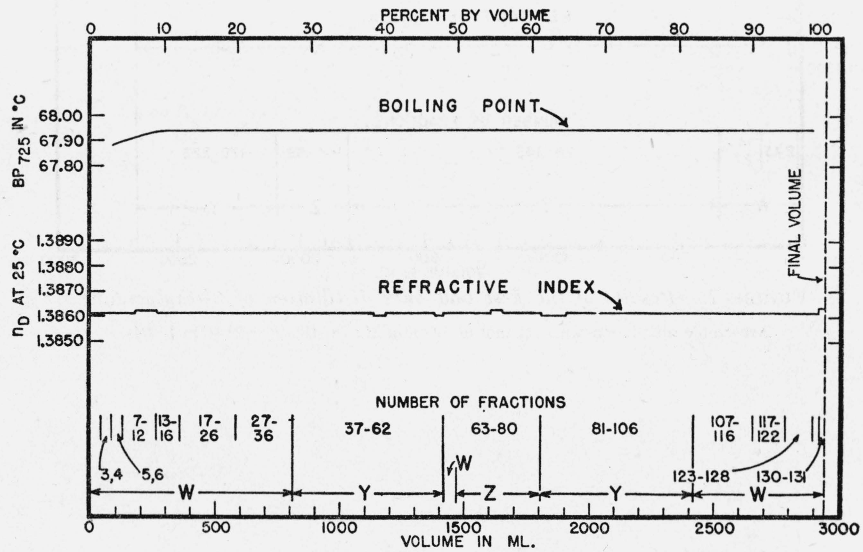

FIGURE 6.—*Resulis of the second and final distillation of 3-methylhexane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 7 (10/17/44 to 11/11/44). See footnote "h" of table 1. 50 ml of fractions 63 to 80 (marked "*W*") was returned to the supplier as a "best" sample.

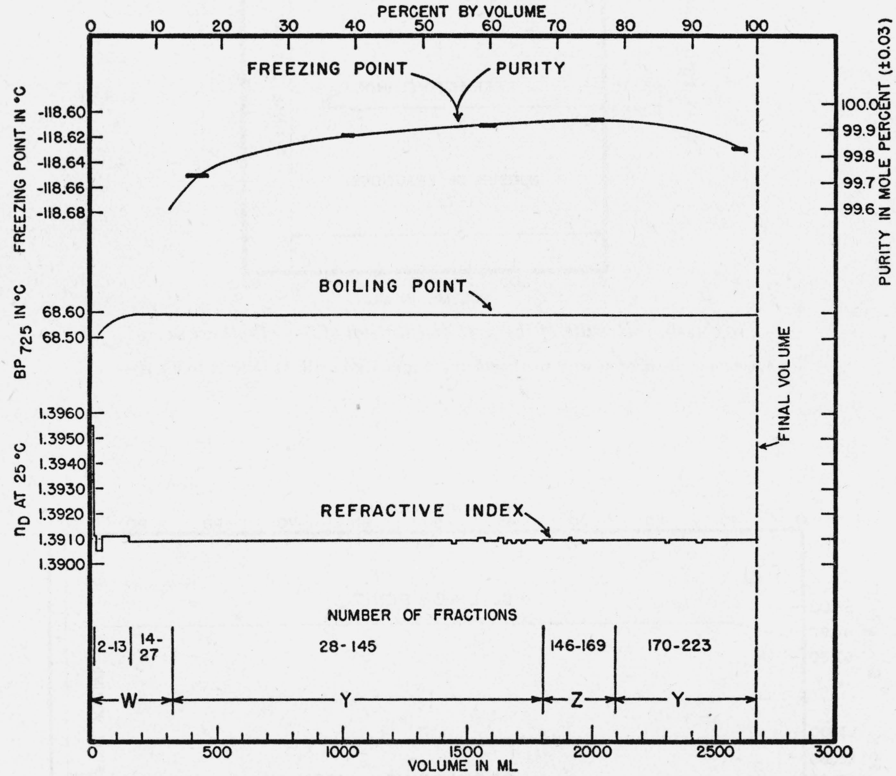

FIGURE 7.—*Results of the first and only distillation of 3-ethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 10 (8/22/44 to 10/4/44).

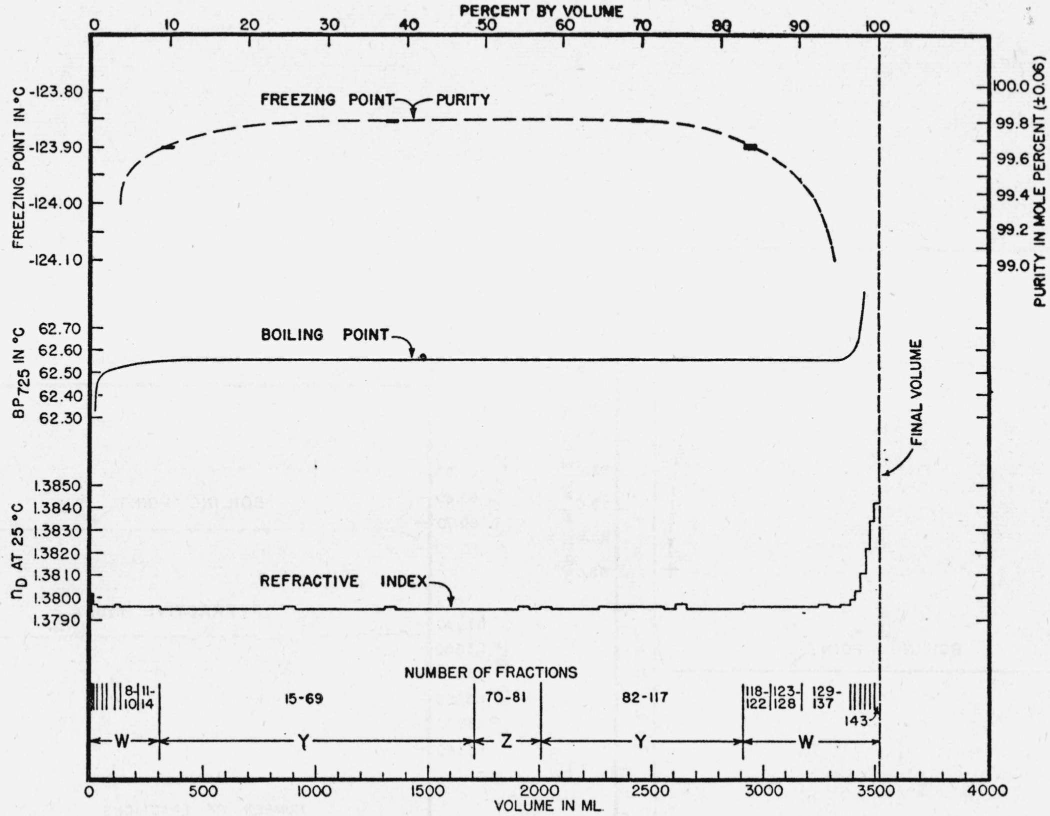

FIGURE 8.—*Results of the first and only distillation of 2,2-dimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 7 (7/31/44 to 8/28/44).

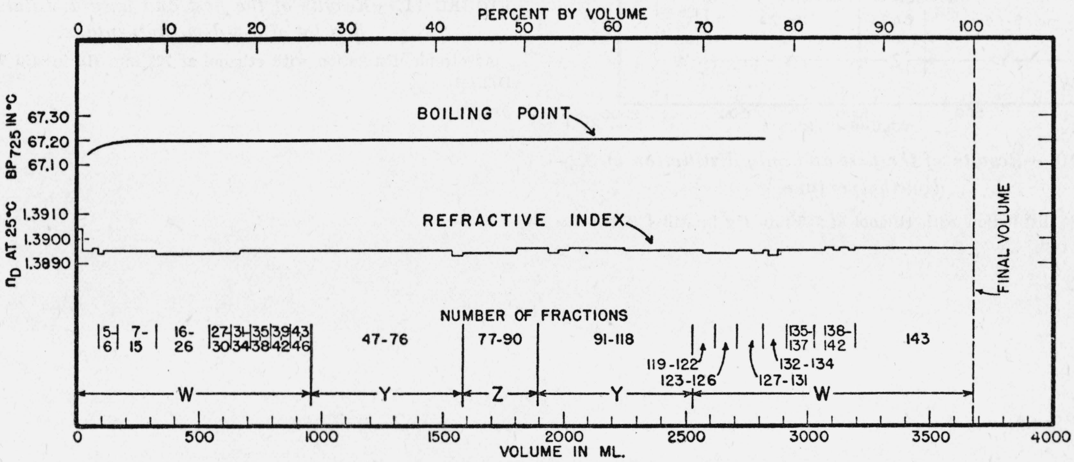

FIGURE 9.—*Results of the first and only distillation of 2,3-dimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 8 (8/16/44 to 9/11/44).

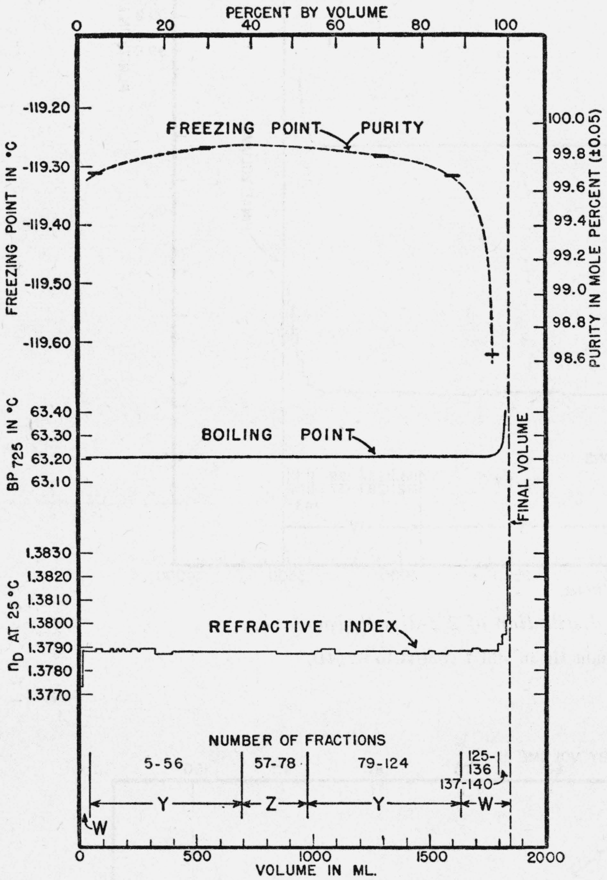

FIGURE 10.—*Results of the first and only distillation of 2,4-dimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 4 (8/14/44 to 9/11/44).

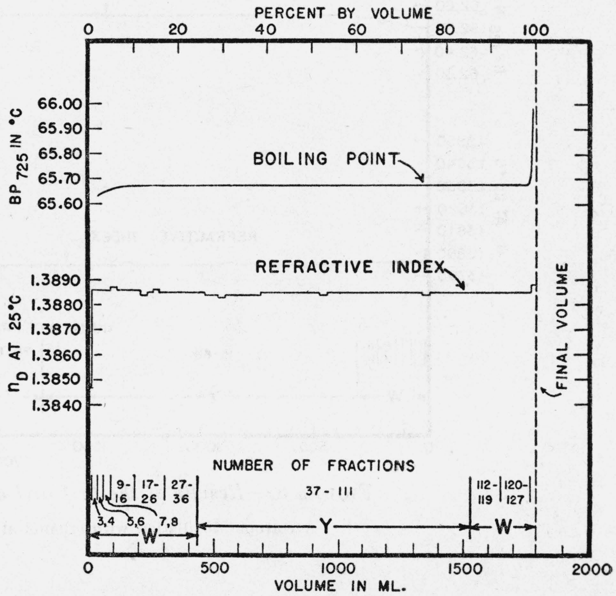

FIGURE 11.—*Results of the first and only distillaiion of the first lot of 3,3-dimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 9 (11/2/44 to 11/27/44).

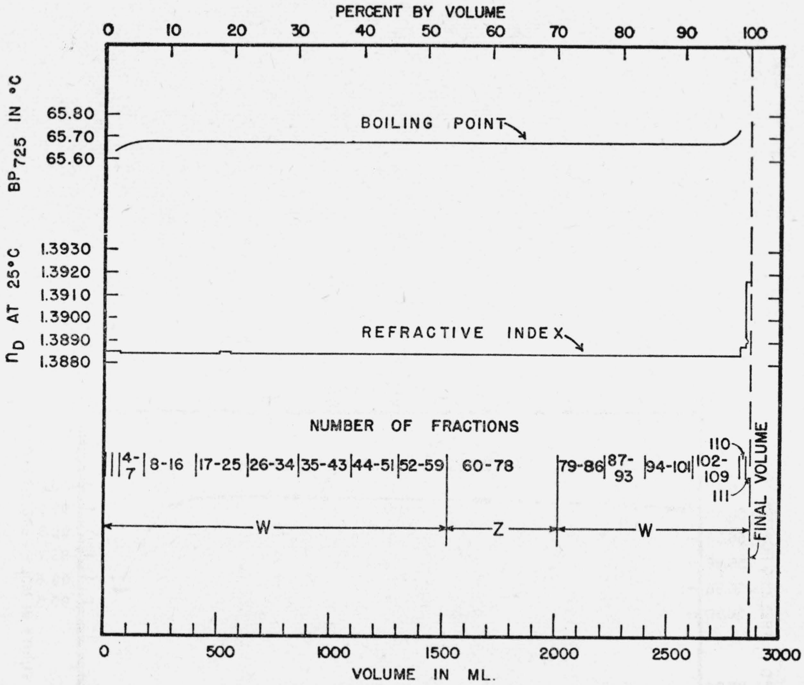

FIGURE 12.—*Results of the first and only distillation of the second lot of 3,3-dimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 7 (1/22/45 to 2/17/45).

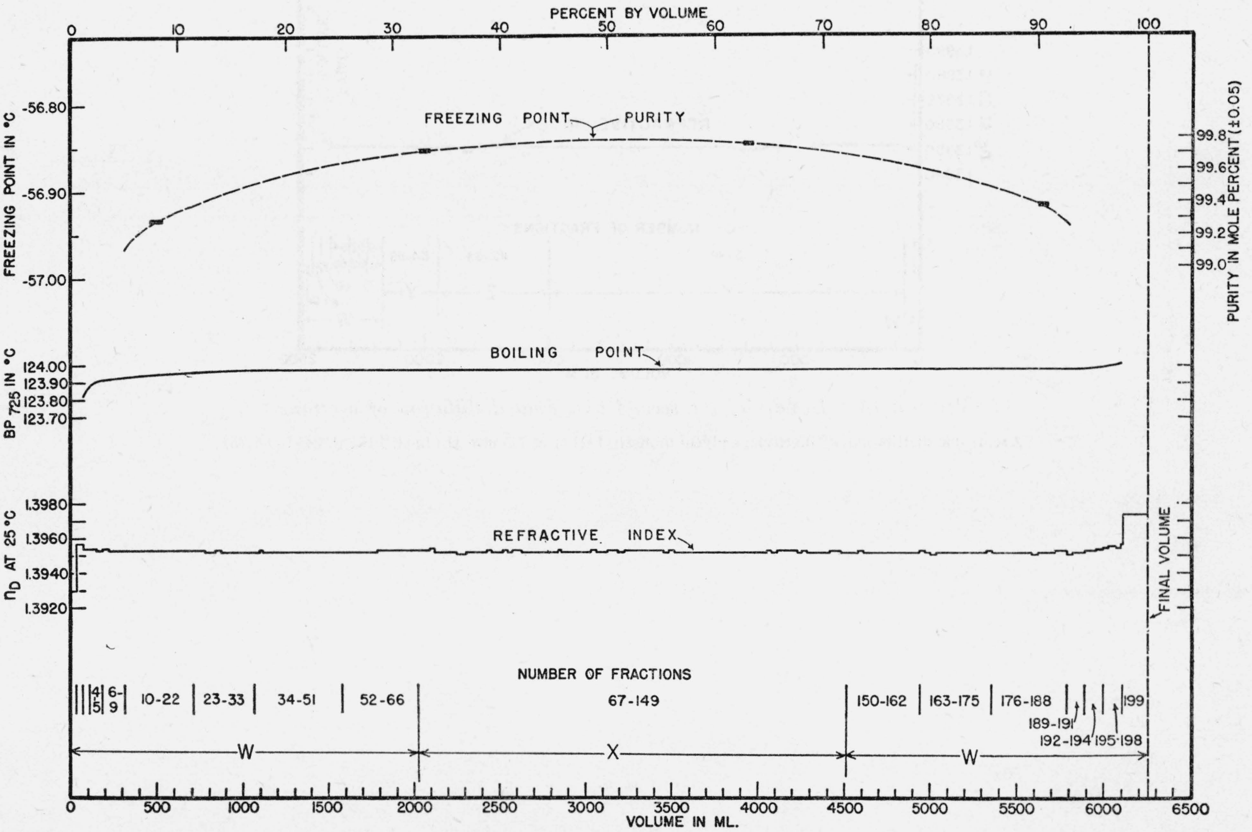

FIGURE 13.—*Results of the first distillation of n-octane.*

Regular distillation at 725 mm Hg in still 13 (4/6/45 to 5/14/45).

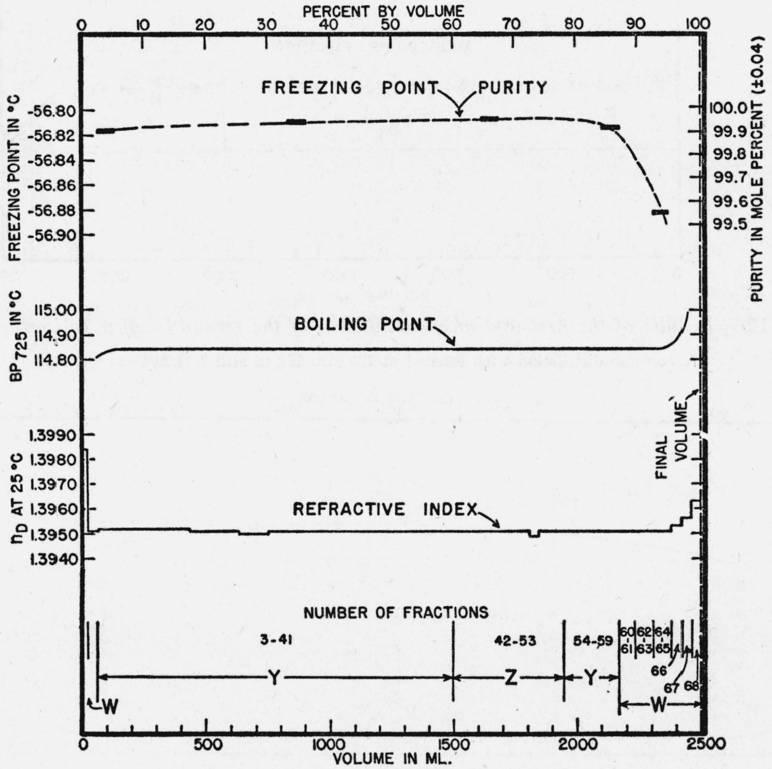

FIGURE 14.—*Results of the second and final distillation of n-octane.*

Azeotropic distillation with ethylene glycol monethyl ether at 725 mm Hg in still 15 (5/26/45 to 6/8/45).

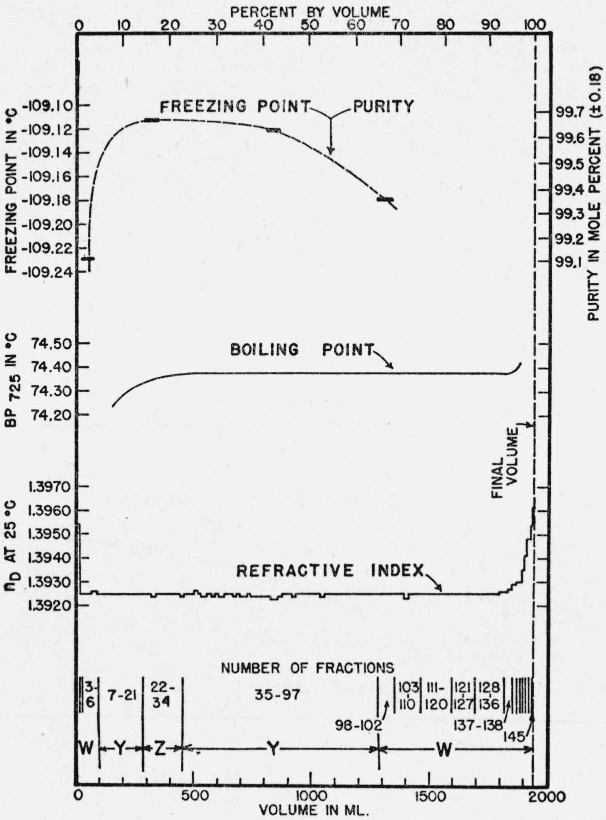

FIGURE 15.—*Results of the first and only distillation of 2-methylheptane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 7 (4/24/45 to 5/20/45).

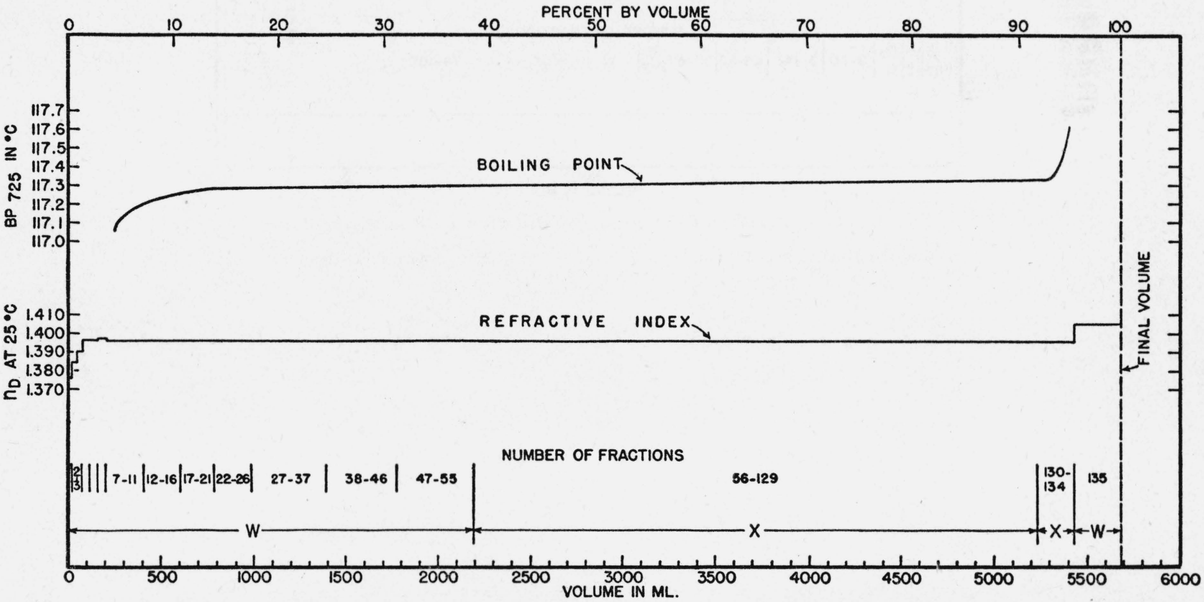

FIGURE 16.—*Results of the first distillation of 3-methylheptane.*

Regular distillation at 725 mm Hg in still 14 (8/30/44 to 9/20/44). Fractions 56 to 129 were used for the charge in the following distillation (see fig. 17), and fractions 130 to 134 were used for the azeotropic distillation in still 8 (see fig. 18 and footnote "w" of table 1).

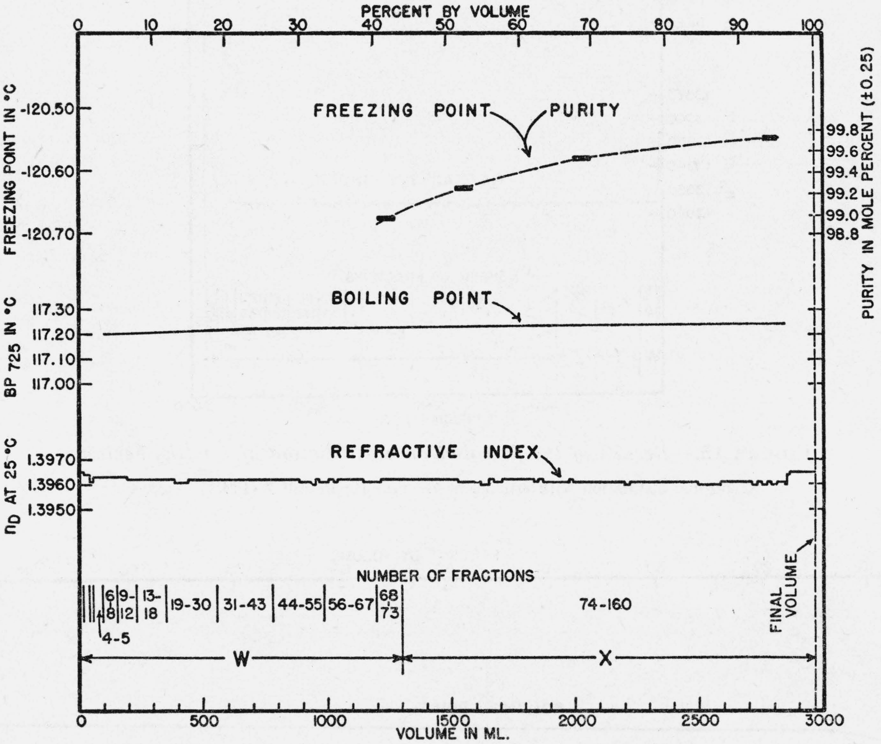

FIGURE 17.—*Results of the second distillation of 3-methylheptane.*

Regular distillation at 725 mm Hg in still 4 (3/3/45 to 4/1/45). See legend of figure 16.

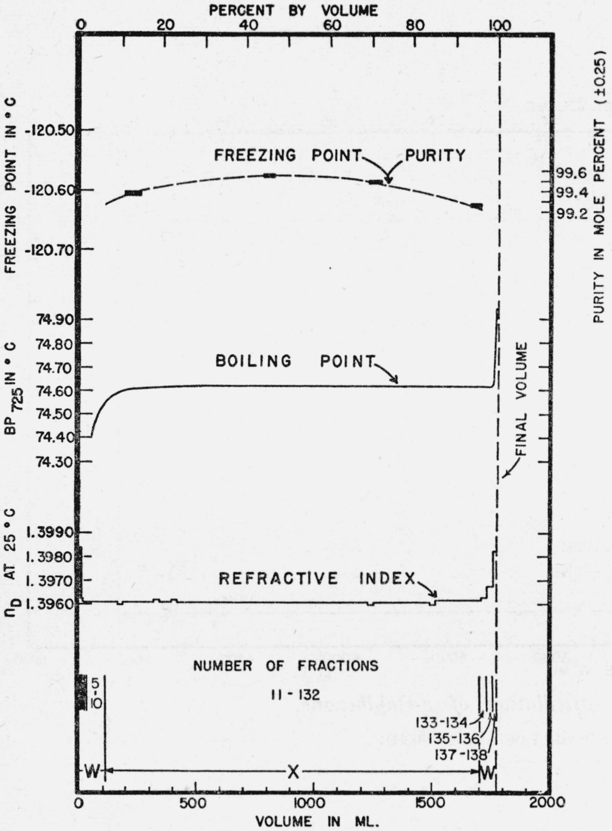

Figure 18.—*Results of the third distillation of 3-methylheptane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 8 (5/7/45 to 5/31/45). See footnote "w" of table 1.

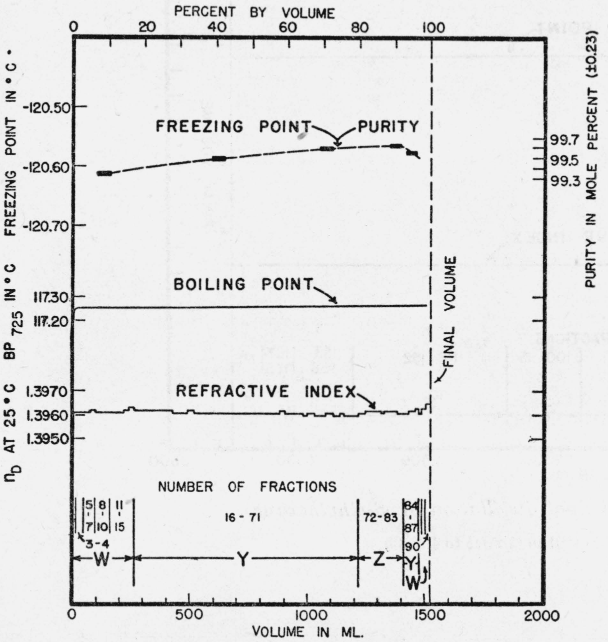

Figure 19.—*Results of the fourth and final distillation of 3-methylheptane.*

Regular distillation at 725 mm Hg in still 4 (6/12/45 to 6/30/45).

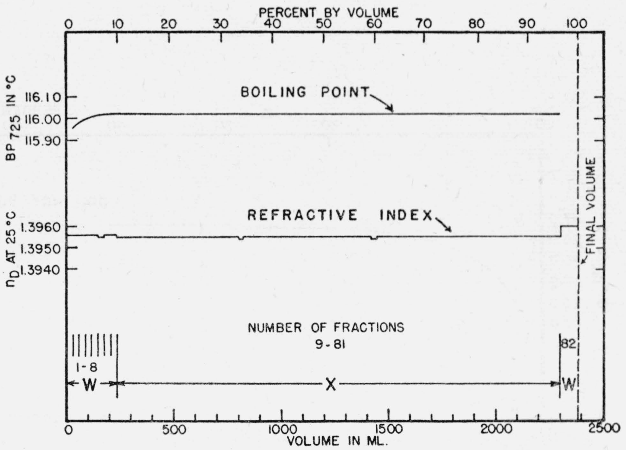

Figure 20.—*Results of the first distillation of 4-methylheptane.*

Regular distillation at 725 mm Hg in still 12 (1/25/45 to 2/18/45).

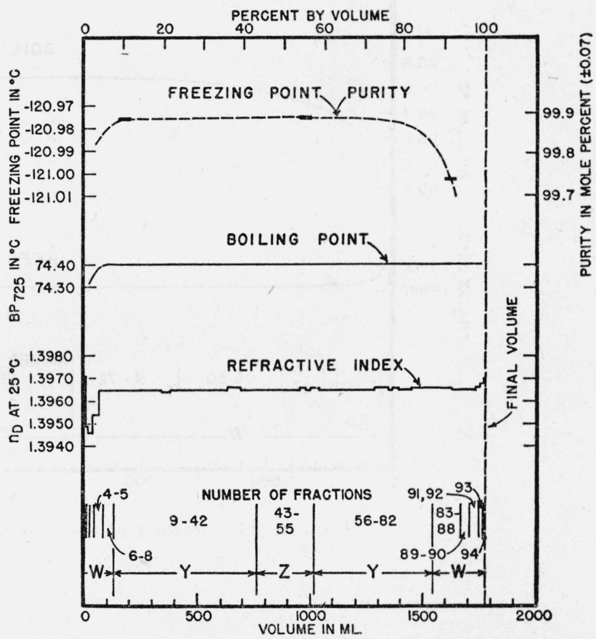

Figure 21.—*Results of the second and final distillation of 4-methylheptane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 14 (3/29/45 to 4/23/45).

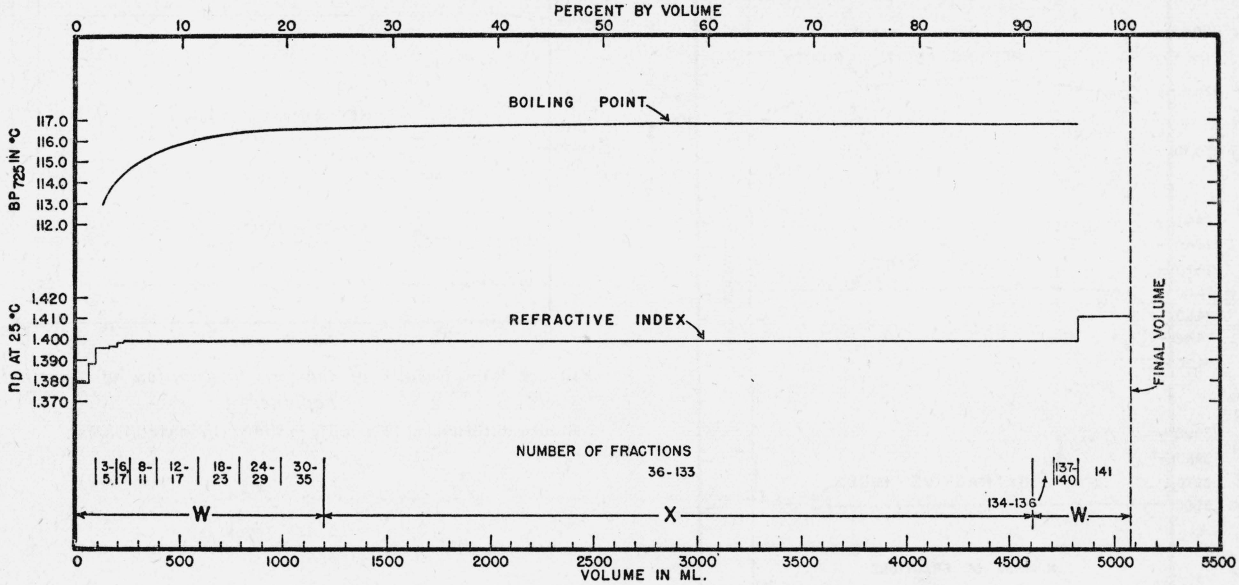

Figure 22.—*Results of the first distillation of 3-ethylhexane.*

Regular distillation at 725 mm Hg in still 7 (9/19/44 to 10/6/44).

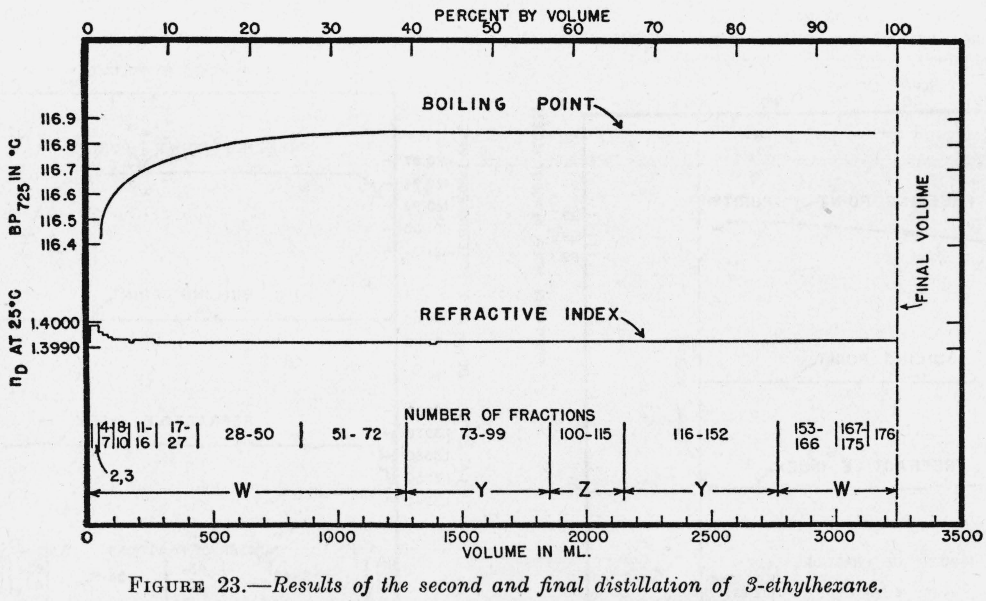

Figure 23.—*Results of the second and final distillation of 3-ethylhexane.*

Regular distillation at 725 mm Hg in still 10 (3/21/45 to 4/23/45).

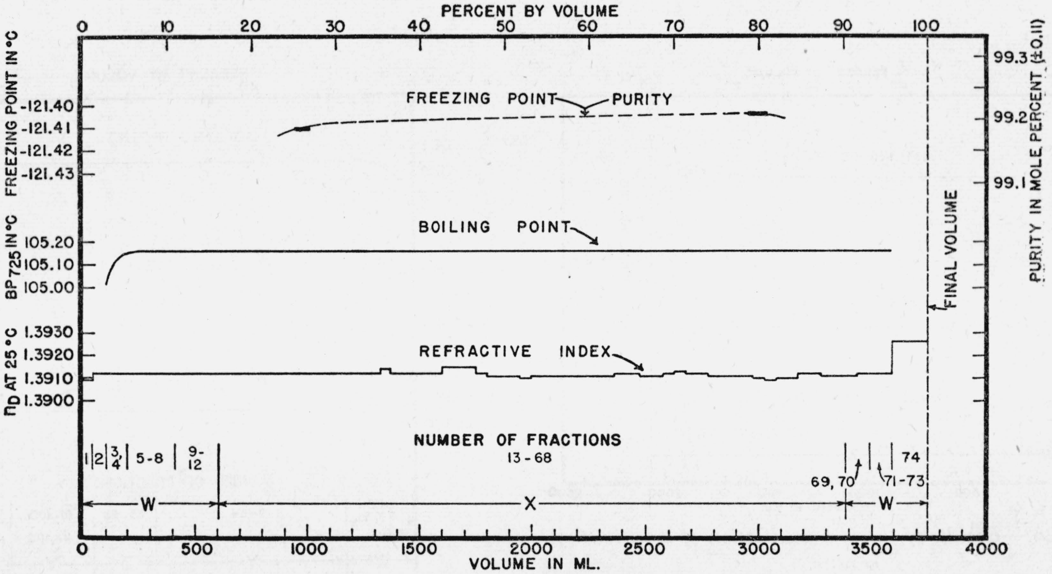

FIGURE 24.—*Results of the first distillation of 2,2-dimethylhexane.*

Regular distillation at 725 mm Hg in still 15 (11/30/44 to 12/15/44).

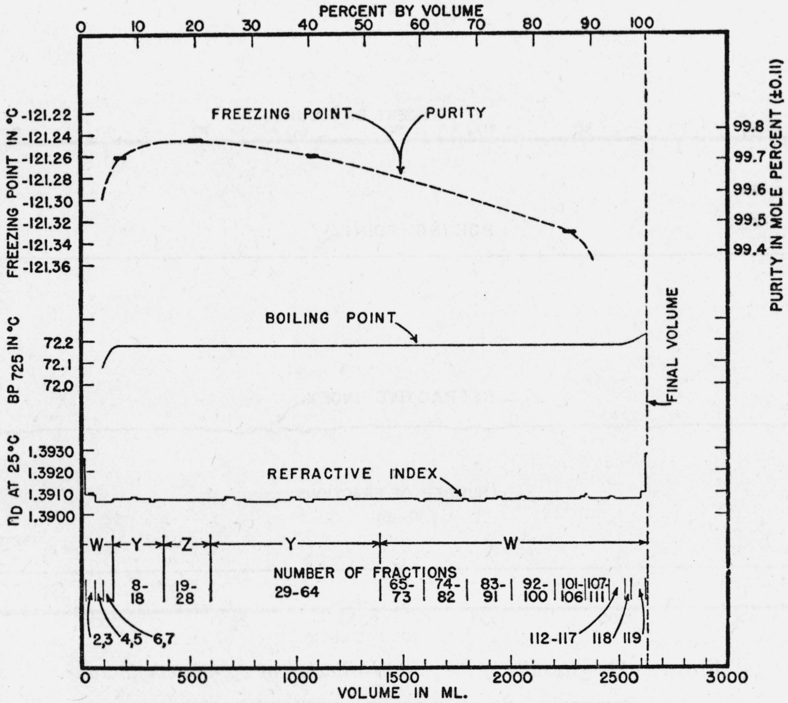

FIGURE 25.—*Results of the second and final distillation of 2,2-dimethylhexane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 13 (1/9/45 to 2/7/45).

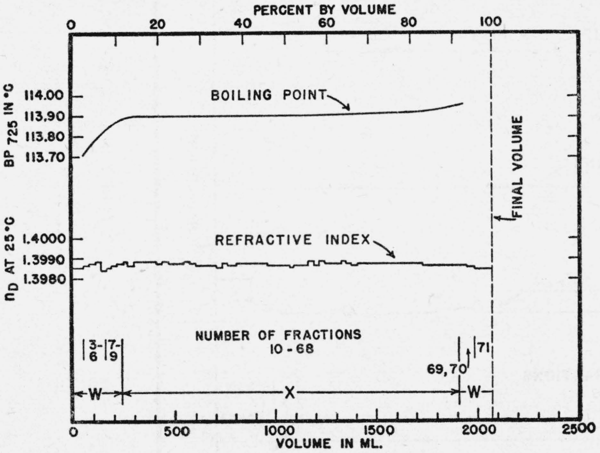

FIGURE 26.—*Results of the first distillation of 2,3-dimethylhexane.*

Regular distillation at 725 mm Hg in still 12 (12/9/44 to 1/2/45).

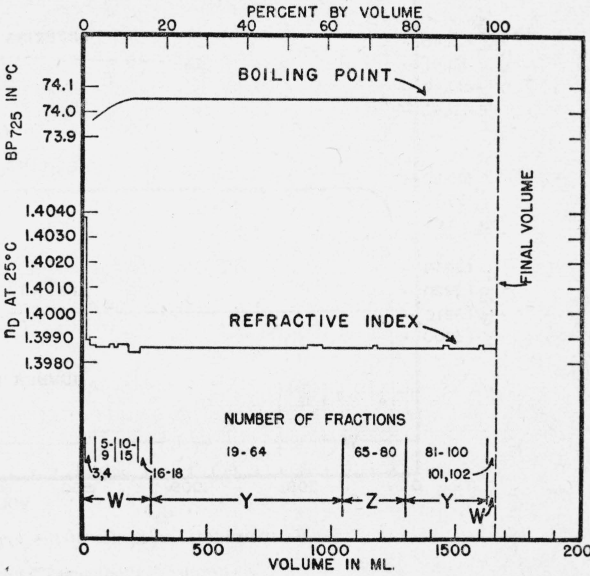

FIGURE 27.—*Results of the second and final distillation of 2,3-dimethylhexane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 8 (2/5/45 to 2/28/45).

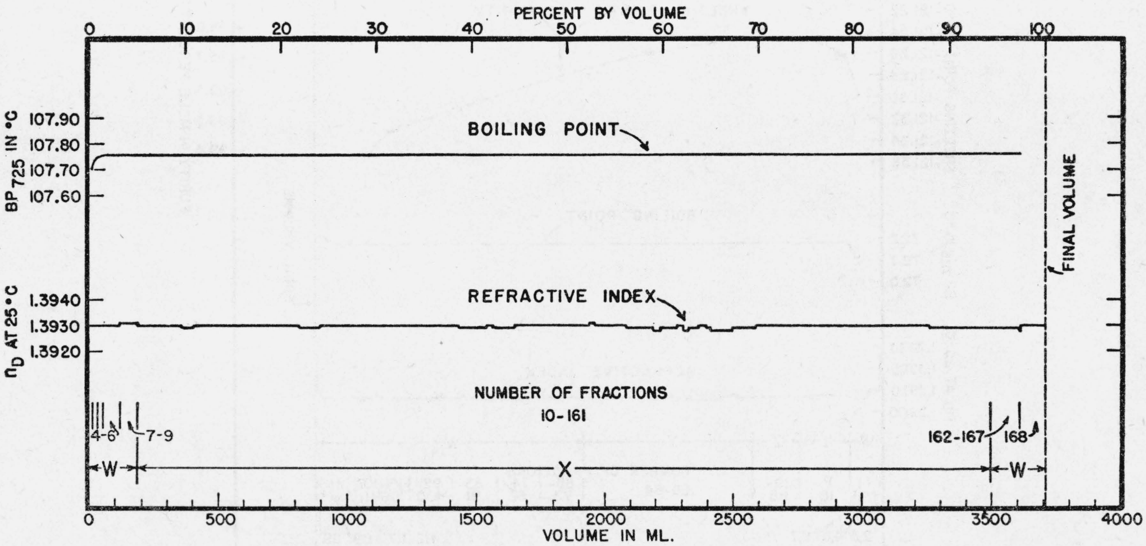

FIGURE 28.—*Results of the first distillation of 2,4-dimethylhexane.*

Regular distillation at 725 mm Hg in still 9 (7/31/44 to 8/30/44).

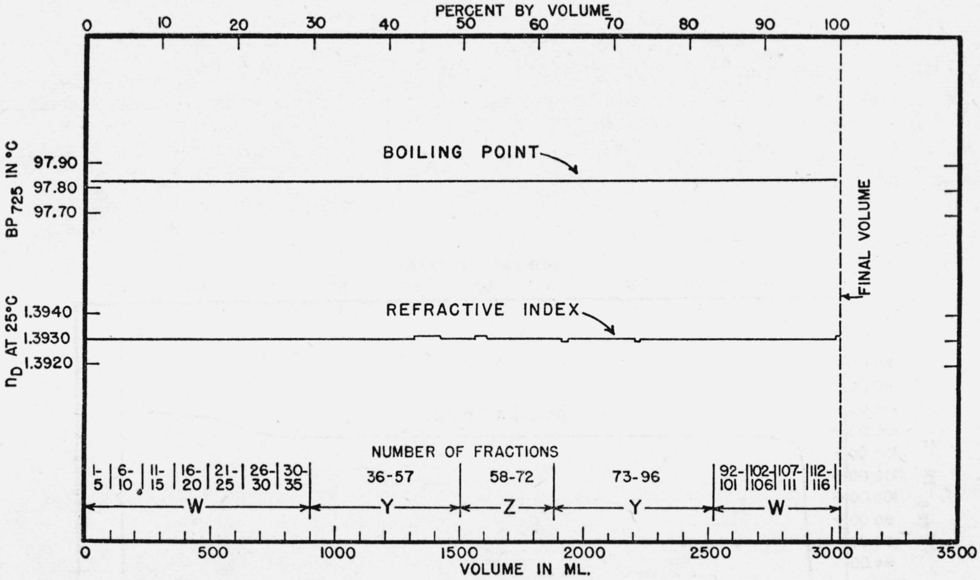

Figure 29.—*Results of the second and final distillation of 2,4-dimethylhexane.*

Azeotropic distillation with ethylene glycol monomethyl ether at 725 mm Hg in still 7 (11/11/44 to 12/8/44).

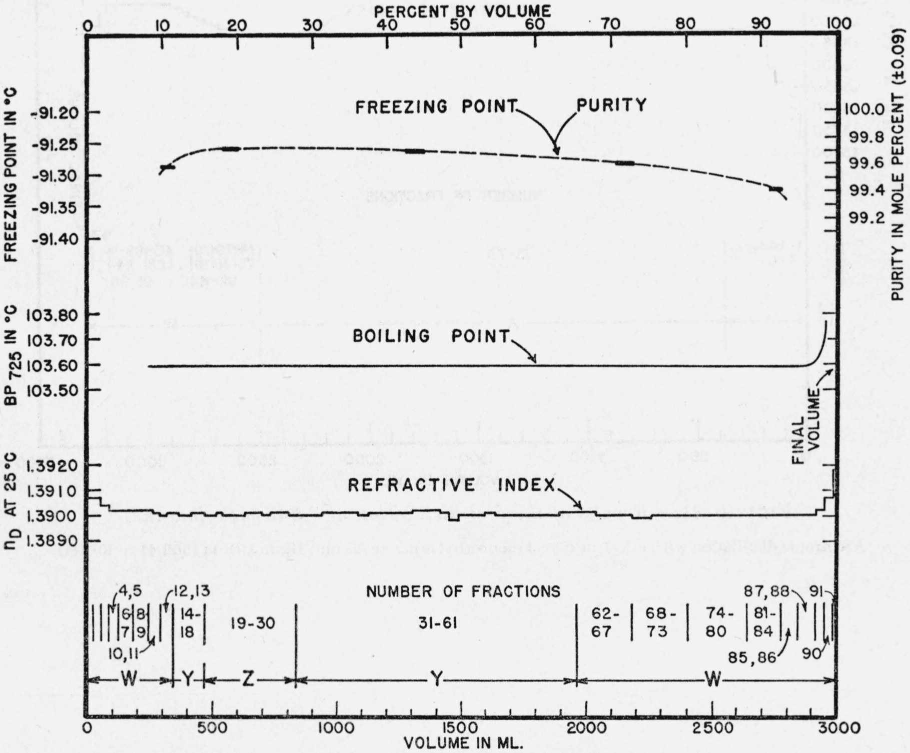

Figure 30.—*Results of the first and only distillation of 2,5-dimethylhexane.*

Azeotropic distillation with ethylene glycol monoethyl ether at 725 mm Hg in still 14 (10/23/44 to 11/12/44).

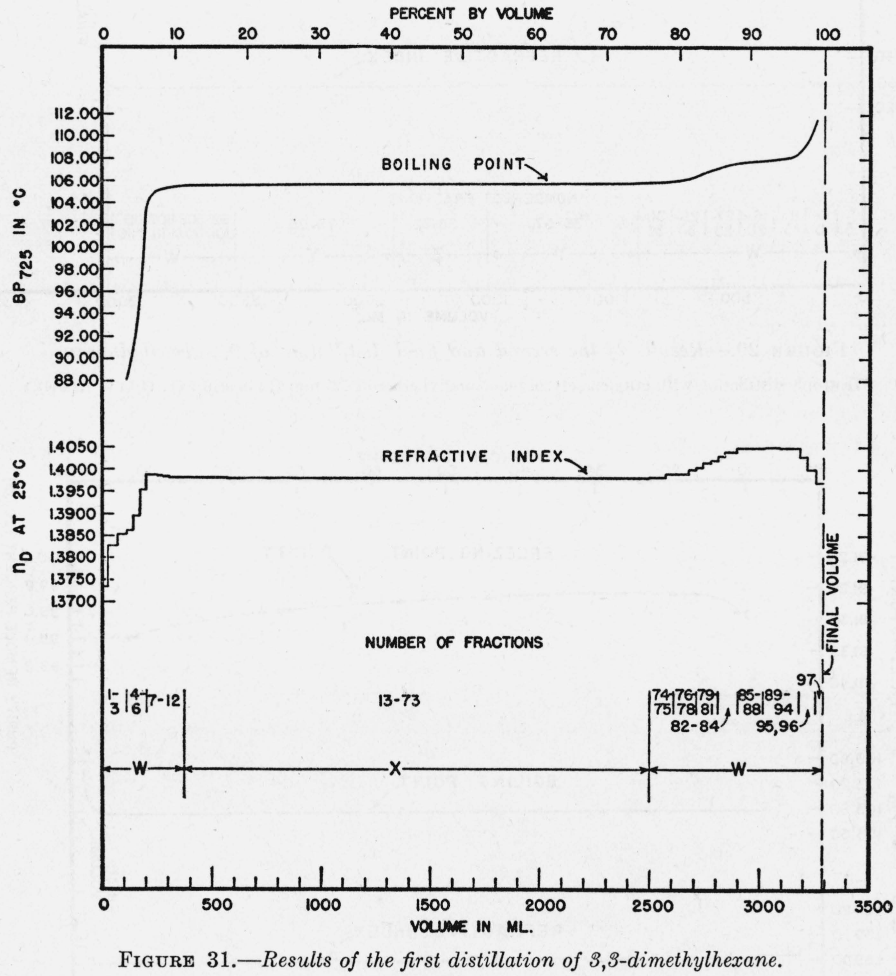

FIGURE 31.—*Results of the first distillation of 3,3-dimethylhexane.*

Azeotropic distillation with ethylene glycol monoethyl ether at 725 mm Hg in still 14 (9/21/44 to 10/7/44).

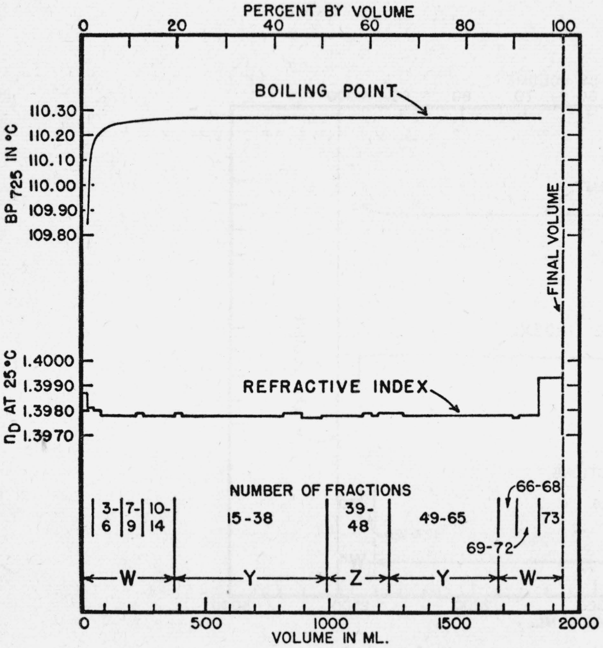

FIGURE 32.—*Results of the second and final distillation of 3,3-dimethylhexane.*

Regular distillation at 725 mm Hg in still 12 (1/3/45 to 1/23/45).

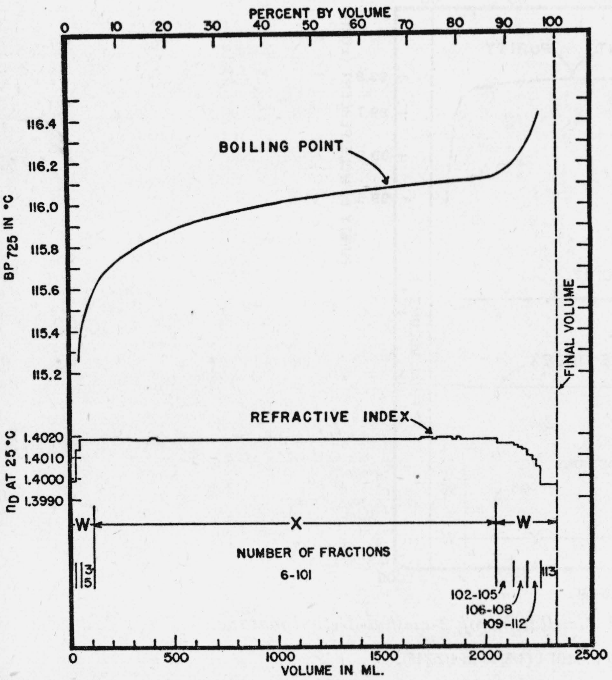

FIGURE 33.—*Results of the first distillation of 3,4-dimethylhexane.*

Regular distillation at 725 mm Hg in still 12 (11/16/44 to 12/8/44).

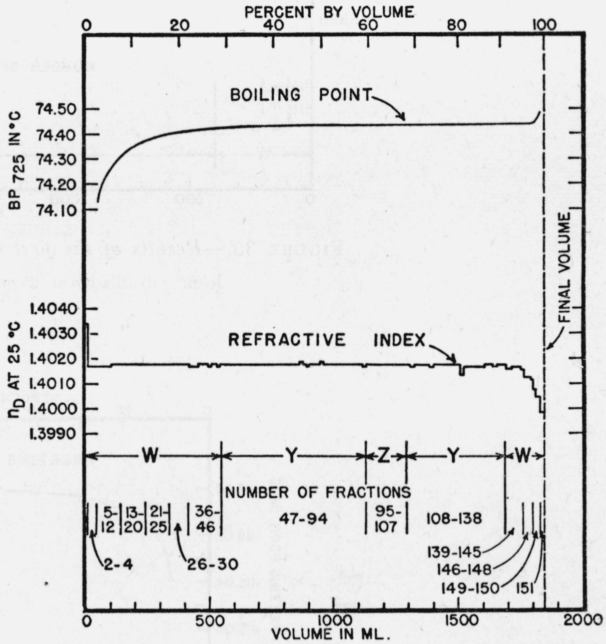

FIGURE 34.—*Results of the second and final distillation of 3,4-dimethylhexane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 8 (4/6/45 to 5/5/45).

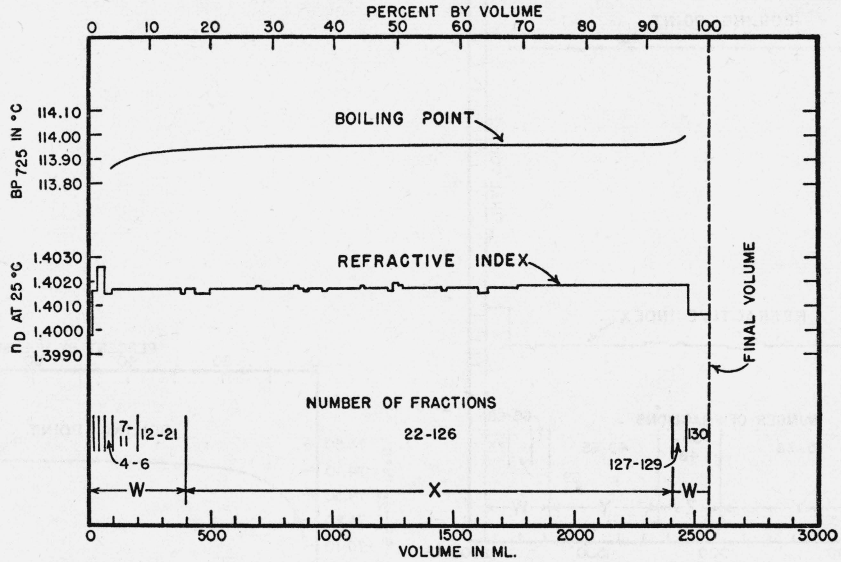

FIGURE 35.—*Results of the first distillation of 2-methyl-3-ethylpentane*

Regular distillation at 725 mm Hg in still 12 (8/30/44 to 9/26/44).

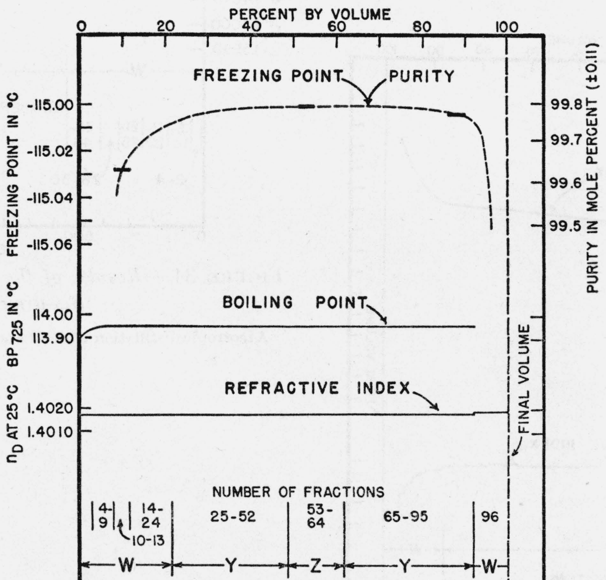

FIGURE 36.—*Results of the second and final distillation of 2-methyl-3-ethylpentane.*

Regular distillation at 725 mm Hg in still 4 (4/3/45 to 4/20/45).

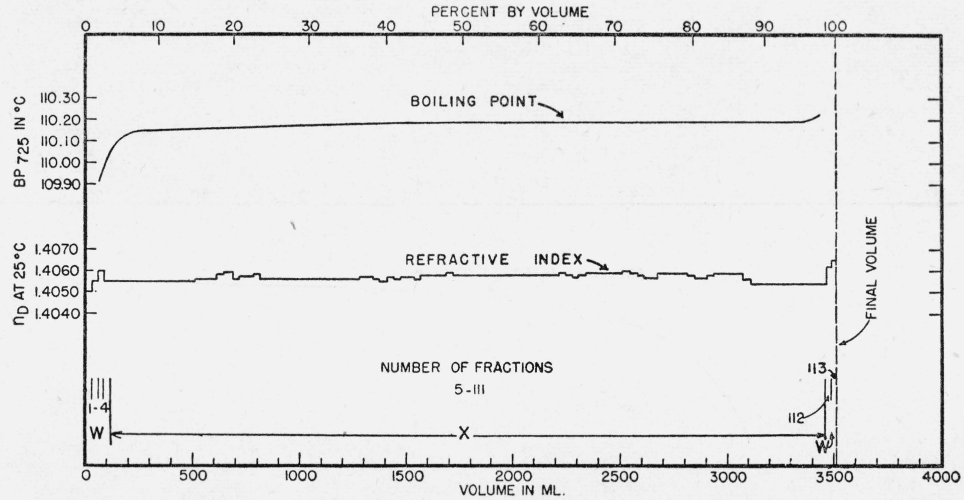

FIGURE 37.—*Results of the first distillation of 3-methyl-3-ethylpentane.*

Azeotropic distillation with ethylene glycol monoethyl ether at 725 mm Hg in still 14 (10/7/44 to 10/23/44).

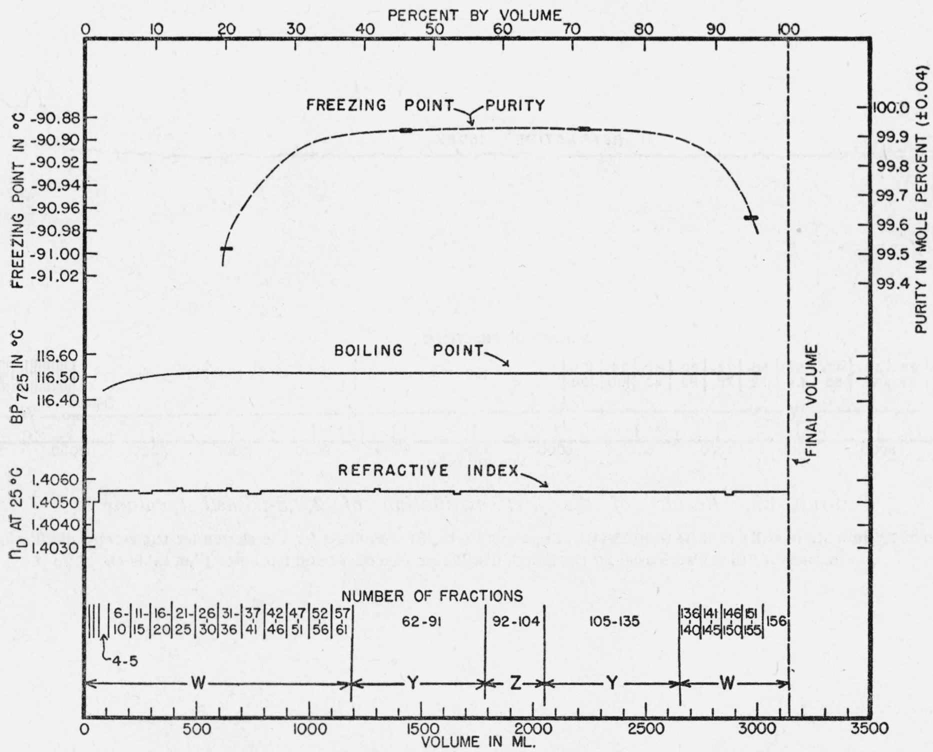

FIGURE 38.—*Results of the second and final distillation of 3-methyl-3-ethylpentane.*

Regular distillation at 725 mm Hg in still 9 (3/1/45 to 3/29/45).

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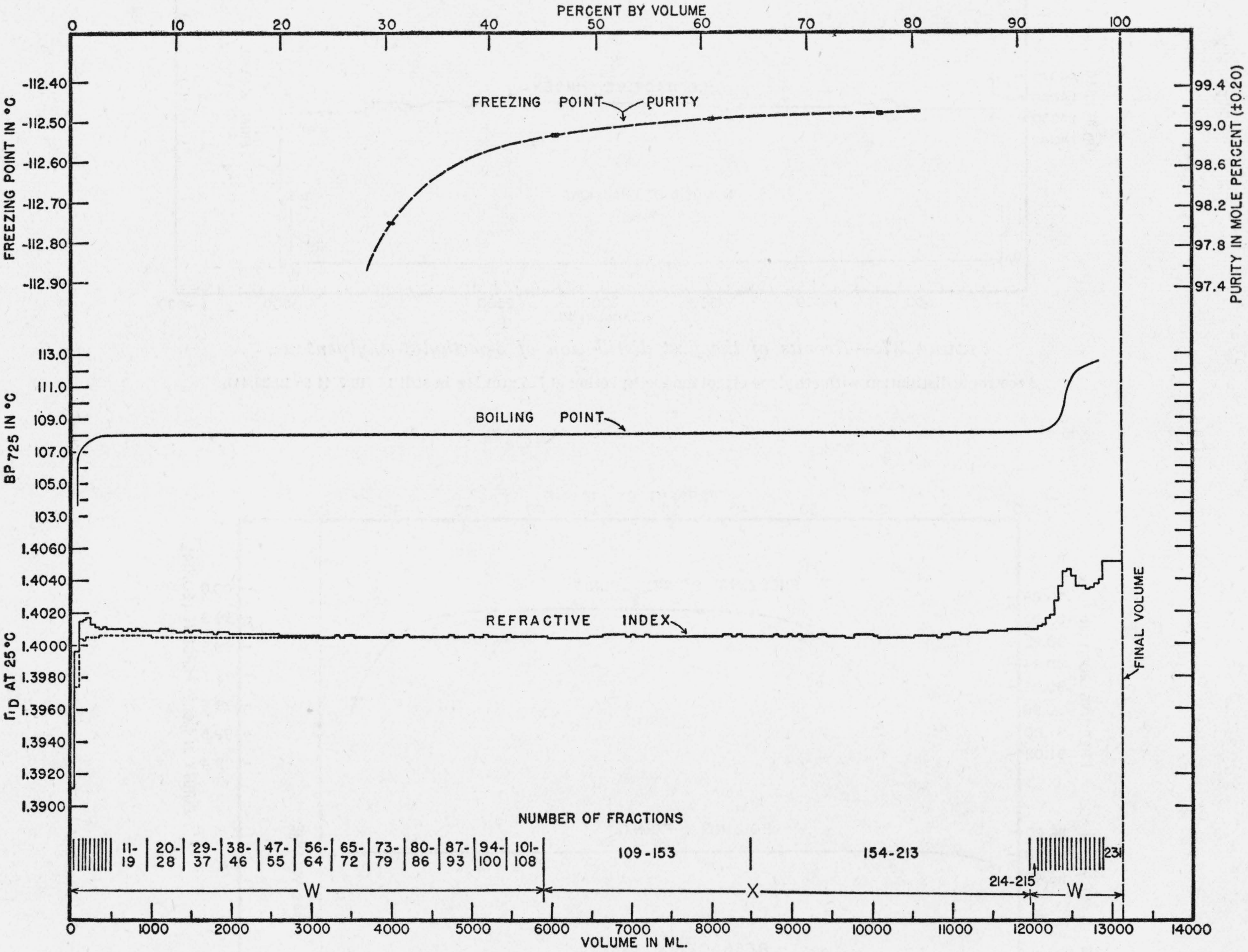

FIGURE 39.—*Results of the first distillation of 2,2,3-trimethylpentane.*

Regular distillation at 725 mm Hg in still 6 (9/12/44 to 10/23/44). Fractions 109 to 153 were used for the charge for the second distillation (see fig. 40). Fractions 154 to 213 were used for the fourth distillation (see fig. 42 and footnote "j" of table 1).

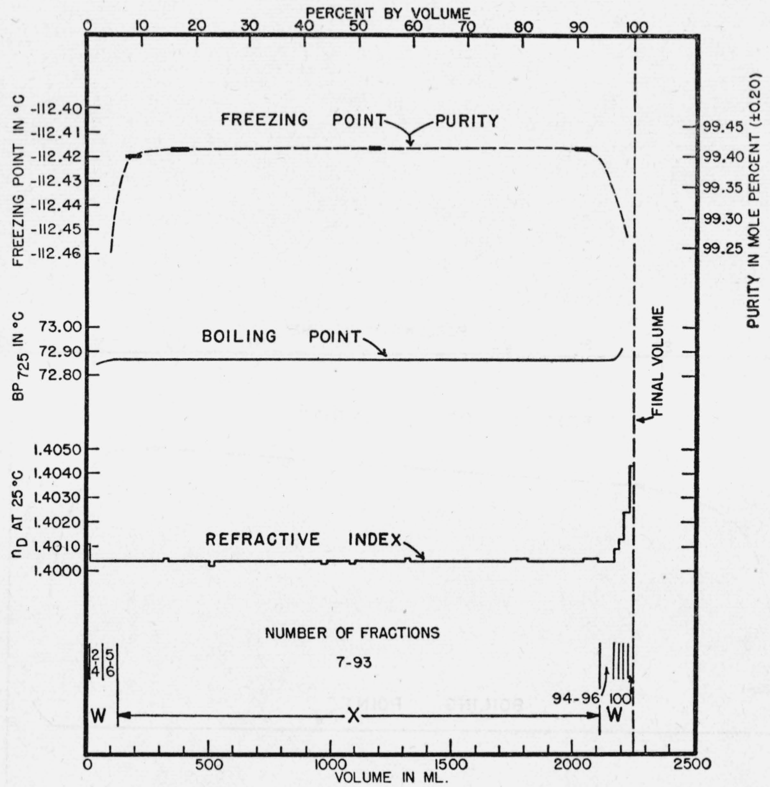

FIGURE 40.—*Results of the second distillation of 2,2,3-trimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 15 (1/3/45 to 1/29/45). See legend for figure 39.

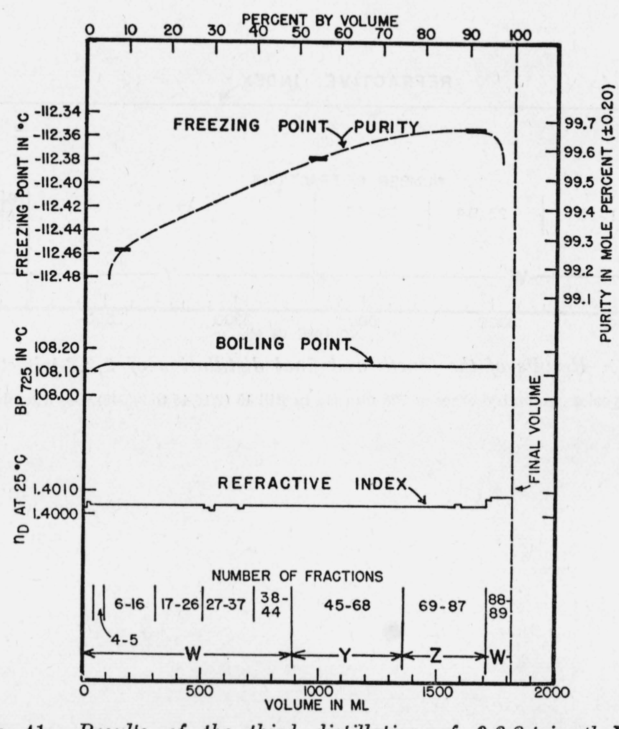

FIGURE 41.—*Results of the third distillation of 2,2,3-trimethylpentane.*

Regular distillation at 725 mm Hg in still 4 (2/14/45 to 3/2/45).

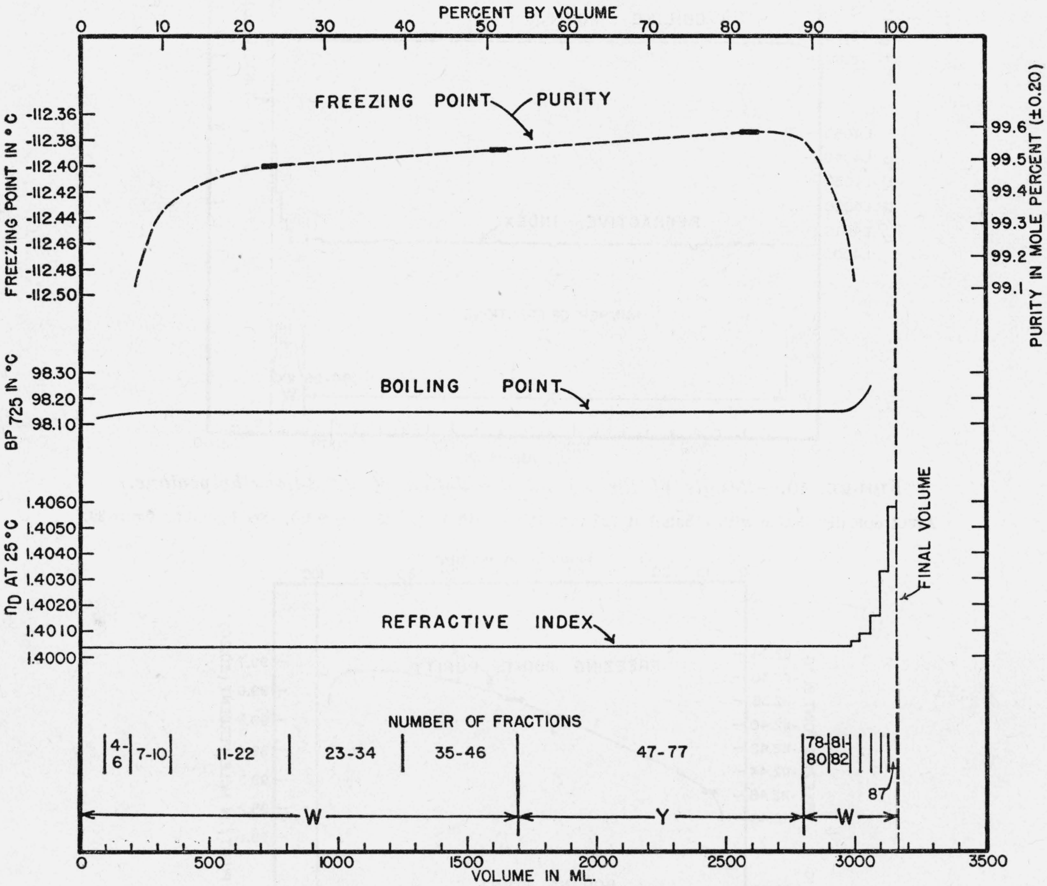

FIGURE 42.—*Results of the fourth and final distillation of 2,2,3-trimethylpentane.*

Azeotropic distillation with ethylene glycol monomethyl ether at 725 mm Hg in still 15 (2/16/45 to 3/5/45). See legend for figure 39 and footnote "j" of table 1.

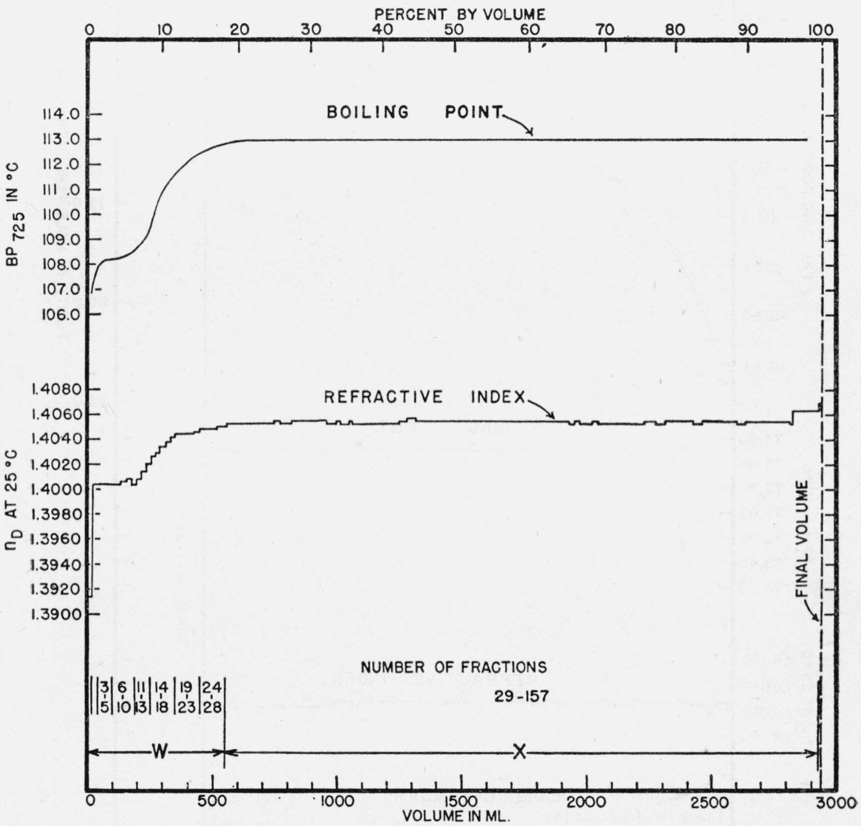

FIGURE 43.—*Results of the first distillation of 2,3,3-trimethylpentane.*

Regular distillation at 725 mm Hg in still 9 (11/27/44 to 12/26/44).

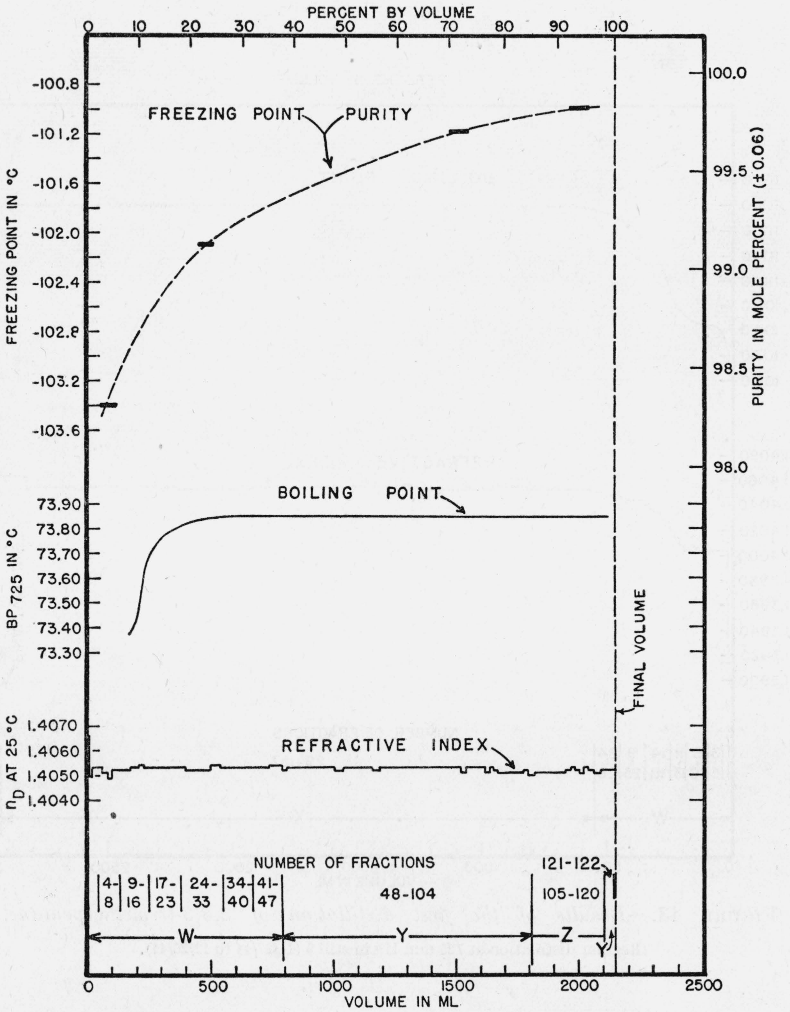

Figure 44.—*Results of the second and final distillation of 2,3,3-trimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 8 (1/8/45 to 2/5/45).

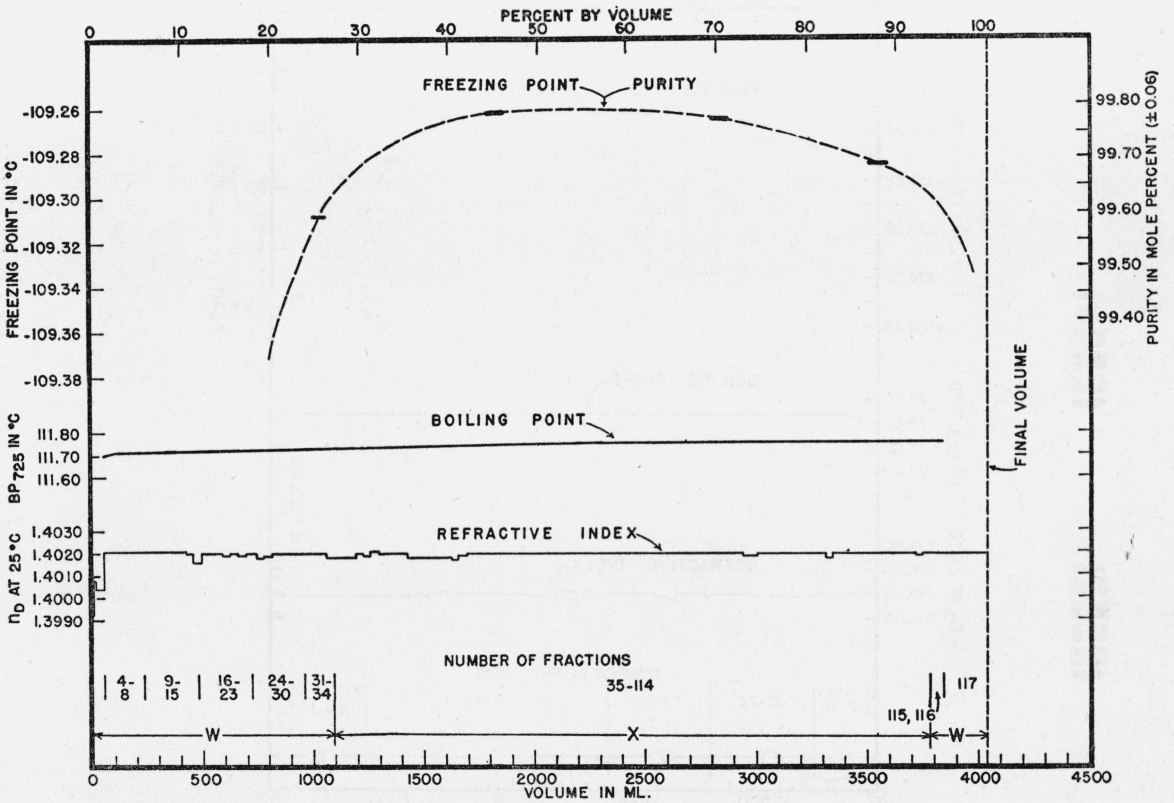

FIGURE 45.—*Results of the first distillation of 2,3,4-trimethylpentane.*
Regular distillation at 725 mm Hg in still 7 (8/28/44 to 9/19/44).

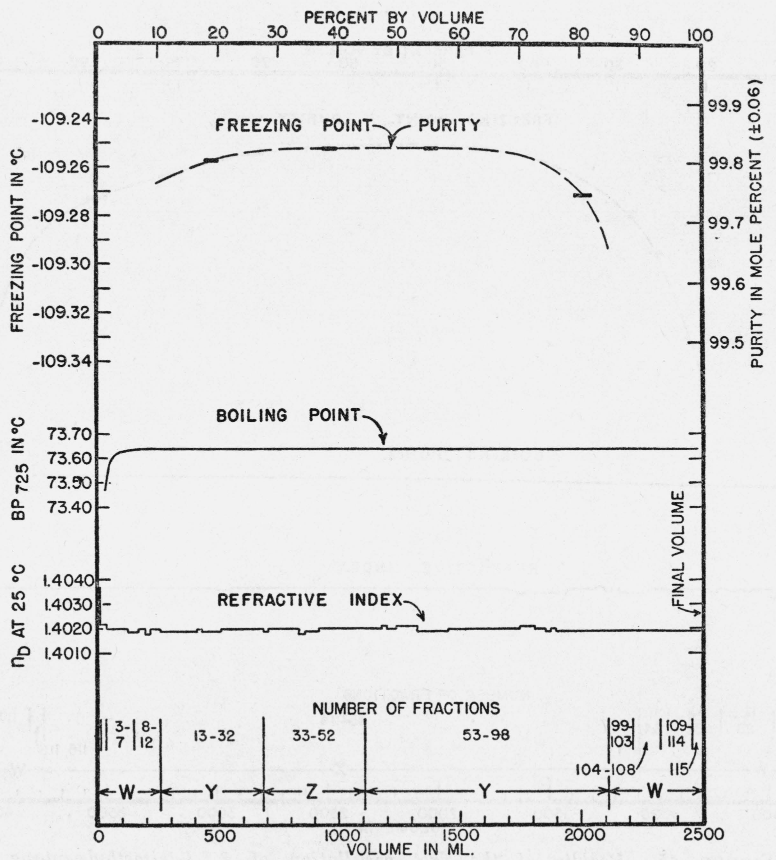

FIGURE 46.—*Results of the second and final distillation of 2,3,4-trimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 14 (12/27/44 to 1/18/45).

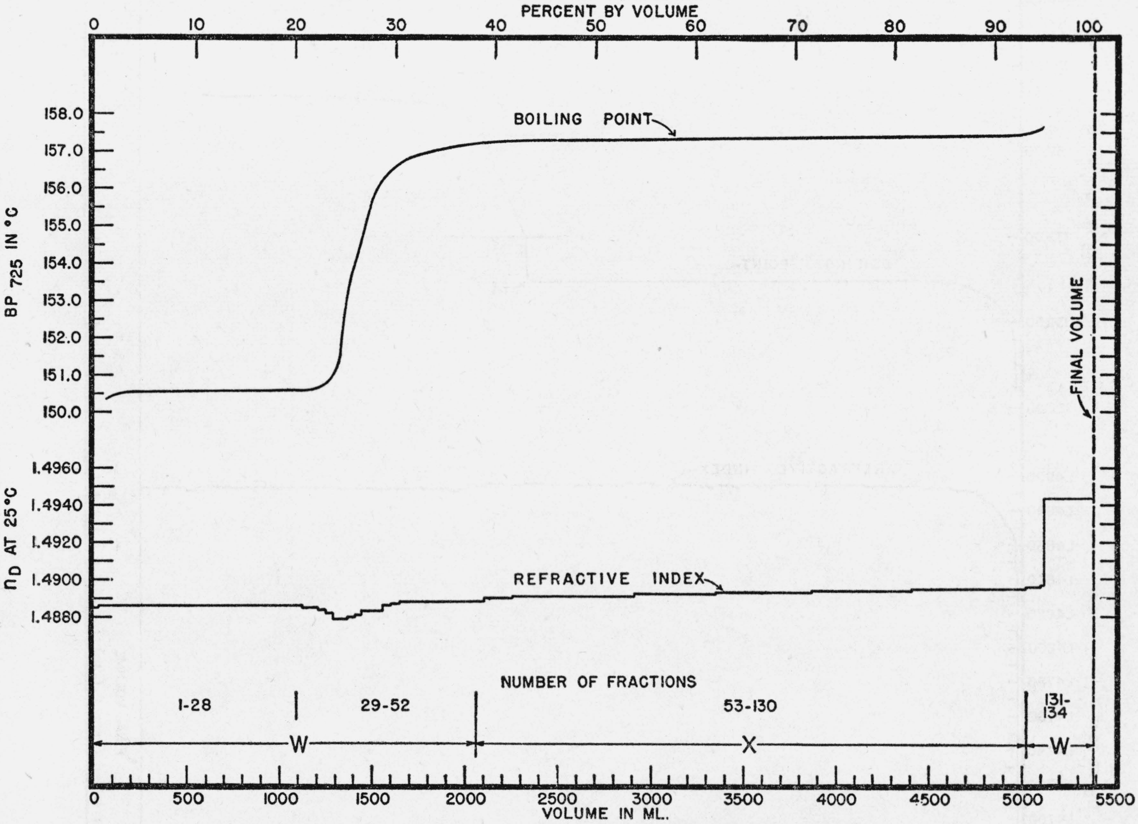

FIGURE 47.—*Results of the first distillation of n-propylbenzene.*

Regular distillation at 725 mm Hg in still 8 (5/23/44 to 6/20/44). This is one of two similar distillations.

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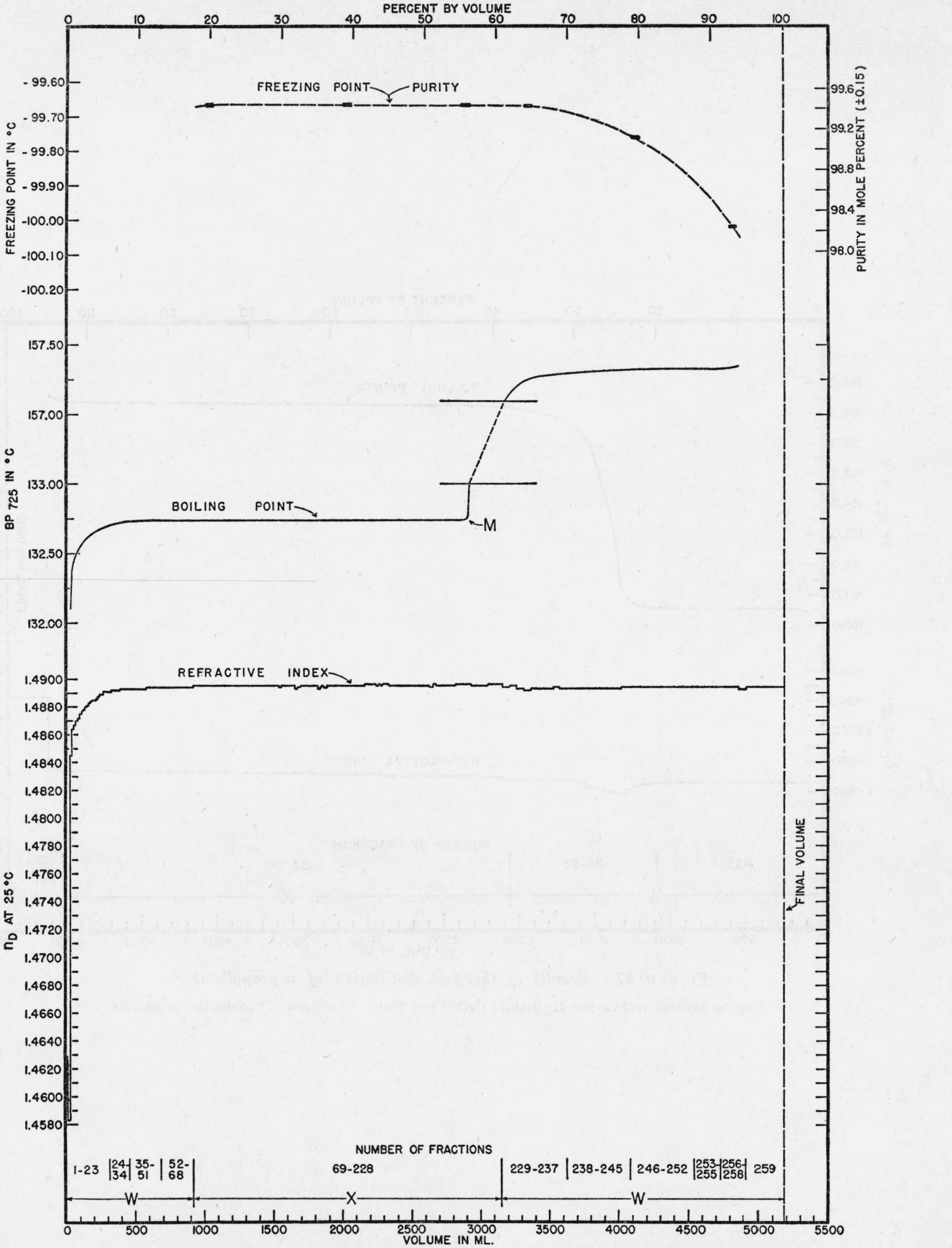

FIGURE 48.—*Results of the second distillation of n-propylbenzene.*

Azeotropic distillation with ethylene glycol monoethyl ether at 725 mm Hg in still 5 (9/5/44 to 10/21/44). See footnote "m" of table 1. At the point marked "*M*" the azeotrope-forming substance was exhausted and the remainder of the distillation was regular.

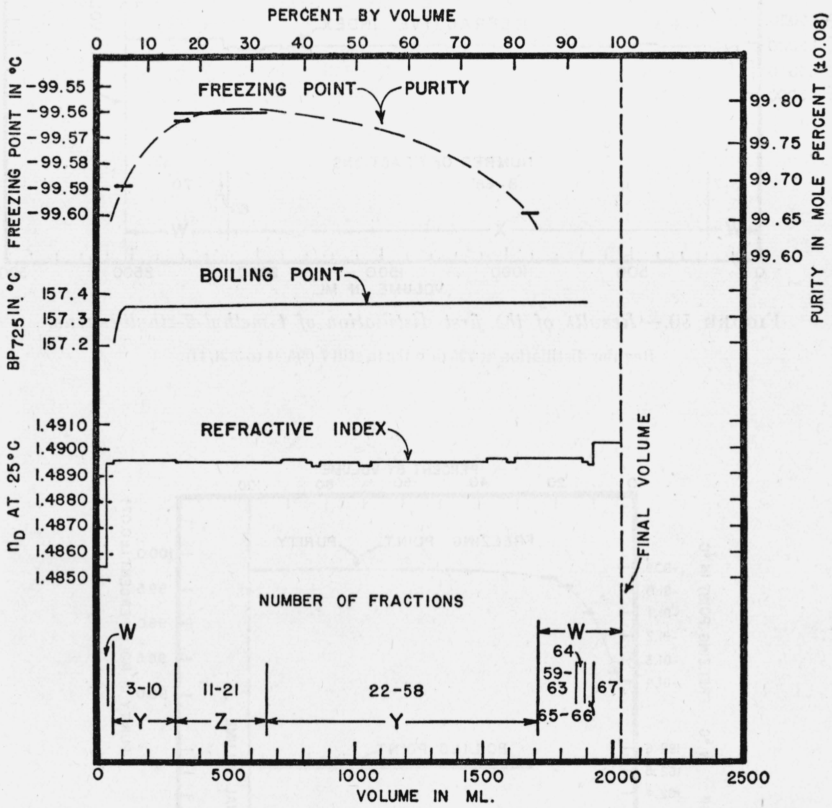

FIGURE 49.—*Results of the third and final distillation of n-propylbenzene.*

Regular distillation at 725 mm Hg in still 13 (12/23/44 to 1/8/45).

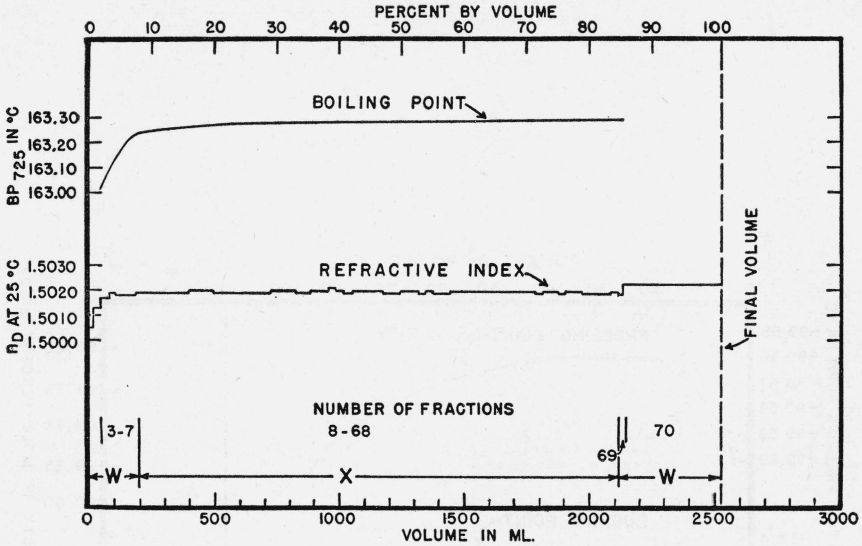

FIGURE 50.—*Results of the first distillation of 1-methyl-2-ethylbenzene.*

Regular distillation at 725 mm Hg in still 7 (5/5/44 to 5/21/44).

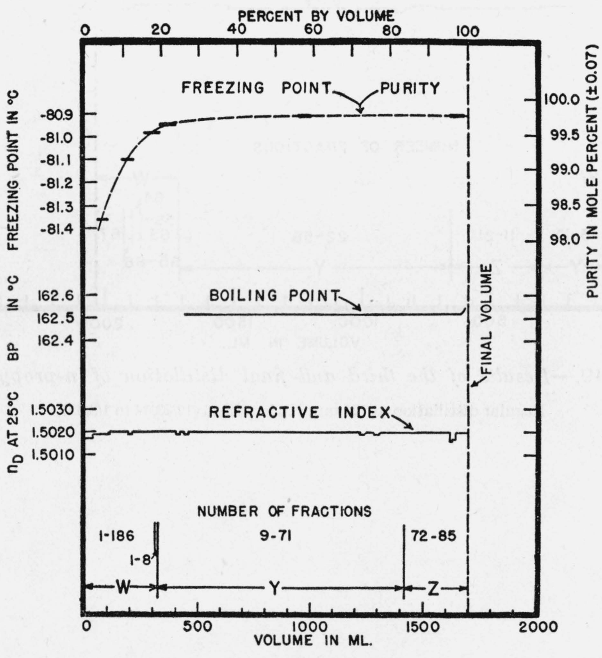

FIGURE 51.—*Results of the second and final distillation of 1-methyl-2-ethylbenzene.*

Azeotropic distillation with ethylene glycol monoethyl ether and diethylene glycol monomethyl ether at 725 mm Hg in still 4 (6/26/44 to 8/15/44). Fractions 1 to 186 in the portion marked "*W*" represent the hydrocarbon which distilled with ethylene glycol monoethyl ether. The remainder of the hydrocarbon was distilled with diethylene glycol monomethyl ether (see footnote "*n*" of table 1).

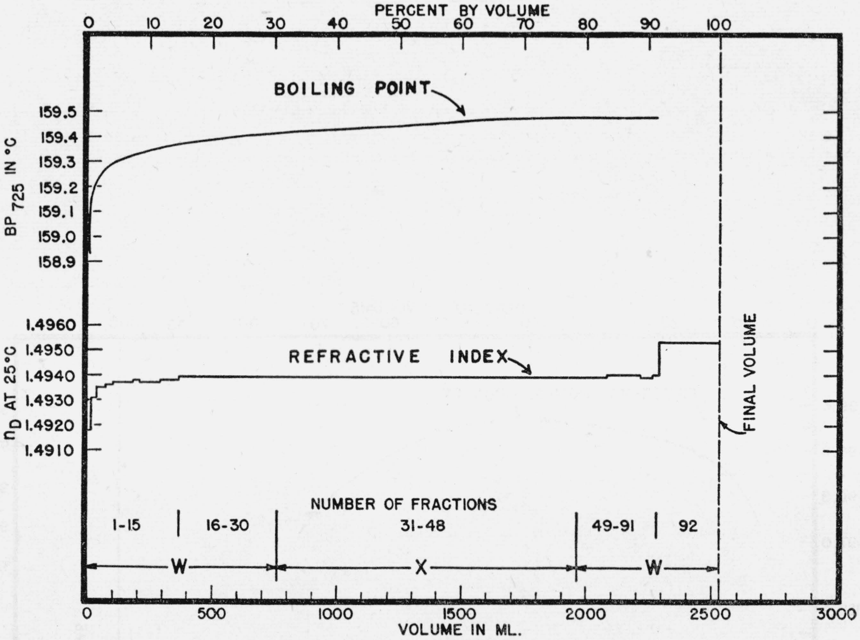

FIGURE 52.—*Results of the first distillation of 1-methyl-3-ethylbenzene.*

Regular distillation at 725 mm Hg in still 8 (3/17/44 to 3/30/44).

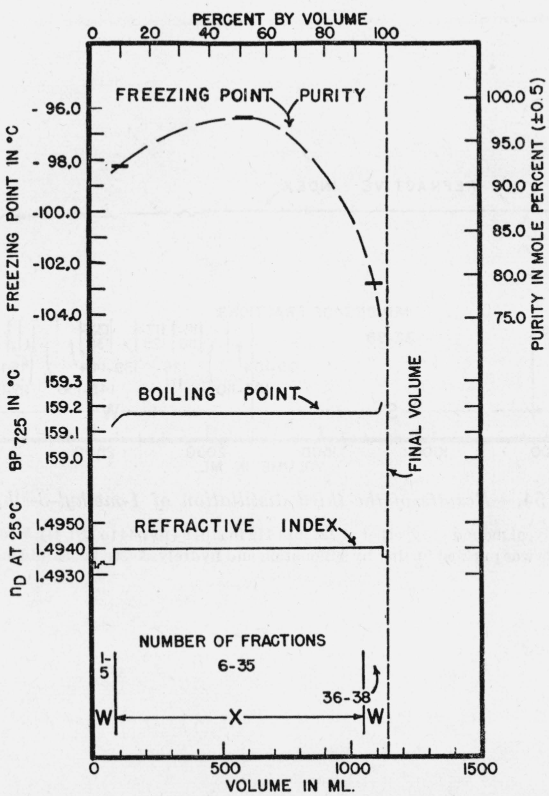

FIGURE 53.—*Results of the second distillation of 1-methyl-3-ethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 8 (4/11/44 to 4/24/44).

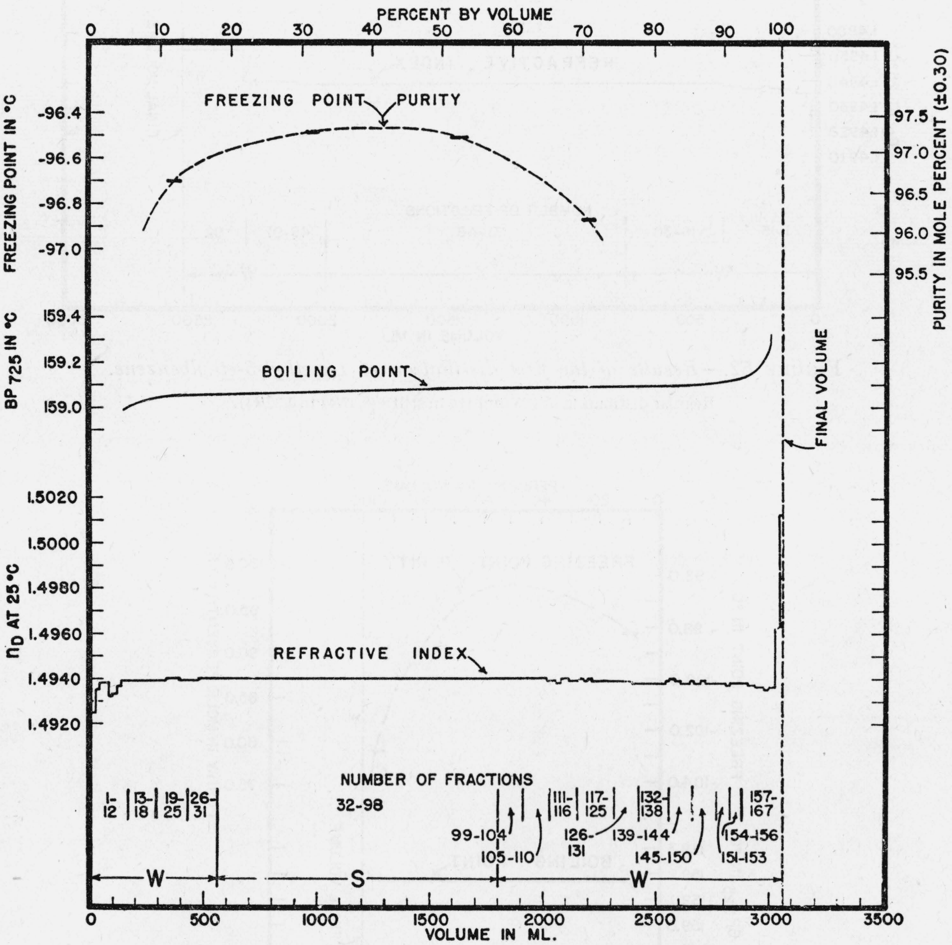

FIGURE 54.—*Results of the third distillation of 1-methyl-3-ethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 9 (10/2/44 to 11/1/44). See footnote "o" of table 1. The portion of the distillate marked "S" was purified further by sulfonation and hydrolysis (see fig. 55 and footnote "p" to table 1).

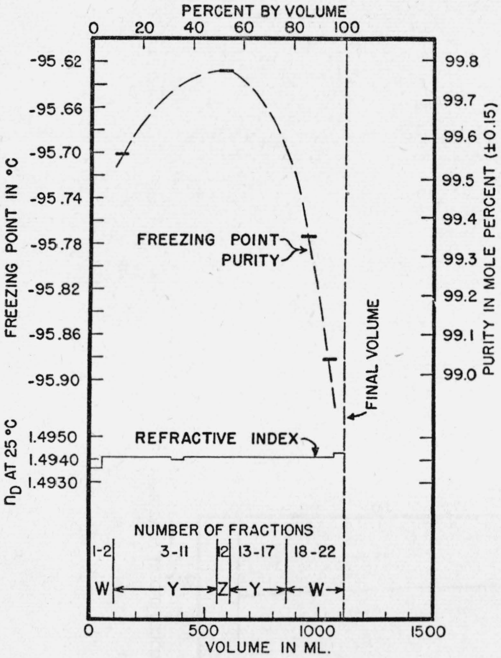

Figure 55.—*Results of final purification of 1-methyl-3-ethylbenzene by sulfonation and hydrolysis.*

See footnote "p" of table 1. (Purification performed 12/11/44).

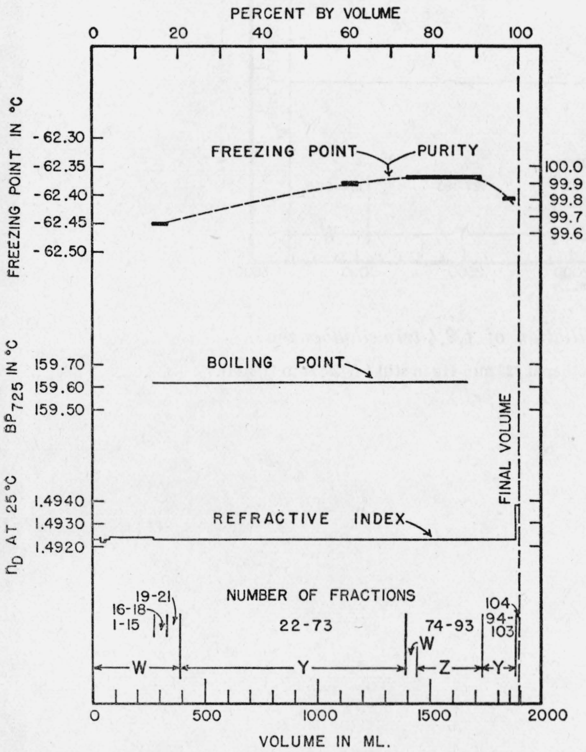

Figure 56.—*Results of first and only distillation of 1-methyl-4-ethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 12 (9/28/44 to 10/21/44). 50 ml of fractions 74 to 93 was returned to the supplier as a "best" sample.

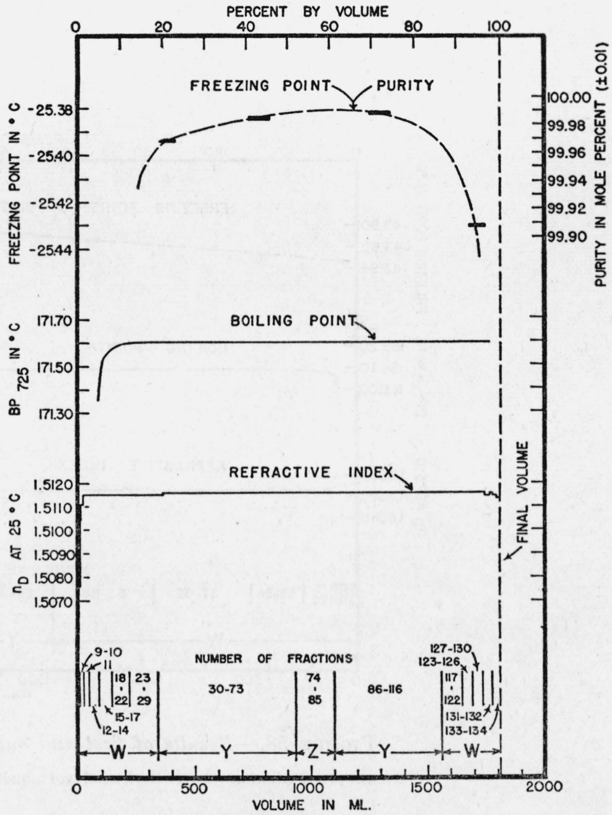

Figure 57.—*Results of first and only distillation of 1,2,3-trimethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 10 (4/24/45 to 5/18/45).

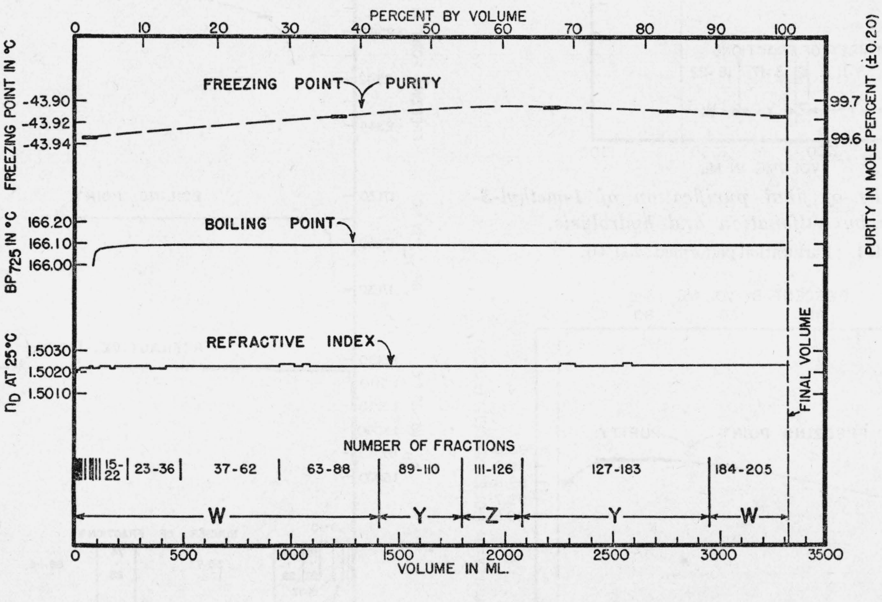

FIGURE 58.—*Results of first and only distillation of 1,2,4-trimethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 4 (9/29/44 to 11/4/44).

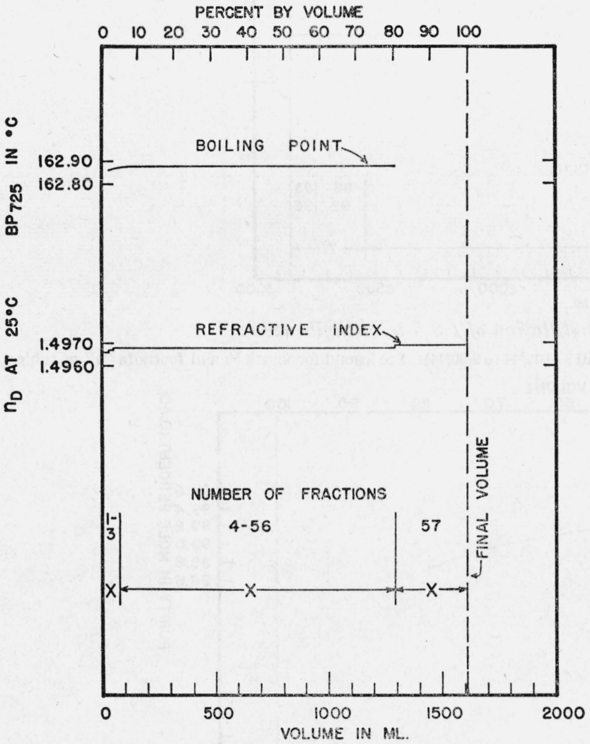

Figure 59.—*Results of the first distillation of 1,3,5-trimethylbenzene.*

Regular distillation at 725 mm Hg in still 8 (3/6/44 to 3/16/44). Fractions 1 to 3 and 57 were included in the charge for the third distillation of this hydrocarbon (see figure 61) and fractions 4 to 56 were redistilled in the second distillation (see figure 60).

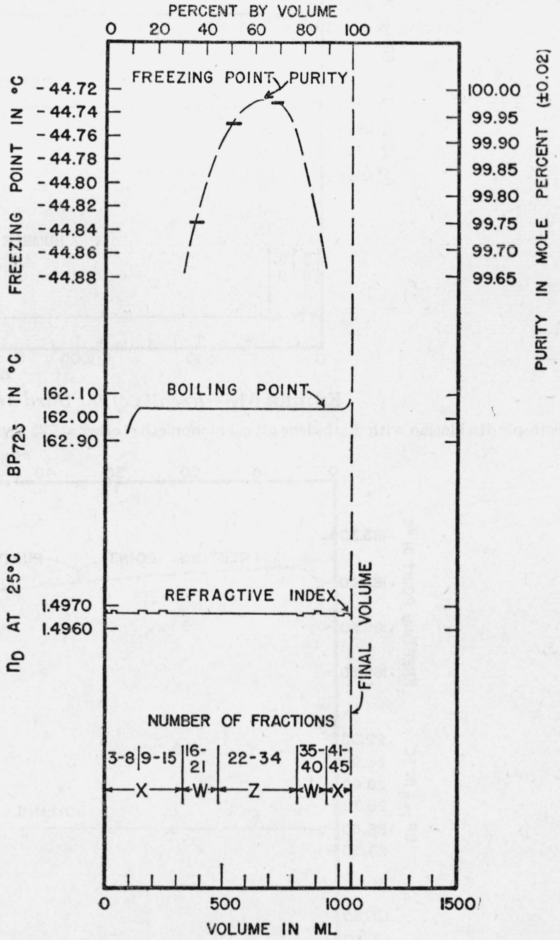

Figure 60.—*Results of the second distillation of 1,3,5-trimethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 8 (5/12/44 to 5/22/44). See legend for figure 59.

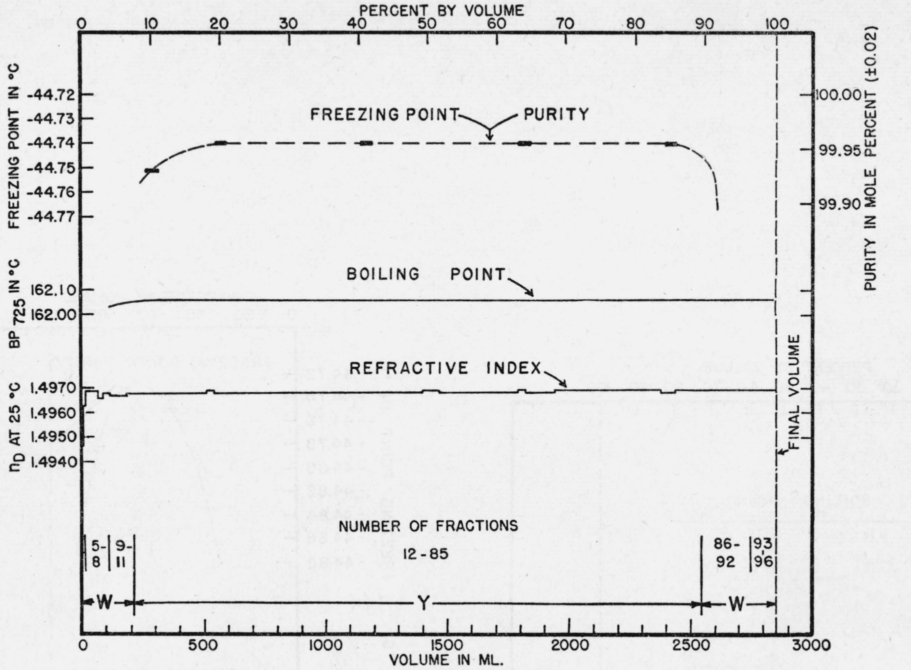

FIGURE 61.—*Results of the third and last distillation of 1,3,5-trimethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 8 (9/12/44 to 9/30/44). See legend for figure 59 and footnote "*q*" of table 1.

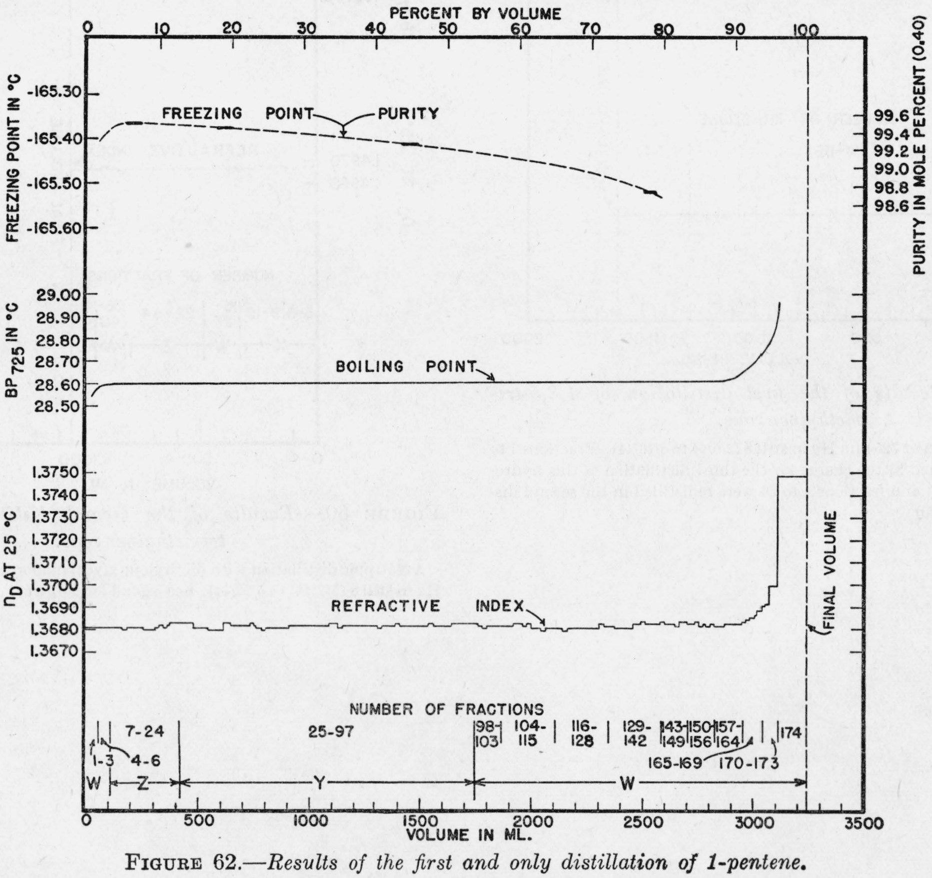

FIGURE 62.—*Results of the first and only distillation of 1-pentene.*

Regular distillation at 725 mm Hg in still 4 (1/9/45 to 2/12/45).

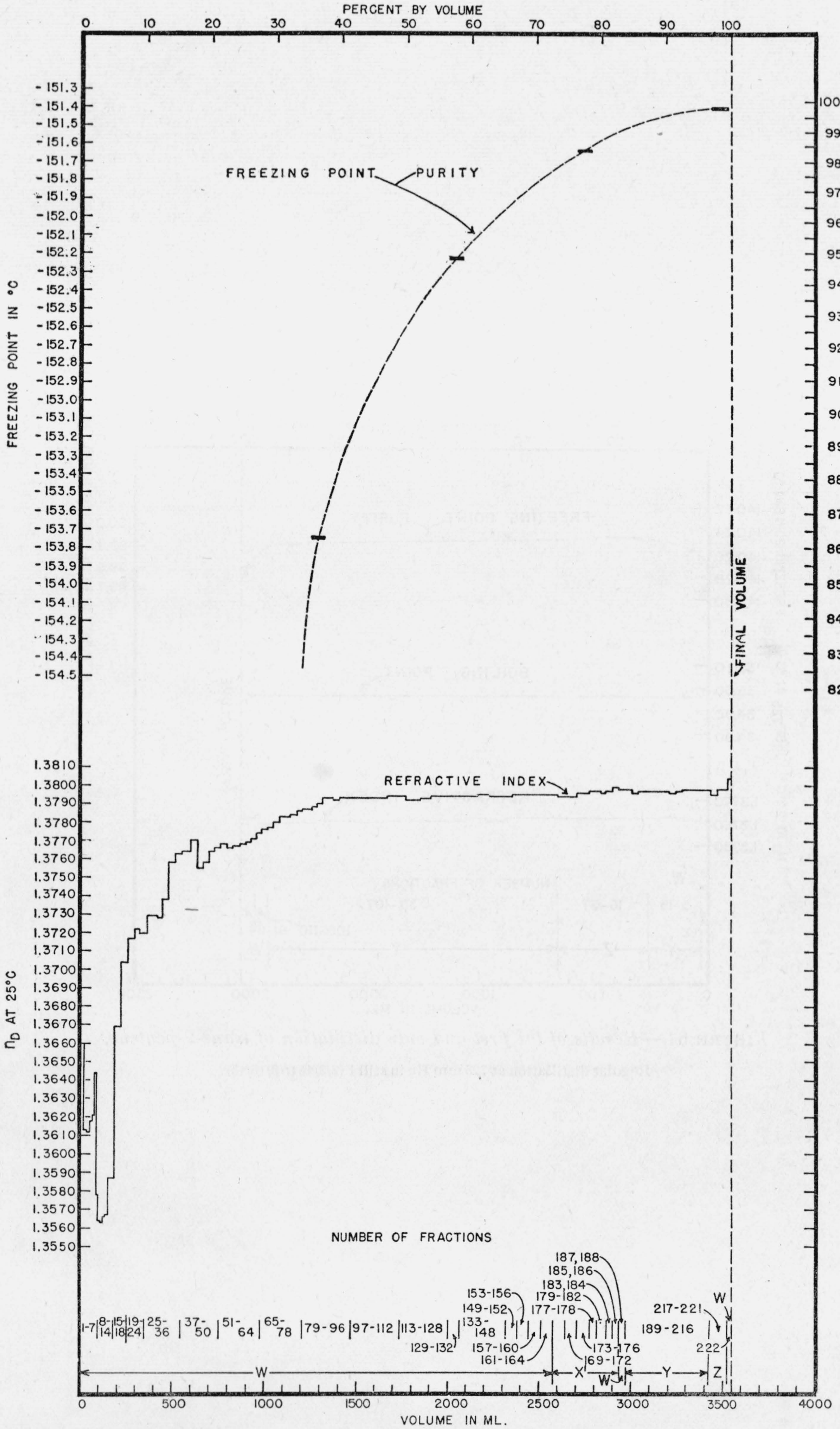

FIGURE 63.—*Results of the first and only distillation of cis-2-pentene.*

Azeotropic distillation with methanol at 725 mm Hg in still 4 (7/16/45 to 9/29/45). The portion maked "*X*" was retained for further processing by the API Research Project 6.

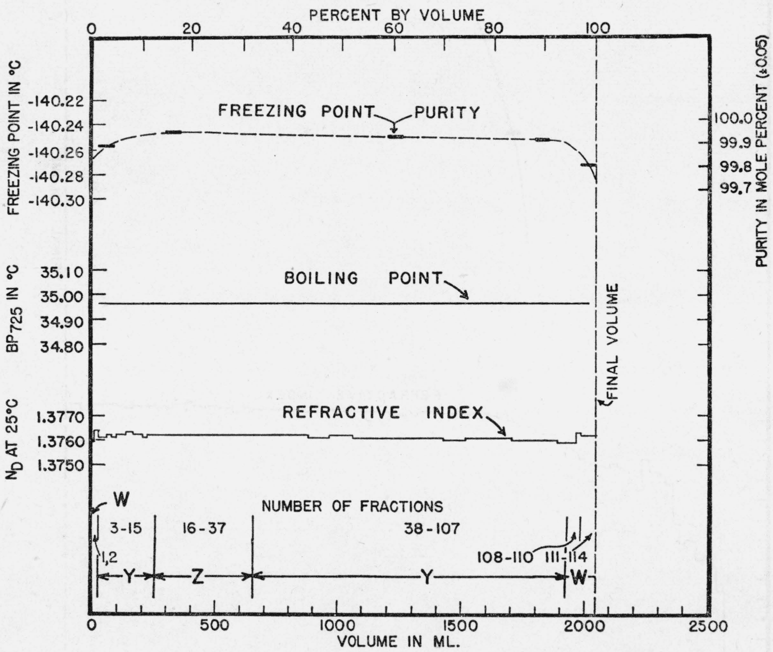

FIGURE 64.—*Results of the first and only distillation of trans-2-pentene.*

Regular distillation at 725 mm Hg in still 1 (2/3/45 to 3/16/45).

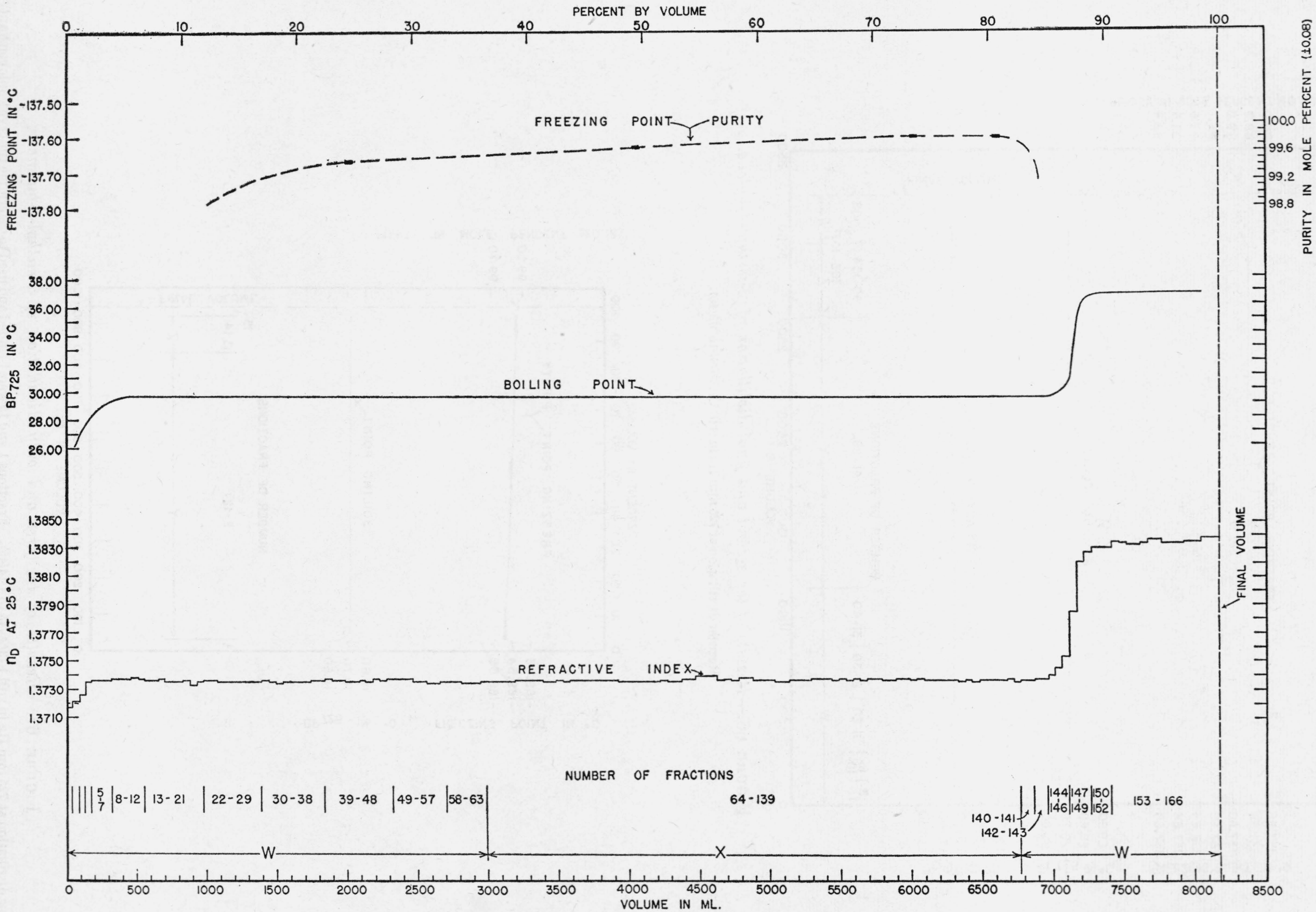

FIGURE 65.—*Results of the first distillation of 2-methyl-1-butene.*

Regular distillation at 725 mm Hg in still 5 (12/8/44 to 1/12/45).

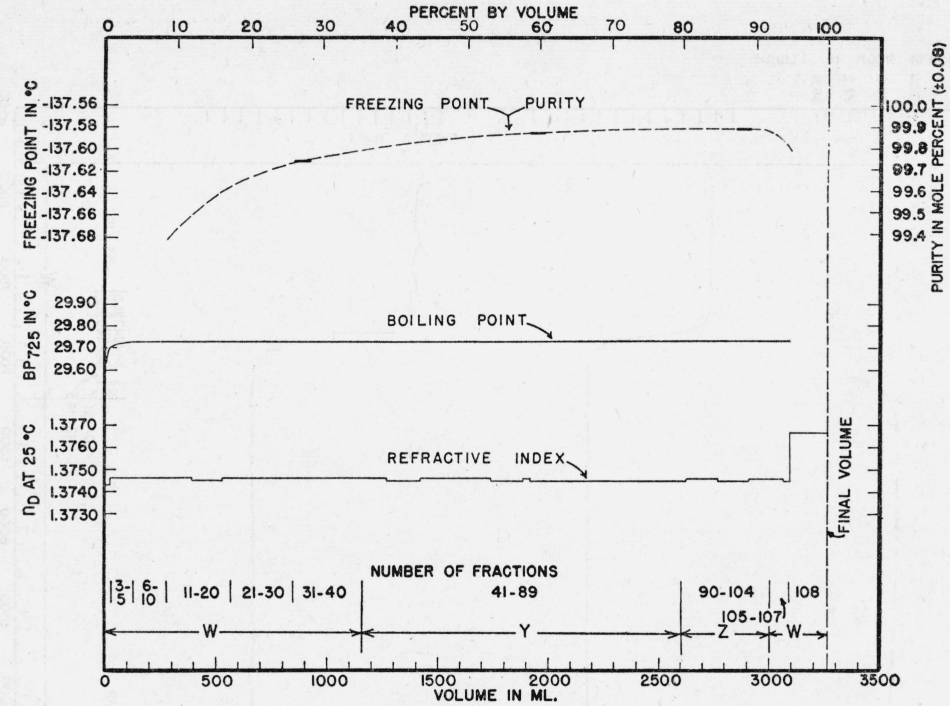

FIGURE 66.—*Results of the second and final distillation of 2-methyl-1-butene.*

Regular distillation at 725 mm Hg in still 13 (2/7/45 to 3/5/45).

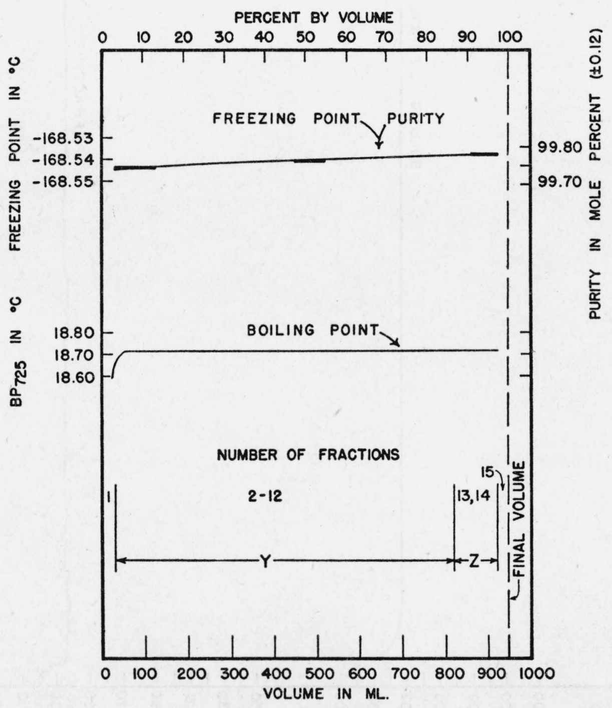

FIGURE 67.—*Results of the first and only distillation of 3-methyl-1-butene.*

Regular distillation at 725 mm Hg in still 1 (3/20/45 to 4/14/45). Fractions 1 and 15 were blended and used to determine the cryoscopic constant.

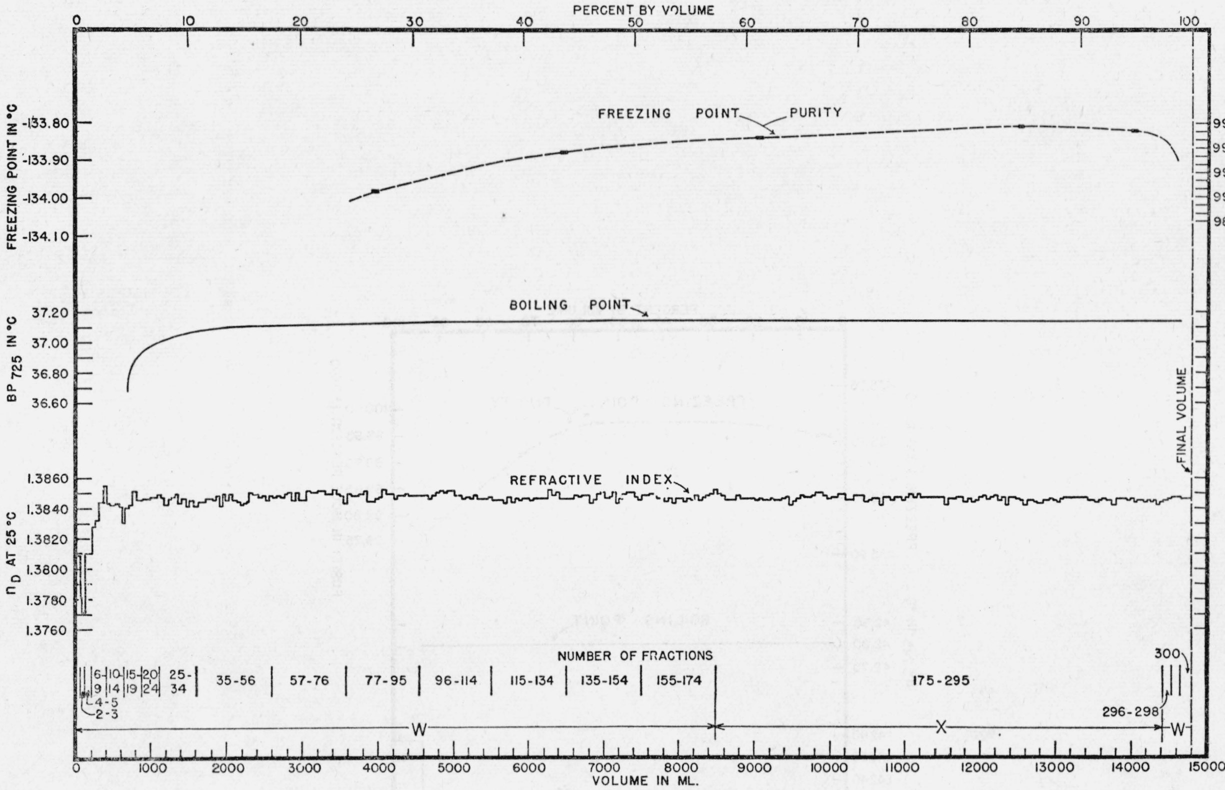

FIGURE 68.—*Results of the first distillation of 2-methyl-2-butene.*
Regular distillation at 725 mm Hg in still 6 (12/4/44 to 2/2/45).

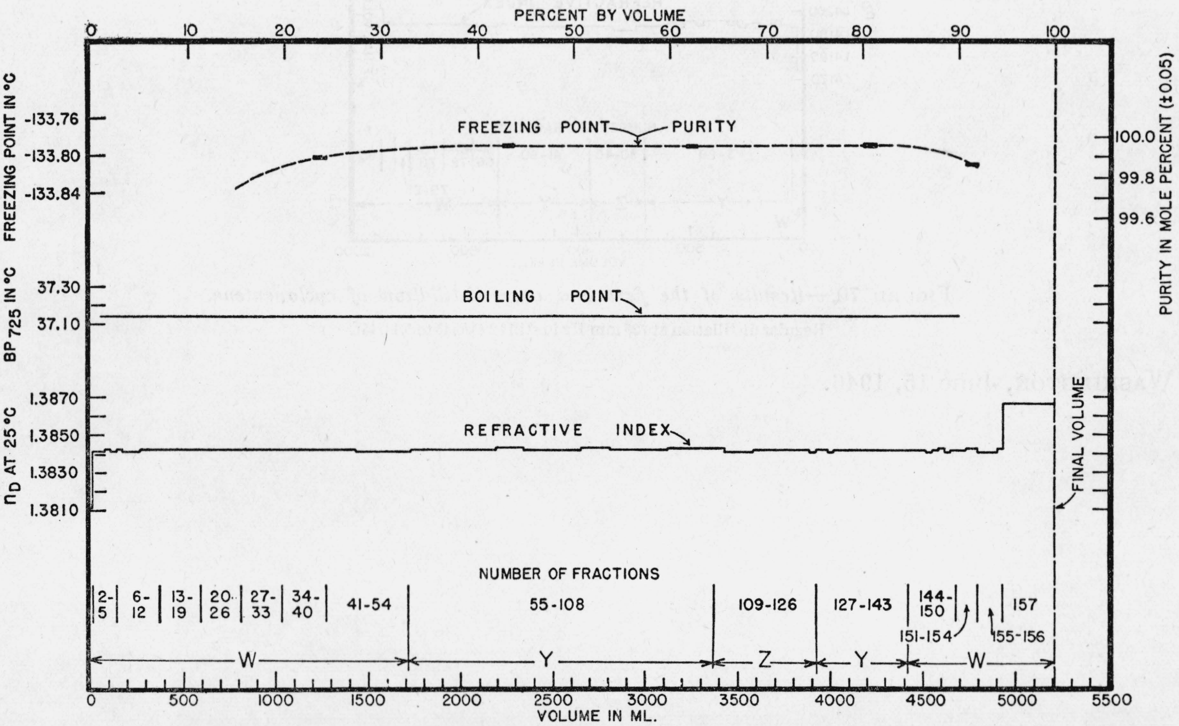

FIGURE 69.—*Results of the second and final distillation of 2-methyl-2-butene.*
Regular distillation at 725 mm Hg in still 8 (3/1/45 to 4/5/45).

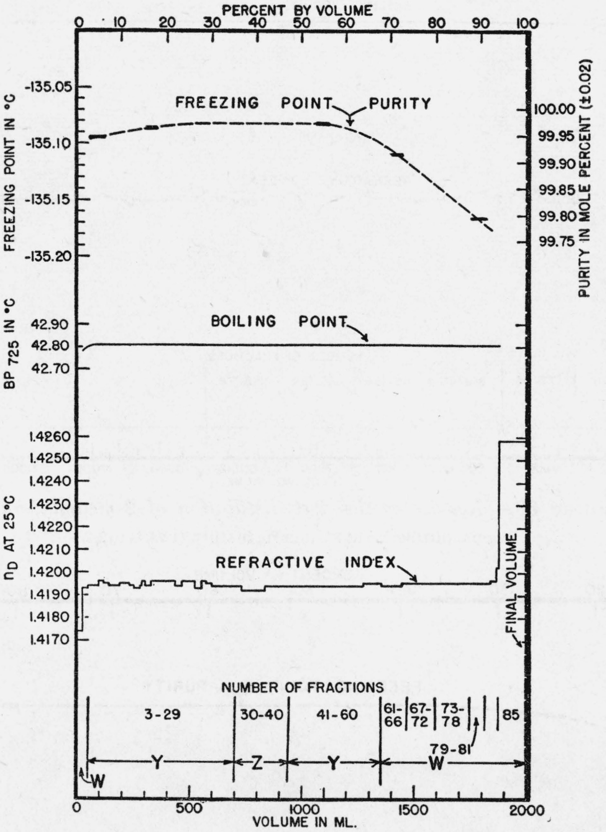

FIGURE 70.—*Results of the first and only distillation of cyclopentene.*

Regular distillation at 725 mm Hg in still 12 (4/6/45 to 5/14/45).

WASHINGTON, June 15, 1946.