[CONTRIBUTION FROM THE BAILEY CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Molecular Addition Compounds of the Group IVa Tetrachlorides with Diphenyl Ether and Anisole

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One of the most important factors involved in the formation of molecular addition compounds is the ability of molecules of one of the components to share pairs of electrons with molecules of the other component. Compound formation through the electron sharing mechanism depends upon the availability of a stable orbital on the acceptor atom, the availability of a pair of electrons on the donor atom, the electronegativities of the donor and acceptor atoms, and on various steric factors.

With the hope of arriving at a better understanding of the process of molecular addition compound formation, a study of various molecular addition compounds has been undertaken. This paper reports the results of a study of the systems of carbon tetrachloride, silicon tetrachloride, germanium tetrachloride, and tin tetrachloride with diphenyl ether and anisole, respectively.

Experimental

Preparation of Materials.—The carbon tetrachloride was purified by repeated fractionation at atmospheric pressure. The silicon tetrachloride was obtained from the Fairmount Chemical Company, and was purified by fractionation at atmospheric pressure. A middle fraction having a constant boiling point of 56° at 735 mm. pressure and freezing at −62.5° was taken. This freezing point is somewhat higher than that reported in the literature. Germanium tetrachloride, obtained from the Eagle-Pitcher Lead Co., was fractionated in the same manner, a middle fraction boiling at 82.2° at 741 mm. pressure and freezing at −49.5° being retained. J. T. Baker C. P. anhydrous tin tetrachloride was further purified by fractionation, a middle fraction boiling at 112° at 738 mm. pressure, and freezing at −30.5° being retained. In all these fractionations a five-foot packed column was used and the material was carefully protected against contact with moisture.

Diphenyl ether obtained from the City Chemical Corporation was purified by repeated recrystallization. The product used in these experiments had a melting point of 28°. Anisole obtained from the Eastman Kodak Company was dried by allowing it to stand over sodium and was purified by fractionation under reduced pressure. A middle fraction boiling at 99° under 130 mm. pressure and freezing at −37.4° was retained.

Procedure.—The systems were studied by the freezing point method, the freezing points being determined by means of cooling curves. The cell used in these experiments was similar to that in similar studies previously reported.[2] The thermocouple well was filled with a mixture of carbon tetrachloride and chloroform to minimize convection effects. The stirrer in the cell consisted of a stainless steel wire coil attached to an iron cylinder coated with stainless steel; the stirrer was operated by means of a solenoid which was wired through a motor driven interrupter, thus allowing constant stirring. Weighed quantities of the components of the system being studied were introduced from a Lunge pipet, the pipet having a ground glass surface of the same taper as the opening. While introducing a sample, another opening was open to the atmosphere through a drying tube filled with calcium chloride. A copper–constantan thermocouple attached to a Leeds–Northrup Micromax self-recording potentiometer was used to measure the temperatures and record the cooling curves; the apparatus was calibrated at the melting point of ice, the boiling point of ammonia, the freezing point of pyridine, the sublimation point of carbon dioxide and the boiling point of oxygen.

The various mixtures were cooled in an ice-salt-bath, in a Dry Ice–carbon tetrachloride–chloroform bath, or in liquid oxygen depending upon the freezing point for the particular mixture. The rate of cooling was regulated by surrounding the cell with one or more test-tubes of larger diameter. The break in the cooling curve was taken as the freezing point; in case of a small amount of supercooling, the level to which the temperature rose immediately after the first break in the curve was taken. Runs in which supercooling was considerable were discarded. All freezing points reported were redetermined at least once. In cases where the tendency to supercool was great, the mixtures were cooled until solidification took place, then warmed rapidly to a temperature just above the freezing point, and then cooled in the regular manner. The tendency toward supercooling was reduced by means of a platinum wire which penetrated the cell wall and thus provided a "cold spot" to start crystallization.

Data obtained by the above method are believed correct to ±1.5°.

The System Carbon Tetrachloride–Diphenyl Ether.—The data obtained for this system are listed in Table I and illustrated graphically in Fig. 1, Curve A. In this and other tables S refers to mole % of tetrachloride, T to freezing point (°C.).

TABLE I

CARBON TETRACHLORIDE–DIPHENYL ETHER

S	T	S	T	
(a) Solid Phase, $(C_6H_5)_2O$		64.4	−12.0	
		67.8	−13.0	
0.0	28.0	68.4	−14.0	
5.4	25.0	69.5	−15.0	
10.4	22.5	75.0	−20.0	
19.8	18.0	79.4	−24.0	
27.3	14.0	82.7	−28.0	
31.2	11.5	86.4	−34.0	−44.5[a]
35.1	9.0	91.0	−41.0	−44.5[a]
39.2	7.0	(b) Solid Phase, CCl_4		
44.5	4.0	93.4	−38.0	−44.5[a]
49.0	1.0	95.9	−30.0	
52.0	−1.0	97.7	−26.0	
55.6	−3.0	100.0	−23.0	
58.9	−6.0			

[a] Complete flattening of curves at this temperature indicates the eutectic equilibrium temperature.

No indication of compound formation is given by these data. The eutectic point occurs at 92 mole per cent. of carbon tetrachloride; a mixture of this composition is in equilibrium with solid

(1) Present address: The Ohio State University, Columbus, Ohio.

(2) Davidson, Sisler and Stoenner, THIS JOURNAL, 66, 779 (1944).

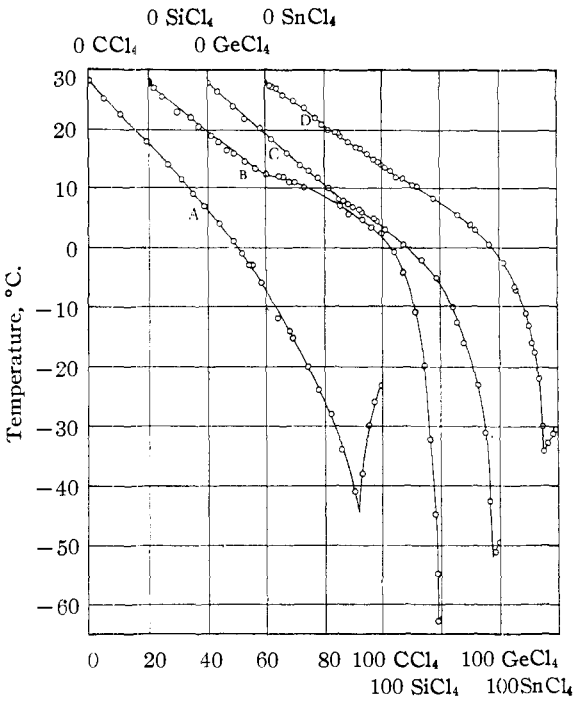


Fig. 1.—The systems diphenyl ether–MCl_4.

carbon tetrachloride and solid diphenyl ether at a temperature of −44.5°.

The System Silicon Tetrachloride–Diphenyl Ether.—The data obtained for this system are recorded in Table II and illustrated graphically in Fig. 1, Curve B.

TABLE II

SILICON TETRACHLORIDE–DIPHENYL ETHER

S	T	S	T	
(a) Solid Phase, $(C_6H_5)_2O$		46.4	12.0	
0.0	28.0	48.6	11.0	
2.4	27.0	50.3	11.0	
5.4	25.5	53.5	10.0	
10.4	23.5	65.8	7.0	
14.9	22.0	68.8	5.5	
17.8	20.5	73.4	4.5	
22.3	19.0	76.7	3.0	
24.2	18.0	80.2	2.0	
27.2	16.5	84.5	− 1.0	
29.5	16.0	87.3	− 4.5	
33.8	14.5	94.6	−20.0	
37.2	13.5	98.6	−45.0	−63.0[a]
		99.3	−63.0	
(b) Solid Phase, $2(C_6H_5)_2O{\cdot}SiCl_4$(?)		(c) Solid Phase, $SiCl_4$		
40.4	12.5	100.0	−62.5	
44.9	12.0			

[a] Complete flattening of the cooling curve at this temperature indicates the eutectic equilibrium temperature.

The data in Table II and Fig. 1, curve B, indicate that compound formation almost certainly occurs between silicon tetrachloride and diphenyl ether. However, since the compound does not melt congruently, its composition is not definitely indicated. Nevertheless, from the course of the curve, and a knowledge of the electronic structure of the molecules involved, it is probable that the mole ratio of the ether to the tetrachloride in the compound is 2:1. Extrapolation indicates that the melting point of the compound would probably be at about 13°. The compound undergoes transition to solid ether and solution at 12.5°. A eutectic point with silicon tetrachloride occurs at more than 99 mole per cent. of diphenyl ether and at a temperature of about −63°.

The System Germanium Tetrachloride–Diphenyl Ether.—The data obtained for this system are listed in Table III and recorded graphically in Fig. 1, curve C.

TABLE III

GERMANIUM TETRACHLORIDE–DIPHENYL ETHER

S	T	S	T	
(a) Solid Phase, $(C_6H_5)_2O$		49.7	7.0	
0.0	28.0	52.0	6.5	
3.6	26.5	52.5	6.0	
8.4	24.0	57.0	5.0	
12.4	22.0	57.4	4.8	
17.9	20.5	60.8	3.0	
21.6	18.5	66.8	0.5	
27.0	16.0	73.0	− 2.0	
31.5	14.0	78.5	− 5.0	
34.2	13.0	83.3	−10.0	
37.7	12.0	85.2	−12.5	
41.0	10.0	87.9	−16.0	
		92.4	−23.0	
(b) Solid Phase, $2(C_6H_5)_2O{\cdot}GeCl_4$(?)		95.1	−31.0	
		96.9	−42.5	−52.0[a]
45.0	8.7	(c) Solid Phase, $GeCl_4$		
46.3	8.0	98.9	−51.0	−52.0[a]
48.1	7.5	100.0	−49.7	

[a] Complete flattening of cooling curve indicates the eutectic temperature.

The general shape of the curve C in Fig. 1 is very similar to that for the silicon tetrachloride–diphenyl ether system except that the tendency toward compound formation is less pronounced. Assuming that a compound of the formula $2(C_6H_5)_2O{\cdot}GeCl_4$ is formed, which is by no means certain from the freezing point data, extrapolation indicates that the compound probably would have a melting point of about 10°. It apparently undergoes transition to solid diphenyl ether and solution at about 9°, and forms a eutectic with germanium tetrachloride at about 98 mole per cent. of the tetrachloride and at a temperature close to −52°.

The System Tin Tetrachloride–Diphenyl Ether.—Data obtained for this system are recorded in Table IV and Fig. 1, curve D.

The curve obtained for the tin tetrachloride–diphenyl ether system is similar to that obtained for the systems of silicon and germanium tetra-

TABLE IV

TIN TETRACHLORIDE–DIPHENYL ETHER

S	T	S	T	
(a) Solid Phase, $(C_6H_5)_2O$		(b) Solid Phase, $2(C_6H_5)_2O{\cdot}SnCl_4$(?)		
0.0	28.0	46.9	11.8	
1.7	27.5	50.0	10.7	
2.0	27.0	52.1	10.5	
4.1	27.0	57.7	8.5	
5.9	26.0	65.8	5.5	
9.6	25.0	70.3	4.0	
13.4	23.7	72.0	3.0	
17.0	22.0	76.9	0.5	
18.9	21.0	81.4	− 2.5	
20.2	20.5	85.5	− 6.5	
21.9	20.0	89.6	−11.0	
23.9	19.5	90.4	−13.0	
25.0	19.5	91.5	−16.0	
25.7	19.0	92.0	−17.5	
28.4	18.0	93.9	−22.0	
30.9	17.0	95.4	−30.0	−34.0[a]
32.3	17.0			
34.8	16.0	(c) Eutectic		
37.0	15.0	96.2	−34.0[a]	
38.3	14.5			
39.5	14.0	(d) Solid Phase, $SnCl_4$		
40.8	13.5	97.3	−33.0	−34.0[a]
42.4	13.0	98.9	−31.0	
44.7	12.0	100.0	−30.5	

[a] Complete flattening of cooling curve indicates the eutectic temperature.

chloride with the same base. As in the case of germanium tetrachloride the tendency for tin tetrachloride to form a compound with diphenyl ether appears to be less than for silicon tetrachloride. It appears, however, that a compound unstable at its melting point and undergoing transition into the solid ether and solution at about 12°, is formed. If we assume the compound to be $2(C_6H_5)_2O{\cdot}SnCl_4$; extrapolation indicates that its melting point would be at about 13°. The compound forms a eutectic with the tetrachloride at about 96 mole per cent. of tin tetrachloride and at a temperature of −34°.

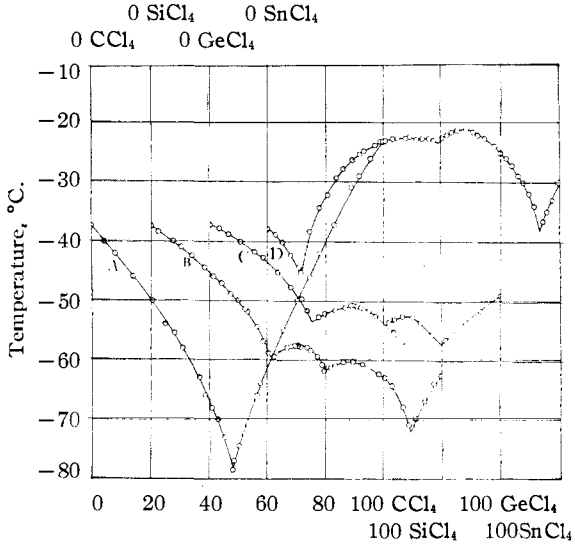
TABLE V

CARBON TETRACHLORIDE–ANISOLE

S	T		S	T	
(a) Solid Phase, $C_6H_5OCH_3$			(b) Solid Phase, CCl_4		
0.0	−37.5		49.2	−77.0	−78.5[a]
4.1	−40.0		51.2	−74.5	
8.5	−42.0		57.3	−66.0	
14.3	−46.0		58.5	−64.0	
20.7	−50.0		66.2	−55.0	
25.4	−54.0		70.9	−50.0	
28.7	−55.5		75.2	−46.0	
31.5	−58.0		78.4	−42.0	
37.2	−63.0		83.3	−37.0	
39.6	−66.0	−78.5[a]	89.1	−31.0	
41.4	−67.0		91.9	−29.0	
43.8	−70.0	−78.5[a]	95.8	−26.0	
46.1	−73.0	−78.5[a]	100.0	−23.0	

[a] Complete flattening of curve indicates the eutectic temperature.

The System Carbon Tetrachloride–Anisole.—The data obtained for this system are listed in Table V and recorded graphically in Fig. 2, curve A.



Mole per cent. tetrachloride.

Fig. 2.—The systems anisole–MCl_4.

The data presented in Table V and Fig. 2, curve A, indicate no tendency toward compound formation between carbon tetrachloride and ani-

TABLE VI

SILICON TETRACHLORIDE–ANISOLE

S	T		S	T	
(a) Solid Phase, $C_6H_5OCH_3$			53.6	−58.0	
0.0	−37.5		55.0	−58.5	
2.8	−38.5		57.3	−59.5	
7.5	−40.0		59.4	−61.0	−62.0[a]
10.2	−41.0		(c) Solid Phase, $C_6H_5OCH_3{\cdot}2SiCl_4$		
14.2	−42.5		61.8	−61.5	
18.6	−44.5		63.5	−61.0	
21.6	−46.0		66.1	−60.5	
24.6	−47.0		69.2	−60.5	
27.9	−49.0		72.7	−61.0	
30.0	−50.0		78.1	−62.0	
32.6	−51.5		80.2	−63.0	
33.5	−52.0		83.1	−64.5	−72.5[a]
36.2	−54.5		87.0	−68.0	−72.5[a]
38.9	−57.0		88.7	−71.0	
40.8	−59.0	−59.5[a]	(d) Solid Phase, $SiCl_4$		
(b) Solid Phase, $C_6H_5OCH_3{\cdot}SiCl_4$			91.0	−70.0	−72.5[a]
42.7	−59.0	−59.5[a]	94.5	−67.0	
47.3	−58.0		97.6	−64.0	
49.5	−57.8		100.0	−62.5	
50.9	−57.7				
51.5	−58.0				

[a] Complete flattening of cooling curve indicates a eutectic temperature.

sole. The eutectic point occurs at about 49 mole per cent. of carbon tetrachloride and at a temperature of about −78.5°. Carbon tetrachloride undergoes a phase transition at about −48°, but this produced only an almost imperceptible irregularity in the freezing point curve.

The System Silicon Tetrachloride–Anisole.—Data obtained for this system are presented in Table VI and Fig. 2, curve B.

The data presented in Table VI and in Fig. 2, curve B indicate that silicon tetrachloride and anisole react to form the compounds $C_6H_5OCH_3 \cdot SiCl_4$ and $C_6H_5OCH_3 \cdot 2SiCl_4$, which have melting points of about −58 and −60.5°, respectively. Eutectic points are obtained at 41 mole per cent. of silicon tetrachloride and a temperature of −59.5°, at 61 mole per cent. of silicon tetrachloride and a temperature of −620°, and at 89 mole percent. of silicon tetrachloride and a temperature of −72.5°.

The System Germanium Tetrachloride–Anisole.—Data for this system are presented in Table VII and Fig. 2, curve C.

TABLE VII

GERMANIUM TETRACHLORIDE–ANISOLE

S	T	
(a) Solid Phase, $C_6H_5OCH_3$		
0.0	−37.5	
3.3	−38.0	
6.6	−39.0	
10.8	−40.5	
15.9	−42.0	
18.4	−43.0	
23.6	−45.5	
28.0	−48.0	
31.2	−50.0	
33.8	−52.0	−54.0[a]
(b) Solid Phase, $C_6H_5OCH_3 \cdot GeCl_4$		
37.6	−53.0	
39.5	−52.5	
40.0	−52.5	
43.5	−52.0	
46.5	−51.5	
48.5	−51.0	
49.7	−51.0	
50.3	−51.0	
52.0	−51.5	
55.1	−52.0	
57.6	−53.0	
(c) Solid Phase, $C_6H_5OCH_3 \cdot 2GeCl_4$		
61.6	−54.0	
63.5	−53.5	−55.5[b]
66.9	−53.0	−58.0[b]
67.3	−53.0	
70.0	−53.0	
72.3	−54.0	
76.6	−56.0	−58.0[a]
(d) Solid Phase, $GeCl_4$		
81.0	−57.0	−58.0[a]
88.0	−54.0	
93.2	−52.0	
100.0	−49.5	

[a] Complete flattening of cooling curve indicates a eutectic temperature. [b] Metastable equilibria.

The data presented in Table VII and Fig. 2 curve C indicate the formation of the compounds $C_6H_5OCH_3 \cdot GeCl_4$ and $C_6H_5OCH_3 \cdot 2GeCl_4$ having melting points of −51° and −53°, respectively. Eutectic points occur at about 35 mole per cent. of germanium tetrachloride and a temperature of −54°, at about 60 mole per cent. of the tetrachloride and −54.5°, and at about 79 mole per cent. of the tetrachloride and a temperature of −58°.

The System Tin Tetrachloride–Anisole.—Data obtained for this system are listed in Table VIII and recorded graphically in Fig. 2, curve D.

TABLE VIII

TIN TETRACHLORIDE–ANISOLE

S	T	
(a) $C_6H_5OCH_3$		
0.0	−37.5	
2.6	−38.5	
5.1	−40.0	−45.0[a]
7.9	−42.0	−45.0[a]
10.2	−44.0	
(b) Eutectic		
11.1	−45.0[a]	
(c) Solid Phase, $C_6H_5OCH_3 \cdot SnCl_4$		
14.2	−38.0	−45.0[a]
17.8	−34.0	
20.5	−32.0	
23.4	−29.0	
29.0	−26.0	
31.4	−25.0	
33.0	−24.5	
36.4	−23.5	
40.0	−23.0	
44.6	−22.3	
47.5	−22.4	
48.5	−22.3	
50.8	−22.5	
51.0	−22.5	
53.0	−22.5	
55.1	−22.7	
56.8	−23.0	
(d) Solid Phase, $C_6H_5OCH_3 \cdot 2SnCl_4$		
60.0	−22.5	
61.3	−22.0	
63.2	−21.5	
65.0	−21.3	
68.0	−21.0	
70.4	−21.5	
72.0	−22.0	
74.4	−22.5	
77.6	−24.0	
79.6	−25.0	
81.5	−26.0	
83.6	−27.0	
85.7	−29.0	
87.6	−30.0	
89.5	−32.0	
91.4	−34.0	−38.5[a]
(e) Solid Phase, $SnCl_4$		
93.5	−38.0	
94.5	−36.5	
95.9	−35.0	−38.5[a]
97.2	−33.0	
98.9	−31.5	
100.0	−30.5	

[a] Complete flattening of cooling curve indicates a eutectic point.

The data presented in Table VIII and Fig. 2, curve D indicate formation of the compounds $C_6H_5OCH_3 \cdot SnCl_4$ and $C_6H_5OCH_3 \cdot 2SnCl_4$ with melting points of about −22 and −21°, respectively. Eutectic points occur at about 11 mole per cent. of tin tetrachloride and a temperature of −45°, at 58 mole per cent. and −23°, and at 93 mole per cent. and −38.5°.

Discussion

Summarizing the results of the experiments presented in this paper, we may state the following observations: (a) carbon tetrachloride does not react either with diphenyl ether or with anisole; (b) diphenyl ether probably reacts with the other three tetrachlorides to form compounds presumably of the formula $2(C_6H_5)_2O \cdot MCl_4$; and (c) anisole reacts with the other three tetrachlorides to form, in each case, compounds of the formulas $C_6H_5OCH_3 \cdot MCl_4$ and $C_6H_5OCH_3 \cdot 2MCl_4$. Because of the complex nature of these phenomena, a thorough theoretical interpretation of these experimental results must await the gathering of more experimental data. Further studies are now in progress.

Certain points may be considered at this time, however. It is interesting to note that carbon tetrachloride shows no tendency toward compound formation with either anisole or diphenyl ether

whereas all the other three tetrachlorides show at least a small tendency toward compound formation with both of these ethers. This would tend to lead one to the conclusion that the availability of a stable orbital on the central atom of the tetrachloride plays a major role in compound formation in these systems. The carbon atom in carbon tetrachloride has no such stable orbital available.

The fact that anisole has a much stronger tendency than diphenyl ether to react with the tetrachlorides is interesting in light of the fact that a phenyl group has a greater electron withdrawing effect than a methyl group. The electron density about the oxygen atom in diphenyl ether is, therefore, less than about the oxygen atom in anisole; hence, anisole would be expected to have a greater tendency to share a pair of electrons than diphenyl.

The effects of the differences in the electronegativities of carbon, silicon, germanium, and tin, as well as various steric effects are undoubtedly of some significance in interpreting the results obtained in this study. It is hoped that further studies will, to some extent at least, aid in the evaluation and delineation of these effects.

Summary

1. The systems of carbon tetrachloride, silicon tetrachloride, germanium tetrachloride and tin tetrachloride with diphenyl ether and anisole, respectively, have been studied throughout the entire concentration range. Carbon tetrachloride showed no tendency toward compound formation with either of these ethers.

2. The existence of the compounds $C_6H_5OCH_3 \cdot SiCl_4$, $C_6H_5OCH_3 \cdot GeCl_4$, $C_6H_5OCH_3 \cdot SnCl_4$, $C_6H_5OCH_3 \cdot 2SiCl_4$, $C_6H_5OCH_3 \cdot 2GeCl_4$ and $C_6H_5OCH_3 \cdot 2SnCl_4$ has been demonstrated.

3. The probable existence of addition compounds of diphenyl ether with silicon tetrachloride, germanium tetrachloride, and tin tetrachloride, presumably of the general formula $2(C_6H_5)_2O \cdot MCl_4$, has been indicated.

COLUMBUS, OHIO RECEIVED SEPTEMBER 23, 1946

[CONTRIBUTION NO. 6 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

The Heat Capacities, Heats of Fusion and Entropies of the Six Pentenes[1]

BY SAMUEL S. TODD, GEORGE D. OLIVER AND HUGH M. HUFFMAN

In continuation of the program[2] of the Bureau of Mines to obtain systematically thermodynamic data on hydrocarbons and related compounds, low-temperature calorimetric studies have been made on the six pentenes over the temperature range 12 to 300 K.

Parks and Huffman[3] have studied 2-methyl-2-butene over the temperature range 93 to 294° K. and also have made measurements on the liquid form of a substance they called pentene-2, which was apparently a mixture of *cis*- and *trans*-2-pentene. Because of incomplete crystallization of this mixture they were unable to calculate a value for its entropy.

The Materials

The hydrocarbons used in this investigation were A.P.I.-N.B.S. samples purified by A.P.I. Research Project 6 at the National Bureau of Standards.[4] The methods of purification and estimates of the purity are given in a report[5] by A.P.I. Research Project 6 (at the National Bureau of Standards).

The Apparatus.—The measurements were made in the apparatus described by Ruehrwein and Huffman,[6] which was loaned to the Bureau of Mines by the California Institute of Technology. Very briefly, the method is as follows: About 0.5 mole of the material under investigation was contained in a sealed copper calorimeter, which was mounted in the adiabatic calorimetric system. A measured amount of electrical energy was supplied to the calorimeter, and at all times the temperature of the environment was maintained at that of the calorimeter to prevent heat interchange. The initial and final temperatures of the calorimeter were meas-

(1) Published by permission of the Director, Bureau of Mines, U. S. Dept. of the Interior.

(2) Douslin and Huffman, THIS JOURNAL, **68**, 173 (1946).

(3) Parks and Huffman, *ibid.*, **52**, 4381 (1930).

(4) These samples of API-NBS hydrocarbons have been made available by the American Petroleum Institute and the National Bureau of Standards through the A.P.I. Research Project 44 on the "Collection, analysis, and calculation of data on the properties of hydrocarbons." The samples were purified at the National Bureau of Standards by the A. P. I. Research Project 6 on the "Analysis, purification and properties of hydrocarbons," under the supervision of Frederick D. Rossini, from material supplied by the following laboratories:

1-Pentene, by the Phillips Petroleum Company, Bartlesville, Okla., through the courtesy of F. E. Frey.

***cis*-2-Pentene** and ***trans*-2-pentene**, by the A. P. I. Research Project 45 on the "Synthesis and properties of hydrocarbons of low molecular weight" at the Ohio State University, under supervision of Cecil E. Boord.

2-Methyl-1-butene and **2-methyl-2-butene**, by the General Motors Corporation, through the courtesy of T. A. Boyd and Wheeler G. Lovell.

3-Methyl-1-butene, by the Houdry Process Corporation through the courtesy of E. A. Smith.

(5) Streiff, Murphy, Sedlak, Willingham and Rossini, *J. Research Natl. Bur. Standards*, **37**, 331 (1946).

(6) Ruehrwein and Huffman, THIS JOURNAL, **65**, 1620 (1943).