AD-776 990

THERMODYNAMIC AND KINETIC DATA OF CARBON-FLUORINE COMPOUNDS

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Rice University

Prepared for:

Army Electronics Command

March 1974

AD 776 990

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Rice University Houston, Texas 77001	Unclassified
	2b. GROUP

3. REPORT TITLE

Thermodynamic and Kinetic Data of Carbon-Fluorine Compounds

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final Report – November 1, 1972 – December 31, 1973

5. AUTHOR(S) (First name, middle initial, last name)

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6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
MARCH 1974	35	12

8a. CONTRACT OR GRANT NO	9a. ORIGINATOR'S REPORT NUMBER(S)
DAAB07-73-C-0056	410041
b. PROJECT NO. C8-3-04251-01-C8-CA	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	ECOM-0056-F

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	U.S. Army Electronics Command Attn: AMSEL-TL-PR Fort, Monmouth, New Jersey 07703

13. ABSTRACT

Samples of the solid fluorocarbons $CF_{0.597}$ and $CF_{0.2369}$ have been prepared and studied to learn more about their thermodynamic properties. Low temperature heat capacity measurements have been made for both of these samples using a hydrogen cryostat calorimeter. For the compound $CF_{0.2369}$, C_p has been measured over the temperature range 15 –309 K. For the compound $CF_{0.597}$, C_p has been measured over the temperature range 20 – 270 K, and in two other series of measurements over the range 60 – 200 K. Smoothed thermodynamic functions have been calculated for these compounds over the 20–300 K temperature range.

The value of $\Delta H^{o}_{f298}(CF_{0.597})$ has been determined by fluorine bomb calorimetry. This datum, coupled with the $\Delta H^{o}_{f298}(CF_{0.2369})$ permits the calculation of a value of E^{o} for the electrochemical processes $CF_{0.2369}(s) + 0.2369\ Li\ (s) \rightarrow 0.2369\ LiF(s) + C\ (s)$ and $CF_{0.597}(s) + 0.597\ Li\ (s) \rightarrow 0.597\ LiF(s) + C\ (s)$.

In order to gather fundamental data to explain the kinetics of the cathode reaction in cells utilizing CF_x (where X = 0.6 to 1.1, or higher), surface area measurements were made on the samples $CF_{1.12}$, $CF_{0.597}$ and $CF_{1.17}$.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Graphite-Fluorine Compounds						
Fluorocarbons						
Polycarbonmonofluoride						
Tetracarbon monofluoride						
Heat Capacities						
Heat of Formation						
Free Energy of Reaction						
Electromotive Force						
Low Temperature Heat Capacities						

THERMODYNAMIC AND KINETIC DATA

OF CARBON-FLUORINE COMPOUNDS

FINAL REPORT

1 NOVEMBER 1972 - 31 DECEMBER 1973

CONTRACT NO. DAAB07-73-C-0056

DA Project No. C8-3-04251-01-C8-CA

Prepared by

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For
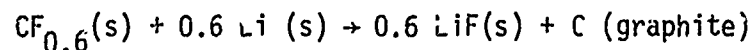U. S. ARMY ELECTRONICS COMMAND, FORT MONMOUTH, N. J.

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INTRODUCTION

The purpose of the research reported herein has been to prepare pure samples of the solid fluorocarbons $CF_{0.6}$, C_4F and $CF_{1.17}$, and to measure certain of their physical properties in order to learn more about their reactions with lithium in an electrochemical cell. These reactions can be written as the idealized processes:

$$CF_{0.6}(s) + 0.6 \; Li \; (s) \rightarrow 0.6 \; LiF(s) + C \; (graphite)$$

and,

$$C_4F \; (s) + Li \; (s) \rightarrow LiF(s) + 4 \; C \; (graphite)$$

In the report that follows, the $CF_{0.6}$ compound was found by chemical analysis to be $CF_{0.597}$, while the C_4F compound was found to be $CF_{0.2369}$. The derived thermodynamic quantities, $S°$, $G°$, and $\Delta H_f°$ 298.16 were based on these formulas. Only the bulk surface area was measured for the compound $CF_{1.17}$.

The description of the experimental work and the results have been divided into four parts. Part I describes the preparation of the samples. Part II describes the low temperature calorimetry of the solid fluorocarbons. Part III describes the fluorine combustion calorimetry of the fluorocarbon $CF_{0.6}$, and Part IV describes the surface area measurements of these solid fluorocarbons.

Part I.   PREPARATION OF SAMPLES

1.   Preparation of $CF_{0.597}$

Spectroscopic grade powdered graphite (Carbon Products Division, Union Carbide Corporation, SP-2) was spread over nickel trays which had already accumulated a layer of NiF. The trays were placed inside a 3 inch i.d. nickel reactor and heated to $452 \pm 2°C$ for the duration of the fluorination. Nitrogen was passed during the heating to the operating temperature in order to dry the graphite and flush out any oxygen contained in the reactor.

A fluorine-nitrogen mixture of 10 cc/min. fluorine and 10 cc/min. nitrogen was started after the reaction temperature had been reached. This mixture was passed until the number of moles of F_2 passed was equal to number of moles of carbon used. This mixture was also allowed to flow while the reactor was cooled to room temperature. The grey product obtained was then sieved through a 140 mesh screen.

The NiF_2 impurities introduced in the preparation were removed by use of the powder classifier described in an earlier report.[1]

2.   Preparation of $CF_{1.17}$

It has been observed in this laboratory that when powdered graphite samples intended for white CF production are heated to a higher temperature range, such as 640-645°C, a very fluffy white material collects at the outlet of the reactor (all other reaction conditions are as those described in Part I above.) A sample of this type was collected and its surface area was measured. This experiment is described in Part IV.

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Part I. LOW TEMPERATURE CALORIMETRY OF THE SOLID FLUOROCARBONS, $CF_{0.2369}(C_4F)$ and $CF_{0.597}$

1.   Apparatus

a.   Cryostat

The cryostat used in this research has been described in the previous report.[1]

b.   Sample container

The sample container used in this research has been described in the previous report.[1]

A new sample container heater was constructed prior to taking the heat capacity measurements on the $CF_{0.597}$ sample. A hollow copper spool slightly smaller in diameter than the heater well of the sample container was fabricated. Approximately 11 feet of 0.0089 inch diameter enameled Evanohm resistance wire was noninductively wound around the spool. The winding was bonded in place with Formvar enamel. The heater assembly was soldered in the heater well with a small amount of Wood's alloy. The heater resistance was found to be 107 ohms. The thermal conductance between the sample container and the heater was found to be markedly superior to that of the old heater configuration. In addition, the Evanohm wire has superior resistance-temperature characteristics as compared to the manganin wire which was used in the old heater.

The internal volume of the sample container is the same as before, 75 cm^3, but the weight complete with heater, thermometer and leads has increased to 88.4 g.

The heat capacity of the sample container was redetermined over the temperature range of 15 to 315 K.

c.   Thermometer and temperature scale

The same thermometer and temperature scale corrections described previously were used in this work. All results reported herein are on the IPTS-68.

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d.   Measurements

The potential measurement apparatus was modified by replacing the Beckman Model 14 D.C. Breaker Amplifier with a Leeds and Northrup Model 9828-3 D.C. Null Detector. The temperature and power circuitry remain as described before.[1]

2.   The Fluorocarbon $CF_{0.2369}$ (C_4F)

a.   Sample

The material used is that described previously.[1]

b.   Heat Capacity and Thermodynamic Functions

Details of the loading of the sample container and the results of heat capacity studies in the temperature range between 15 and 57 K were given previously.[1]

The heat capacity was subsequently measured in the temperature range between 58 and 311 K. The experimental heat capacity points are presented in Table I in the order in which they were measured. They are corrected for the He present in the sample container.

The precision is better than 0.1% between 90 and 310 K, decreased to 0.15% at 30 K and 0.5% at 15 K.

The data was smoothed, extrapolated to zero Kelvin and used to generate the thermodynamic functions by means of the FITAB program.[2] The smoothed heat capacity and other thermodynamic functions at rounded temperatures are presented in Table II. The estimated uncertainty in the entropy at 298.15K is 0.15%.

3.   The Fluorocarbon $CF_{0.597}$

a.   Sample

The material used in this research was analyzed by Schwartzkopf Micro-analytical Laboratory in Woodside, New York. The mean results and their standard deviations of three sets of duplicate analysis are:

$$\% \text{ F} \ : \ 51.46 \pm 0.31$$

$$\% \text{ C} \ : \ 48.59 \pm 0.34$$

$$\% \text{ Ni} \ : \ 0.06 \pm 0.01$$

The above analysis indicates a composition of $CF_{0.597}$.

b.   Heat Capacity and Thermodynamic Functions

The sample container was loaded with 55.6219 g <u>in vacuo</u> of $CF_{0.597}$. Prior to loading, the material was pressed into pellets 3 mm in diameter by 3 mm long. The pellets were not firm and were very easily broken up but were more compact than the powdered material from which they were made.

The experimental heat capacity points are presented in Table III in the order in which they were measured. They are corrected for the He present in the sample container and for the presence of NiF_2. The heat capacity data of Catalano and Stout[3] were used to make the latter corrections.

As in the case of $CF_{1.1}$, the behavior with respect to thermal conductivity was poor at the lowest temperatures in the liquid hydrogen range and the data taken below 20 K were not usable. In addition, the heat capacity seems to vary with the thermal history of the sample. Initially, the sample was cooled to 14 K and data was taken up to 55 K. The sample was held at this temperature for four days and then data was taken up to 275 K. These data are given in Series A. After being held at room temperature for five days, the sample was cooled to 54 K and data was taken up to 305 K. These data are given in Series B. It was noted in Series B that the length of time

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required to reach temperature equilibrium after shutting off the power input to the sample container was noticably and consistently shorter than in Series A. The sample container, after being held at room temperature for two days, was cooled to 273 K and the data of Series C were taken. At this time, work-up of the experimental data was begun and it was discovered tnat Series A and B were slightly but significantly different. The sample container, after being held at room temperature for 18 days was cooled to 54 K and the data of Series D were taken.

The differences between the series are shown graphically in Figure I. The data of Series B, C and D were fitted to a smoothing polynomial with the FITAB program and the deviations of all data points from this polynomial were plotted against temperature. The dotted lines represent the error in the sample heat capacity caused by a $\pm$ 0.03% error in the total heat capacity (i.e. the heat capacity of sample and sample container). This represents the probably maximum precision of the data. It appears that there is a small systematic difference between Series B and D but it approaches insignificance. The difference between Series A and Series B and D is obvious and quite real. Tne possible reason for the differences is postulated in the discussion.

Since Series A contains the only data taken below 55 K, it will be used to calculate the entropy and other thermodynamic functions. Since the different series seem to converge above 250 K, the data of Series B, C and D above 250 K were also used.

Additionally, the values of $s_{298.15}-s_{55}$ calculated from Series A and from Series B, C and D differ by only 0.25%.

The thermodynamic functions for $CF_{0.597}$ at rounded temperatures are presented in Table IV. The tentatively assigned uncertainty in the entropy at 298.15 K is 0.25%.

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FIGURE 1
DEVIATION PLOT FOR
EXPERIMENTAL HEAT CAPACITY
DATA OF $CF_{0.6}$
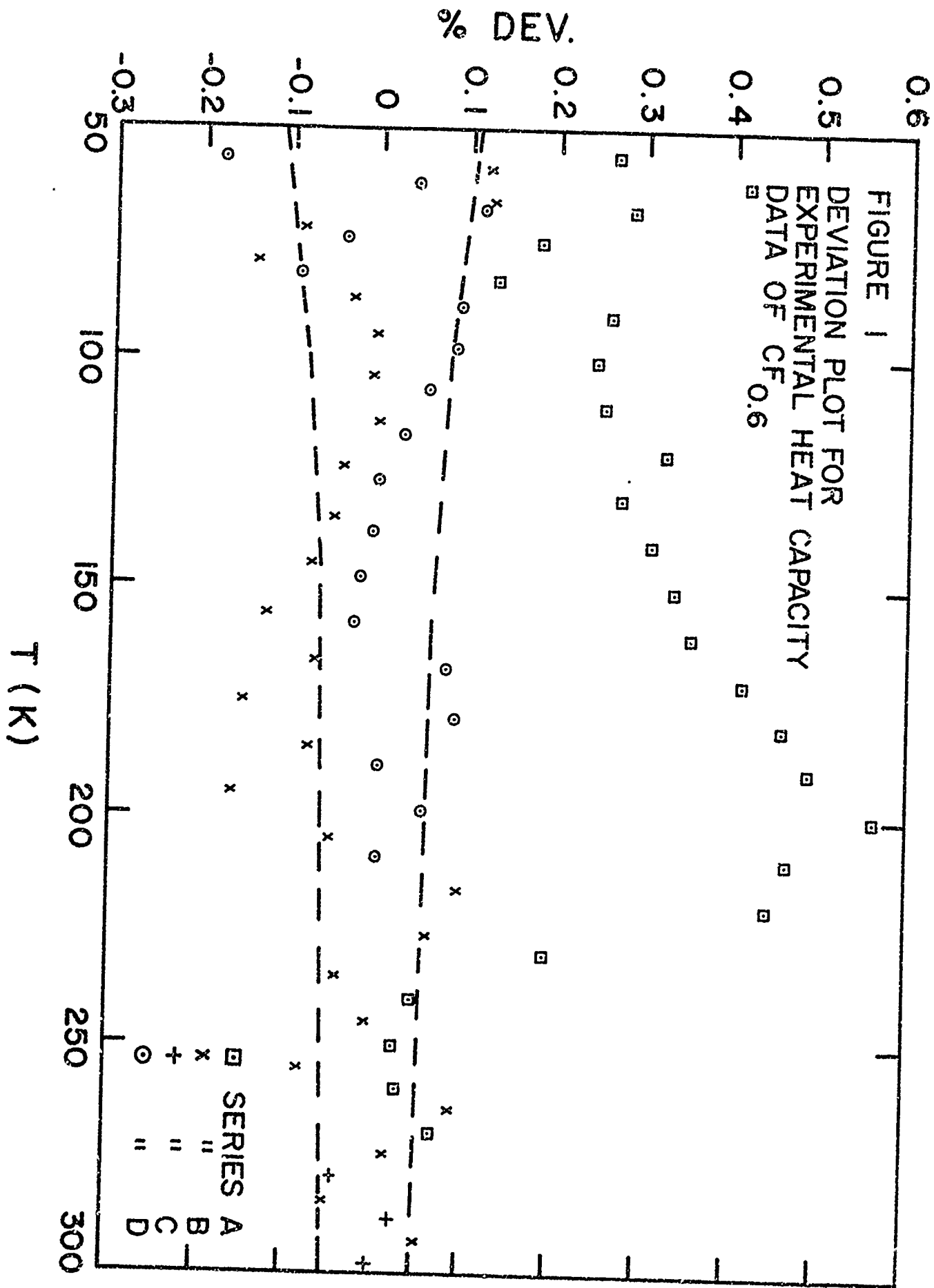
TABLE I

THE HEAT CAPACITY OF C_4F.

T (K)	c_p (J/g K)	T (K)	c_p (J/g K)	T (K)	c_p (J/g K)
Series A		Series B (cont.)		Series C (cont.)	
15.55	0.01649	134.18	0.3352	112.24	0.2697
17.19	0.01901	142.48	0.3593	122.02	0.2986
18.78	0.02150	150.80	0.3842	129.54	0.3209
20.70	0.02427	159.51	0.4101	137.48	0.3444
22.79	0.02750	168.22	0.4356	145.80	0.3693
25.34	0.03213	176.70	0.4609	154.54	0.3939
28.23	0.03752	185.05	0.4852	163.97	0.4233
31.32	0.04351	194.01	0.5116	172.60	0.4486
34.85	0.05074	203.07	0.5378	181.80	0.4757
38.63	0.05945	211.89	0.5634	191.19	0.5032
42.79	0.06949	220.71	0.5889	200.18	0.5293
47.43	0.08103	229.76	0.6144	207.71	0.5510
52.26	0.09364	238.56	0.6381	216.63	0.5768
57.58	0.1082	247.37	0.6619	225.76	0.6033
		259.08	0.6951	234.97	0.6285
Series B		267.66	0.7187	243.98	0.6528
58.52	0.1107	276.23	0.7417	252.79	0.6770
64.22	0.1270	284.41	0.7644	264.30	0.7091
70.26	0.1443	292.82	0.7873	273.60	0.7344
76.09	0.1615	301.98	0.8121	282.71	0.7593
82.11	0.1794	311.37	0.8369	291.72	0.7840
88.54	0.1988			300.52	0.8087
95.50	0.2198	Series C		309.06	0.8304
102.75	0.2419	84.97	0.1881		
110.90	0.2659	91.49	0.2074		
118.13	0.2869	98.38	0.2285		
125.95	0.3102	105.24	0.2498		

TABLE II

THE THERMODYNAMIC FUNCTIONS OF C_4F AT ROUNDED TEMPERATURES.

T (K)	c_p (J/g K)	s (J/g K)	$(h-h_o)/T$ (J/g K)	$-(g-h_o)/T$ (J/g K)
0	0.0	0.0	0.0	0.0
5	0.00289	0.00159	0.00104	0.00056
10	0.00882	0.00532	0.00338	0.00195
15	0.01575	0.01019	0.00633	0.00386
20	0.02324	0.01573	0.00961	0.00612
25	0.03149	0.02179	0.01315	0.00864
30	0.04079	0.02834	0.01696	0.01137
35	0.05123	0.03539	0.02110	0.01429
40	0.06269	0.04297	0.02557	0.01740
45	0.07491	0.05105	0.03037	0.02069
50	0.08770	0.05960	0.03546	0.02415
55	0.1010	0.06858	0.04081	0.02778
60	0.1149	0.07796	0.04640	0.03156
65	0.1291	0.08772	0.05221	0.03551
70	0.1436	0.09781	0.05822	0.03959
75	0.1584	0.1082	0.06444	0.04382
80	0.1733	0.1189	0.07074	0.04818
85	0.1882	0.1299	0.07722	0.05266
90	0.2033	0.1411	0.08380	0.05726
95	0.2183	0.1525	0.09048	0.06197
100	0.2333	0.1640	0.09725	0.06678
110	0.2631	0.1877	0.1110	0.07669
120	0.2929	0.2118	0.1249	0.08694
130	0.3225	0.2364	0.1390	0.09750
140	0.3521	0.2614	0.1531	0.1083
150	0.3816	0.2867	0.1674	0.1194
160	0.4112	0.3123	0.1817	0.1306
170	0.4409	0.3381	0.1961	0.1421
180	0.4704	0.3642	0.2105	0.1537
190	0.4999	0.3904	0.2249	0.1654
200	0.5291	0.4168	0.2394	0.1774
210	0.5579	0.4433	0.2539	0.1894

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TABLE II

Thermodynamic Functions of C_4F (cont.)

220	0.5864	0.4699	0.2684	0.2015
230	0.6145	0.4966	0.2828	0.2138
240	0.6423	0.5233	0.2972	0.2261
250	0.6698	0.5501	0.3116	0.2385
260	0.6971	0.5769	0.3259	0.2510
270	0.7245	0.6037	0.3401	0.2636
273.15	0.7332	0.6122	0.3446	0.2676
280	0.7520	0.6306	0.3543	0.2762
290	0.7796	0.6574	0.3685	0.2889
298.15	0.8019	0.6794	0.3801	0.2993
300	0.8069	0.6843	0.3827	0.3016
310	0.8332	0.7112	0.3968	0.3144

TABLE III

THE HEAT CAPACITY OF $CF_{0.6}$

T (K)	c_p (J/g K)	T (K)	c_p (J/g K)	T (K)	c_p (J/g K)
Series A		Series A		Series B	
20.35	0.01057	200.19	0.5382	215.99	0.5798
22.23	0.01256	209.80	0.5648	225.90	0.6066
24.33	0.01488	220.48	0.5939	235.63	0.6321
26.57	0.01737	230.46	0.6198	245.19	0.6574
29.12	0.02038	240.23	0.6448	254.79	0.6817
31.84	0.02414	250.21	0.6706	264.61	0.7077
34.92	0.02892	259.53	0.6945	274.19	0.7310
38.80	0.03533	269.37	0.7194	284.21	0.7551
43.31	0.04407			293.81	0.7795
48.01	0.05426	Series B		303.19	0.8018
52.98	0.06611	59.85	0.08433		
56.82	0.07623	65.67	0.1013	Series C	
62.32	0.09163	71.88	0.1206	279.03	0.7425
68.36	0.1013	79.00	0.1442	288.60	0.7665
75.46	0.1327	86.79	0.1711	298.14	0.7897
83.15	0.1588	95.45	0.2014	308.10	0.8143
91.62	0.1885	104.34	0.2324		
100.69	0.2202	113.61	0.2644	Series D	
110.57	0.2546	123.96	0.2995	56.54	0.07516
120.86	0.2900	134.68	0.3350	61.71	0.08952
130.98	0.3239	145.23	0.3692	67.48	0.1069
141.02	0.3570	155.67	0.4021	74.17	0.1282
150.94	0.3890	165.89	0.4340	81.41	0.1525
160.92	0.4205	175.46	0.4625	89.33	0.1802
170.91	0.4514	185.26	0.4919	98.25	0.2114
180.41	0.4802	195.22	0.5202	107.19	0.2424
190.19	0.5091	205.66	0.5503	116.77	0.2753

TABLE III

The Heat Capacity of $CF_{0.6}$ (continued)

T (K)	c_p (J/g K)	T (K)	c_p (J/g K)	T (K)	c_p (J/g K)
				Series D (continued)	
				127.27	0.3106
				137.52	0.3445
				147.67	0.3772
				158.01	0.4098
				168.23	0.4418
				178.53	0.4728
				189.29	0.5040
				199.49	0.5335
				209.40	0.5611

TABLE IV

THE THERMODYNAMIC FUNCTIONS OF $CF_{0.6}$ AT ROUNDED TEMPERATURES

T (K)	c_p (J/g K)	s (J/g K)	$(h-h_0)/T$ (J/g K)	$-(g-h_0)/T$ (J/g K)
0	0.0	0.0	0.0	0.0
5	0.00087	0.00046	0.00030	0.00016
10	0.00308	0.00168	0.00109	0.00058
15	0.00629	0.00350	0.00226	0.00124
20	0.01040	0.00585	0.00376	0.00209
25	0.01547	0.00870	0.00558	0.00312
30	0.02163	0.01205	0.00773	0.00432
35	0.02898	0.01592	0.01022	0.00569
40	0.03762	0.02033	0.01309	0.00724
45	0.04758	0.02533	0.01636	0.00897
50	0.05985	0.03091	0.02004	0.01088
55	0.07134	0.03710	0.02412	0.01298
60	0.08496	0.04388	0.02862	0.01526
65	0.09956	0.05125	0.03351	0.01774
70	0.1150	0.05919	0.03877	0.02042
75	0.1312	0.06768	0.04439	0.02328
80	0.1480	0.07668	0.05034	0.02634
85	0.1652	0.08616	0.05659	0.02957
90	0.1827	0.09610	0.06311	0.03299
95	0.2002	0.1064	0.06986	0.03658
100	0.2178	0.1172	0.07682	0.04034
110	0.2528	0.1396	0.09123	0.04834
120	0.2871	0.1630	0.1061	0.05691
130	0.3207	0.1874	0.1213	0.06600
140	0.3536	0.2123	0.1368	0.07556
150	0.3859	0.2378	0.1523	0.08553
160	0.4176	0.2637	0.1679	0.09585

TABLE IV

THERMODYNAMIC FUNCTIONS OF $CF_{0.6}$ (continued)

170	0.4487	0.2900	0.1835	0.1065
180	0.4791	0.3165	0.1991	0.1174
190	0.5087	0.3432	0.2146	0.1286
200	0.5374	0.3700	0.2300	0.1400
210	0.5653	0.3969	0.2453	0.1515
220	0.5923	0.4239	0.2605	0.1634
230	0.6187	0.4508	0.2755	0.1753
240	0.6445	0.4776	0.2903	0.1873
250	0.6701	0.5045	0.3050	0.1995
260	0.6954	0.5312	0.3195	0.2117
270	0.7206	0.5580	0.3339	0.2240
273.15	0.7284	0.5664	0.3384	0.2279
280	0.7453	0.5846	0.3482	0.2364
290	0.7698	0.6112	0.3623	0.2489
298.15	0.7896	0.6328	0.3737	0.2591
300	0.7941	0.6377	0.3763	0.2614
310	0.8192	0.6642	0.3902	0.2740

Part III.   FLUORINE COMBUSTION CALORIMETRY OF $CF_{0.597}$

1.   Experimental Apparatus

The apparatus used for the combustion of $CF_{0.6}$ has been described.[1]
The only change made was a rearrangement of the fuse assembly. Difficulty
was encountered in maintaining electrical continuity due to the fuse wire
slipping out of position. This problem was overcome by introducing two
short bends in the fuse wire such that it was held in place by the tension
of the wire.

2.   Combustion Technique

The combustion technique used was essentially the same as that used
in the combustion of C_4F.[1] The only change made was a rearrangement of the
fuse assembly. Difficulty was encountered in maintaining electrical continuity
due to the fuse wire slipping out of position. This problem was overcome by
introducing two short bends in the fuse wire such that it was held in place
by the tension of the wire.

It was found that a somewhat higher proportion of silicon was necessary
to insure complete combustion. Nevertheless, residues typically amounted to
about 1.2% of the sample weight were obtained after each combustion run.

3.   Results of Combustion Runs

Analyses of the gaseous products of the combustion was carried out with
a 10 cm gas IR cell. The only detectable product was $CF_4(g)$.

The solid residues from each combustion were weighed to ±0.02 mg. X-ray
powder patterns of these residues indicated them to be unburned $CF_{0.6}$. The
combustion of C_4F yielded a residue that was shown to be graphite.[1] The results

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of the combustion of $CF_{0.6}$ can be explained by the higher fluorine content. This would lower the temperature of the fluorine flame and produce $CF_{0.6}$ rather than graphite.

The auxiliary data used for deriving the energy of combustion of $CF_{0.6}$ was taken from Table VII, Reference 1. The computation of Δt_c was carried out with a computer program, CALOR,[4] which uses a least squares fit for the initial and final temperature periods, and a trapezoidal integration of the main period temperature data.

The correction to the standard states of 25°C, and 1 atmosphere pressure appears as ΔE (contents) and ΔE (gas) in Table I. The techniques for making these corrections are described by Hubbard.[5]

All weights have been corrected to mass in vacuo.[6]

A series of six calibration runs were carried out, using National Bureau of Standards, Standard Sample 391 benzoic acid. This series yielded a value for E (calor) of $3698.7 \pm .6$ cal deg^{-1}.

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TABLE V

Summary of Combustion Data on $CF_{0.6}$ in Fluorine at 298.16 K
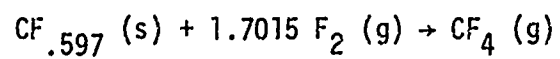
	70 – I	71 – I	73 – I	74 – I	80 – I
m (compound), g	.27927	.28989	.27062	.27289	.28503
m (tungsten), g	.29418	.29430	.23709	.23775	.25668
m (silicon), g	.03918	.03452	.04133	.03898	.03824
m (residue), g	.00382	.00560	.00399	.00317	.00393
Δt_c, deg	.95457	.95667	.90770	.90787	.94242
E (calor)($-\Delta t_c$), cal	-3530.67	-3538.44	-3357.31	-3357.94	-3485.73
ΔE (contents), cal[a]	-1.10	-1.11	-1.04	-1.03	-1.08
ΔE (silicon), cal	537.62	473.68	567.12	534.88	524.72
ΔE (tungsten),cal	656.58	656.85	529.16	530.63	572.88
ΔE (gas), cal[b]	-.07	-.07	-.07	-.07	-.07
ΔE (ign), cal	.65	.65	.65	.65	.65
$\Delta E°/M$ (compound), cal/g	-8484.26	-8471.77	-8481.75	-8500.96	-8497.44

$$\Delta \bar{E}°_c/M = -8487.24 \pm 5.3^c \text{ cal/g}$$

[a] ΔE (contents) = E^i (cont)(t^i-25) + E^f(cont)(25-^{f} + Δt corr); See Reference 5.   [b] Sum of items 32 and 34 in Reference 5.   [c] Standard deviation of the mean.
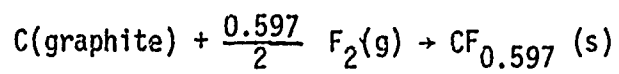
TABLE VI

Derived Data for $CF_{0.597}$ at 298.16 K

$$CF_{.597} \; (s) + 1.7015 \; F_2 \; (g) \rightarrow CF_4 \; (g)$$

$$\Delta E_C^\circ = -828.98 \pm 0.52 \; kJ/mole$$

$$\Delta H_C^\circ = -831.46 \pm 0.52 \; kJ/mole$$

$$C(graphite) + \frac{0.597}{2} \; F_2(g) \rightarrow CF_{0.597} \; (s)$$

$$\Delta H_f^\circ = -101.74 \pm 0.91 \; kJ/mole$$

Part IV.   SURFACE AREA MEASUREMENTS

1.   The Fluorocarbon $CF_{1.17}$

Duplicate analyses of the fluffy white fluorocarbon were carried out by Schwartzkopf Laboratories, these results are shown below:

C	H	F
35.03	0.04	65.32
35.36	0.00	64.76

Taking the average carbon and fluorine values and making the assumption that the percentage hydrogen reported represents random error in the determinations, the formula for this compound becomes $CF_{1.17}$.

2.   The Fluorocarbons $CF_{1.12}$ and $CF_{0.597}$

The white fluorocarbon $CF_{1.12}$ has been described previously,[1] and the fluorocarbon $CF_{0.6}$ is described in Part II of this report.

3.   Method and Apparatus

The method used to determine the surface areas of the three fluorocarbons was adsorption isotherms. In this case, plots of nitrogen adsorption against its partial pressure at a constant temperature (77 K). The Brunauer, Emmett, Teller (BET) theory was used to interpret the data obtained.

The measurements were carried out on a BET apparatus in the Rice University Chemical Engineering Department.[7]

4.   BET Surface Areas

The preliminary results of the BET isotherms are given in Table VII. As expected, the fluffy white fluorocarbon had a greatly increased surface area over that of the white and gray samples. More precise calibration experi-

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ments are needed in order to be completely certain as to the trend in the surface area with extent of fluorination.

TABLE VII.

BET Surface Areas of Some Solid Fluorocarbons

Compound	Formula	Surface Area (m^2/g)
gray CF	$CF_{0.6}$	230
white CF	$CF_{1.12}$	270
fluffy white CF	$CF_{1.17}$	520

Part V.   CONCLUSIONS

1.   Discussion of Heat Capacity Data

The heat capacity curves of the substances studied in this report and the previous report[1] all show one feature which is unusual but not unexpected: all require inclusion of quadratic terms in the extrapolation of the heat capacity data to zero; i.e. the low temperature heat capacity is of the form:

$$c_p = aT^2 + bT^3 + cT^4 + dT^5 + \cdots$$

In contrast to this behavior, most crystalline substances at low temperature follow the Debye heat capacity approximation; i.e.,

$$c_p = AT^3 + BT^5 + CT^7 + \cdots$$

Since the heat capacity of graphite at low temperature depends quadratically upon temperature,[9] the low temperature behavior of the carbon-fluorine compounds is not unexpected.

Re-evaluation of the analytical data for the substance CF which was assigned the composition $CF_{1.09}$(1), indicates that a composition of $CF_{1.125}$ is more probably correct.

The molar heat capacities of graphite,[8] $CF_{0.237}$, $CF_{0.597}$ and $CF_{1.125}$ are presented in Table VIII and in Figure 2. One mole of the fluorocarbons is defined as the amount of material containing one mole of carbon.

Examination of Figure 2 shows that the heat capacity curve of $CF_{0.237}$ is inordinately high at low temperatures. This would indicate that the fluorine is more loosely bound in $CF_{0.237}$ than in the other fluorocarbons. This contention can be tested by studies which elucidate the structures of these materials; e.g. Raman and infra-red spectroscopy.
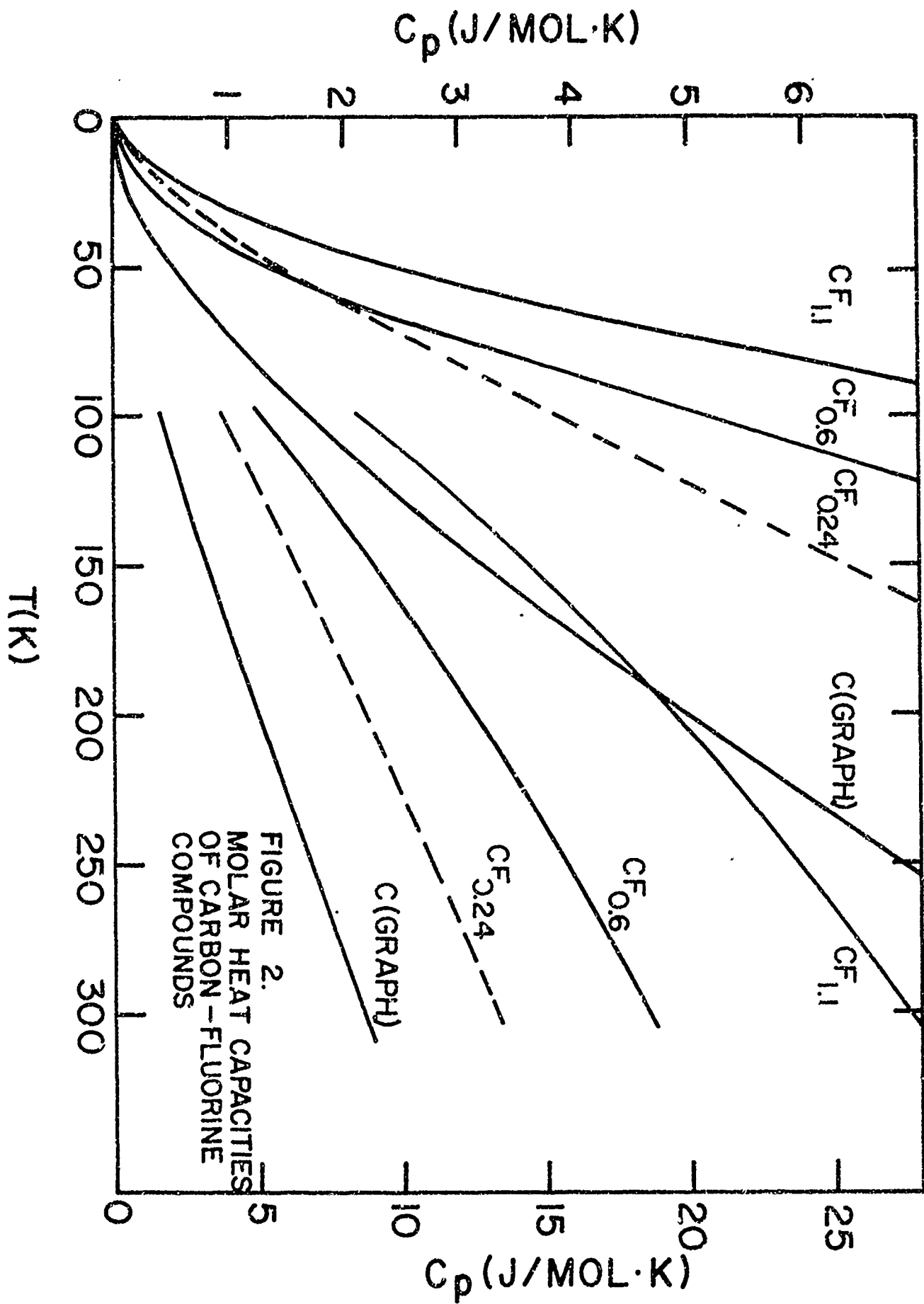
FIGURE 2.
MOLAR HEAT CAPACITIES
OF CARBON–FLUORINE
COMPOUNDS

The entropies of the materials are presented in Table IX and the molar entropies are plotted as a function of fluorine content in Figure 3. It can be seen that the entropy of $CF_{0.237}$ is inordinately high.

TABLE VIII

Molar Heat Capacities of C-F Compounds

T (K)	c(graphite) (J/mole K)	$CF_{0.237}$ (J/mole K)	$CF_{0.597}$ (J/mole K)	$CF_{1.125}$ (J/mole K)
15	0.0427	0.2600	0.1469	0.3175
25	0.1255	0.5199	0.3612	0.7363
50	0.5063	1.448	1.347	2.449
75	1.046	2.615	3.064	5.185
100	1.658	3.852	5.086	8.468
150	3.229	6.300	9.011	14.51
200	4.937	8.735	12.55	19.45
250	6.816	11.06	15.65	23.70
300	8.590	13.32	18.54	27.57

TABLE IX

Entropies of C-F Compounds

	$S_{298.15}$ (J/gm K)	$S_{298.15}$ (J/mole K)
C(graphite)	0.1142	5.74
$CF_{0.237}$	0.6794	11.22
$CF_{0.597}$	0.6328	14.71
$CF_{1.126}$	0.7081	23.64

As noted earlier, the heat capacity of the sample of $CF_{0.597}$ seems to vary slightly with the thermal history of the sample. The effect, although small, is apparently real. Further heat capacity work will be done in an attempt to duplicate Series A. In addition, X-ray studies and infra-red spectroscopy studies will be done on samples cycled between different low temperatures. It is believed that an energetically small, slow, non-isothermal transistion to a new phase more stable at very low temperature than the form stable at room temperature can explain the anolomous behavior in the heat capacity data. The above mentioned studies hopefully will clarify the situation.

2. Calculation of Thermodynamic Quantities for the Cell Reaction

In the calculations to follow, the JANAF data[10] given below will be used:

$$\Delta H_{f298} \text{ (LiF, s)} = -616.93 \text{ KJ/mole}$$

$$S_{298} \text{ (LiF, s)} = 35.66 \text{ J/mole K}$$

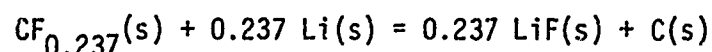$$S_{298} \text{ (Li, s)} = 29.10 \text{ J/mole K}$$

$$S_{298} \text{ (C, s)} = 5.69 \text{ J/mole K}$$

a. Cell reaction of $CF_{0.237}$ with Li

Using the value for the heat of formation of $CF_{0.237}$[1]

$$\Delta H_{f298} \text{ } (CF_{0.237}, \text{ s}) = -25.43 \text{ kJ/mole}$$

and the JANAF value for the heat of formation of LiF, we obtain for the reaction

$$CF_{0.237}(s) + 0.237 \text{ Li(s)} = 0.237 \text{ LiF(s)} + C(s)$$

$$\Delta H_{298} = -120.72 \text{ kJ/mole}.$$

Using the value for the entropy of $CF_{0.237}$

$$S_{298} \text{ } (CF_{0.237}, \text{ s}) = 11.22 \text{ J/mole K}$$

and the JANAF values for the entropies of graphite, Li, and LiF we obtain for the

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above reaction

$$\Delta S_{298} = -3.98 \text{ J/mole K.}$$

The cell reaction Gibbs free energy change, standard potential, and temperature coefficient of standard potential are readily found to be

$$\Delta G_{298} = -119.5 \text{ kJ/mole}$$

$$E_{298} = 5.23 \text{ volt}$$

$$\left(\frac{dE}{dT}\right)_{298} = -0.2 \text{ mvolt/K}$$

b. Cell reaction of CF_n (0.6 <n<1.1) with Li

In the previous report[1], values of E_{298} for the cell reaction were calculated for various values of n. A serious error was introduced by using an extrapolation procedure for the heat of formation of CF_n using the heats of formation of $CF_{1.12}$ and fluorocarbons with a greater fluorine content. Other assumptions also contributed to the error.

In the treatment to follow, the heat of formation and the entropy of CF_n will be calculated by linear interpolation of the corresponding data for $CF_{0.597}$ and $CF_{1.125}$.

From the following data:

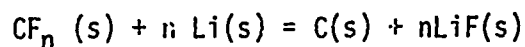|	ΔH_{f298}	S_{298}
$CF_{0.597}$	-107.74 kJ/mole	14.71 J/mole K
$CF_{1.125}$	-195.73 kJ/mole	23.64 J/mole K

we obtain

$$\Delta H_{f298} (CF_n, s) = (4.53 - 178.01n) \text{kJ/mole}$$

$$S_{298} (CF_n, s) = (4.62 + 16.91n) \text{J/mole K}$$

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Using these results and the JANAF values given above, we obtain for the reaction

$$CF_n (s) + n\ Li(s) = C(s) + nLiF(s)$$

$$\Delta H_{298} = -(438.92n + 4.53)\ kJ/mole$$

$$\Delta S_{298} = (1.07 - 10.35n)\ J/mole\ K$$

$$\Delta G_{298} = -(435.83n + 4.85)\ kJ/mole$$

The values of ΔG_{298}, E_{298}, and $dE/dT)_{298}$ are then readily calculated for any value of n between 0.6 and 1.1. The quantities at rounded values of n are presented in Table X.

TABLE X

Thermodynamic Properties of Cell Reaction

of CF_n with Li for various values of n

n	$-\Delta G_{298}$	E_{298}	$\frac{dE)}{dT)_{298}}$
	(kJ/mole)	(v)	(mv/K)
0.597	265.0	4.60	-0.09
0.7	309.9	4.59	-0.09
0.8	353.5	4.58	-0.09
0.9	397.1	4.57	-0.10
1.0	440.7	4.57	-0.10
1.125	.. ˙ 2	4.56	-0.10

FIGURE 3.
MOLAR ENTROPY
AT 298.15 vs. n FOR CF_n

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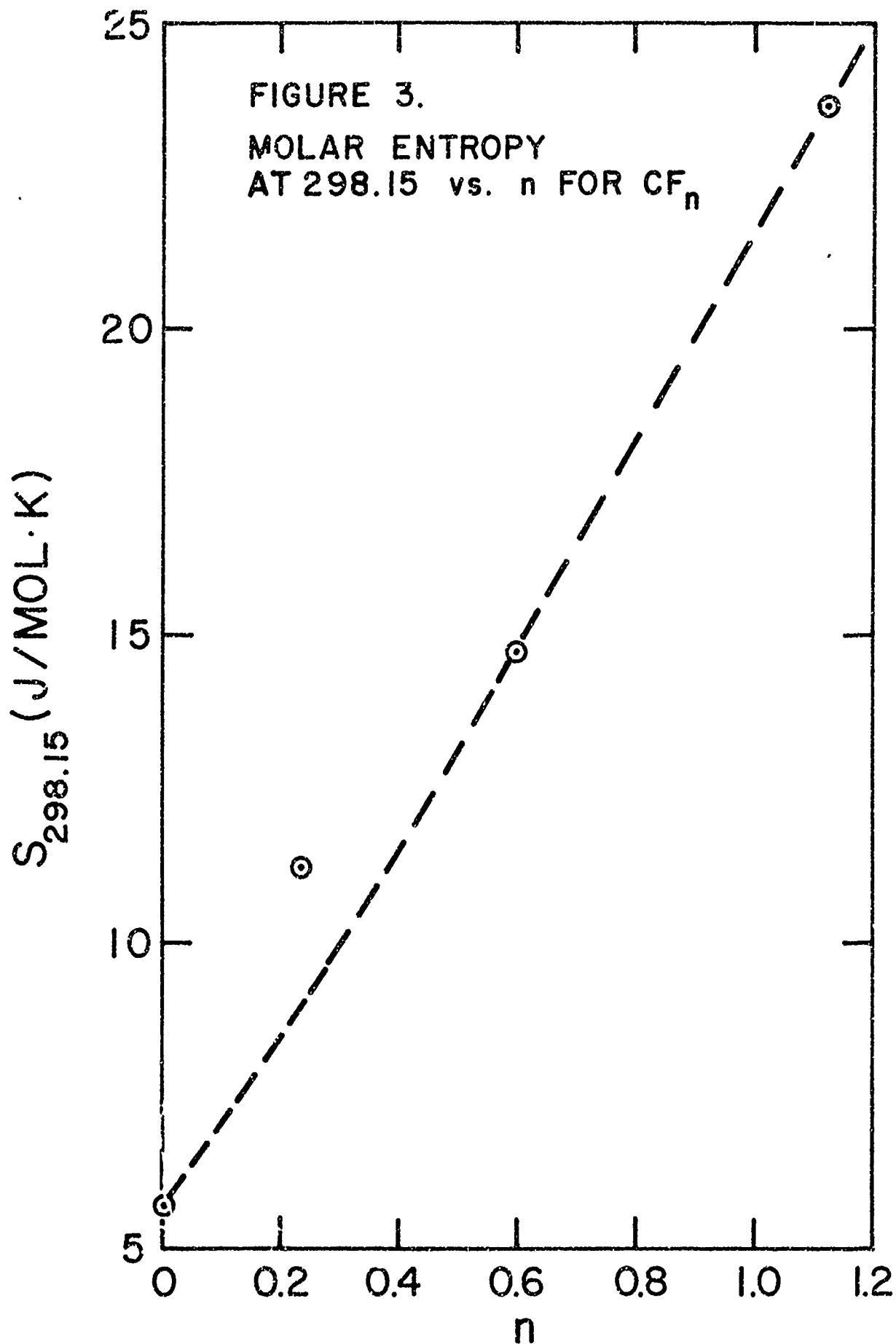
3. Discussion of BET Surface Areas of Fluorocarbons

The BET theory allows easy comparison between samples of various surface area if the same adsorbate is used. The values reported in Table VII were not compared against the starting SP-2 graphite, but reasonable values[11] range between 11 and 85 m^2/g. The fluffy white sample, $CF_{1.17}$, appears to have a surface area greater than that of carbon black, which is about 340 m^2/g.[12] The general trend is noticed that greater fluorination produces a greater surface area, at least i. the care of $CF_{1.17}$ compared with the other two samples. It is possible that the $CF_{1.17}$ material has the greater surface area because of fewer C-C bonds within the graphite-like lattice, but no X-ray data are available to confirm this assumption.

With a surface area almost double that of white CF, it would be interesting to see if attained discharge rates for Li batteries made with this material would be greater.

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