

# Heat Capacity of Gaseous Perfluoropropane

Joseph F. Masi, Howard W. Flieger, Jr., and John S. Wicklund

An accurate flow calorimeter, previously described, has been used to measure the heat capacity of gaseous perfluoropropane ( $C_3F_8$ ) at three pressures up to 1.5 atmospheres at each of the temperatures  $-30^\circ$ ,  $+10^\circ$ ,  $+50^\circ$ , and  $+90^\circ$  C. The results, believed accurate to 0.1 percent, have been extrapolated to zero pressure at each temperature, in order to obtain the ideal-gas heat capacity ( $C_p^0$ ) and the pressure coefficient of heat capacity. Values of  $C_p^0$  are 31.10, 34.22, 37.02, and 39.49 calories mole $^{-1}$  degree C $^{-1}$ , respectively, at the four temperatures of measurement.

## 1. Introduction

Experimental gas heat capacities, obtained at several low pressures and over a range of temperatures, can be helpful in interpreting molecular structure and spectroscopic data and in studying equations of state at low pressure. The present investigation was undertaken as part of a comprehensive study of the thermodynamic and structural properties of fluorocarbons. The heat capacities of gaseous hexafluoroethane<sup>1</sup> and perfluorocyclobutane<sup>2</sup> have previously been reported.

## 2. Experimental Procedure

### 2.1. Material

A specially purified sample of perfluoropropane ( $C_3F_8$ ) was very kindly furnished by the Minnesota Mining & Manufacturing Corp. The entire sample was evaporated in a closed system while surrounded with a mixture of carbon tetrachloride and chloroform, cooled with dry ice to about 2 deg below the normal boiling point of  $C_3F_8$  ( $-38^\circ$  C). The vapor was condensed in a trap at liquid-nitrogen temperature. During this distillation the system was continuously pumped with a high-vacuum apparatus. First and last portions (about 25 g each) of the distillate were discarded. There was obtained a sample of about 450 g for use in the experiments.

A mass-spectrograph analysis of the sample, performed after most of the heat-capacity data had been taken, showed only a trace (less than 0.1 percent) of  $CF_2Cl^+$  and  $CF_2H^+$  ions. A gravimetric determination of the amount of carbon dioxide and moisture present was made by passing the entire flow-calorimeter sample, as vapor, through tubes of Anhydrone and Ascarite. Absorption of less than 0.01 percent was obtained. It was indicated that impurities should affect the heat-capacity measurements by much less than 0.1 percent.

### 2.2. Apparatus and Method

The construction and operation of the flow calorimeter have been described in detail;<sup>3</sup> a résumé has also been published.<sup>4</sup>

The heat capacity was determined at a number of different flow rates at each temperature and pressure, so that the effect of any residual heat leak could be eliminated by extrapolation to the zero of reciprocal rate. "Blank" determinations were made at several rates at each temperature and pressure to measure the amount of cooling,  $\delta T$ , experienced by the gas in passing through the calorimeter when no heat was applied. A total of 57 heat-capacity experiments and 67 blank experiments was made.

## 3. Results

The important data for all of the heat-capacity experiments are given in table 1. The values of heat capacity,  $C$ , (column 7) were calculated from the power,  $W$ ; the flow rate,  $F$ ; the rise in temperature,  $\Delta T$ ; and the temperature fall,  $\delta T$ , in the corresponding blank experiment, by the relation

$$C = \frac{W}{F(\Delta T + \delta T)}$$

These have been corrected by the amounts in column 8 in order to bring all results to the nominal mean pressure,  $p_m$ , and mean temperature,  $T_m$ , to yield the values of " $C_p$  (observed)" appearing in column 9.

The values of " $C_p$  (observed)" were plotted against the reciprocal of flow rate, and straight lines were fitted by least squares. Typical plots are given in figure 1, which shows the results at  $10^\circ$  C. An analysis of variance, performed under the direction of W. J. Youden of the Bureau's Applied Mathematics Division, indicated that, for the data as a whole, the variation in slope of these lines was statistically significant. Consequently, the least-square intercepts have been retained in all cases as the desired value of heat capacity at each temperature and pressure, indicated as "extrapolated value" in table 1. The precision of the data is indicated by the value of  $\sigma$ , where  $\sigma = \sqrt{\sum d^2 / (n-1)}$ ,  $d$  is the deviation of each point from the appropriate line, and  $n$  is the number of experiments for each line. The average value of  $\sigma$  is equivalent to  $\pm 0.03$  percent of the heat capacity.

Results are summarized in table 2, having been converted to calories mole $^{-1}$  degree $^{-1}$ . (The defined calorie, equal to 4.1840 j, is used here.) A slight correction has been made, where necessary, for the

<sup>1</sup> J. S. Wicklund, H. W. Flieger, Jr., and J. F. Masi, J. Research NBS **51**, 91 (1953) RP2437.

<sup>2</sup> J. F. Masi, J. Am. Chem. Soc. **75**, 5082 (1953).

<sup>3</sup> J. F. Masi and B. Petkof, J. Research NBS **48**, 179 (1952) RP2303.

<sup>4</sup> J. F. Masi, J. Am. Chem. Soc. **74**, 4738 (1952).

TABLE 1. Data on perfluoropropane

Reciprocal of rate, $F^{-1}$	Mass of sample, $m$	Power, $W$	Pressure drop, $\Delta p$	Temperature rise, $\Delta T$	Blank correction, $\delta T$	Heat capacity, $C$	Correction for $T_m$ and $p_m$ , $\Delta C$	Heat capacity, $C_p$ (observed)
-30.00° C = 243.16° K; 1.00 atm								
<i>sec g<sup>-1</sup></i>	<i>g</i>	<i>w</i>	<i>mm Hg</i>	<i>° K</i>	<i>° K</i>	<i>j g<sup>-1</sup> deg<sup>-1</sup></i>	<i>j g<sup>-1</sup> deg<sup>-1</sup></i>	<i>j g<sup>-1</sup> deg<sup>-1</sup></i>
9.1325	57.5097	0.753506	74.42	9.5427	0.1208	0.71210	+0.00038	0.71248
10.4708	71.9782	.612918	55.83	8.9149	.0933	.71243	+ .00031	.71274
11.7710	65.1171	.615517	44.20	10.0930	.0757	.71250	+ .00003	.71253
14.8430	88.1819	.491159	28.41	10.1797	.0517	.71254	- .00017	.71237
17.8982	46.0844	.413501	19.17	10.3433	.0367	.71300	- .00037	.71263
28.3768	44.6435	.248342	7.14	9.8719	.0150	.71278	- .00024	.71254
28.8342	38.2730	.247685	7.37	10.0048	.0162	.71268	- .00018	.71250
Extrapolated value-----								0.71258
$\sigma$ -----								$\pm 0.00010$
0.67 atm								
9.2277	108.1488	0.750862	111.95	9.6622	0.1648	0.70506	+0.00043	0.70549
11.6910	104.6250	.614240	65.89	10.0704	.1036	.70583	- .00027	.70556
14.6602	43.3911	.491138	42.97	10.1400	.0733	.70498	- .00003	.70495
17.4329	50.1947	.411872	30.45	10.1267	.0567	.70508	- .00001	.70507
28.0026	41.4276	.247657	11.73	9.8091	.0318	.70471	- .00012	.70459
29.7293	38.4368	.248370	10.98	10.4511	.0305	.70446	- .00033	.70413
Extrapolated value-----								0.70607
$\sigma$ -----								$\pm 0.00018$
0.33 atm								
12.0251	81.4694	0.614151	140.00	10.3706	0.1933	0.69910	-0.00018	0.69892
14.8191	62.4984	.491274	84.97	10.2924	.1287	.69861	- .00044	.69817
14.8249	58.9523	.489272	82.40	10.2445	.1254	.69947	- .00054	.69893
17.1889	55.1834	.412296	61.64	10.0468	.0987	.69857	- .00027	.69830
28.8417	30.3918	.246727	22.79	10.1415	.0425	.69874	- .00017	.69857
Extrapolated value-----								0.69875
$\sigma$ -----								$\pm 0.00034$
+10.00° C = 283.16° K; 1.50 atm								
7.6341	88.4219	0.964866	80.32	9.4063	0.0803	0.77645	+0.00060	0.77705
11.9426	63.3854	.616531	32.92	9.4435	.0345	.77685	+ .00058	.77743
15.5622	38.0904	.494454	19.41	9.8831	.0226	.77680	+ .00029	.77709
24.0445	39.9908	.328796	8.25	10.1606	.0150	.77693	+ .00002	.77695
31.7895	32.1109	.247218	4.68	10.0937	.0133	.77758	+ .00006	.77764
Extrapolated value-----								0.77699
$\sigma$ -----								$\pm 0.00026$
1.00 atm								
7.8857	78.2654	0.963962	119.17	9.7483	0.1103	0.77106	+0.00043	0.77149
12.1578	44.1411	.616923	49.72	6.6800	.0489	.77094	+ .00053	.77147
15.4957	51.0117	.493985	29.93	9.8900	.0270	.77187	+ .00032	.77219
18.4080	47.5825	.414090	21.82	9.8584	.0194	.77169	+ .00040	.77209
23.2923	43.5259	.328493	13.28	9.8988	.0131	.77194	+ .00004	.77198
31.4505	35.7164	.247232	7.26	10.0655	.0094	.77178	+ .00008	.77170
Extrapolated value-----								0.77162
$\sigma$ -----								$\pm 0.00030$
0.50 atm								
9.5808	73.4262	0.617011	161.50	7.5868	0.1406	0.76500	+0.00186	0.76686
15.7018	41.9239	.493877	59.04	10.0547	.0580	.76683	- .00010	.76673
23.6735	38.3678	.329408	26.08	10.1422	.0269	.76686	- .00020	.76666
31.9499	33.6054	.246343	14.49	10.2447	.0175	.76695	- .00023	.76672
Extrapolated value-----								0.76687
$\sigma$ -----								$\pm 0.00006$

TABLE 1. *Data on perfluoropropane—Continued*

Reciprocal of rate, $F^{-1}$	Mass of sample, $m$	Power, $W$	Pressure drop, $\Delta p$	Temperature rise, $\Delta T$	Blank correction, ( $T$ )	Heat capacity, $C$	Correction for $T_m$ and $p_m$ , $\Delta C$	Heat capacity, $C$ —(observed)
+50.00° C = 323.16° K; 1.50 atm								
<i>sec g<sup>-1</sup></i>	<i>g</i>	<i>w</i>	<i>mm Hg</i>	<i>° K</i>	<i>° K</i>	<i>j g<sup>-1</sup> deg<sup>-1</sup></i>	<i>j g<sup>-1</sup> deg<sup>-1</sup></i>	<i>j g<sup>-1</sup> deg<sup>-1</sup></i>
8.3615	69.1872	0.973454	77.59	9.7307	0.0508	0.83214	+0.00034	0.83248
16.7869	52.7321	.4812918	19.69	9.7010	.0146	.83159	+0.00034	.83193
24.0516	28.5482	.345982	9.69	9.9928	.0076	.83211	+0.00014	.83225
32.5992	22.6392	.243888	5.43	0.5597	.0045	.83128	+0.00044	.83172
Extrapolated value...								0.83261
$\sigma_{..}$								±0.00021
1.00 atm								
8.5834	63.0260	0.973891	112.88	01.0070	0.0714	0.82943	+0.00008	0.82951
16.9441	27.7200	.481379	29.27	9.8184	.0209	.82897	+0.00017	.82914
23.8000	33.9298	.345495	14.99	9.9039	.0125	.82921	+0.00011	.82932
36.1370	35.5804	.244058	6.69	10.6325	.0070	.82894	-0.00039	.82855
Extrapolated value...								0.82981
$\sigma_{..}$								±0.00019
0.50 atm								
12.1633	116.3520	0.687173	117.66	10.0371	0.0752	0.82654	+0.00011	0.82665
17.2428	82.3232	.481102	58.93	10.0040	.0407	.82586	+0.00020	.82606
25.2559	31.9494	.345631	27.28	10.5514	.0205	.82570	-0.00020	.82550
34.7789	21.7759	.243559	14.02	10.2411	.0114	.82621	-0.00011	.82610
Extrapolated value...								0.82662
$\sigma_{..}$								±0.00042
+90.00° C = 363.16° K; 1.50 atm								
8.2178	89.1452	1.088710	91.27	10.0689	0.0350	0.88548	+0.00015	0.88563
16.3840	56.9990	0.542204	23.18	10.0315	.0083	.88482	+0.00009	.88491
23.8928	29.8241	.362959	11.04	9.8054	.0035	.88410	+0.00024	.88434
35.7239	24.9024	.272077	5.53	10.9996	.0013	.88353	-0.00048	.88305
Extrapolated value...								0.88644
$\sigma_{..}$								±0.00009
1.00 atm								
8.2735	79.4052	1.088739	137.93	10.1385	0.0563	0.88356	-0.00008	0.88348
17.0922	45.7350	0.542399	32.51	10.4810	.0108	.88362	-0.00037	.88325
25.8957	40.1121	.363091	14.50	10.6396	.0028	.88349	-0.00046	.88303
32.5131	24.8082	.272998	9.27	10.0527	.0006	.88290	-0.00008	.88282
Extrapolated value...								0.88371
$\sigma_{..}$								±0.00002
0.50 atm								
11.8229	91.7568	0.768290	137.67	10.2451	0.0591	0.88152	-0.00022	0.88130
16.7215	61.3767	.540098	69.10	10.2177	.0303	.88127	-0.00020	.88107
24.4192	34.9221	.362947	32.21	10.0491	.0094	.88113	-0.00008	.88105
33.7577	28.0348	.272367	17.42	10.4279	.0055	.88125	-0.00028	.88097
Extrapolated value...								0.88138
$\sigma_{..}$								±0.00007

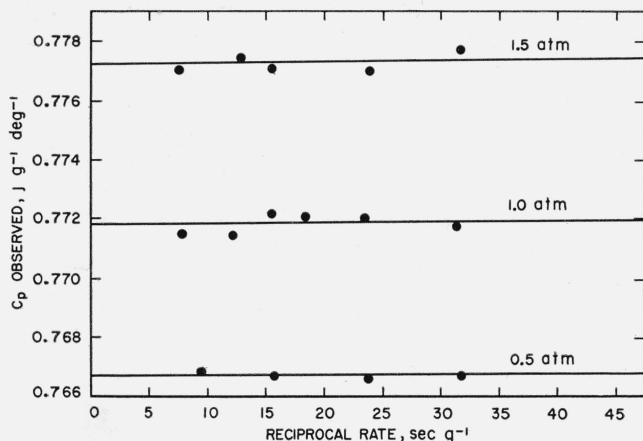


FIGURE 1. Measured heat-capacity values for perfluoropropane at 10° C and three pressures.

effect of curvature of the heat capacity-temperature function. Values of the heat capacity of the ideal gas  $C_3F_8$  were obtained by extrapolation of the results to zero pressure at each temperature of measurement, and are given as " $C_p^0$ , observed" in table 2.

There has been no complete assignment of the vibration fundamentals of perfluoropropane, and consequently statistical calculation of the ideal-gas heat capacity cannot yet be made. Also, there are no density data available for  $C_3F_8$  gas, so the values of the pressure coefficient of heat capacity, given in the last line of table 2, cannot yet be used in determining the constants of a low-pressure equation of state.

The experimental values of  $C_p^0$  for hexafluoroethane (see footnote 1), perfluoropropane, and perfluorocyclobutane (see footnote 2), together with a calculated value<sup>5</sup> for carbon tetrafluoride, are compared at one temperature (50°) in figure 2 by plotting against molecular weight. Similar plots are obtained at other temperatures. It is seen that a nearly constant increment of heat capacity per mole (amounting to about 10.3 cal deg<sup>-1</sup> mole<sup>-1</sup> at 25° C) may be indicated for each added  $CF_2$  group, at least

<sup>5</sup> Rita M. Potocki and D. E. Mann (informal communication).

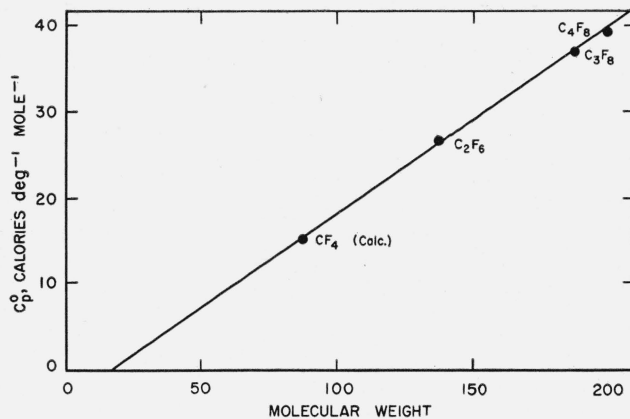


FIGURE 2. Variation with molecular weight of the ideal-gas heat capacities at 50° C of four saturated fluorocarbons.

TABLE 2. Heat capacity of gaseous perfluoropropane ( $C_3F_8$ )

Summary of results				
Temperature, ° C	-30.00	+10.00	+50.00	+90.00
	Calories mole <sup>-1</sup> degree <sup>-1</sup>			
$C_p$ , 1.50 atm		34.93	37.42	39.84
1.00 atm	32.02	34.68	37.29	39.71
0.67 atm	31.73			
0.50 atm		34.45	37.15	39.61
0.33 atm	31.40			
$C_p^0$ , observed	31.10	34.22	37.02	39.49
	Calories mole <sup>-1</sup> degree <sup>-1</sup> atm <sup>-1</sup>			
$\Delta C_p / \Delta P$	0.93	0.47	0.27	0.23

in the straight-chain series. In the case of paraffin hydrocarbons, constancy of heat-capacity increments per added  $CH_2$  group occurs in the higher members of the series, beginning at about *n*-hexane.

WASHINGTON, September 29, 1953.