tane, 2774.1 kj./mole.[16] and other data[20] to obtain the free energy of formation. Free energy of isomerization to isobutene may also be calculated. These values together with the corresponding values for cyclopropane and cyclopentane are given in Table VI. The values given are consistent with the observation that synthesis of cyclobutane has been difficult.

TABLE VI

FREE ENERGY OF FORMATION ($\Delta F^0_{f\,298°}$) AND ISOMERIZATION ($\Delta F^0_{i\,298°}$) OF CYCLIC HYDROCARBONS

Hydrocarbon	$\Delta F^0_{f\,298°}$, kcal./mole	$\Delta F^0_{i\,298°}$ (to most stable alkene), kcal./mole
Cyclopropane[13]	24.98	− 9.99
Cyclobutane	26.31	−11.73
Cyclopentane	9.23	5.04

Our analysis of cyclobutane suggests that some other strained cyclic compounds may also have double minimum potential functions with barriers sufficiently low so that similar effects might be observed. Spectroscopic investigation has confirmed this expectation in the cases of cyclopentene and cyclopentane. Preliminary spectroscopic investigation of octafluorocyclobutane has yielded negative results.

We are indebted to Professor R. S. Halford for helfpul suggestsions and advice in connection with this problem.

NEW YORK, N. Y.
BERKELEY, CALIF.

(20) "Properties of Hydrocarbons," Project #44, American Petroleum Institute.

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Condensed Gas Calorimetry. V. Heat Capacities, Latent Heats and Entropies of Fluorine from 13 to 85°K.; Heats of Transition, Fusion, Vaporization and Vapor Pressures of the Liquid[1]

BY JIH-HENG HU, DAVID WHITE AND HERRICK L. JOHNSTON

RECEIVED JULY 2, 1953

Heat capacities of fluorine were measured from 14 to 85°K. A first-order transition was found at 45.55°K. with heat of transition equal to 173.90 ± 0.04 cal./mole. The melting point of pure fluorine was found to be 53.54°K. and the heat of fusion, 121.98 ± 0.5 cal./mole. The heat of vaporization at 84.71°K. and 738 mm. was found to be 1563.98 ± 3 cal./mole. The vapor pressure of liquid fluorine was measured between the melting point and 90°K., and the data were fitted to the equation: $\log P_{\mathrm{mm}} = 7.08718 - \frac{357.258}{T} - \frac{1.3155 \times 10^{18}}{T^8}$. The normal boiling point, calculated from this equation, is 85.02 ± 0.02°K. Thermodynamic functions of fluorine have been computed from 0 to 85°K. The entropy in the ideal gas state at 85.02°K., from the calorimetric measurements, is 39.58 ± 0.16 e.u. Values calculated from spectroscopic data by Haar and Beckett, and by Cole, Farber and Elverum (39.56 ± 0.01 and 39.62 ± 0.02 e.u., respectively) are in good agreement with the calorimetric value.

Introduction

At present there are very few accurate measurements of the physical properties of fluorine at low temperatures. The calorimetric measurements by Kanda[2] show considerable uncertainties and do not agree with the results obtained from spectroscopic data. Furthermore, Murphy and Rubin[3] have pointed out, from a careful examination of these data, that a transition in the solid may have been overlooked.

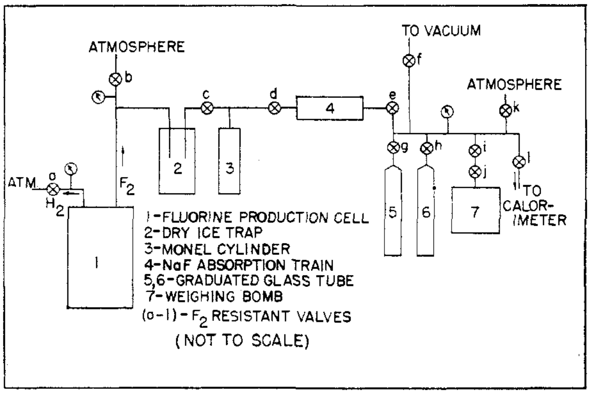

Fig. 1.—Purification system.

Because of a variety of important commercial uses for fluorine, considerable interest in accurate thermal properties of this molecule has been evident recently. We therefore deemed it desirable to reinvestigate the thermal properties of F_2 with our improved instruments and techniques which were not available to the earlier investigators.

Materials

The fluorine used in our calorimetric study was produced by a Harshaw laboratory-size fluorine cell. Its electrolyte was a mixture of KF, 2HF and 1.0–1.5% LiF. The cell was allowed to operate several hours before F_2 was allowed to collect in the purification system. The procedure for purifying the material and filling the calorimeter is shown schematically in Fig. 1. All tubings and valves in this system were made of Monel or nickel, the valves were packed with Teflon, and all joints were silver-soldered.

The system was first evacuated and flushed with fluorine several times before use. After leaving the Harshaw electrolytic cell (1) and passing through a dry ice trap (2) to remove most of the HF vapor, 100 cc. of liquid fluorine was condensed into a Monel cylinder (3). The greatest part of the remaining HF was removed from the material by an NaF absorption train before it was further purified by repeated bulb to bulb distillations, (3) to (5), (5) to (6), and finally from bulb (6) to the high-pressure Monel bomb (7) in which the material was carefully weighed at room temperature before condensing into the calorimeter. The amount of F_2 condensed in the calorimeter, determined by weighing the bomb (7) before and after filling the calorime-

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[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] E. Kanda, *Bull. Chem. Soc. Japan*, **12**, 473 (1937).

[3] G. M. Murphy and E. Rubin, *J. Chem. Phys.*, **20**, 1179 (1952).

ter, on a balance which had an accuracy of approximately 5 mg., was 97.616 g. (2.5688 moles). A more detailed description of the condensation has been given in a previous paper dealing with HF.[4]

The purity of the sample was estimated as 99.97% from the melting point determinations (see Section III of this text, on freezing point determination).

Experimental Results and Procedure

I. **Heat Capacities** of Solid I, Solid II and the Liquid.—The experimental procedure in determining the heat capacities was identical to that previously described for condensed gas calorimetry.[5] The experimental heat capacities are summarized in Table I and plotted in Fig. 2 along with the data of Kanda.[2] The heat capacity curve of the solids shows a normal shape from 13 to 45.55°K. at which temperature a first-order transition occurs before the substance melts at 53.54°K. The heat capacity of the liquid shows a minimum, before steadily increasing.

Table I

Experimental Heat Capacity of Fluorine (F_2)

T_{av}, °K.	C_p, cal./mole/deg.	T_{av}, °K.	C_p, cal./mole/deg.	T_{av}, °K.	C_p, cal./mole/deg.
13.89	1.505	Transition at		Melting point	
15.49	1.871	45.55°K.		53.54°K.	
17.08	2.322	48.51	11.585	58.14	13.685
18.86	2.778	49.42	11.729	62.27	13.685
21.37	3.568	50.39	11.839	67.05	13.556
24.16	4.406	51.49	12.728	71.86	13.567
27.60	5.358	52.09	17.331	76.60	13.714
31.60	6.462			81.32	13.797
36.99	7.919				
41.48	9.222				

II. **Transition Temperature and Heat of Transition.**—The temperature at which the transition occurs in solid fluorine was obtained from heating curves for a constant rate of energy input. The system was found to remain at a constant temperature of 45.55 ± 0.02°K., until the transition was complete. This constant value was taken as the transition temperature of solid fluorine. The heat of the transition was obtained by subtracting off from the total energy input that part of the energy which was used in heating the sample up to, and beyond, this transition temperature. Two determinations were made, and the results obtained are summarized in Table II.

Table II

The Heat of Transition of Solid Fluorine (F_2)

Run no.	Temp. interval, °K.	ΔH_T (heat of transition), cal./mole
1	42.40–47.88	173.86
2	42.32–47.17	173.94
	Average	173.90 ± 0.04

Transition temperature 45.55 ± 0.02°K.

III. **Melting Point and Heat of Fusion.**—The melting point of fluorine was obtained by studying the temperature of the sample as a function of the fraction of the material melted and then extrapolating to an infinite amount melted. This extrapolation should give a value which corresponds to the melting point of the pure substance. The experimental data can be expressed by the relation

$$T = 53.54 - (0.069/x) \qquad (1)$$

where x is the fraction melted. Putting $1/x = 0$, *i.e.*, for infinite dilution, one obtains the melting point of pure fluorine, equal to 53.54 ± 0.02°K. The value reported by Kanda[2] is 55.2°K. The experimental values of the temperature and those calculated from equation 1 for various fractions of the solid melted are given in Table III. The deviation is ±0.01°K.

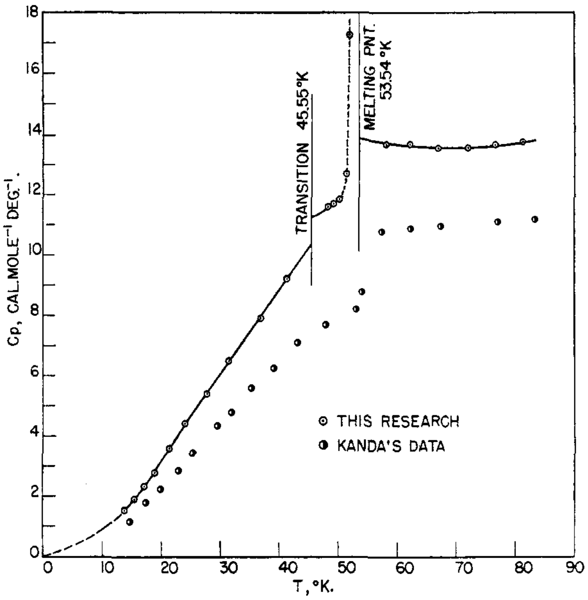

Fig. 2.—Heat capacity of fluorine.

Table III

Melting Point of Fluorine (F_2)

x, fraction melted	$T_{expt.}$, °K.	$T_{calcd.}$, °K.
0.395	53.37	53.37
.555	53.41	53.42
.718	53.44	53.44
.888	53.47	53.46

Melting point of the pure substance 53.54 ± 0.02°K.

From a theoretical point of view, the relation between T and x, for an ideal dilute solution, should be

$$T = T_f - K/x \qquad (2)$$

where

$$K = (RT_f^2/\Delta H_f)y$$

T_f is the melting point of pure substance, ΔH_f is the heat of fusion, and y is the number of moles of soluble impurities. By substituting the values of K, T_f and ΔH_f into equation 2, solving for y, and assuming that the mean molecular weight of the impurities is about 20 (which is approximately equal to the molecular weight of HF), the purity of the sample is estimated to be 99.97%.

The heat of fusion was obtained in the usual way. The sample was heated from a temperature below the melting point to one above. By subtracting from the total input energy that part of energy which was used for heating the sample up to, and beyond, the melting point (obtained from the heat capacity of solid and liquid fluorine), the heat of fusion was obtained. Four determinations were made and

Table IV

Heat of Fusion of Fluorine (F_2)

Run no.	Temp. interval, °K.	ΔH_f (heat of fusion), cal./mole
1	53.18–54.50	121.63
2	52.42–56.16	121.91
3	53.25–56.55	122.46
4	50.99–53.86	121.93
	Average	121.98 ± 0.5

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[4] J. H. Hu, D. White and H. L. Johnston, This Journal, **75**, 1232 (1953).

[5] H. L. Johnston, J. T. Clarke, E. B. Rifkin and E. C. Kerr, *ibid.*, **72**, 3933 (1950).

the results are summarized in Table IV. The present value is equal to about one-third of the value given by Kanda.[8]

IV. **Heat of Vaporization.**—Four determinations of the heat of vaporization, ΔH_v, have been made. During the vaporization, the pressure was held constant to within 5 mm. by observing the pressure on a Monel Bourdon gage and manually controlling the rate of recondensation into the Monel bomb (7) by means of a valve (see Fig. 1). The amount of fluorine evaporated from the calorimeter (Fig. 1) was determined by weighing the Monel bomb before and after each run. The error introduced, due to weighing, was about 0.1%. Since the total correction to the energy input for the heat leak was never greater than 20 cal./mole, and could be determined to within 10–15%, the total error in the heat of vaporization should not exceed ±0.2%. The experimental results are summarized in Table V; they agree very well with the values given by Kanda.[2]

TABLE V

HEAT OF VAPORIZATION OF FLUORINE (F_2)

Run no.	Amount of F_2 evaporated, g.	ΔH_v at 84.71°K. 738 mm., cal./mole
1	12.241	1562.71
2	9.706	1561.95
3	9.729	1567.32
4	9.690	1563.95
	Average	1563.98 ± 3

V. **Vapor Pressures of Liquid Fluorine.**—Vapor pressure measurements on liquid F_2 were carried out by using a glass U-tube filled with "fluorolube," a substance which is non-reactive in the presence of F_2. One side of this U-tube was connected to the calorimeter, and the other side to a mercury manometer which was read with a cathetometer to within ±0.03 mm. The difference in the heights of the fluorolube columns in the two arms of the U-tube, was observed by another cathetometer, and was always adjusted to a minimum value. The pressure exerted by the fluorolube column, in terms of mm. of mercury, was determined by intercomparing the fluorolube manometer with the mercury manometer before and after the vapor pressure measurements. The final results are given in Table VI along with the data of Cady and Hildebrand.[6]

The best equation representing the data of the present investigation was found to be

$$\log_{10}P_{\text{mm}} = 7.08718 - \frac{357.258}{T} - \frac{1.3155 \times 10^{13}}{T^8} \quad (3)$$

This equation gives a triple point pressure of 1.66 mm. at 53.54°K., and gives 85.02 ± 0.02°K. for the normal boiling point, compared with 84.93 ± 0.1°K., 85.12 ± 0.1°K. and 85.4°K., given by Cady and Hildebrand,[6] by Claussen[7] and by Kanda,[8] respectively.

In order to compare the consistency of these results with the calorimetric data, the heat of vaporization was calculated at 84.71°K. and 738 mm. from the Clausius–Clapeyron relation, using the vapor pressure equation 3. The vapor and liquid densities were obtained from determinations of the second virial coefficient of gaseous fluorine and its liquid density, both measured by the authors[9,10] in this Laboratory. The value thus calculated is 1558 cal./mole, which agrees closely with the calorimetric value of 1564 ± 3 cal./mole at the same temperature and pressure.

TABLE VI

VAPOR PRESSURES OF LIQUID FLUORINE (F_2)

The values appearing in the parentheses in column 5 were obtained by extrapolation of Cady and Hildebrand's vapor pressure equation, above and below the range (72.53–85.99°K.) of their experimental data.

T, °K.	$P_{\text{expt.}}$, mm.	$P_{\text{calcd.}}$, mm.	Deviation	P,[a] mm.
53.56	1.67	1.67	0.00	(2.07)
53.84	1.84	1.84	.00	(2.25)
54.99	2.73	2.71	+ .02	(3.18)
55.69	3.46	3.39	+ .07	(3.95)
57.56	5.94	5.91	+ .03	(6.49)
59.03	8.84	8.82	+ .02	(9.47)
60.50	12.89	12.85	+ .04	(13.57)
61.95	18.26	18.18	+ .08	(19.00)
63.49	25.93	25.74	+ .19	(26.68)
65.02	35.28	35.59	− .31	(36.70)
66.52	48.12	48.11	+ .01	(49.45)
68.00	63.66	63.76	− .12	(65.40)
69.57	84.30	84.72	− .42	(86.75)
71.07	109.22	109.64	− .42	(112.13)
72.56	139.67	140.06	− .39	143.06
75.59	223.73	223.19	+ .54	227.38
77.17	280.40	280.14	+ .26	284.85
78.54	338.89	338.44	+ .45	343.38
80.03	412.75	412.50	+ .25	417.34
81.59	504.10	503.42	+ .68	507.55
83.06	604.12	603.03	+1.09	605.64
84.58	722.98	721.59	+1.39	721.35
85.05	763.08	761.60	+1.48	760.16
86.60	907.07	907.32	−0.25	(901.50)
87.52	1002.72	1003.07	−0.35	(992.12)
88.59	1122.29	1124.55	−2.26	(1107.40)
89.40	1219.89	1223.57	−3.68	(1200.75)

[a] Calculated from Cady and Hildebrand's equation.

Entropy of Fluorine in the Ideal Gas State

The entropy calculations are given in Table VII. The correction for gas imperfection is calculated from the results obtained by the authors[9] for their measurements of the second virial coefficient of gaseous fluorine. In calculating the entropy from 0–14°K. it was found that the experimental values of C_p at low temperatures (14–20°K.) do not follow the T^3 law. By plotting C_p against T^3 and estimating the slope of the curve near the absolute zero,

TABLE VII

ENTROPY OF FLUORINE (F_2)

	e.u.
Solid I, 0–14°K. (extrapolation)	0.629
14–45.55°K. (Simpson's rule)	5.970
Transition at 45.55°K. (173.90/45.55)	3.818
Solid II, 45.55–53.54°K. (Simpson's rule)	1.891
Fusion at 53.54°K. (121.98/53.54)	2.278
Liquid, 53.54–84.71°K. (Simpson's rule)	6.274
Vaporization at 84.71°K. (378 mm.) (1563.98/84.71)	18.463
Entropy change from 84.71°K. (378 mm.) to 85.02°K. (700 mm.)	−0.036
Correction for gas imperfection	0.29
Entropy of ideal gas at 85.02°K. (760 mm.)	39.58 ± 0.16

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(6) G. H. Cady and J. H. Hildebrand, THIS JOURNAL, **52**, 3829 (1930).

(7) W. H. Claussen, *ibid.*, **56**, 614 (1934).

(8) E. Kanda, *Bull. Chem. Soc. Japan*, **12**, 463 (1937).

(9) D. White, J. H. Hu and H. L. Johnston, "The density and surface tension of liquid fluorine between 65 and 80K." (submitted for publication).

(10) D. White, J. H. Hu and H. L. Johnston, "Measurements on the second virial coefficient of gaseous F_2 from 80–300°K." (unpublished results).

θ_D was found to be approximately 78. With this value of θ_D, and also taking into consideration the temperature dependence of experimental values of C_p at the lowest temperatures (14–20°K.), the increase of entropy from 0 to 14°K. is estimated to be 0.63 e.u. with an uncertainty of ±0.06 e.u. The uncertainties in the entropy calculations, due to errors in the measurements of the heat of vaporization and heat capacity and in the estimation of gas imperfections, are estimated, respectively, to be ±0.03, ±0.04 and ±0.03 e.u. The total uncertainty in the entropy of F_2 is therefore about ±0.16 e.u.

TABLE VIII

THERMODYNAMIC FUNCTIONS OF FLUORINE (F_2)

Temp., °K.	C_p, cal./mole/ deg.	S, cal./mole/ deg.	$(H - H_0)/T$, cal./mole/ deg.	$-(F - H_0)/T$, cal./ mole/ deg.
		Solid I		
15	1.745	0.741	0.5226	0.218
20	3.104	1.422	0.9915	.431
25	4.609	2.276	1.564	.712
30	6.031	3.245	2.192	1.053
35	7.427	4.281	2.842	1.439
40	8.778	5.363	3.502	1.861
45	10.142	6.475	4.164	2.311
45.55	10.290	6.599	4.237	2.362
		Solid II		
45.55	11.120	10.417	8.055	2.362
50	11.792	11.486	8.359	3.127
53.54	12.210	12.308	8.600	3.708
		Liquid		
53.54	13.700	14.586	10.879	3.708
55	13.698	14.955	10.954	4.001
60	13.680	16.146	11.182	4.964
65	13.607	17.239	11.372	5.867
70	13.558	18.245	11.529	6.716
75	13.642	19.182	11.666	7.516
80	13.793	20.067	11.794	8.273
85	13.948	20.907	11.916	8.991
85.02	13.948	20.909	11.917	8.992
85.02 (Vapor)	....	39.287	30.281	8.996
85.02 (Ideal gas)	....	39.577	.....	...

The entropy of F_2 in the ideal gas state has been calculated at various temperatures from spectroscopic data by Cole, Farber and Elverum,[11] and by Haar and Beckett.[12] Their values of entropy at 85.02°K. are, respectively, 39.62 ± 0.02 and 39.56 ± 0.01 e.u., which are in close agreement with the value obtained from our calorimetric data (39.58 ± 0.16).

Derived Thermodynamic Functions

The heat capacity and the derived thermodynamic functions for F_2 at selected integral values of temperature are given in Table VIII.

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[11] L. G. Cole, M. Farber and G. W. Elverum, Jr., *J. Chem. Phys.*, **20**, 586 (1952).

[12] L. Haar and C. W. Beckett, National Bureau of Standards Report 1435 (1952).

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Heat of Combustion of Cerium[1]

BY ELMER J. HUBER, JR., AND CHARLES E. HOLLEY, JR.

RECEIVED MAY 14, 1953

A precise measurement has been made of the heat of combustion of cerium metal. It was found to be 7749 ± 10 joules/g. at an oxygen pressure of 25 atm. The heat of formation of CeO_2 at 25° is calculated to be −1088.6 ± 1.4 kjoules/mole. This value differs by 7 to 12% from those found in the literature.

Introduction.—Values in the literature[2–4] for the heat of formation of CeO_2 are in poor agreement, presumably because of the use of impure cerium metal. This paper reports the results of the combustion of analyzed cerium metal to determine the heat of formation of its dioxide.

Method.—The method involved the determination of the heat evolved from the burning of a weighed sample of the metal in an oxygen bomb calorimeter at a known pressure. The energy equivalent of the calorimeter was determined from the heat of combustion of standard benzoic acid and also was determined electrically. The completeness of combustion was determined by treating the combustion products with 6 *N* perchloric acid and measuring the amount of hydrogen evolved from any unburned metal present.

The uncertainties given are twice the standard deviations.

The results are expressed in absolute joules and also in defined calories; 1 defined calorie = 4.1840 absolute joules.

Apparatus.—The details of the construction and calibration of the calorimeter have been described.[5] The energy equivalent of the calorimeter with oxygen at 25 atmospheres pressure was 10,096.6 ± 3.1 joules/deg.

Cerium Metal.—The cerium metal was supplied by Dr. F. H. Spedding of the Ames Laboratory of the A. E. C. This metal was analyzed at the Los Alamos Scientific Laboratory with the following results: Na, 0.05%; Mg, 0.01; Ca, 0.005; La, 0.01; C, 0.0090; N, 0.0975; O, 0.244 and H, < 0.001. Any other metallic impurities were present in amounts too small to be detected by the spectroscopic method used. The metal was thus about 99.57% cerium. The chemical state of the impurities is not known. However, if it is assumed that the oxygen, nitrogen and carbon are combined with cerium as CeO_2, CeN and CeC_2, respectively, and not combined with the metallic impurities, then the material is 97.48 atomic per cent. cerium metal. A Debye X-ray pattern of the metal showed only lines of the metal in the cubical form.

Combustion of Cerium.—The cerium was burned as chunks on sintered discs of cerium dioxide supported on a platinum platform weighing 103.8 g. New discs were used

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[1] This work was done under the auspices of the A. E. C.

[2] W. Muthmann and L. Weiss, *Ann.*, **331**, 1 (1904).

[3] H. Hirsch, *Trans. Electrochem. Soc.*, **20**, 57 (1911).

[4] J. Moose and S. Parr, THIS JOURNAL, **46**, 2656 (1924).

[5] C. E. Holley, Jr., and E. J. Huber, Jr., *ibid.*, **73**, 5577 (1951).