Studies on Fluorine at Low Temperatures. VIII. Determination of Molecular Heat, Heat of Fusion of Condensed Fluorine and the Entropy of Fluorine.

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The molecular heats of oxygen, nitrogen and other ordinary elements in the forms of condensed gases have been determined at low temperatures, and accordingly their entropies are already known. But such determinations have not been made at all on fluorine and volatile fluorides (except hydrogen fluoride). The present author measured the specific heat of fluorine at low temperatures, and in addition, determined the melting point, heat of fusion and entropy of fluorine, using a method by which he previously measured the specific heat of organic compounds at low temperatures.(1)

I. Method and Apparatus. The apparatus for the experiment is shown in Fig. 1.

(1) *Cooling device.* The measurement was made in a range from −190°C. to −258°C., the cooling being done by liquid nitrogen or liquid hydrogen or solid hydrogen. The apparatus illustrated in Fig. 1 is for cooling by solid hydrogen or liquid hydrogen. In this apparatus, A is a Dewar vessel made of German silver which is intended for liquid nitrogen, and B is a glass Dewar vessel for liquid hydrogen. B has a brass cap D in its upper part, which is connected with the Dewar vessel by means of rubber packing and is kept air-tight. The cap D has an opening at which the calorimeter is held, an opening for the double-walled pipe through which liquid hydrogen is poured in, a device for indicating the depth of liquid hydrogen, an opening at which the mercury pressure gauge is held, and an exhaust opening. Filling B with liquid hydrogen is done by connecting it with V_1 by means of the double-walled pipe, and the liquid is sucked in by a pump attached to M.

For lowering the temperature of the liquid hydrogen under its boiling point −252°C., the pump of large capacity attached to M is worked, and the liquid is vaporized vigorously at the decreased pressure. When

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(1) Aoyama and Kanda, *Sci. Repts. Tôhoku Imp. Univ.*, Ser. I, **24** (1935), 116.

the vapour pressure of the liquid hydrogen is 40 mm., the hydrogen gradually solidifies, and reaches the triple point, that is, $-258°$C.

(2) *Apparatus for determining the temperature.* Inside the device for measuring the specific heat, there is a platinum resistance thermometer which is made by winding a platinum thread around a copper cylinder insulated with bakelite. The precision of this thermometer is determined in advance by comparing its resistance with the temperature of the gas thermometer.(2) The resistance is shown in Table 1.

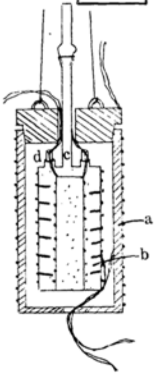

Fig. 2.

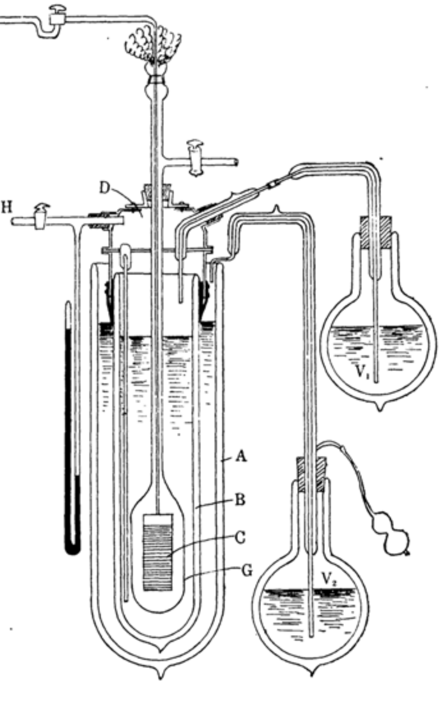

Fig. 1.

Table 1.

Temperature (°C.)	Resistance (ohm)
0°	20.1550
−25.50	18.2597
−39.10	17.1710
−68.38	14.8130
−125.55	10.1146
−158.75	7.3203
−183.40	5.2059
−195.85	4.2633
−252.66	0.9652
−254.53	0.8154
−256.50	0.6637
−258.17	0.5324

At temperatures lower than $-252.66°$C., the calibration was made by means of a hydrogen vapour thermometer.(3)

According to the formula

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(2) Aoyama and Kanda, this Bulletin, **10** (1935), 472.

(3) Wrede-Rankine-Keesom's formula (Onnes and Keesom, *Commun. Phys. Lab. Univ. Leiden*, Suppl. No. 23) is used, which is

$$\log p_{\text{cm.}} = 4.6063 - \frac{58.40}{T} + \frac{61}{T^2}.$$

$$R_t = \alpha R_0\left[\frac{1}{\alpha}+t+\delta\left(1-\frac{t}{100}\right)\frac{t}{100}+\beta\left(1-\frac{t}{100}\right)\left(\frac{t}{100}\right)^3\right],$$

the relation between the resistance and the temperature at −252.66°C. and upward can be expressed in

$$R_t = 0.0038745 \times 20.1550 \times \left[258.097+t+1.4950 \times \left(1-\frac{t}{100}\right)\frac{t}{100}+ \right.$$
$$\left. 0.11251 \times \left(1-\frac{t}{100}\right)\left(\frac{t}{100}\right)^3\right].$$

(3) *Apparatus for measuring the specific heat.* The apparatus for measuring the specific heat was nearly the same as one formerly used in the measurement on organic substances, but was made suitable for condensed gases.

In Fig. 2, a is a case made of a thick copper plate. The temperature is adjusted by means of a heating coil around the outside of the case. b is a cylinder made of a thin copper plate and has a resistance thermometer and a few ledges in it with a heating coil of a constantan wire on the outside. There are junction points of a thermocouple on the inside and outside of a and b respectively for determining the difference in temperature between the two sides. The exit d for the platinum resistance wire is sealed with fused glass as shown in the figure. The sample is introduced through C and condensed in b. This device is put in a glass bulb G, which is set up in the cooling vessel.

(4) *Determination of the amount of the sample.* The determination of the amount is very difficult in the case of condensed gases. This is especially the case with fluorine, for which a gas reservoir cannot be used. The author used a 200 c.c. gas-burette, in which glycerine was placed on the mercury as shown in Fig. 3.

(5) *Apparatus for determining the heating energy.* The electrical connections for measuring the temperature of the sample and heating energy electrically applied to the calorimeter are illustrated in Fig. 4. To make the construction of the device well understood and to give an exact idea of the apparatus, the platinum thermometer, the sample, the heating coil, and the case are separately illustrated.

The measuring apparatus consists of a system in which the current in the heating coil and the potential difference between the ends of the coil are measured and of a system in which the resistance of the platinum thermometer is measured. In both systems there are standard resistances connected with the potentiometers. The heating energy was

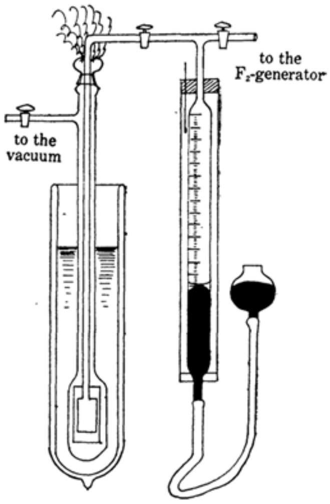

Fig. 3.

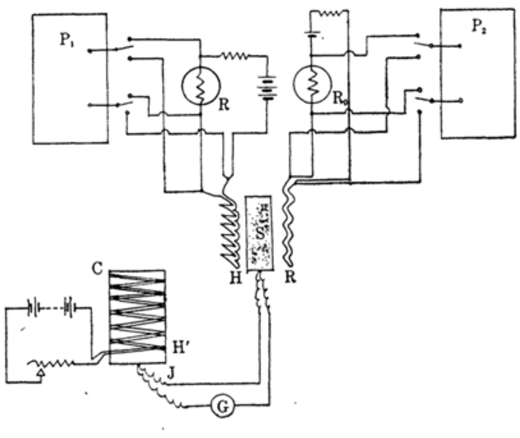

Fig. 4.

determined by means of the Leeds and Northrup type potentiometer, and the potentiometer for low potential free from thermoelectromotive force was used for the resistance thermometer.

(6) *Construction of the calorimeter and heat loss.* For obtaining a desired low temperature, dry air or dry hydrogen gas was introduced into the glass bulb G in Fig. 2, and the low temperature of the liquid nitrogen or liquid hydrogen on the outside was transmitted to the case and the calorimeter by conduction of this gas. The temperature of the sample was observed by means of the platinum thermometer, and when a proper temperature was reached, G was cleared of the hydrogen gas, and was made highly vacuous (about 10^{-5} mm. Hg). In this way the inward transmission of cold through the wall of G was prevented. Further, for preventing cooling of the calorimeter by conduction of any remaining gas, the case was heated slowly through the coil on its surface. The difference in temperature between the outer surface of the calorimeter and the inner surface of the case was observed even while the specific heat was being measured by means of a galvanometer, and the heating current on the case was adjusted during the rise of temperature so that the difference might not exceed 0.5°. Although this process is far more complicated than one in which the calorimeter is simply hung in G, it greatly decreases the heat loss due to radiation and conduction, and minimizes the error.

Supposing that the vacuum in G is about 10^{-5} mm. Hg, that the temperature at which the specific heat is to be measured is -200°C., and that the difference in temperature between the walls of G and b is 50°, the heat loss of the calorimeter due to radiation q_r and due to conduction q_g will be approximately expressed by

$$q_r \fallingdotseq \frac{F_i}{\frac{1}{C}+\frac{F_i}{F_e}\left(\frac{1}{C}-\frac{1}{C_b}\right)}(T_e^4-T_i^4) \fallingdotseq F_iC(T_e^4-T_i^4)\ , \quad \text{and}$$

$$q_g = \frac{a}{2-a}\eta p\sqrt{\frac{273}{T_i}}(T_e-T_i)F_i \fallingdotseq \eta p\sqrt{\frac{273}{T_i}}(T_e-T_i)F_i\ ,$$

where F_i is the surface area of the calorimeter, F_e that of glass bulb G, T_i temperature of the calorimeter, T_e the surface temperature of G, C radiation constant of the material of the calorimeter, etc., C_b that of the black body, a the accommodation coefficient of the gas (air or hydrogen), η a constant dependent upon the viscosity, and p the pressure of the remaining gas (mm. Hg).

For example, in case $F_i=50$ cm.^{2}, $T_i=73$°K (−200°C.), and $T_e=23$°K (−250°C.), we have $q_r=5.86\times10^{-5}$ cal./sec., and $q_g=27.8\times10^{-5}$ cal./sec.

In the actual measurement, the temperature of the sample is raised usually by 0.2° for every 5 minutes. For 5 minutes $q_r'=0.0176$ cal., $q_g'=0.0834$ cal., and $\Sigma q'=0.101$ cal.

The test fluorine (about 20 g.) actually requires about 1 cal. at this temperature or neighbourhood for a rise of 0.2°, and so the above-mentioned heat loss amounts to more than 10%. If, however, the temperature of the wall of the case is kept at −199.5°C. by adjusting against −200°C. of the device, we shall have $\Sigma q'=0.0088$ (for 5 minutes).

This shows that the heat loss is about 0.9% of the heat required. In this way the heat loss must be kept small for making the experiment with a very small temperature rise of the sample and for obtaining a specific heat as near the true one as possible.

II. **Measurment of Specific Heat.** (1) Quantity of heat which is electrically given is (a) consumed in the temperature rise of the sample and (b) consumed in the temperature rise of the calorimeter itself, and (c) escapes outward, resulting in heat loss.

$$Q = I^2RZ = (CM+w)\times\Delta t+q = (CM+w)\times\Delta t'\ ,$$

where I is electric current flowing through the heating coil of the calorimeter, R resistance of the heating coil of the calorimeter, Z duration of heating, C specific heat of the sample, M mass of the sample, w water equivalent of the device, and Δt rise of the temperature. Of these, w was determined in advance at various temperatures.

The heat escaping outward was, as stated before, about 1 to 2%, and was determined experimentally by a temperature-time curve. Thus the specific heat of the sample could be determined by the foregoing formula.

(2) *Correction for the heat loss and determination of the temperature rise.* As for the correction for the heat loss and the determination of the true temperature rise, the resistance of the platinum thermometer and the time were observed before and after the heating of the sample and the temperature-time curve was constructed (Fig. 5). From this curve the true rise of temperature was obtained. For instance, let us suppose that the temperature of the sample is not kept perfectly constant but has a tendency slightly to rise before the heating (A–B) and that the heating is begun at B (the time Z_1) and ends at C (the time Z_2), the sample then gradually being cooled along the C–D line. The lines AB and CD are extended as in the figure, and F is taken on the extension of the DC line so that ΔZ may be equal to $\mathrm{BCE}/\Delta t$. If G is the point of intersection of the ordinate through F and the extension of the AB line, $\mathrm{FG}=\Delta t'$ will be the true rise of temperature. The area BCE is determined on section paper.

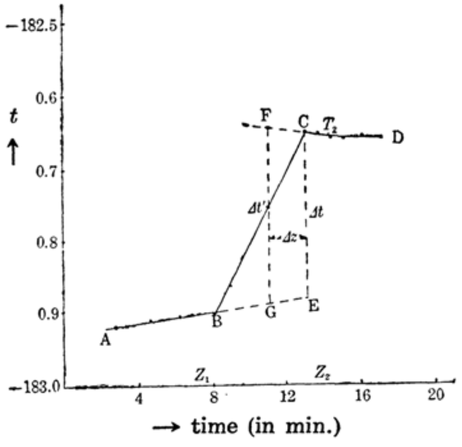

Fig. 5.

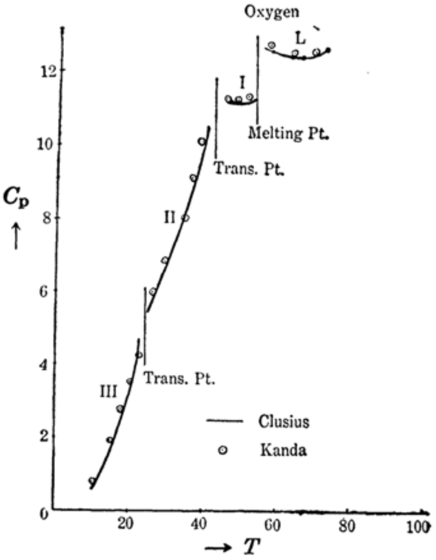

Fig. 6.

(3) *Water equivalent of the calorimeter.* See Table 2.

Table 2.

Temperature	Water equivalent	Temperature	Water equivalent
0°	2.141	−159.17	1.608
−15.50	2.120	−172.15	1.521
−37.85	2.074	−185.55	1.480
−50.17	2.041	−192.50	1.293
−58.56	2.024	−199.13	1.209
−67.21	2.005	−207.21	1.121
−86.17	1.950	−211.50	1.063
−94.54	1.921	−219.10	0.941
−103.13	1.889	−225.86	0.841
−118.55	1.821	−232.10	0.705
−127.34	1.782	−238.11	0.558
−134.85	1.744	−250.18	0.221
−145.76	1.690	−258.22	0.0045

III. Results of the Measurements. (1) *Oxygen.* In the preliminary experiment, measurement was carried out on liquid oxygen and solid oxygen. It was intended only for comparing its result with those already obtained by Eucken(4) and Clusius(5) (see Fig. 6). The values are shown in Table 3. The values obtained in the author's experiment were somewhat greater than those obtained by Clusius for liquid and solid I, but were close to the values reached by Eucken, which, however, are not given here.

Table 3.

Author	Eucken	Clusius	Kanda
Transition point I	23.5°K	23.8°K	24.1°K
„ „ II	42.5	43.5	42.9
Melting point	54.1	54.1	54.3

(2) *Fluorine.* The quantity of the sample used in each experiment was about 0.5 mol. The result as reduced to the molecular heat according to the value of specific heat is tabulated below.

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(4) Eucken, *Verhandl. Phys. Ges.*, **18** (1915), 4.

(5) Clusius, *Z. physik. Chem.*, B, **3** (1929), 41.

(a) Molecular heat. See Table 4.

Table 4.

T	C_p	C_v	θ	T	C_p
14.91	1.167	11.59	99.8	47.95	7.741
17.75	1.807	1.786	100.2	52.98	8.210
20.01	2.240	2.203	101.0	53.98	8.761
23.10	2.841			55.20	Melting point
25.42	3.440			57.50	10.84
29.50	4.310			62.51	10.92
32.00	4.795			67.49	10.98
35.40	5.561			77.10	11.12
39.11	6.280			83.41	11.20
43.10	7.120			85.19	Boiling point

(b) Melting point and heat of fusion. According to thermal analysis, the melting point is 55.20°K. The heat of fusion was determined by measuring the total heat quantity used for heating from a point a little below the melting point up to a point a little higher than this point, and by subtracting from this total heat quantity the sensitive heat used for the respective rises of temperature from the values of the specific heat of the solid and liquid. The heat of fusion is $Q_s=372$ cal./mol. The value of C_p is given in Fig. 7.

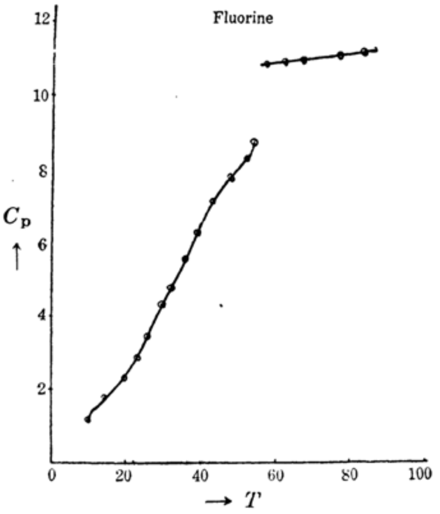

Fig. 7.

IV. Characteristic Temperature and Entropy as Determined from the Result of Measurements.

(1) *Characteristic temperature.* Debye's law of T^3 for the atomic heat at constant volume is, strictly speaking, applicable only in the case of a monatomic and cubic system. But if the molecule of crystal of solid fluorine also can be regarded as making Debye's vibration at a temperature below 20°K as if it were a single atom, its molecular heat may be said to be proportional to the cube of

the absolute temperature. On this assumption, the characteristic temperature Θ was obtained from the molecular heat at three points below 20°K.

For determining the molecular heat at constant pressure, the following formula was used:

$$C_v = C_p - 0.0214\frac{T}{T_s}C_p^2 ,$$

where T_s is the melting point, 55.20°K.

The characteristic temperature Θ was determined from the value of C_v by using

$$C_v = \frac{12\pi^4}{5}R\left(\frac{T}{\Theta}\right)^3 .$$

The results obtained at three points below 20°K well coincide with one another and show the above-mentioned assumption is right. Thus we have $\Theta = 100.3$.

(2) *Entropy of fluorine vapour.* The entropy of fluorine vapour is obtained from

$$S = \int_0^T \frac{C_p}{T} dT .$$

There being no measured value of the molecular heat at temperatures below 15°K, the author made integration, using Debye's function and putting $\Theta = 100.3$.

For determining $\int_0^T \frac{C_p}{T} dT$ as to the solid and liquid between 15°K and 55.2°K, and 56.2°K and 85.19°K, by using $T_s = 55.2$, $Q_s = 372$ cal. at the melting point and $T_\sigma = 85.19$, $Q_\sigma = 1581$ cal. (from the vapour pressure data) at the boiling point, a curve is drawn for the measured values of C_p at various temperatures against $\ln T$, and mensuration was graphically made of $\int C_p d\ln T$.

Further, to the value of entropy of such an ideal gas must be added correction for the entropy of a real gas.

From Berthelot's equation of state

$$PV = RT\left[1 + \frac{9}{128}\frac{PT_c}{P_cT}\left(1 - 6\frac{T_c^2}{T^2}\right)\right] ,$$

where T_c is the critical temperature (144 for fluorine) and P_c is the critical pressure (55 atm.), and from the thermodynamical relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$, we have

$$\Delta S = S_{\text{real}} - S_{\text{ideal}} = \frac{27}{32} R \frac{T_c^3}{T^3} \frac{P}{P_c} .$$

Putting $T=85.19°\text{K}$ (boiling point), $T_c=144°\text{K}$, $P_c=55$ atm., and $P=1$ atm. in this equation, we have $\Delta S=0.15$ cal./degree mol.

In fine, the entropy of fluorine vapour at the boiling point of 85.19°K is as follows:

$\int_0^{15} \frac{C_p}{T} dT = 0.49$ according to Debye's law, $\int_{15}^{55.2} C_p d \ln T = 5.86$ from the molecular heat of solid, $Q_s/T_s = 6.73$ at melting point, $\int_{55.2}^{85.19} C_p d \ln T = 5.46$ from the molecular heat of liquid, $Q_\sigma/T_\sigma = 18.60$ at boiling point, $\Delta S = 0.15$ correction for real gas, entropy of fluorine vapour at boiling point $= 37.29$ entropy unit.

Conclusion. As the results of the investigations recorded in the papers I–VIII the various properties of fluorine, knowledge of which is necessary for the study of fluorine at low temperatures, have been made clear. The experiments, however, were of such a nature that one or two instruments or apparatus were not enough for dealing with several kinds of materials or problems, but one material had to be studied from various points of view, and therefore various apparatus had to be devised for the purposes. Of these apparatus, some will not stand further use, because their lives have been exhausted by the highly corrosive nature of fluorine, while others will be usable in future studies of condensed gases.

In conclusion the author expresses his deepest gratitude to Prof. Aoyama, who advised him to get about the present investigation and who kindly directed him throughout his work. And he also wishes to express his heartful thanks to Prof. Katayama of the Tokyo Imperial University, who encouraged him throughout these studies. Sincere thanks are also due to Mr. Katsumi Oeda, who earnestly and incessantly assisted the author in the experiments dealing with very unmanageable and dangerous test substances. Further, the author embraces this opportunity of thanking the Japan Society for the Promotion of Scientific Research, who gave him great assistance for many years and placed at his disposal various kinds of apparatus required in the investigation and of thanking the Saitô Gratitude Foundation, who provided the Research Institute for Iron, Steel and Other Metals with the useful apparatus for obtaining low temperatures.

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