Studies on Fluorine at Low Temperatures. II. Vapour Pressure of Fluorine.

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In the study of liquid and solid fluorine, the vapour pressure of fluorine must first of all be determined. The present authors determined the boiling point and the vapour pressure of fluorine, and calculated heat of vaporization.

I. Apparatus for the Experiment. The method was nearly the same as employed in the measurements of the vapour pressure of oxygen and nitrogen,[1] both the quartz film pressure gauge and the platinum film pressure gauge being used in the present experiment. The platinum film pressure gauge is shown in Fig. 1. The hatched part is made of copper. Concentric waves are impressed, by means of a stamp separately devised, on the platinum film (containing 10% rhodium), 0.04 mm. thick. The film is inserted between c and d and is made gas-tight by fastening it to the copper body with a number of screws. A needle is set in the centre of the film and the mirror m at the end of the needle turns on its stem s with the vertical movement of the film. The movement of the mirror is

(1) Aoyama and Kanda, this Bulletin, **10** (1935), 482.

observed by means of a telescope and a scale at a distance of 1 metre. The lower surface of the platinum film p is exposed to, and under the pressure of, the fluorine, and the upper surface is under the air pressure. This air pressure acts on the mercury pressure gauge through the pipe l. The gauge is used as a zero instrument, always having an accuracy of 0.05 mm. Hg.

The device in which the quartz film pressure gauge is used as the zero instrument is illustrated in Fig. 2. The life of the quartz film will be rather short if it is under ordinary pressure of fluorine vapour.

The cryostat is shown in Fig. 2,[2] in which a liquid hydrogen vessel is used for adjusting the temperature when measurement is to be made at −195°C. and below.

Fluorine was produced in an electrolyser more than 20 hours after the start of electrolysis. The fluorine was introduced at A after a number of fractional distillations, and was condensed in the bulb B.

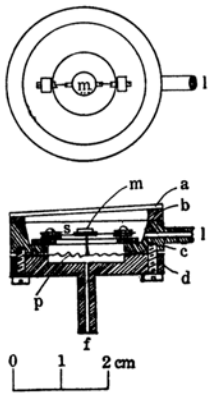

Fig. 1.

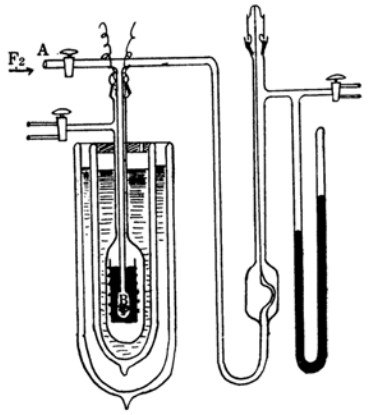

Fig. 2.

II. Results of Measurements. (1) Measurements were made at about 14 points between −187°C. and −213°C. It has been found that the vapour pressure can be expressed by the following equation:

$$\log p_{\text{mm.}} = -\frac{442.72}{T} + 9.1975 - 0.013150\,T\,.$$

The observed and the calculated values are given in Table 1.

(2) For particulars, see (1).

Table 1.

T	$p_{obs.}$	$p_{cal.}$	$p_{cal.}-p_{obs.}$
59.90	10.10	10.445	+ 0.35
63.61	26.30	25.20	− 0.90
65.00	35.50	34.02	− 1.50
68.70	65.20	70.78	+ 5.6
69.99	92.05	89.56	− 2.4
72.85	143.35	145.34	+ 2.0
75.01	209.10	203.70	− 5.4
77.51	289.50	292.81	+ 3.3
79.35	381.50	375.66	− 5.8
79.98	402.35	407.85	− 4.5
83.43	608.10	622.30	+14.2
84.52	712.75	704.85	+ 7.9
85.00	740.10	743.70	+ 3.6
86.21	845.20	848.20	+ 3.0

From the same equation the boiling point at $p = 760$ mm. was calculated as follows:

$$T_o = 85.19°\text{K}\ (-188°\text{C.}),$$

while Clausen[3] gives 85.21°K, Cady[4] 84.93°K, and Moissan[5] 86°K.

From the above equation for the vapour pressure we have for the heat of vaporization:

$$Q_o = 1581 \text{ cal, according to } Q_o = RT^2 \frac{d \ln p}{dT}.$$

(2) Vapour pressure of solid fluorine is given in Table 2.

Table 2.

T	55.15	54.50	53.90	52.55	51.85
p	2.70	2.10	1.75	1.55	0.10

(3) *J. Am. Chem. Soc.*, **56** (1934), 614.
(4) *Ibid.*, **52** (1930), 3839.
(5) *Compt. rend.*, **125** (1897), 505.

It gives $\log p_{\text{mm.}} = -\frac{430.06}{T} + 8.233$. This equation gives $Q \fallingdotseq 1970$ cal. for the heat of vaporization of solid fluorine. From this value and the heat of vaporization of the liquid, $Q_S \fallingdotseq 390$ cal. was obtained for the heat of fusion.

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