Studies on Fluorine at Low Temperatures. IV. Separation of Fluorine from Oxygen by Adsorption and Rectification.

By Eizo KANDA.

(Received August 12th, 1937.)

As was stated in the first paper, fluorine is often contaminated with oxygen, the boiling points, −188°C. and −183°C. respectively, being rather close. Removal of oxygen from fluorine with chemical reagents would be practically impossible, because fluorine acts upon almost all substances at ordinary temperature. Besides, it is desired to handle fluorine at low temperatures to avoid its chemical activity. Therefore, the author examined the possibility of separation of fluorine from oxygen by adsorption upon charcoal at low temperatures.

Experiments on separation were also made by means of a rectification still, because the difference between the boiling points is as small as 5°, and accordingly the separation by fractional distillation of the liquid might be very difficult.

I. Experiment on Adsorption. (1) *Apparatus.* The ordinary method of determining the adsorption of gases, in which the sample of the adsorbent (for instance, charcoal) is placed in a glass or quartz vessel and the variation of the volume or pressure of the gas due to adsorption is determined by reading the mercury column, was not applicable in this case, because glass, quartz and mercury are attacked by fluorine. The author, therefore, used the method with a spring balance for reducing the error.

In Fig. 1, A is a trap in which pure liquid fluorine is kept and which is cooled by liquid nitrogen. In the trap is a heating coil H. The fluorine is vaporized in a desired quantity and the vapour is carried into B. B has a spring balance in it, and at the end of the balance a platinum-plated quartz scale is hung by a platinum filament. T is a thermocouple made of copper and constantan wires, which is placed near the test piece for determining the temperature. An outline of the apparatus for obtaining desired low temperatures is represented by two Dewar vessels, which are similar to one used by the author for calibrating thermocouples by means of a hydrogen thermometer[1].

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

Spring balance. A quartz thread 0.4 mm. in diameter was wound in the form of a spring having a diameter of about 15 mm., the number of turns being 60 and the sensitivity 25 mm./0.1 g. The platinum-filament was fitted with the scale at its lower end in advance, and platinum weights of 0.1 g., 0.2 g.,.... 2 g. were placed on the scale. The elongation of the spring was determined by a cathetometer and was calibrated against the weights. As illustrated, the upper end of the spring was connected to a platinum thread, which was wound round a cock placed on the top of B, and the scale was brought into a proper position by turning the cock. Otherwise, the temperature of the test piece would have varied with the movement of the scale, which must take place as the result of expansion

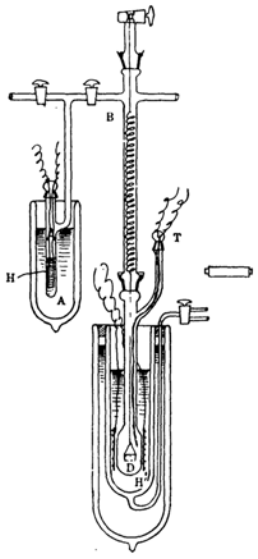

Fig. 1.

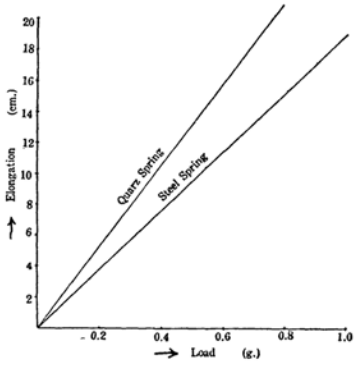

Fig. 2.

and contraction of the spring due to variation of the weight of the test piece during the experiment. The quartz thread was covered with platinum film for fear of its being destroyed by fluorine. A steel spring (0.2 mm.) was also used. The weights were examined before and after each experiment. An example of the results of experiments is given in Fig. 2.

(2) *Adsorption of oxygen gas.* The adsorption of oxygen gas was determined at −160°, −100°, −40°C. and at the pressures of 600, 400, 350, and 200 mm. As for the adsorbent, cocoanut-charcoal was baked at 700°C., activated with oxygen, and made vacuous while it was being baked.

The adsorption for 1 g. of charcoal as expressed in c.c. at N.T.P. was shown in Table 1. This result, together with the adsorption of fluorine, is illustrated in Fig. 4.

(3) *Adsorption of fluorine gas.* Similar experiments were made with fluorine. The progress of adsorption with the lapse of time is given in Fig. 3. The time required for saturation was about 3 hours.

Table 1.

Temp. (°C.) / Press. (mm.)	−160	−100	−40	0
760	136	50	32	10
600	123	44	26	—
400	104	30	20	—
200	80	18	—	—

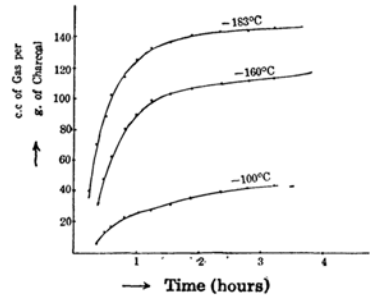

Fig. 3.

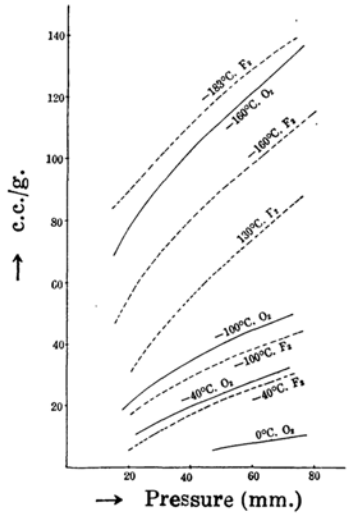

Fig. 4.

The amounts of adsorption in the saturated state are given in Table 2. Fluorine gas was introduced slowly after the charcoal had attained the temperature of the cooling vessel lest it should act upon charcoal. Further, the spring balance was examined several times.

The author expected that fluorine would be adsorbed in a greater quantity than oxygen because of its chemical reactivity against charcoal at ordinary temperature, but the reverse was the case. Oxygen was adsorbed in a greater quantity than fluorine at every temperature. The difference of the amounts of adsorption between them became greater with the fall of temperature. After a mixture of 96% fluorine and 3.7%

Table 2.

Temp. (°C.) / Press. (mm.)	−183	−160	−100	−40	0
760	142	111	44	30	13
600	128	98	40	24	—
400	109	80	30	16	—
200	86	60	17	—	—

oxygen was adsorbed upon the charcoal at −180°C., the remaining gas contained 97% fluorine and 2.8% oxygen. After the same operation was repeated 5 times, the gas was refined up to 99.4% fluorine and 0.4% oxygen. Adsorption, therefore, may be used for refining fluorine.

II. Experiment on Rectification. A rectifier made of Pyrex glass and filled with glass beads was used for the experiment (Fig. 5). V_1 and V_2 are Dewar vessels, and the inside of V_1 forms the rectifying tower. A heating coil H is placed on the bottom, and a mixed liquid of fluorine and oxygen is vaporized in it. The still is 80 cm. long, and is filled with glass beads 5 mm. in diameter. The top of the still has a glass tube C inserted, and is made air-tight with plaster. Liquid air is poured into C from another Dewar vessel, V_3. The temperature of the liquid air in C is controlled by varying its composition and serves as a condenser. A part of the vapour rising in the still is condensed by this condenser, and

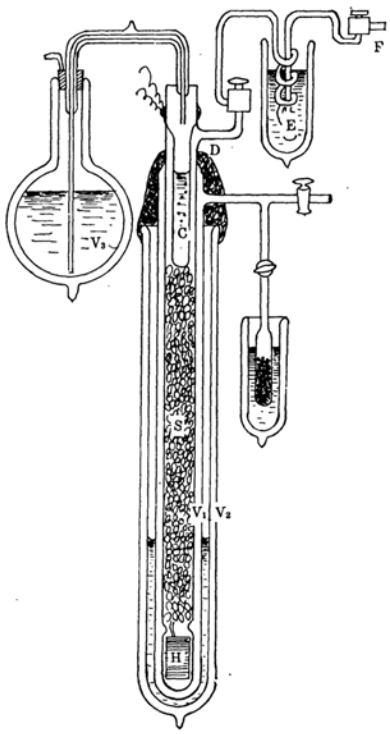

Fig. 5.

the vapour which has become fluorine-rich goes through D and is condensed in the trap E which has been cooled by liquid nitrogen. The substance which has been collected in E is taken out through F, and then subjected to the analysis of fluorine using mercury.

The vaporizer, still, and condenser are fitted with thermocouples for observing the temperature. Dewar vessel V_2, the gas-introducing tube attached on the outside of the Dewar vessel V_1, and the charcoal trap serve for cooling the rectifying tower and keeping it at a proper temperature. By using this refining apparatus, 99% pure fluorine could be obtained in E from an original liquid containing 95% fluorine.

In short, purification of fluorine must always be done at a low temperature, but the purest fluorine that can be obtained by the rectifying process is 99%, and therefore a percentage higher than this can be reached only by means of adsorption.

In conclusion, the author expresses his cordial thanks to Prof. Aoyama who advised him through this work. The author also expresses his hearty thanks to the Japan Society for the Promotion of Scientific Research for a grant.

Cryogenic Section,
Research Institute for Iron, Steel and other Metals,
Tohoku Imperial University.