Studies on Fluorine at Low Temperatures. IX. Experiment on the Reaction between Solid Fluorine and Liquid Hydrogen.

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The reaction between fluorine and hydrogen is much complicated. Although close investigations have been made and numerous papers are still being published on the reactions between other halogens and hydrogen in the gaseous state, any systematic study has scarcely been made on the reaction between fluorine and hydrogen. Moreover, strange to say, the results obtained by the few who have studied this problem have been contradictory to one another. For illustrating this fact, the present authors will give the results of their tentative study on the reaction between solid fluorine and liquid hydrogen, and state their own opinion about it.

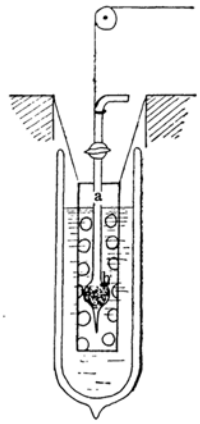
Moissan and Dewar(1) reported that explosion took place when a kind of test-tube with solid fluorine placed on its bottom was dipped into liquid hydrogen and the two elements were brought in contact with each other by breaking the bottom of the tube with a metallic bar thrust in at the upper end of the tube. But Wartenberg(2) and Eyring(3) reported that they saw no remarkable reaction between fluorine and hydrogen at ordinary or low temperatures, though they made no such experiment as Dewar's.

The present authors carried out the following experiments for ascertaining validity of these conflicting reports and the conditions for an explosion of this kind, if any.

I. **Experiments and Results.** Experiments such as Dewar's, in which, as stated above, a metallic bar is thrust in at the upper end of the tube, have the following drawback: (i) Air may be mixed in the samples, and (ii) it is doubtful whether the hydrogen and fluorine will come in contact with each other respectively in the true liquid and solid states, because the temperature of the metal is probably higher than that of the liquid hydrogen.

(1) Moissan and Dewar, *Compt. rend.*, **136** (1903), 641.
(2) Wartenberg, *Nachr. Ges. Wiss. Göttingen*, **1** (1930), 119.
(3) Eyring, *J. Am. Chem. Soc.*, **55** (1933), 2796.

In the authors' experiment, an apparatus as shown in the figure was used. A brass cylinder was hung in the liquid hydrogen. In this cylinder was also hung a glass bulb containing condensed fluorine. A thread by which the bulb was suspended through a roller was drawn out, and the bulb was dropped. A thin-walled capillary tube of the bulb was broken at the bottom of the cylinder, whereby the solid fluorine and liquid hydrogen touched each other. The following is the summary of the results of experiments:



(1) With an inside diameter of about 10 mm. at a and about 1 c.c. of fluorine in b; the weather cloudy. Immediately after the thread was drawn out and the bulb dropped, a slight explosion was heard and flames were seen on the surface of the liquid hydrogen (surface burning). In about one minute, the Dewar vessel burst, perhaps on account of explosion of the liquid hydrogen (or hydrogen gas) or of thermal strain in the vessel.

(2) With an inside diameter of 1 mm. at a and about 1 c.c. of fluorine in b; exposed directly to the sun. Even after the capillary tube was broken, no explosion took place. When the bulb, with the broken capillary tube but still containing the solid fluorine, was taken out, a slight explosion was heard.

(3) With an inside diameter of 6 mm. at a and about 1 c.c. of fluorine in b; exposed directly to the sun. Explosion took place after the breakage of the capillary tube and the Dewar vessel burst shortly after the explosion.

(4) With a diameter of 13 mm. at a and about 1 c.c. in b; exposed directly to the sun. Violent explosion was experienced and even the brass cylinder was crushed.

All these experiments being carried out outdoors and examined at a distance of about 1 metre from the apparatus, the observation might not be very accurate. Nevertheless, a little smoke of light brown colour was seen rising at the opening of the vessel in each case of (1), (3), and (4) after the breakage of the end of the tube.

II. **Discussion of the Results.** (1) Eyring's denial of the explosion of solid fluorine at the temperature of liquid hydrogen has no ground in experiments. The present authors' experiment was the first to be made after Dewar's investigation. The authors cannot fall in with Eyring's views that there is no explosion between solid fluorine and liquid hydrogen, and that the explosion, if any, is caused by contaminating organic matters (Eyring admitted explosion of a mixture of hydrogen gas and fluorine gas at an ordinary temperature, but attributed it to organic matters such as rubber). In the authors' experiment, grease or other organic matters were not used.

(2) Explosion did not always occur. With a capillary tube as used in experiment (2), no explosion took place.

(3) The explosion was more frequent and violent with a tube having a larger diameter. In the authors' opinion, the reaction in question may be one not between the solid and liquid but in the gas phase existing over the solid and liquid, thus resulting in the above-mentioned explosion.

(4) No explosion, however, was experienced when the gases of the two elements were mixed in a large glass vessel at ordinary temperature —even when the vessel was exposed to the sun or to the light of a mercury lamp. (Explosion sometimes occurred when the wall of the vessel was fresh.) If so, how is the explosion at such a low temperature explained? The following questions arose in the authors' mind:

(a) Does a condensed gas become chemically more active when it is liquefied or vaporized?

(b) Is there any transition into an active form in solid fluorine at this temperature?

(c) Does any negative catalyser exist in this reaction in the gas phase? Can the explosion not be explained by degeneration at low temperature of the negative catalyser?

As for (a), fluorine fresh from the electrolyser was found, in the authors' experiment, more apt to chemical reaction than one which was first liquefied and condensed and then vaporized, but there was no ground for answering (a) in the negative.

As for existence of the transition referred to in (b), although there was a slight change in the colour of the solid fluorine at the temperature of the liquid hydrogen, such is also the case with other halogens. Determination of the molecular heat showed no transition.

As for degeneration of a negative catalyser, the results of the authors' investigation on the reaction of gases $H_2 + F_2 \rightarrow 2HF$ have shown that this reaction is greatly affected by the wall of the vessel used, and have pointed to the probability of negative catalysis of SiF_4 coming from the glass wall. It may also be conceived that a negative catalyser of this kind will completely freeze and will degenerate at such a low temperature as that of liquid hydrogen.

The foregoing, however, is a mere supposition, and the authors cannot give any definite opinion about the reaction in these seemingly heterogeneous phases until the reaction between hydrogen and fluorine in the gas phase is thoroughly investigated.

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