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Thermochemical Studies of XeF_4 and XeF_6

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MASTER

Abstract

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The reduction of xenon tetrafluoride and xenon hexafluoride with hydrogen is being studied with an isothermal calorimeter at 120 to 130°C. Each compound reacts rapidly with hydrogen in this temperature region, forming xenon and hydrogen fluoride:

$$XeF_4(g) + 2H_2(g) \rightarrow Xe(g) + 4HF(g) \qquad (1)$$

$$XeF_6(g) + 3H_2(g) \rightarrow Xe(g) + 6HF(g). \qquad (2)$$

Preliminary values of the heats of reaction obtained thus far are $\Delta H = -202$ kcal./mole XeF_4 for reaction (1) and $\Delta H = -306$ kcal./mole XeF_6 for reaction (2). The approximate heats of formation are calculated to be:

$$\Delta H_{f.XeF_4(g)} = -55 \text{ kcal./mole}$$

$$\Delta H_{f.XeF_6(g)} = -79 \text{ kcal./mole.}$$

From the present measurements the average xenon-fluorine bond energy is found to be 32.0 kcal. in the tetrafluoride and 31.5 kcal. in the hexafluoride.

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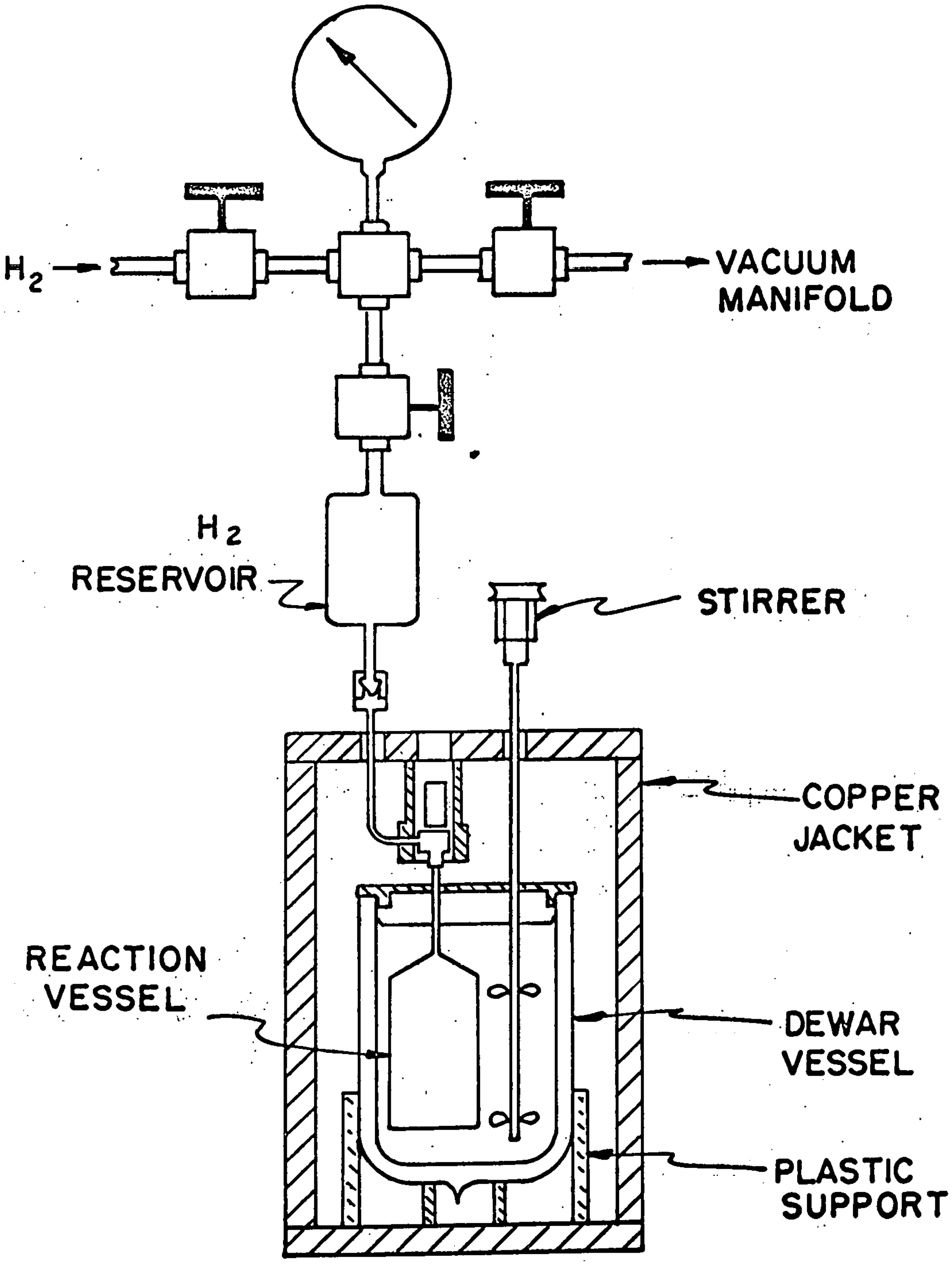
DISCLAIMER

Previous investigators (2-4) have shown that xenon fluorides can be reduced quantitatively with excess hydrogen at 400° to form xenon and hydrogen fluoride. The reactions of xenon tetrafluoride and hexafluoride with hydrogen are now being studied at lower temperatures with an isothermal calorimeter in order to obtain heats of formation of these compounds. The tetrafluoride does not react with hydrogen to any noticeable extent at 25° but reacts slowly at 70° and rapidly at 130°. The hexafluoride behaves erratically when mixed with hydrogen at 25°; in some instances a spontaneous reaction occurs, in other instances no reaction is observed. At 130°, the hexafluoride is rapidly reduced by hydrogen. The first experiments with the calorimeter have therefore been carried out in the interval 120 to 130°, with the reactions regulated by the rate of hydrogen addition. Since complete results will be published at a later date, only a brief description of the experimental procedure and some preliminary results will be given here.

Apparatus

The calorimeter, shown in Figure 1, consists of a silvered Pyrex Dewar vessel mounted inside a cylindrical copper jacket. The top, side, and bottom of the jacket are heated by separate electric windings. The Dewar contains a nickel reaction vessel, 300 cc. of mineral oil. a twin-bladed stirrer, a 25 ohm platinum resistance thermometer (not shown), and a 400 ohm calibration heater (not shown). Both the Dewar cover, which is made of thin Transite, and the top of the jacket are split into halves for easy assembly.

Figure 1. Calorimeter for studying the reactions of xenon fluorides with hydrogen.


H_2
VACUUM MANIFOLD
H_2 RESERVOIR
STIRRER
COPPER JACKET
REACTION VESSEL
DEWAR VESSEL
PLASTIC SUPPORT

The reaction vessel consists of a nickel can of approximately 130 cc. volume attached to a small bellows valve and a vacuum coupling by thin-walled Monel tubing. The volume of the tubing between the can and the valve point comprises less than 0.1 per cent of the total volume. When the calorimeter is assembled, the valve is inserted into an electrically heated copper sleeve, where it is clamped with a set screw. The vacuum coupling is then attached to the hydrogen reservoir, which is also electrically heated. Above the reservoir, the metal vacuum line contains a 0-4000 mm. Bourdon gauge, several cold traps (not shown), and manifold connections to a hydrogen cylinder and oil diffusion pump.

Thermocouples indicate the temperature of the sleeve, reservoir, and jacket at several points. A double microvolt potentiometer, Rubicon Model No. 2773, is used for electrical measurements with the resistance thermometer and calibration heater. The current measurements are made with standard resistors manufactured by Leeds and Northrup Company and Gray Instrument Company. Time intervals are measured with a Beckman EPUT meter, Model No. 7350 C.

Experimental Procedure

After the reaction vessel has been thoroughly prefluorinated at 500°, it is evacuated, weighed, filled on a vacuum line with XeF_4 or XeF_6, and again weighed to determine the amount of compound added. The weighings are made with an analytical balance, using a second vessel as a tare. The calorimeter is assembled with 300 cc. of mineral oil in the Dewar and is then heated to 120° or slightly higher. When temperature equilibrium is established, the heat capacity is measured one or more times by electrical calibration with the 400 ohm heater. Prepurified hydrogen (99.97%) from a cylinder is passed through a Deoxo unit, through a cold trap at -195°, into the hydrogen reservoir, which is initially at the same temperature as the calorimeter. The reaction is then carried out by cracking open the small valve and allowing hydrogen at 3500 to 4000 mm. pressure to enter the calorimeter until a large excess has been added. Generally the hydrogen addition is completed in 3 to 5 minutes, and a temperature rise of the order of one degree is observed. After the reaction, the heat capacity is again determined by electrical calibration, the calorimeter is cooled to room temperature and disassembled, and the reaction vessel is washed with acetone, dried, and weighed to determine the amount of hydrogen added. As a check on the stoichiometry of the reaction, in some instances additional weighings are made as follows: the excess hydrogen is pumped out at -195°, the vessel is weighed to determine the amount of xenon plus hydrogen fluoride present, the xenon is then pumped out at -160°, and the vessel is weighed to determine the amount of hydrogen fluoride remaining.

Preliminary Results

Thus far three experiments have been completed with XeF_4 and three experiments with XeF_6. Both compounds were originally believed to be of 99 per cent or higher purity from chemical and infrared analyses, but further tests of the same preparations indicate that only the XeF_4 is this pure. The XeF_6 has been found to contain XeF_4 and another unidentified substance, and its purity has been revised to 95 per cent or slightly higher. For further calorimetric experiments, attempts are being made to purify both compounds more extensively.

Preliminary results obtained from the first experiments are shown in Table 1. Under the conditions which are used at present, all reactants and products are in the gaseous state, and no corrections for vaporization are necessary. The reactions occurring in the calorimeter are as follows:

$$XeF_4(g) + 2H_2(g) \rightarrow Xe(g) + 4HF(g) \qquad (1)$$

$$XeF_6(g) + 3H_2(g) \rightarrow Xe(g) + 6HF(g). \qquad (2)$$

The hydrogen fluoride is assumed to be entirely monomeric, since the concentration of polymers is very low at 120°.

The total energy change in each experiment is shown in column 2. Since hydrogen is added from a source outside of the calorimeter, the incoming gas does work on the contents of the calorimeter which must be subtracted from the total energy change to obtain $\Delta E_{Reaction}$. The correction term, calculated as nRT, where n is the number of moles of hydrogen added, R is the gas constant, and T is the absolute temperature, is given in column 3. From $\Delta E_{Reaction}$ and the increase in the total number of moles of gas [Equation (1) or (2)], $\Delta H_{Reaction}$ is readily calculated. No correction of the enthalpy from the actual temperature to 25° is made at present, since the experimental error is larger than

Table 1

A. Reduction of XeF_4 with excess H_2:

Weight of XeF_4 (mg.)	Total Energy Change (cal.)	Correction for PV work (cal.)	$\Delta H_{Reaction}$ (kcal./mole XeF_4)
690.9	685.8	7.4	-202.2
326.3	325.6	9.9	-199.0
329.2	337.1	9.5	-204.7
		average =	-202.0

B. Reducton of XeF_6 with excess H_2:

Weight of XeF_6 (mg.)	Total Energy Change (cal.)	Correction for PV work (cal.)	$\Delta H_{Reaction}$ (kcal./mole XeF_6)
493.0	626.0	7.8	-305.2
382.1	489.9	9.4	-306.0
298.4	388.1	10.2	-308.3
		average =	-306.5

the correction and since the heat capacities of gaseous XeF_4 and XeF_6 have not yet been determined.

Using the value -64.2 kcal./mole for the heat of formation of hydrogen fluoride (5), the approximate heats of formation of XeF_4 and XeF_6 are calculated as follows:

From Equation (1),

$$\Delta H_{\text{Reaction}} = 4\Delta H_{f.HF(g)} - \Delta H_{f.XeF_4(g)}$$

$$-202.0 = 4(-64.2) - \Delta H_{f.XeF_4(g)}$$

$$\Delta H_{f.XeF_4(g)} = -54.8 \text{ kcal./mole}$$

From Equation (2),

$$\Delta H_{\text{Reaction}} = 6\Delta H_{f.HF(g)} - \Delta H_{f.XeF_6(g)}$$

$$-306.5 = 6(-64.2) - \Delta H_{f.XeF_6(g)}$$

$$\Delta H_{f.XeF_6(g)} = -78.7 \text{ kcal./mole.}$$

The present value for the heat of formation of gaseous XeF_4 can be compared with the value obtained by Gunn and Williamson (6) for crystalline XeF_4.

Taking the heat of dissociation of fluorine to be 36.7 kcal./mole (7), the average bond energies in XeF_4 and XeF_6 are calculated as follows:

$$\text{average B. E. in } XeF_4 = \frac{54.8 + 2(36.7)}{4} = 32.0 \text{ kcal.}$$

$$\text{average B. E. in } XeF_6 = \frac{78.7 + 3(36.7)}{6} = 31.5 \text{ kcal.}$$

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