

The Reactions of Xenon and Fluorine to Form Xenon Fluorides

B. H. DAVIS, J. L. WISHLADE, AND P. H. EMMETT

*From The Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218*

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The present paper recounts experiments that we have been carrying on since 1963 in an effort to ascertain whether the principal reactions involved in the formation of xenon fluorides from xenon and fluorine are heterogeneous or homogeneous. The results here presented clearly indicate that the reactions are heterogeneous and occur for the most part on the fluorinated walls of the Monel reaction vessels or on the surface of added metal fluorides. CoF_3 , NiF_2 , and CaF_2 all exhibited catalytic activity for the fluorine-xenon reactions.

The formation of xenon fluorides (1-3)— XeF_2 , XeF_4 , and XeF_6 —from fluorine and xenon has received a good deal of attention in the time that has elapsed since Bartlett (4) prepared the first compound containing xenon in 1962. Most experimental work has, however, been directed toward structural studies (5, 6) of the xenon fluorides and toward the measurement of the equilibria (7) involved. The present paper recounts experiments that we have been carrying on since 1963 in an effort to ascertain whether the principal reactions involved in the formation of xenon fluorides from xenon and fluorine are heterogeneous or homogeneous. The results clearly indicate that the reactions are heterogeneous and occur for the most part on the walls of the metallic nickel reaction vessels or on the surface of added metallic fluorides.

EXPERIMENTAL

Originally the experiments were planned in such a way that identical fluorine-xenon mixtures would be admitted simultaneously to two reaction vessels—one empty and one packed with a known surface area of a metallic fluoride. The apparatus is shown schematically in Fig. 1. Two 150-cc Monel reaction vessels V_1 and V_2 were connected to their respective gauges and separated from each other by

a Hoke valve. A trap, T, with valves as indicated was provided for condensing out the xenon while preparing the fluorine-xenon mixture. A ballast bulb B was in the all-metal gas-tight system to assist in preparing the gas mixtures. Tank xenon and fluorine purified by passage through sodium fluoride traps for removing HF could be admitted as shown. The entire apparatus (except for the reaction vessels and hot portions of connecting tubing) was constructed of copper. The apparatus was, in all cases, prefluorinated to zero reaction rate with pure fluorine prior to use.

Three slightly different techniques were used during the work. These will be briefly described in connection with the three sets of experimental results presented in Figs. 2 to 4.

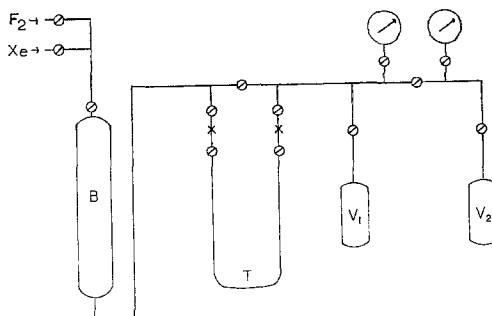


FIG. 1. Apparatus

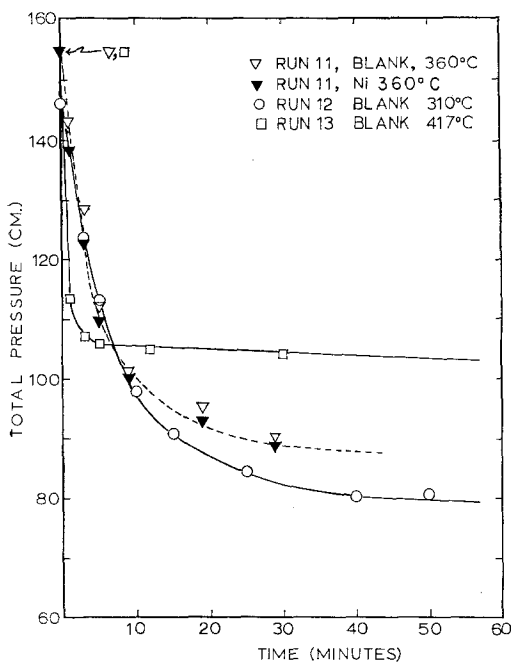


FIG. 2. Pressure vs. time curve for preliminary runs with xenon-fluorine mixtures. Runs 12 and 13 were blanks made on the empty fluorinated Monel reaction vessel. Run 11 involved two reactors, one containing 37 g (5.7 m^2) of fluorinated nickel powder. The two sets of symbols distinguish the portion of Run 11 that was a blank from the portion containing the nickel powder.

RESULTS

One of the authors (J. L. Wishlade) constructed the apparatus and carried out a series of preliminary runs. Four of these are shown in Fig. 2. In these experiments the xenon was first put into the reaction vessel and measured. Then a small amount of fluorine was added and the mixture was frozen into the reaction vessel by cooling the latter in liquid nitrogen. Repeated fluorine additions and condensation finally yielded a mixture of the desired composition. The xenon and part of the fluorine was then frozen in the trap cooled in liquid nitrogen. When the reaction vessel had been heated to the desired temperature, the xenon-fluorine mixture was flushed to full pressure in a few seconds by being immersed in a bath of boiling water. As will be described below, a simple calculation will show the composition of the gas in the

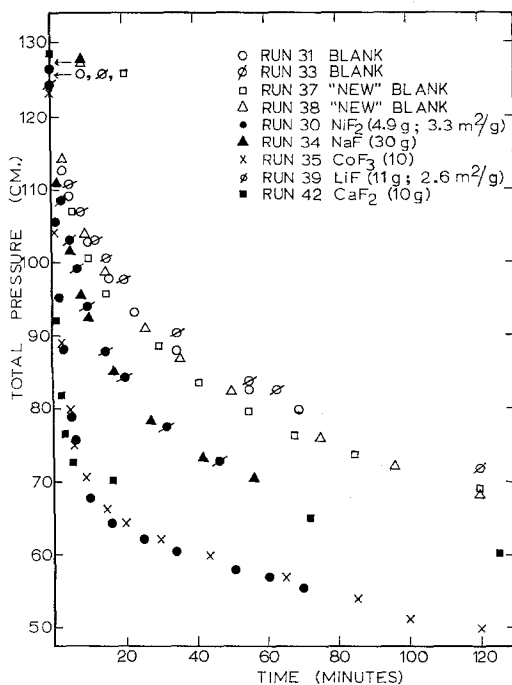


FIG. 3. Reaction rate curves for fluorine-xenon gas mixtures in empty reaction vessels (blanks), and in reaction bulbs containing NaF, LiF, CaF, NiF_2 , or CoF_3 . Gas mixture seemed to be about 2.5:1 F_2 :Xe in the reactor (see Table 1).

reactor consistent with equilibria and with total pressure change. These calculations indicate the overall F_2 to Xe ratios in the reactor were 1.53 for the 410° and 1.9 for the 360° and 300° runs. It appears, from the curve in Fig. 2, that the reaction was so fast that it was impossible to say in these runs whether the initial reaction was heterogeneous or homogeneous.

To better differentiate between the rates of runs with no added catalyst and rates with added material, the temperature was lowered to 300°C and the apparatus redesigned to give a volume, outside the reactor, of 35 cc per reactor instead of 75 cc (used with the four preliminary experiments). The xenon was added to the reservoir system (including the ballast tank B but not the reaction vessel). It was then frozen in trap T and fluorine was added to a given pressure. Finally, the xenon was permitted to evaporate into the fluorine in the lines to some initial total pressure and

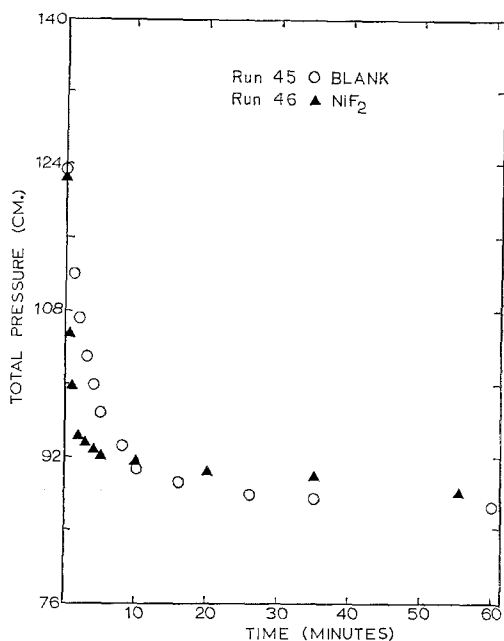


Fig. 4. Reaction rate curves for two fluorine-xenon runs in which better mixing of the reactants was attempted. The fluorine-to-xenon ratios in the reactor were in the range 4:1 to 5:1. The 12 g of NiF_2 in Run 46 probably had a surface area of about 90 m^2 as judged by area measurements on a different but similar sample.

then the reaction vessel was opened. The group of blank runs and runs with added material as catalyst are shown in Fig. 3. All runs were at temperatures in the range 300° to 308° . Only a single reaction vessel was used. Sometimes it was empty as a blank and sometimes partially filled with CoF_3 , NiF_2 , NaF , CaF_2 , or LiF .

The fluorine:xenon ratios as judged by the initial pressure measurements with the reaction vessel closed off were about 6:1. However, it was realized that the location of the xenon trap made it certain that the filling of the reaction vessel would favor the pickup of xenon. The final calculated composition (see Table 1) indicates that the gas mixture in the reaction vessel was in the range 2.6:1 to 2.9:1 F_2 :Xe.

It is evident that the rate of reaction is much greater in the presence of CoF_3 , NiF_2 , and CaF than in the absence of these substances. Even LiF and NaF cause some acceleration though they are less effective than the CoF_3 , NiF_2 , or CaF_2 .

Finally, in Fig. 4, are shown two runs in which some effort was made to mix the gases. After the xenon was expanded from the cold trap into the fluorine, the mixture in trap B was cooled to -78° and then expanded. This was repeated a second time. The calculated ratio of fluorine to xenon was about 6:1. The composition that actually got into the reactor appears to have been in the range 4:1 to 5:1. Even here the NiF_2 run is distinctly faster than the blank runs though both were considerably faster than the blank runs in Fig. 3.

DISCUSSION

The basic purpose of the present work was to ascertain whether the reaction of xenon and fluorine to form the xenon fluorides was homogeneous or heterogeneous. We conclude on the basis of the runs shown in Figs. 3 and 4 that the reaction is at least partly heterogeneous. In the absence of an added catalyst the reaction appears to be taking place on the fluorinated nickel wall. This agrees with the conclusion reached by Weaver (8) who found that the rate was 13 times faster in a 1.59-cm tube than in one 6.8 cm in diameter. This observation by Weaver, together with the fact that he was able to almost stop the reaction by poisoning the walls, enabled him to conclude that the reaction was primarily heterogeneous and not homogeneous. A similar conclusion was reached by Baker and Fox (9) in experiments carried out on a hot nickel filament in a cooled quartz reactor. Incidentally, their observation that the reaction rate was zero order with respect to xenon is very puzzling if the reaction involves adsorption equilibrium between the gases and the surface. However, Weaver has shown that a similar zero order behavior with respect to xenon observed in his work can be explained by assuming the slow step involves the dissociation of adsorbed fluorine molecules into adsorbed fluorine atoms.

Difficulties of mixing the reactants properly made kinetic measurements in the present work inconclusive. It is certain that in the experiments shown in Fig. 2 the fluorine-to-xenon ratio was probably high

at the start of the run but decreased to a value of about 1.9 as the reaction proceeded and the xenon-rich gas came in from the connecting tubes. In the data in Fig. 3, the ratio of 6:1 fluorine to xenon calculated from the partial pressures of xenon and fluorine added to the system including ballast bulb B and connecting tubes (but not the reactor) was certainly much higher than the ratio in the mixture that reached the reactor. The latter composition was apparently about 2.5:1. Only in the two runs in Fig. 4 was fair mixing obtained but even here the composition of the gas in the reactor may well have changed some during the run. About all that one can say is that in the runs in Figs. 2 and 4 the time for half-pressure drop was the order of 1 or 2 min. Considering that the reactor was about 4 cm in diameter, this result is reasonably consistent with the half-times found by Weaver (0.3 to 5 min depending on the gas composition and reactor diameter.) The reason for the much longer half-times in the blank runs in Fig. 3 compared to the blank in Figs. 2 and 4 is not clear. The consistency of the various blank runs in Fig. 3, however, makes it unlikely that the slower rates resulted from any poisoning action. It probably is related to the gas composition. The initial F_2 :Xe ratios in the experiments of Figs. 2 and 4 were both probably higher than in those of Fig. 3. This, according to Weaver's results, would be expected to yield a faster rate than obtained when the F_2 :Xe ratio is lower.

Although the composition of the gas in the connecting lines and gauge lines at the end or during a run are not known, it is possible to calculate with fair accuracy the total amount of fluorine and xenon that entered the reactor up to any time. From this, in turn, one can calculate the gas composition that would exist at equilibrium with respect to the various xenon fluorides.

The total gas entering the reactor is simply the initial total gas (calculated from P_0 and the known volume of the systems) less the amount left in the gauge and connecting lines at the time for which the calculation was being made. The reactor, in all cases, had an absolute volume of 150 cc.

The connecting tubes and gauges had a total absolute volume of 35 cc per reactor for runs in Figs. 3 and 4, and 75 cc for the experiments in Fig. 2. The contraction from the initial equivalent pressure based on all of the gas that eventually went into the reactor to the final observed pressure P_f enables one to calculate the partial pressures of xenon, XeF_2 , XeF_4 , XeF_6 , and F_2 present if equilibrium existed at the time selected for calculation. It also permits the calculation of the fluorine-to-xenon ratio actually entering the reaction vessel during the run. The results of these calculations are shown in Table 1.

Some consequences of these calculations should be pointed out. To begin with, for the first three runs in which the fluorine-to-xenon ratios were in the range 1.5:1 to 1.9:1, the increasing pressure drop with decreasing temperature is consistent with the shift to more XeF_4 compared to XeF_2 in the product. These shifts are, of course, based on calculations involving the equilibrium data shown in Table 2.

We satisfied ourselves that fluorides were being formed in these runs by condensing and crystallizing the product in several different experiments. The product was monoclinic and, therefore, was not XeF_2 . It appeared to be XeF_4 though the solid $XeF_2 \cdot XeF_4$ is also monoclinic and could have been present.

In the absence of detailed information on the composition of the product formed, the exact gas composition in the reactor as a function of time and the lack of knowledge as to the exact kinetics over the pressure range and gas composition used, no conclusions can be drawn in regard to the temperature coefficient. The results are, however, consistent with the small temperature coefficients (12 to 15 kcal) found by Weaver (8).

One other item should be mentioned. In the experiments shown in Fig. 3, the reaction to form the xenon fluorides is, we believe, substantially complete by the time the pressure drops to about 650 to 700 mm. The drop in pressure beyond this point is believed due to the diffusion of the xenon fluorides out of the reactor with condensation in the colder part of the apparatus

TABLE 1
 THE FORMATION OF XENON FLUORIDES FROM THEIR ELEMENTS

| Run | Temp. | Catalyst added ^a | P ₀ (mm Hg) | P _f ^b | Time (min) | Last reading hot reactor | | P in cold reaction at ~20 hr | Calculated composition ^c at P _f (mm Hg) | | | | | |
|-----|-------|-----------------------------|------------------------|-----------------------------|------------|--------------------------|------|------------------------------|---|------------------|------------------|------------------|----------------|--------------------|
| | | | | | | P | Time | | Xe | XeF ₂ | XeF ₄ | XeF ₆ | F ₂ | F ₂ /Xe |
| 13 | 417° | None | 1540 | 990 | 90 | 990 | 90 | — | 15 | 525 | 335 | — | 115 | 1.53 |
| 11 | 360° | Ni | 1540 | 900 | 69 | 815 | 159 | — | 1 | 227 | 570 | 2 | 100 | 1.9 |
| 12 | 310° | None | 1485 | 800 | 50 | 800 | 50 | — | 1 | 105 | 648 | 6 | 40 | 1.92 |
| 30 | 300° | NiF ₂ | 1272 | 630 | 20 | 552 | 70 | — | — | 17 | 466 | 17 | 130 | 2.24 |
| 31 | 304° | None | 1250 | 700 | 120 | 502 | 345 | — | — | 6 | 365 | 29 | 300 | 2.8 |
| 33 | 300° | None | 1255 | 715 | 120 | 658 | 142 | 210 | — | 6 | 379 | 30 | 300 | 2.66 |
| 34 | 304° | NaF | 1278 | 704 | 56 | 571 | 180 | 127 | — | 6 | 363 | 31 | 304 | 2.9 |
| 35 | 299° | CoF ₃ | 1230 | 600 | 45 | 135 | 440 | ~30 | — | 14 | 420 | 16 | 150 | 2.42 |
| 36 | 304° | NiF ₂ | 600 | 340 | 11 | 119 | 420 | ~20 | — | 9 | 209 | 7 | 115 | 2.5 |
| 37 | 300° | None | 1240 | 686 | 120 | 595 | 190 | — | — | 6 | 365 | 29 | 286 | 2.8 |
| 38 | 305° | None | 1272 | 686 | 120 | 595 | 180 | 143 | — | 7 | 391 | 28 | 260 | 2.7 |
| 39 | 302° | LiF | 1232 | 660 | 85 | 660 | 85 | 160 | — | 10 | 415 | 25 | 210 | 2.44 |
| 42 | 302° | CaF ₂ | 1285 | 702 | 17 | 544 | 235 | 90 | — | 8 | 403 | 29 | 262 | 2.6 |
| 45 | 309° | None | 1230 | 850 | 120 | 750 | 968 | — | — | 2 | 265 | 33 | 550 | 3.78 |
| 46 | 308° | NiF ₂ | 1215 | 876 | 70 | 680 | 1260 | — | — | 2 | 194 | 29 | 651 | 5.1 |
| 50 | 306° | NiF ₂ | 1225 | 586 | 24 | 416 | 151 | — | — | 23 | 440 | 12 | 111 | 2.25 |

^a The weights and, when available, the surface areas of added catalysts was as follows: Run 11, 37 g Ni, 5.7 m²; Runs 30 and 36, 4.9 g NiF₂, 16.5 m²; Run 34, 30 g NaF, 3.0 m²; Run 35, 10 g CoF₃; Run 39, 11 g LiF, 28.6 m²; Run 42, 10 g CaF₂; Runs 46 and 50, 12 g NiF₂ (probably about 90 m²).

^b P_f is chosen as the point at which the pressure drop ceased or merged into a slow linear form. It is assumed in the calculations that at this point all of the xenon fluorides were vapors in the hot reactor.

^c The calculated values are consistent with the observed values of P_f, the equilibrium constants (see Table 2) for the formation of the various xenon fluorides, and the initial pressure, P₀.

(connecting lines) or to the reaction with the added catalyst to form complexes. The blank runs seems to indicate that the diffusion times may be as high as 15 to 20 hr. However, the run with CoF₃ showed a very low pressure at 7 hr. The data suggest that for both CoF₃, and probably NiF₂ complexes are formed with some of the xenon fluorides. The rate is slow compared to the rate of reaction of the xenon and fluorine to form the xenon fluorides but fast compared to diffusion out of the reaction vessel. We have no evidence as to which fluoride of

xenon is involved. However, data in the literature suggests (2, 10) that XeF₆ reacts with NaF preferentially with respect to XeF₄ and XeF₂. It seems likely, therefore, that XeF₆ gradually combines with the CoF₃ to form a complex capable of continually removing XeF₆ from the reaction zone even at 300°C. This would mean a gradual consumption of fluorine in converting XeF₄ to XeF₆. We realize that XeF₆ formation is usually slow but suspect that in the presence of added CoF₃ or NiF₂, the formation of XeF₆ or of complexes such as

 TABLE 2
 EQUILIBRIUM CONSTANTS FOR THE XENON-FLUORINE SYSTEM^a

| Reaction | Temperature (°K) | | | | |
|--|-------------------------|------------------------|------------------------|------------------------|------------------------|
| | 298.15° | 523.15° | 573.15° | 623.15° | 673.15° |
| Xe + F ₂ = XeF ₂ | 1.23 × 10 ¹³ | 8.79 × 10 ⁴ | 1.02 × 10 ⁴ | 1.67 × 10 ³ | 3.59 × 10 ² |
| XeF ₂ + F ₂ = XeF ₄ | 1.37 × 10 ¹¹ | 1.43 × 10 ³ | 1.55 × 10 ² | 27.2 | 4.86 |
| XeF ₄ + F ₂ = XeF ₆ | 8.6 × 10 ⁵ | 0.944 | 0.211 | 0.0558 | 0.0182 |

^a Units are in atmospheres. This table was taken directly from the paper by Malm *et al.* (3).

$\text{XeF}_6 \cdot \text{CoF}_3$ and $\text{XeF}_6 \cdot \text{NiF}_2$ may take place. In line with this we noted that at least half the product formed in the presence of CoF_3 was evolved only when the reactor was heated to about 380°C .

The runs containing NiF_2 follow the run with CoF_3 closely down to a pressure of 400 mm; unfortunately, no NiF_2 run was continued in a hot reactor to longer times. However, the pressures in the cold vessel at the end of a run (about 20 hr) were about the same for runs with NiF_2 and CoF_3 and was definitely smaller than for other runs. This suggests that NiF_2 , as well as CoF_3 , was forming complexes, thereby preferentially removing XeF_6 and consuming both fluorine and some of the XeF_4 .

Calcium fluoride appears intermediate in its behavior. Like NiF_2 and CoF_3 , it seems to catalyze the formation of the xenon fluorides; however, it follows the blank runs closely after a pressure of 700 mm or so is obtained. Presumably, it does not form a complex with the xenon fluorides stable under the conditions of these experiments at 300°C .

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