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The Xenon–Fluorine System

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Equilibrium constants have been obtained in the Xe–F_2 system in the temperature range 250–500°. The data show that only three binary fluorides, XeF_2, XeF_4, and XeF_6, are present. There is no evidence for the existence of XeF_8 at 250° and up to 500 atm of F_2. A preparation of pure XeF_6 is described. A molecular weight determination, some infrared measurements, and vapor pressure data obtained with this sample are reported. Values for the thermodynamic properties of formation of XeF_2, XeF_4, and XeF_6 are derived from the equilibrium constant data. The average value of the two missing vibrational modes of XeF_4 is evaluated to be 246 ± 10 cm^{-1} from an analysis of the equilibrium constant and molecular data. Thermodynamic properties of XeF_2 and XeF_4 are calculated from molecular data. The value of $S°$ for XeF_4 at 25° is 75.6 cal mole^{-1} deg^{-1}, in agreement with a value of 75.3 cal mole^{-1} deg^{-1} calculated from calorimetric data and the heat of sublimation. A number of molecular models for XeF_6 are examined in terms of their consistency with the equilibrium constant data. A definite choice among the various models is not possible, but the analysis favors a low symmetry for XeF_6. Values of $S°$ for XeF_6 at 25° are derived for each model and may be useful to help determine the symmetry of XeF_6 when calorimetric data become available. The average bond energy of XeF_2 is 31.0 kcal and that of XeF_4 is 30.9 kcal. For XeF_6 the average bond energy is 29.7 kcal, so that the average energy for forming the last two bonds in XeF_6 is 27.3 kcal.

Introduction

A study of equilibrium conditions in the Xe–F_2 system as a function of temperature, pressure, and composition will be described in this paper.[1] The research was undertaken to determine the thermodynamic stability of the three known binary xenon fluorides, XeF_2, XeF_4, and XeF_6, and to answer the question of whether other binary xenon fluorides are present at equilibrium in significant amounts. An analysis of our preliminary data had suggested the possible existence of XeF_5, although this conclusion was shown to be unlikely from later measurements.[2] A major experimental difficulty that had to be solved to avoid artifacts of this type was the development of a reliable procedure for the quantitative transfer of xenon fluorides without fractionation and without change in composition. Experimental procedures relating to this problem will be described in detail, partly to establish the reliability of the present work and partly because they are pertinent to a number of questions that have arisen about the reliability of other investigations of noble gas compounds. In this respect, XeF_6 is of particular interest because of the ease with which it is converted to its oxygenated counterpart, $XeOF_4$. Although the position has been taken that "no new principles are involved in the understanding of the nature of the chemical bond in these (noble gas) molecules,"[3] XeF_6 has not been sufficiently characterized to make this judgment for it and more careful experimental work with XeF_6 is necessary. If the structure of XeF_6 turns out to be unsymmetrical, then further theoretical work will be needed to rationalize this structure within the present theoretical framework.

Experimental Section

Materials.—Xenon obtained from the Linde Division of the Union Carbide Corp. was used. Mass spectrometric analysis of the xenon showed 0.3 mole % O_2 and 0.5 mole % N_2. Prior to use, these impurities were removed by a sublimation procedure. The fluorine was supplied by the General Chemical Division of the Allied Chemical Corp. Preceding its analysis or use, the fluorine was purified from HF by passage through a liquid oxygen cooled U tube and was transferred to a 2.5-l. Monel storage cylinder by condensation with liquid nitrogen. Fluorine from two different commercial tanks was used in the experiments; tank 1 was 96.53 ± 0.16 mole % F_2 upon analysis and tank 2 was 98.68 ± 0.13 mole % F_2. The impurity had the composition of air. Analytical details are given in the section on Fluorine Analysis.

Apparatus.—A main manifold similar to that described elsewhere[4] was used to measure the quantities of Xe and F_2 taken. It contained two Monel U tubes, a Bourdon gauge, and a 2.5-l. Monel cylinder. The parts were assembled using $^3/_8$-in. Monel high-pressure tubing, fittings, and valves (Autoclave Engineers, Erie, Pa.). The gauge had a Monel Bourdon tube and a 0–1000 mm, 8-in. dial face with 5-mm divisions (Helicoid Gauge Division, American Chain and Cable Co., Bridgeport, Conn.). The gauge was calibrated against a Hg manometer; the readings reproduced to ±1.5 mm. The volume of the manifold was determined by gas expansion using a calibrated glass flask as the standard.

Monel reactors sealed by Heli-arc welding and fitted with a high-temperature, high-pressure Monel valve (Autoclave Engineers) were used. The distinguishing feature of the valve is a long valve stem, which allows the Teflon packing to be sufficiently removed from the heated zone to prevent its deterioration. The reactors used in the low-pressure experiments were of 200-ml capacity. For the high-pressure experiments, 15-ml reactors were used. The reactor used at the highest pressure was designed for 5000 psi at 400° (Autoclave Engineers) and was tested hydrostatically at 9700 psi at room temperature. The reactor volumes were determined at room temperature by filling with water and weighing; corrections were applied for the expansion of Monel under the experimental conditions.

A cylindrical electrical furnace, vertically mounted, was used for heating the reactor and part of the valve body. The temperature was controlled by a Model 402 Capicitrol (Wheelco Instruments Division, Barber-Colman Co., Rockford, Ill.), using a thermocouple as the sensing element, or by a Model 1053A

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[1] Presented in major part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964.

[2] B. Weinstock, E. E. Weaver, and C. P. Knop, "Noble Gas Compounds," H. H. Hyman, Ed., The University of Chicago Press, Chicago, Ill., 1963, pp 50–60 (particularly the footnote on p 59).

[3] J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chem. Rev.*, **65**, 199 (1965).

[4] B. Weinstock and J. G. Malm, *J. Inorg. Nucl. Chem.*, **2**, 380 (1956).

Thermotrol (Hallikainen Instruments, Berkeley, Calif.), using a nickel resistance bulb as the sensing element. The reaction temperature was measured with a chromel–alumel thermocouple attached to the midpoint of the reactor. The thermocouple was calibrated against an NBS calibrated, platinum resistance thermometer.

Thermocouples were also placed at the top and at the bottom of the reactor to measure the temperature uniformity. Because of heat loss through the valve the top of the reactor tended to be at lower temperature than the body. An auxiliary tape heater wound on the valve body was used to achieve uniform temperature. The reactor temperature was taken to be uniform and constant to ±0.5°.

Special vessels were made for weighing xenon and the xenon fluorides and for chemical analysis of the xenon fluorides and of fluorine. The cylinder wall and bottom plate of the weighing vessels were of 30-mil nickel; the top plate $^1/_8$-in. Monel. They were connected to No. 321 stainless steel, Teflon-packed valves (Hoke, Inc., Cresskill, N. J.) by Hoke tube fittings. Their volume was 74 ml and their weight 180 g. Similar light-weight nickel U tubes were also used in the analytical procedures. Hg was added to the weighing vessels and U tubes when a chemical analysis for fluorine was desired. Weighings made with these containers were uncertain to ±0.2 mg.

The main manifold was connected to the reactor through a submanifold, which contained these nickel U tubes and weighing vessels. A xenon fluoride sample, contained in a nickel vessel, was attached to this manifold and was used to season the manifold parts that were exposed to air during the attachment and removal operations necessary for the weighings.

Procedure.—Wherever possible, the equipment was reduced with H_2 and heated with F_2 prior to its initial use.[4] The desired amount of xenon was first introduced into the evacuated reactor by condensation. The quantity of xenon taken was estimated from *PVT* measurements and was also determined by weight. This weight of xenon taken was used in the subsequent calculations. The *PVT* data provided a check against an accidental error; the two measurements agreed within experimental error, or better than 1%.

Fluorine was next introduced into the measuring manifold to a pressure of about 1000 mm and then condensed into the reactor using liquid nitrogen. This process usually was repeated several times in order to obtain the desired quantity of fluorine. The amount of fluorine taken was calculated from the difference between the initial and final pressures (about 700 mm). In this calculation correction was made for the purity of the fluorine, but not for nonideality (the maximum correction for nonideality would be 0.1% at 1000 mm pressure). There is the possibility of fractionation between the fluorine and its air impurity in the transfer operations. However, an analysis of the particular operations employed showed that this error should be much less than the measuring uncertainty.

The reactor was then heated and maintained at a selected temperature for a period of time that varied from 20 to 400 hr. The reaction was stopped by rapid removal of the furnace, followed by immersion of the reactor in ice water.

Fluorine Analysis.—After quenching the reaction, the reactor was cooled with liquid oxygen, the reactor valve opened to the measuring manifold, and the pressure of unreacted fluorine (and the air impurity) read with the Bourdon gauge. For most experiments, a single pressure measurement sufficed. In the event the pressure was greater than 1000 mm (the limit of the gauge), successive expansions were made. The amount of fluorine was calculated from the gas laws, correction being made for the amount of air initially present in the fluorine. In this calculation, the temperature of the reactor was taken as that of boiling oxygen; the correction for the volume occupied by the condensed xenon fluorides was negligible. Experiments were done to show that adsorption or entrainment of fluorine by the xenon fluorides did not give a measurable effect. Thus, when the reactor was warmed to vaporize the xenon fluorides and was then cooled again, no change in pressure was observed. Expansion of a known pressure of F_2 from the reactor to the evacuated measuring system also gave the expected pressure change.

When the amount of unreacted fluorine was too small to be measured directly with sufficient accuracy, a chemical analysis for fluorine was made. The unreacted fluorine was first expanded into a cooled weighing vessel containing Hg. The valve of the weighing vessel was then closed and the reaction between fluorine and mercury initiated by warming with a heat gun. When this reaction appeared complete, the weighing vessel was cooled and the procedure repeated a number of times. The weighing vessel was eventually evacuated (while cooled to 0°) and its weight increase gave a direct measure for fluorine. The fluorine content of the residual gas in the system was determined by iodometry. The gas was passed through NaBr heated to 150°, and the liberated bromine was collected in cooled glass U tubes. This bromine was then allowed to react with a KI solution, and the iodine liberated was titrated with sodium thiosulfate, using starch as an indicator.[5]

The purity of the fluorine used in the equilibrium experiments was determined by reaction with mercury. The fluorine sample to be analyzed was introduced into a liquid oxygen cooled, evacuated weighing vessel containing mercury. (Fractionation of the gas components is unlikely in this procedure.) The increase in weight of the vessel gave the weight of sample taken, about 350 mg. To ensure complete reaction between mercury and fluorine, the vessel was kept in an oven at 80° for 3–6 hr and was shaken frequently. Finally, the vessel was cooled with ice water, evacuated, and weighed. The increase in weight over the initial weight gave the fluorine content. Three analyses were made for each fluorine supply that was used. The results of these analyses and their average deviations were given previously. One sample of the unreacted impurity was collected and analyzed mass spectrometrically. This analysis showed a composition similar to that of air.

Analysis for Xenon and the Xenon Fluorides.—After the collection and analysis of fluorine was completed, the unreacted xenon and the xenon fluorides were transferred from the reactor and were measured. The development of a reliable procedure for this step offered a major difficulty in this research. Two processes contribute most importantly to this problem. First, the xenon fluorides being of relatively low volatility adsorb strongly on the metallic surfaces of the equipment used. This not only makes complete recovery of the xenon fluorides difficult, but also results in a fractionation of the xenon fluorides. Second, even limited exposure to air of the connectors used to attach the analytical vessels to the manifold appears to produce significant hydrolysis of the xenon fluorides. The latter difficulty was unexpected since reasonable precautions (such as flowing dry nitrogen over the exposed parts, warming, and pumping) were not entirely effective in preventing hydrolysis.

The procedure that was finally adopted to minimize errors arising from these effects was to season the reactor, the transfer manifold, and the exposed connectors before use with a xenon fluoride mixture of similar composition to that expected for the final product. In each operation, the seasoning compound was removed from the system in an analogous fashion to that used for the transfer of the xenon fluoride sample. Of particular importance was the use of a pumping period of similar duration to that used in the transfer operation.

Some experiments that were done to test the reliability of the transfer procedure will be described next. The transfer of xenon offered no difficulty. A sample of xenon was weighed, transferred to the reactor, and then transferred back to the weighing vessel. Typically, three successive weights obtained following this procedure gave 0.30907 ± 0.00018 g, which result is consistent with an estimated uncertainty of ±0.2 mg per weighing. The procedure adopted for collecting the xenon fluoride reaction products was tested in the following way. Two weighed U tubes were attached in series to the small manifold, with dry

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[5] A. E. Florin, I. R. Tannenbaum, and J. F. Lemons, *J. Inorg. Nucl. Chem.*, **2**, 368 (1956).

nitrogen gas flowing through a tee at the connection to the small manifold to minimize exposure to moisture. The newly connected portion of the system was evacuated to a gauge pressure below 10^{-5} torr. The system was then exposed for 30 min to a mixture of xenon fluorides (XeF_x) provided by the seasoning can. This XeF_x sample was recondensed into the seasoning can and the system pumped for 1 hr ($P < 10^{-5}$ torr). (Any HF formed is removed from the seasoning can by cooling with Dry Ice and pumping.) A weighed sample of XeF_x was then condensed into the reactor. The reactor valve was closed and the reactor warmed to room temperature. After 40 min, the reactor valve was opened and the XeF_x sample was allowed to condense into the far U tube, which was cooled with liquid nitrogen. The reactor was then pumped on through the U tubes for 45 min. Finally, the near U tube was cooled with liquid nitrogen and the pumping continued another 15 min. The two U tubes were then weighed and the XeF_x recovery determined. The above procedure was also tested in two experiments where F_2 gas was condensed into the reactor together with the XeF_x sample. In these latter experiments, the reactor was first cooled to the temperature of liquid oxyen to remove the bulk of the fluorine before attempting to transfer the XeF_x sample.

In general, better than 99% of the XeF_x sample was found in the far U tube (45 min pumping time). The samples of XeF_x introduced weighed about 0.5 g. The average uncertainty of the recovery procedure was ±1.5 mg. Longer pumping times were used for the larger samples that were transferred in the actual experiments. In those experiments when a relatively large amount of XeF_x was found in the near U tube, the reactor was pumped on for an additional period of time.

Two other variations from this procedure were used in the actual experimental XeF_x recoveries. The U tubes contained mercury, so that a chemical analysis of the XeF_x samples could be made. Also, the U tubes were cooled with a $-100°$ bath, so that unreacted xenon would pass through and could be collected in a liquid nitrogen cooled U tube in the large measuring system.

Measurable quantities of unreacted xenon were not found except in the few experiments at the highest temperature, 500°, and at the low equilibrium F_2 pressure, <3.4 atm. However, small quantities of gas that passed through the $-100°$ U tube were usually collected in the other experiments. This gas was presumed to be SiF_4 formed by corrosion of the Monel reactor, although a definite proof of this assumption has not been obtained.

The increase in weight of the U tubes gave the weight of xenon fluorides formed. Their fluorine content was taken as this weight less the weight of xenon taken initially (except where unreacted xenon was recovered as noted above).

A chemical analysis of the xenon fluorides was made to permit a mass balance for xenon and for fluorine and to give a measure of the over-all reliability of the experimental results. The analysis consisted of allowing the xenon fluorides to react with mercury in the U tube at 80° with subsequent collection and weighing of the xenon released.[6] Additionally, the loss in weight of the U tube gave an independent measure of the xenon content of the sample. To ensure complete reaction of the xenon fluorides with the Hg, the process of heating and shaking the U tube and of removing and collecting xenon was repeated until the U tube and its contents reached a constant weight.

For 28 experimental samples analyzed in this way, the average deviation between the initial weight of xenon taken in the experiment (ranging from 305 to 648 mg) and the weight of xenon recovered after analysis was ±1.40 mg. Four other analyses gave larger errors; one could be explained as the result of incomplete reaction, and the other three could be explained by incomplete reaction followed by distillation of some XeF_x along with the xenon. The amount of xenon determined by the loss in weight of the U tube agreed with the corresponding xenon recovery weight with similar consistency.

These mass balance data for xenon give us a measure of reliability for the weight of xenon fluoride product. In the subsequent error analysis this uncertainty is taken as ±1.5 mg; most of the error arises from the transfer operation (as explained earlier) rather than from the weighing.

Fluorine Mass Balance.—A mass balance for fluorine was made by subtracting the amount of fluorine found in the xenon fluorides from the amount of fluorine taken initially and comparing it with the amount of unreacted fluorine found at the end of the experiment. This comparison was made for 30 experiments. In 25 of them, less fluorine was found at the end of the experiment that would be expected from the fluorine lost as xenon fluorides; in the other 5 more fluorine was found. This result suggests that some fluorine was lost by corrosion of the reactor. However, the discrepancies are small and no correlation with time, pressure, or temperature is evident in the data. The average deviation between the two fluorine determinations was ±0.135 mmole; the individual amounts of unreacted fluorine at equilibrium ran from 0.7 to 53 mmoles. The uncertainty of each gauge reading of ±1.5 mm corresponds to an uncertainty of ±0.024 mmole. This reasonable mass balance for fluorine adds to the confidence in the reliability of the data. In computing the equilibrium fluorine pressure, both fluorine determinations were used. At least double weight was given to the measured values of unreacted fluorine and a small correction for corrosion was made to the values derived from the fluorine consumption. For the experiments when the fluorine pressure was very low and measured analytically (see Fluorine Analysis), this value was used directly.

Equilibrium Fugacity of Fluorine.—The pressure of fluorine, P_F, in the reaction vessel at equilibrium was calculated using the equation of state

$$P_F = \frac{n_F RT}{V}\left(1 + \frac{nB}{V}\right)$$

where n_F is the number of moles of fluorine measured at the end of the experiment, R is the gas constant, T is the absolute temperature of the experiment, V is the volume of the reactor corrected for the experimental conditions, and n is the total number of moles in the vapor state at equilibrium. The second virial coefficient, B, of fluorine at the reaction temperature was used in the calculations. These values of B are summarized in Table I, where $T^* = T/(\epsilon/k)$, $B^* = B/(^2/_3\pi N\sigma^3) = B/b_0$, and $b_0 = 59.3$ cm³. The force constants given by White, Hu, and Johnston[7] were used: $\epsilon/k = 121°$ and $\sigma = 3.61$ A; and the value of B^* as a function of T^* was taken from Table I-B of Hirschfelder, Curtis, and Bird.[8] The Boyle point for F_2 is $T_B = 3.42(\epsilon/k) = 413.8$°K, so that B is positive in the experimental range reported here.

TABLE I

SECOND VIRIAL COEFFICIENT FOR F_2

T, °K	T^*	B^*	B, cm³
300	2.479	−0.3223	−19.11
523.15	4.324	0.1644	9.75
573.15	4.737	0.2158	12.80
623.15	5.150	0.2577	15.28
673.15	5.563	0.2933	17.40
774.15	6.398	0.3469	20.57

The fugacity of fluorine, f, is then calculated from the relation

$$\ln\,(f/P_F) = \frac{BP}{RT}\left(1 - \frac{BP}{2RT}\right)$$

where P is the total pressure in the system.

The use of the virial coefficient of F_2 in the equation of state

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[6] E. E. Weaver, B. Weinstock, and C. P. Knop, *J. Am. Chem. Soc.*, **85**, 111 (1963).

[7] D. White, J. Hu, and H. L. Johnston, *J. Chem. Phys.*, **21**, 1149 (1953).

[8] J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, "Molecular Theory of Gases and Liquid," John Wiley and Sons, Inc., New York, N. Y., 1954, pp 1114–1115.

introduces an error because the xenon fluorides are also an important constituent of the vapor phase. However, the error is probably not significant compared with the experimental uncertainty. The largest correction for nonideality occurs in the experiments at the highest pressures that were done to test the possible existence of XeF_8. In the extreme case, the fluorine pressure was 440 atm and the mole fraction of fluorine in the vapor 0.94. The total correction for nonideality was about 20%. A 10% uncertainty in the virial coefficient would then introduce a 2% error in the fugacity. The highest fluorine pressure in the experimental data used to calculate equilibrium constants was 186 atm, and the mole fraction of fluorine was 0.916. The total correction for nonideality was 6.4%, so that a 20% uncertainty in the virial coefficient would introduce a 1.3% error in the fugacity. A correction for the dissociation of F_2 was necessary only in the experiment at the highest temperature and lowest pressure (C-14). The correction was less than 1%.

Results

The experiments were done at five different temperatures. There were 11 runs at 250°, 9 runs at 300°, 6 runs at 350°, 10 runs at 400°, and 5 runs at 500°. The reaction times used for the experiments were 135–400 hr at 250°, 65–120 hr at 300°, 41–168 hr at 350°, 42–114 hr at 400°, and 19–70 hr at 500°. The detailed experimental results have been transmitted to the American Documentation Institute in tabular form.[9] These tables include the reaction temperature, the reactor volume, the number of moles of Xe and F_2 taken initially, the reaction time, the weight of xenon fluorides recovered, the unreacted xenon, the xenon recovery from XeF_x, the xenon mass balance, the amount of unreacted fluorine, the fluorine mass balance, and the calculated uncertainty in the amount of unreacted fluorine.

Equilibrium Constants.—The experimental data can be fitted to three equilibrium constants, which suggests that only three binary xenon fluorides are present in significant amounts. The three equilibria are

$$Xe + F_2 = XeF_2 \tag{1}$$

$$Xe + 2F_2 = XeF_4 \tag{2}$$

$$Xe + 3F_2 = XeF_6 \tag{3}$$

The corresponding equilibrium constants are

$$K_2 = k_2 = (XeF_2)/(Xe)(F_2) = n_2/n_0f \tag{4}$$

$$K_4 = (XeF_4)/(Xe)(F_2)^2 = n_4/n_0f^2 \tag{5}$$

$$K_6 = (XeF_6)/(Xe)(F_2)^3 = n_6/n_0f^3 \tag{6}$$

or, alternatively

$$k_4 = (XeF_4)/(XeF_2)(F_2) = n_4/n_2f \tag{7}$$

$$k_6 = (XeF_6)/(XeF_4)(F_2) = n_6/n_4f \tag{8}$$

In the evaluation of the equilibrium constants the number of moles, n_0, n_2, n_4, and n_6, was used for the activity of Xe, XeF_2, XeF_4, and XeF_6 respectively. For the activity of F_2, f, the fugacity was used.

Experimentally, the individual xenon fluorides could not be measured separately; the composition and amount of the xenon fluoride mixture, XeF_x, was obtained. Using the mass balance relations given below, the equilibrium constants could be derived without directly measuring the individual amounts of each compound. The mass balance equation for xenon is

$$n^0_{Xe} = n_0 + n_2 + n_4 + n_6 \tag{9}$$

where n^0_{Xe} is the number of moles of xenon taken initially. The g-atoms of fluorine chemically bound as a xenon fluoride, n_F, is determined experimentally and is given by

$$n_F = rn^0_{Xe} = 2n_2 + 4n_4 + 6n_6 \tag{10}$$

The parameter, r, is the ratio n_F/n^0_{Xe}. Combining eq 4, 5, 6, 9, and 10 gives the relationship

$$r + (r - 2)K_2f + (r - 4)K_4f^2 + (r - 6)K_6f^3 = 0 \tag{11}$$

The individual equilibrium constants can then be derived from eq 11, using the experimental values of r and f. In this evaluation the experimental data were separated into three groups: from one group the value of k_2 could be derived most reliably from the data, from another group k_4, and from the remaining group k_6. It was necessary to use preliminary estimates for two of the constants in every case, and the final evaluations were arrived at by successive refinements of these estimates.

The experimental data used in this evaluation and the final equilibrium constants derived are given in Table II for the five temperatures studied. Where the equilibrium constant is given in parentheses the values were not used in the final averages. This was done because we did not want to derive two equilibrium constants from the same data. (For example, expt C-9 at 523.15°K was used to derive k_4 but not k_6.) These values in parentheses are included in the table to show the consistency of the data. In other cases the equilibrium data were excluded because of excessive deviation from the final average arrived at and these values are marked with an asterisk. (For example, expt B-20, B-6, and A-4 at 523.15°K.)

The column heading Δk(calcd) gives our estimates of the uncertainty in each equilibrium constant based on the uncertainties in the experimental data. (The formulas used for this evaluation are given in the American Documentation Institute document[9] mentioned previously.) The reciprocals of these numbers were used as weighting factors for deriving the average value of the equilibrium constants. The weighted average value for the equilibrium constant at each temperature is given below each data grouping, together with the weighted average deviation from the mean. Below the experimental average equilibrium constant for k_4 is given the value of that constant calculated from thermodynamic considerations k_4(th)

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(9) Detailed experimental results have been deposited as Document No. 9096 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

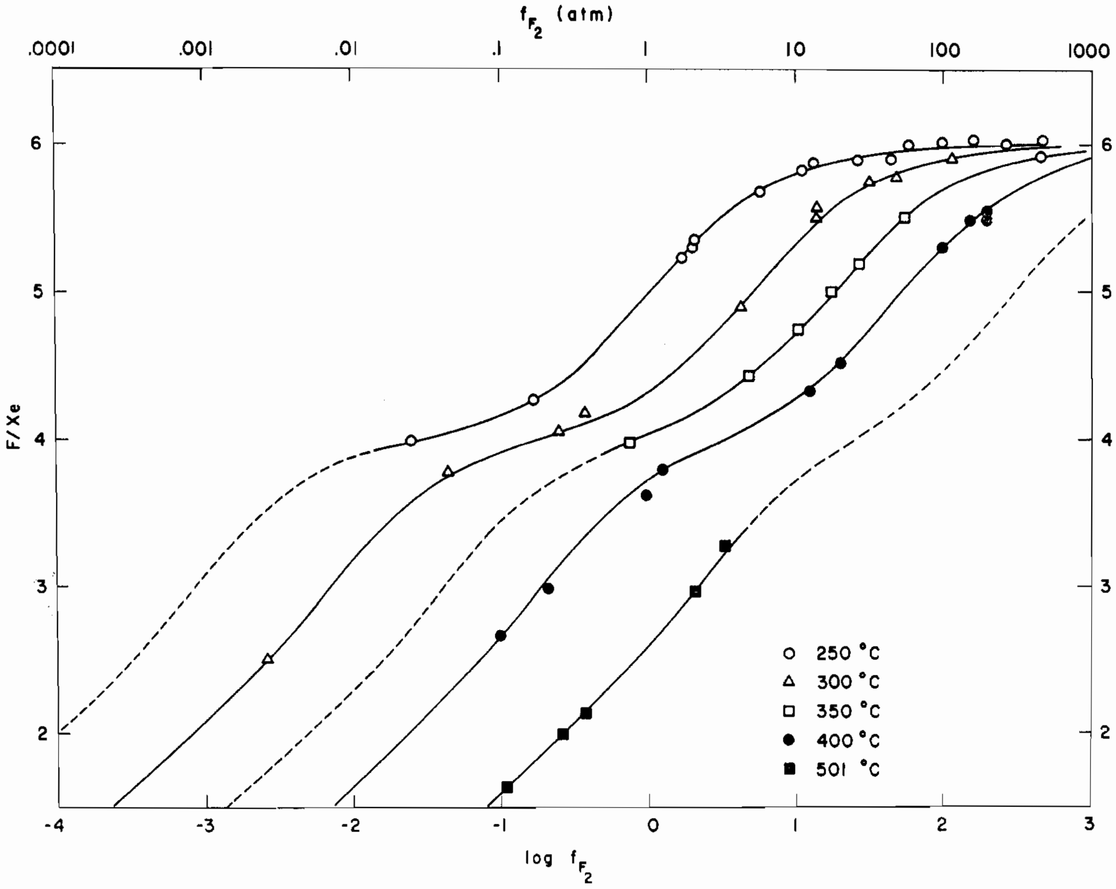

Figure 1.—The variation or r = F(bound)/Xe(total) with F_2 fugacity, f, in the range 250–501°.

and for k_6 the value calculated from an interpolation formula, eq 18. These values are the best values for k_4 and k_6 that we can derive from our data. Their derivation will be discussed in the section on Thermodynamic Calculations. The experimental data are displayed in Figure 1; the lines drawn there are calculated from the final values of the equilibrium constants.

Another potentially important source of error is the possible change in composition that occurs during the quenching procedure. This would introduce a systematic error in the data, in that the temperatures that we have taken as the equilibrium temperatures would always be too high or equivalently the equilibrium constants would be too high for the assigned temperature. The error would be greatest at the highest temperature and would become progressively less important at the lower temperatures because the rate of change of composition would depend exponentially on the temperature for the most part. Additionally, the effect would increase the relative concentration of the higher xenon fluorides at the expense of the lower xenon fluorides (the value of r would become greater).

It is difficult to make a quantitative estimate of this error, but we do not believe that it contributes an important uncertainty to our measurements. The variation of lengths of time used in the experiments was intended to give information relative to this question. If the time the reactor were kept at the equilibrium temperature were not long enough, then the value of r observed would be smaller than the true equilibrium value. The shorter times used at each temperature reflect our desire to have kept the reactors at temperature for at least twice the minimum assymptotic equilibrium time. The choices were somewhat arbitrary in that only qualitative attempts were made to determine the minimum equilibrium times. Our procedure for removing the furnace and immersion of the reactor in the ice bath was also intended to minimize this error. The elapsed time was 10 sec. The consistency of the data themselves argues strongly against the possibility of an important quenching error. Another point is worth noting in more detail. It has to do with the kinetics of the reactions. Since a lower temperature results in the formation of higher xenon fluorides at the expense of the lower xenon fluorides, the effect should be strongly dependent on the fluorine pressure. In the data used to evaluate k_6 at 673.15°K (Table II), the fluorine pressure changed from 12 atm (B-14) to 198 atm (A-19) and no trend toward higher values of k_6 or of r is seen. The data for expt B-19 at 198 atm, which was excluded because it deviated excessively from the average, deviate in the wrong direction to arise from a quenching error. The data at 774.15°K for k_4 also show no trend. If one pessimistically assumed the value of k_4 derived in expt C-17 to be too high because of quenching, then the temperature assigned would be about 4° low (dk_4/dT = 0.01 atm^{-1} deg^{-1}). More likely, the quenching error at this

TABLE II

EQUILIBRIUM CONSTANTS

Expt	f, atm	r(exptl)	r(calcd)	k, atm^{-1}	Δk, atm^{-1}
T = 523.15°K					
C-9	0.0251	3.992	3.983	1.43×10^3	880
			k_4(exptl)	$1.43 \pm 0.88 \times 10^3$	
			k_4(th)	1.22×10^3	
C-9	0.0251	3.992	3.983	(1.144)	0.684
C-8	0.1706	4.279	4.267	0.999	0.146
D-5	1.701	5.227	5.237	0.931	0.067
A-18	2.043	5.301	5.321	0.911	0.077
B-3	2.085	5.354	5.333	0.999	0.088
B-2	5.891	5.684	5.701	0.892	0.121
B-1	10.92	5.828	5.823	0.988	0.216
A-3	11.17	5.821	5.828	0.911	0.172
B-20	13.57	5.882	5.855	1.159*	0.178
B-6	26.73	5.907	5.924	0.768*	0.307
A-4	43.74	5.909	5.953	0.471*	0.187
			k_6(exptl)	0.944 ± 0.014	
			k_6(eq 18)	0.948	
T = 573.15°K					
D-7	0.00263	2.505	2.501	(8570)	3450
			k_2(eq)	1.02×10^4	
D-7	0.00263	2.505	2.501	148	12
D-8	0.0448	3.782	3.760	164	26
D-6	0.2527	4.055	4.045	186	138
			k_4(exptl)	155 ± 5	
			k_4(th)	146	
A-11	4.302	4.901	4.923	0.192	0.014
B-8	13.92	5.518	5.470	0.228	0.022
A-6	14.24	5.572	5.478	0.260	0.027
A-7	31.87	5.758	5.727	0.230	0.037
B-5	49.34	5.785	5.816	0.169	0.030
A-5	116.00	5.912	5.918	0.185	0.077
			k_6(exptl)	0.211 ± 0.011	
			k_6(eq 18)	0.203	
T = 623.15°K					
B-11	0.766	3.988	3.980	27.2	12.3
B-9	4.78	4.399	4.402	(17.9)	28.8
			k_4(exptl)	27.2 ± 12.3	
			k_4(th)	24.8	
B-11	0.766	3.988	3.980	(0.0610)	0.0296
B-9	4.78	4.399	4.402	0.0548	0.0060
T = 623.15°K (*Continued*)					
A-12	10.51	4.751	4.726	0.0581	0.0043
B-7	17.67	4.998	4.985	0.0565	0.0040
A-17	26.80	5.189	5.190	0.0550	0.0039
A-8	56.92	5.507	5.514	0.0542	0.0052
			k_6(exptl)	0.0558 ± 0.0006	
			k_6(eq 18)	0.0555	
T = 673.15°K					
D-9	0.0996	2.604	2.657	(385)	280
C-11	0.2088	2.993	3.058	(235)	237
			k_2(eq)	360	
D-9	0.0996	2.604	2.657	4.89	0.36
C-11	0.2088	2.993	3.058	4.91	0.29
D-10	0.9620	3.631	3.712	4.23	0.41
C-12	1.266	3.809	3.790	6.02	0.92
B-14	12.68	4.329	4.350	(2.90)	2.19
			k_4(exptl)	4.86 ± 0.16	
			k_4(th)	5.49	
C-12	1.266	3.809	3.790	(0.0266)	0.0138
B-14	12.68	4.329	4.350	0.0170	0.0020
B-15	20.59	4.526	4.540	0.0181	0.0016
B-17	101.97	5.308	5.311	0.0168	0.0014
B-16	151.66	5.494	5.477	0.0195	0.0018
A-19	198.50	5.558	5.577	0.0177	0.0018
B-19	198.55	5.502	5.573	0.0153*	0.0014
			k_6(exptl)	0.0182 ± 0.0003	
			k_6(eq 18)	0.0184	
T = 774.15°K					
C-14	0.111	1.639	1.632	30.3	1.7
C-16	0.261	1.989	1.994	29.1	2.2
C-15	0.367	2.143	2.137	(31.0)	3.4
D-16	2.071	2.976	2.980	(26.0)	7.2
			k_2(exptl)	29.8 ± 0.4	
C-14	0.111	1.639	1.632	(0.518)	0.106
C-16	0.261	1.989	1.994	(0.471)	0.045
C-15	0.367	2.143	2.137	0.495	0.033
D-16	2.071	2.976	2.980	0.480	0.032
C-17	3.354	3.280	3.232	0.535	0.035
			k_4(exptl)	0.502 ± 0.012	
			k_4(th)	0.482	

temperature is less than 1° and negligible at the lower temperatures.

Intermediate Fluorides.—In a report of our preliminary experimental study of the xenon–fluorine system,[2] the possibility of the existence of XeF_5 was reported. In a footnote to that report, some experiments were described that made this possibility appear unlikely. The artifact appears to have been connected with the difficulty of obtaining a reliable and quantitative transfer of the xenon fluorides formed. This was discussed in some detail in the Experimental Section.

There is no evidence in our present results for the existence of any binary fluoride of xenon other than the three compounds XeF_2, XeF_4, and XeF_6. To test this point, we have included in Table II a column headed r(calcd). These values were calculated from eq 11, using the fugacities and the derived equilibrium constants. If any intermediate fluoride was present as a significant compound in our gas mixture then we would expect large deviations between r(exptl) and r(calcd), particularly in the region corresponding to the formula of the intermediate compound. None was found.

The Effect of Oxygen.—The fluorine used in our experiments contained the order of 1% oxygen. It was therefore important to determine whether or not the presence of this oxygen had an effect on our equilibrium data, particularly in view of the existence of a stable well-characterized xenon oxyfluoride, $XeOF_4$. This question was examined in the following way. Two experiments were performed at 573.15°K with similar amounts of xenon and fluorine, but with the difference that in one experiment the reaction mixture contained additionally 4.6 times as much oxygen as fluorine. (The pressure of O_2 at equilibrium in this system was 149 atm.) The results of the two experiments were the same within the experimental error and indicated that the presence of the large amount of oxygen probably had no greater effect than to increase the fugacity of the reactants. The results of the experiments are given in Table II; expt A-6 had no added oxygen and expt B-8 included the large excess of oxygen. Aside from the agreement of the equilibrium constant in expt B-8, the mass balance data and the chemical analyses also support the conclusion that $XeOF_4$ is not present within our limits of detection.

Xenon Octafluoride.—The possibility of the existence of xenon octafluoride, XeF_8, has been reported by Slivnik, *et al.*[10,11] The data given in Table II cover the range of experimental conditions they describe, but do not show an anomaly that would suggest the presence of XeF_8. We have further extended our experimental conditions to investigate the possibility of the existence of XeF_8. A series of experiments was done at 250° and at F_2 pressures up to the limit of our equipment. The experimental results are summarized in Table III. The first column gives the initial ratio of g-atoms of fluorine to xenon, $(F/Xe)_0$; the second column, the fugacity of F_2 at equilibrium; the third column, the experimental value of r, which is the ratio of g-atoms of fluorine in the xenon fluoride product to the initial g-atoms of xenon in the system; r(calcd) is the value of r for the experiment calculated from the experimental conditions and the equilibrium constants; the final column, Δr(calcd), gives the uncertainty in r calculated from the error analysis of the experimental data.

TABLE III

HIGHER XENON FLUORIDES

$(F/Xe)_0$	f, atm	r(exptl)	r(calcd)	r(calcd) − r(exptl)	Δr(calcd)
32.6	98.3	6.026	5.979	−0.047	0.035
50.7	161.4	6.048	5.987	−0.061	0.035
60.9	271.4	6.008	5.992	−0.016	0.051
60.0	477.5	5.922	5.996	+0.074	0.025
62.3	494.5	6.043	5.996	−0.047	0.026

Although several of the values of r(exptl) exceed 6, the values are equal to 6 within experimental error (compare the last two columns of Table III). Furthermore, there is no significant increase in the value of r(exptl) as the fluorine fugacity is increased from 100 to 500 atm. From these data, we conclude that the observations of Slivnik, *et al.*, are in error and that XeF_8 does not exist as a significant molecular species in an equilibrium gas mixture within the range covered. It is also worth noting that in unloading the reactor the connecting tubing was kept refrigerated at ∼−15° to minimize decomposition of XeF_8 (if it existed) during the transfer operations. In all cases the xenon recovered upon analysis agreed with the initial xenon, which eliminates the possibility of a nonvolatile XeF_8 product.

Pure Xenon Hexafluoride.—The study of XeF_6 had been complicated by the presence of small amounts of XeF_4 and $XeOF_4$ in the samples. These compounds are of similar volatility to XeF_6 and have absorption bands in the infrared that are close to some of the XeF_6 bands. We therefore decided to make a XeF_6 preparation that would be substantially free of these compounds and that could be fractionated to test the purity of the sample.

A sample of xenon fluorides weighing 6.4295 g and consisting mainly of XeF_6 and XeF_4 was condensed into a high-pressure reactor along with fluorine. At the end of 192 hr at 200° the fluorine measured back corresponded to a calculated pressure of 162 atm in the reactor. The xenon fluorides now weighed 6.5463 g and consisted mainly of XeF_6.

The sample was transferred to a special portable manifold for purification and also for monitoring the process by infrared spectroscopy. The portable manifold consisted of a 1.7-l. Monel cylinder, which contained the 6.5 g of XeF_6, an infrared cell, and two small reservoirs. The sample of XeF_6 was allowed to vaporize in the 1.7-l. can and then slowly condensed by cooling to −20°. Any volatile impurities would remain in the large vapor phase. This vapor was found to contain XeF_4 and $XeOF_4$ as indicated by the infrared absorption bands. This impure vapor was discarded by transferring for 10 min to a reservoir cooled with liquid nitrogen. The 1.7-l. cylinder was then warmed again and the cycle repeated until the bands at 928 cm^{-1} for $XeOF_4$ and 581 cm^{-1} for XeF_4 disappeared and the spectrum of pure XeF_6 was recorded. The infrared spectrum obtained in the region 500–650 cm^{-1} is shown in Figure 2 after subtraction of the background.

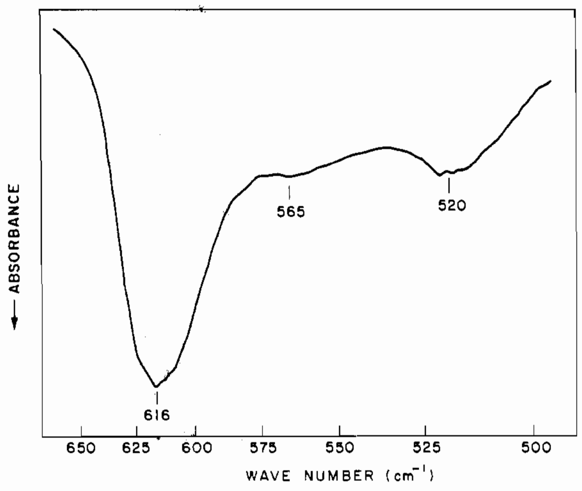

Figure 2.—Infrared spectrum of XeF_6 in the region 500–650 cm^{-1}.

It is similar to that reported by Smith,[12] but the band at 520 cm^{-1} is sharper and a possible, partly resolved band at 565 cm^{-1} is present. The strongest absorption is at 616 cm^{-1}.

The balance of this sample was used for chemical analysis, molecular weight determination, and vapor pressure measurement.

Vapor Pressure of XeF_6.—The vapor pressure apparatus contained an absolute oil manometer, a differential oil manometer, and a 14-in. long vertical Monel

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[10] J. Slivnik, B. Volavšek, J. Marsel, V. Vrščaj, A. Šmalc, B. Frlec, and A. Zemljič, ref 2, pp 64–67.

[11] J. Slivnik, B. Volavšek, J. Marsel, V. Vrščaj, A. Šmalc, B. Frlec, and A. Zemljič, *Croat. Chem. Acta*, **35**, 81 (1963).

[12] D. F. Smith, ref 2, pp 295–303.

barrier tube (i.d. 1/8 in.) connected directly above the main manifold. The barrier tube could be closed off from the rest of the system by two valves and evacuated separately.

To determine the pressure in the main manifold, the evacuated barrier tube was first filled with XeF_6 vapor. The lines connecting the other end of the barrier tube and the manometers were filled with dry nitrogen at the expected pressure of the sample. The barrier was then opened to the differential manometer and the difference in pressure noted. The procedure was then repeated until the differential manometer gave only a slight change. The final vapor pressure reading consisted of the sum of the absolute oil manometer reading corrected for the differential manometer reading. The readings were made with a Wild cathetometer. The results obtained are summarized in Table IV. The data were fitted to the equation

$$\log P_{\text{mm}} = -3400.12/T + 12.86125 \qquad (12)$$

The heat of sublimation of XeF_6 calculated from this equation is 15,600 cal mole^{-1}. This is a high value for a hexafluoride molecule and consistent with the fact that XeF_6 is by far the least volatile hexafluoride molecule. The heat of sublimation of orthorhombic PtF_6, a relatively nonvolatile hexafluoride molecule, is 11,400 cal mole^{-1} at 3°, where its vapor pressure is 32.5 mm. A graph of XeF_6 vapor pressures obtained by a combination of infrared absorption measurement and direct measurement has been reported by Smith.[13] His data are in general agreement with ours, but are somewhat higher at the lower temperatures and lower at the higher temperatures. His plot gives 13,200 cal mole^{-1} for the heat of sublimation of XeF_6.

TABLE IV

VAPOR PRESSURE OF XeF_6

Temp, °C	Vapor press, mm	
	Obsd	Eq 12
0.04	2.70	2.60
9.78	7.11	6.98
18.10	15.10	15.38
22.67	23.43	23.31

Molecular Weight Determination.—Preliminary attempts to determine the molecular weight of XeF_6 by vapor density measurements had consistently given high results. The difficulty appeared to be caused by adsorption of XeF_6 in the measuring system because the adsorbed material would be collected and weighed along with the vapor. To minimize this error, we carefully measured the pressure before and after removing the sample for weighing. The pressures were measured with the vapor pressure system described above. The results of two determinations are given in Table V. The agreement with the formula weight is good and it is concluded that XeF_6 is not associated in the vapor at these pressures.

The effect of adsorption on the apparent molecular weight can be seen in Table VI. Here a sample of known weight was kept in the manifold for varying lengths of time prior to measuring its pressure. The decrease in pressure with time as well as the apparent increase in molecular weight is clear. Corrections were made for the sample removed in the process of measuring the pressure.

TABLE V

MOLECULAR WEIGHT OF XeF_6

P_1, mm	13.26	15.83
P_2, mm	7.22	11.22
ΔP, mm	6.04	4.61
Sample wt, mg	211.1	158.9
Temp, °C	25.6	24.8
Vol., cm^3	2609.5	2609.5
Mol wt	249.6	245.5

Theoretical 245.3

TABLE VI

APPARENT MOLECULAR WEIGHT OF XeF_6[a]

Time in vessel, min	Press, mm	Apparent mol wt
70	16.46	262.2
334	16.10	266.2
1629	15.83	269.4

[a] Initial sample 605.65 mg; room temperature 25.0°; volume 2609.5 cm^3.

Chemical Analysis.—Since the XeF_6 sample represented a relatively pure xenon compound we also did a chemical analysis of the sample. This analysis served not only to confirm the formula, XeF_6, but also to check the reliability of our analytical procedures, described previously. The results were as follows: sample taken, 0.3538 g; weight of xenon, by weight loss, 0.1895 g (by recovery, 0.1905 g); weight of fluorine, as "HgF_x," 0.1644 g; ratio of F/Xe, 5.996. As in the analytical procedure adopted for the analysis of the equilibrium data, the amount of xenon was taken from the loss of weight of the mercury can.

Thermodynamic Calculations

Xenon Difluoride, XeF_2.—The thermodynamic properties of XeF_2 were calculated by the usual methods of statistical mechanics.[14] In this and the subsequent calculations the IUPAC fundamental constants based on $^{12}C = 12$ were used. The structure of XeF_2 was taken as linear symmetric, symmetry $D_{\infty h}$ with a bond length of 2.00 A.[15] The fundamental vibrational frequencies were taken as $\nu_1 = 513$, $\nu_2 = 213$, and $\nu_3 = 557$ cm^{-1}.[12] The value of ν_1 was taken from $(\nu_1 + \nu_3) = 1070$ less ν_3 (557 cm^{-1}), rather than use the Raman value of 496 cm^{-1} found for the solid.[12] The calculated values at the temperatures of interest here are summarized in Table VII.

The thermodynamic properties for the formation of XeF_2 (eq 1) are given in Table VIII. The last three columns of this table give the values of $S°$, $\Delta(G° - H°_0)$, and $-\Delta(H° - H°_0)$ that were calculated from statistical mechanics. In this computation, the thermodynamic properties of F_2 were recalculated, following the paper of

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(13) D. F. Smith, ref 2, p 45.

(14) J. E. Mayer and M. G. Mayer, "Statistical Mechanics," John Wiley and Sons, Inc., New York, N. Y., 1940.

(15) H. A. Levy and P. A. Agron, *J. Am. Chem. Soc.*, **85**, 241 (1963).

TABLE VII

THERMODYNAMIC PROPERTIES OF XeF_2 IN THE IDEAL GASEOUS STATE AT 1 ATM PRESSURE (CAL MOLE^{-1} DEG^{-1})

T, °K	$-(G° - H°_0)/T$	$(H° - H°_0)/T$	$S°$
298.15	51.987	10.070	62.057
523.15	58.094	11.621	69.715
573.15	59.166	11.846	71.012
623.15	60.165	12.044	72.209
673.15	61.101	12.219	73.320
774.15	62.830	12.515	75.345

Cole, Farber, and Elverum.[16] The recalculation was necessary because it was not possible to obtain sufficient accuracy from their table by interpolation and because of the change in fundamental constants. The only temperature in common with their table was at 298.15°K: we obtained $S° = 48.500$ cal mole^{-1} deg^{-1} compared to their value of 48.506 and $-(G° - H°_0)/T = 41.447$ compared to 41.432.

TABLE VIII

THERMODYNAMICS OF FORMATION OF XeF_2

T, °K	K_2, atm^{-1}	$\Delta(G° - H°_0)$, cal mole^{-1}	$-\Delta(H° - H°_0)$, cal mole^{-1}	$-\Delta S°$, cal deg^{-1} mole^{-1}
298.15	1.23×10^{13}	7,461	584	26.982
523.15	8.80×10^{4}	13,483	404	26.544
573.15	1.02×10^{4}	14,808	357	26.459
623.15	1670	16,129	311	26.382
673.15	360	17,446	265	26.310
774.15	29.8	20,097	172	26.182

$\Delta H°_0 = -25{,}319$ cal mole^{-1}

Using the experimental value $K_2 = 29.8$ atm^{-1} at 774.15°K, we obtained $\Delta G° = -5222$ cal mole^{-1}. The value of $\Delta H°_0$ for the formation of XeF_2 is then $-25{,}319$ cal mole^{-1}. By combining this value of $\Delta H°_0$ with the statistical calculations of $-\Delta(G° - H°_0)$, the values for $-\Delta G°$ are obtained for the other temperatures; the corresponding values of K_2 were then computed from the $-\Delta G$ values.

The points of comparison that can be made with other experimental K_2 values from our data are at 673.15 and 573.15°K. As can be seen in Table II, expt D-9 and C-11 gave values of 385 and 235 for K_2 compared with our derived value of 360 atm^{-1}; and expt D-7 gave 0.857×10^4 for K_2 compared to the derived value of 1.02×10^4 atm^{-1}. The agreement is well within the estimated experimental uncertainty.

It would have been desirable to have more data with which to evaluate K_2, but experimental difficulties were the limiting factor. Actually higher temperatures are necessary in order to have reasonable equilibrium fluorine pressures, but then corrosion of the reactor limits the reliability of the data. At the lower temperatures the equilibrium pressures tend to become very low. The three data points mentioned above were used to calculate k_4 rather than K_2 because of the greater reliability afforded. It was felt that the thermodynamic extrapolation of the K_2 data was much more reliable than the use of these data.

Xenon Tetrafluoride, XeF_4.—X-Ray diffraction[17-19] and neutron diffraction[20] studies with crystalline XeF_4 show the molecule to have a square-planar configuration with a Xe–F bond distance (corrected for thermal motion) of 1.95 A.[20] The infrared spectrum of XeF_4 vapor and the Raman spectrum of the solid[21] are interpreted in terms of D_{4h} symmetry (symmetry number 8) in agreement with the diffraction measurements with the solid. There are seven fundamental vibrational frequencies. Five of these have been assigned[21] and the frequencies (with degeneracies given in parentheses) are: ν_1 (1) 543, ν_2 (1) 291, ν_3 (1) 235, ν_5 (1) 502, and ν_6 (2) 586 cm^{-1}. Since ν_1 and ν_5 are assigned from Raman data with the solid, we have assigned different frequencies for these fundamentals for the vapor based on binary bands observed in the infrared spectrum of the vapor.[21] For ν_1 we obtain 550 cm^{-1} from $\nu_1 + \nu_6 = 1136$, and for ν_5 we obtain 519 cm^{-1} from $\nu_5 + \nu_6 = 1105$. Although ν_3 was also observed for the solid, it was taken as 235 cm^{-1} in the absence of other information. The b_{1u} inactive fundamental, ν_4, has been estimated at 221 cm^{-1} based on the assignment of a solid Raman band at 442 cm^{-1} as $2\nu_4$, but this assignment is regarded as questionable.[21] The second e_u infrared-active fundamental, ν_7, was originally assigned as 123 cm^{-1}, but this band has since been shown to have been due to HF.[22] In view of the uncertainties presently existing for two of the XeF_4 vibrational fundamentals, it was not possible to make a reliable calculation of the thermodynamic properties of XeF_4. Instead we have used the equilibrium constant data to derive an estimate for the two missing frequencies. The procedure used was to find values for the two vibrational frequencies that gave the best agreement between the thermodynamic properties of the reacting molecules and the temperature variation of the equilibrium constant data.

The equilibrium constants, k_4 (eq 7), that we obtained for the reaction

$$XeF_2 + F_2 = XeF_4 \qquad (13)$$

are listed in the second column of Table IX. These numbers differ from the values in Table II in that they contain one more significant figure. The next column, labeled ω, gives the weight assigned to each equilibrium constant in the least-squares calculations. These weighting factors are the equilibrium constant divided by the average deviation of its mean value (Table II). At the two temperatures where only one datum point was obtained, the weighting factor used was $k/\Delta k$, where Δk is the estimated uncertainty of the equilibrium constant measured. This procedure gave much more weight to the equilibrium constants at the tem-

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[16] L. G. Cole, M. Farber, and G. W. Elverum, Jr., *J. Chem. Phys.*, **20**, 586 (1952).

[17] W. C. Hamilton and J. A. Ibers, ref 2, p 195.

[18] J. A. Ibers and W. C. Hamilton, *Science*, **139**, 106 (1963).

[19] D. H. Templeton, A. Zalkin, J. D. Forrester, and S. M. Williamson, ref 2, p 203; *J. Am. Chem. Soc.*, **85**, 242 (1963).

[20] J. H. Burns, P. A. Agron, and H. A. Levy, ref 2, p 211; *Science*, **139**, 1208 (1963).

[21] H. H. Claassen, C. L. Chernick, and J. G. Malm, *J. Am. Chem. Soc.*, **85**, 1927 (1963).

[22] H. H. Claassen, "The Noble Gases," D. C. Heath and Co., Boston, Mass., 1966, p 88.

Table IX

Thermodynamic Fitting of k_4

T, °K	k_4(exptl), atm^{-1}	ω	k_4 (eq 15), atm^{-1}	k_4 (th), atm^{-1}	$-\Delta H°_0$, cal mole^{-1}	$\Delta S°$(exptl − calcd), cal deg^{-1} mole^{-1}
298.15			1.38×10^{11}	1.33×10^{11}		
523.15	1431	1.6	1220	1220	25,019	0.316
573.15	154.9	30.4	147	146	24,918	0.116
623.15	27.22	2.2	24.9	24.8	24,967	0.188
673.15	4.857	30.5	5.53	5.49	24,685	−0.246
774.15	0.5020	42.9	0.484	0.482	24,915	0.079
					24,850 ± 90	+0.003 ± 0.143

peratures where many data points were averaged, a procedure that was felt desirable.

The equilibrium constants were fitted by least squares to a three-constant equation of the form

$$\log k_4 = A/T + B \log T + C \qquad (14)$$

Since least-squares fitting generally loses the physical significance of the parameters used, it was decided to assign the value of B from the thermodynamic properties of the reacting species of eq 13. In this case B is related to $\Delta C_p°$, which is taken to be constant over the range of interest. The procedure we followed was to assign provisional values for ν_4 and ν_7 of XeF_4 and then calculate the thermodynamic functions for eq 13. The values used for the thermodynamic properties of F_2 and XeF_2 were discussed in the previous section; for XeF_4 we used the molecular constants given at the beginning of this section. We then assigned a value for B (eq 14) from the thermodynamic calculations and derived values for A and C by least squares.

Experimental values of $\Delta G°$ for eq 13 were calculated in the usual way from the equilibrium constants, and experimental values of $\Delta H°$ were obtained by differentiation of eq 14 (van't Hoff relation). From these values experimental values of $\Delta S°$ were obtained. Theoretical values of $\Delta S°$ for eq 13 were calculated from the molecular properties and these were compared with the experimental values at each temperature. The best fit for ν_4 and ν_7 was taken as that which gave the weighted sum of $\Delta S°$(exptl) − $\Delta S°$(theor) equal to zero.

An equivalent, but less convenient, procedure used the values of $\Delta H°_0$ derived for eq 13. Values for $\Delta H°_0$ were obtained from the experimental values of $\Delta G°$ and the theoretical values of $\Delta(G° - H°_0)$. Similarly values of $\Delta H°_0$ were obtained from the experimental values of $\Delta H°_0$ and the theoretical values of $\Delta(H° - H°_0)$. The weighted average values of $\Delta H°_0$ obtained in these two ways became equal for the ν_4 and ν_7 frequency assignments that gave $\Delta S°$(exptl − calcd) equal to zero.

For the best fit of all the data we found ν_4 = 237 and ν_7 = 250 cm^{-1}. The variation of k_4 with temperature over the temperature range 523.15–774.15°K is given by

$$\log k_4 = 5728.231/T + 0.86628 \log T - 10.21724 \qquad (15)$$

The values of k_4 calculated from eq 15 are given in the fourth column of Table IX, as well as the value of k_4 extrapolated to 298.15°K. In the next column of Table IX the values of k_4 calculated from the theoretical values of $\Delta(G° - H°_0)$ and $\Delta H°_0 = -24{,}850$ cal mole^{-1} are given. The extrapolated value of $k_4 = 1.33 \times 10^{11}$ atm^{-1} at 298.15°K is probably more reliable than the value obtained by extrapolation of eq 15, but the difference between the two values is only 4%.

The next column of Table IX lists the values of $\Delta H°_0$ calculated using the experimental values of k_4 and the theoretical values of $\Delta(G° - H°_0)$. The weighted average value of $\Delta H°_0$ = 24,850 cal mole^{-1} to four significant figures and the weighted average deviation of the values is 90 cal mole^{-1}. The value of $\Delta H°_0$ calculated from the $\Delta H°$ data is the same, but does not show the scatter of the experimental data.

The last column of Table IX gives the difference between $\Delta S°$(exptl) and $\Delta S°$(calcd). The weighted absolute deviation of the entries is ±0.143 cal deg^{-1} mole^{-1}.

Thermodynamic properties of XeF_4 using our frequency assignments are listed in Table X and the corresponding thermodynamic functions for the formation of XeF_4 are listed in Table XI. Calculated equilibrium constants for the formation of XeF_4, K_4 (eq 2), are also listed in Table XI. These were calculated using $\Delta H°_0 = -50{,}169$ cal mole^{-1} and the listed values of $\Delta(G° - H°_0)$.

Table X

Thermodynamic Properties of XeF_4 in the Ideal Gaseous State at 1 Atm Pressure (cal mole^{-1} deg^{-1})

T, °K	$-(G° - H°_0)/T$	$(H° - H°_0)/T$	$S°$
298.15	60.992	14.584	75.576
523.15	70.222	18.174	88.396
573.15	71.905	18.698	90.603
623.15	74.488	19.158	92.646
673.15	74.983	19.563	94.546
774.15	77.766	20.253	98.019

The particular frequencies assigned to ν_4 and ν_7 are of course not unique. An equivalent fit could probably be obtained if, for example, we increased ν_7 by 10 cm^{-1} and decreased ν_4 by 20 cm^{-1}. It would be more appropriate to describe our result by saying the average

TABLE XI

THERMODYNAMICS OF FORMATION OF XeF_4

$Xe + 2F_2 = XeF_4$

T, °K	K_4, atm^{-2}	$\Delta(G° - H°_0)$, cal mole^{-1}	$-\Delta(H° - H°_0)$, cal mole^{-1}	$-\Delta S°$, cal deg^{-1} mole^{-1}
298.15	1.64×10^{24}	17,135	1342	61.973
523.15	1.07×10^{8}	30,948	860	60.800
573.15	1.49×10^{6}	33,982	730	60.563
623.15	4.14×10^{4}	37,004	599	60.344
673.15	1.98×10^{3}	40,016	466	60.139
774.15	14.4	46,071	197	59.767

$\Delta H°_0 = -50{,}169$ cal mole^{-1}

value of these frequencies, $(\nu_4 + 2\nu_7)/3$, is 246 cm^{-1}. However, if the value of $\nu_4 = 221$ cm^{-1}, based on the Raman assignment of $2\nu_4$, is correct, then the frequency of ν_7 derived should be only 8 cm^{-1} higher than the value we assign.

Claassen,[23] on the basis of force constant considerations, has estimated that $\nu_4 = 232$, $\nu_7 = 183$, and $\nu_6 = 608$ cm^{-1}. The average value of $(\nu_4 + 2\nu_7)$ from his estimates is then 199 cm^{-1}, which gives poor agreement for $\Delta S°$(exptl − calcd). Following the same procedure as that outlined above we obtain $\Delta S°$(exptl − calcd) to be 1.255 cal deg^{-1} mole^{-1} when $\nu_4 = 232$ and $\nu_7 = 183$ are used.

The average deviation of $\Delta S°$(exptl − calcd) = ±0.143 cal deg^{-1} mole^{-1} provides a measure of the reliability of these frequency assignments. A similar attempt was made to fit the equilibrium data using $\nu_4 = 235$ and $\nu_7 = 242$, the average value of these frequencies being 240 cm^{-1}. We obtained $\Delta S°$(exptl − calcd) = 0.139 cal deg^{-1} mole^{-1}. Thus a change of 6 cm^{-1} in the average frequency value (246 cm^{-1} average gave the best fit) gave a discrepancy of one standard deviation. From this it would appear that our assignment of 246 cm^{-1} as the average frequency of ν_4 and ν_7 is probably good to about 10 cm^{-1}.

The equilibrium constant data can be analyzed directly (without recourse to statistical calculations) to yield values for $\Delta H°$ and $\Delta S°$ at the average temperature of our measurements. To do this we made a least-squares fit to a two-constant equation and obtained

$$\log k_4 = 5492.73/T - 7.41206 \tag{16}$$

From this we obtain $\Delta H° = -25{,}133$ cal mole^{-1}. Taking the average of $1/T$ over the temperature range, we obtain 622.01°K as the average temperature. From eq 16 $\Delta G°$ at this temperature is −4037 cal mole^{-1} and $\Delta S° = -33.92$ cal deg^{-1} mole^{-1}. The value of $\Delta H°$ derived from eq 15 at 622.01°K is −25,139 cal mole^{-1}, so that the fit to the statistical calculations has not altered the inherent validity of the data.

Johnston, Pilipovich, and Sheehan have reported preliminary values of the heat capacity of XeF_4 from 20°K to room temperature.[24] From these data they obtain the entropy of solid XeF_4 at 298.16°K to be 35.0 cal deg^{-1} mole^{-1}. Using the heat of sublimation of XeF_4 of 15.3 kcal mole^{-1} [25] and an entropy of compression (from 3 mm to 1 atm) of −11.0 cal deg^{-1} mole^{-1}, we estimate $S°$ for XeF_4 to be 75.3 cal deg^{-1} mole^{-1} at 298.16°K. This value is in fine agreement with the value of 75.6 cal deg^{-1} mole^{-1} (Table X) that we calculated from molecular properties. However, the agreement is probably somewhat fortuitous because of the uncertainties in the two vibrational frequencies of XeF_4, in the entropy of sublimation, in the vapor pressure, and in the purity of the calorimetric XeF_4 sample studied.

Xenon Hexafluoride, XeF_6.—The equilibrium constants, k_6 (eq 8), that we obtained for the reaction

$$XeF_4 + F_2 = XeF_6 \tag{17}$$

are listed in the second column of Table XII. (They contain one more significant figure than the corresponding values given in Table II.) The weighting factors, ω, used in least-squares treatment of these data were assigned in the same way as described for Table IX. The data are fitted with good accuracy by a two-constant equation

$$\log k_6 = 4018.682/T - 7.70472 \tag{18}$$

TABLE XII

THERMODYNAMIC FITTING OF k_6

T, °K	k_6(exptl), atm^{-1}	ω	k_6 (eq 18), atm^{-1}	k_6 (eq 19), atm^{-1}	$-\Delta H°_0$, cal mole^{-1}	$\Delta S°$(exptl − calcd), cal deg^{-1} mole^{-1}
298.15			(5.9×10^5)	(8.2×10^5)		
523.15	0.9435	66.9	0.9484	0.9503	17,920	−0.0210
573.15	0.2112	19.0	0.2026	0.2017	17,980	0.0941
623.15	0.05582	96.2	0.05552	0.05533	17,937	0.0181
673.15	0.01822	60.7	0.01842	0.01852	17,905	−0.0379
					17,928 ± 16	−0.0007 ± 0.0298

The equilibrium constants calculated from eq 18 are given in the fourth column of Table XII and are seen to agree with the experimental data well within the uncertainty of the measurements.

Using eq 18 the values of the thermodynamic functions for eq 17 at the average temperature of the

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[23] H. H. Claassen, private communication; W. A. Yeranos, *Mol. Phys.*, **9**, 449 (1965).

[24] W. V. Johnston, D. Pilipovich, and D. E. Sheehan, ref 2, pp 139–143.

[25] J. Jortner, E. G. Wilson, and S. A. Rice, *J. Am. Chem. Soc.*, **85**, 814 (1963).

measurements, 598.62°K, are: $\Delta H° = -18{,}390$ cal mole^{-1}, $\Delta G° = 2716$ cal mole^{-1}, and $\Delta S° = -35.25$ cal deg^{-1} mole^{-1}.

The molecular structure of XeF_6 is not presently known. Even the qualitative question of whether XeF_6 has a symmetrical or an unsymmetrical structure cannot be definitely answered from the vibrational spectra.[12,26] Theoretical considerations also are at variance about the symmetry of XeF_6. For example, molecular orbital theory appears to favor O_h symmetry[27,28] while the localized electron-pair bond model predicts an unsymmetrical structure.[29]

In view of the uncertainty about the structure of XeF_6 and of the potential theoretical importance that a clarification of its structure might have, an attempt was made to differentiate among several possiblities in terms of our data. The following procedure was adopted. The Xe–F distance was taken at 1.95 A. A moment of inertia corresponding to that of a regular octahedron with this bond distance was used to calculate the rotational contributions to the thermodynamic properties for all of the models considered. The differences among the various models for rotation then arose only from the change in symmetry number. The assignment of the 15 vibrational degrees of freedom was rather arbitrary and was used as the parameter in fitting the data. Details of this procedure will be discussed later.

The correlation of the molecular model chosen with the equlibrium constant data was made in an analogous fashion to the method used to derive the missing vibrational frequencies of XeF_4. The equilibrium constant data were fitted to a three-constant equation of the form given by eq 14, with the constant B being calculated from the molecular data. To calculate B, an estimate of the vibrational frequencies had to be made. As a starting point in the analysis the vibrational frequencies were adjusted to give the experimentally determined value of $\Delta S° = -35.25$ cal deg^{-1} mole^{-1} at 598.62°K. The constants A and C of eq 14 (k_4 is now k_6) were then derived by a weighted least-squares fit of the equilibrium data given in Table XII. Values for $\Delta S°$(exptl) and $\Delta S°$(theor) were then derived as explained in the XeF_4 section and the process was repeated (after adjustment of the vibrational frequencies) until the weighted average of $\Delta S°\text{(exptl)} - \Delta S°\text{(theor)}$ was equal to zero.

Fifteen hexafluoride molecules, including four that have a dynamic Jahn–Teller effect, are known to possess O_h symmetry.[30] As a starting point in this analysis, O_h symmetry was therefore adopted. The fifteen vibrational degrees of freedom in O_h symmetry are described by six normal modes, which are listed with their usual designation, their degeneracy in parentheses, and their spectral activity (R = Raman, IR = infrared, and I = inactive) in the first column of Table XIII. The first three modes, which account for six degrees of freedom, may be regarded as stretching modes and the last three modes, which account for the nine remaining degrees of freedom, as bending modes. Three Raman shifts have been obtained by Begun with solid XeF_6 at 655, 635 and 582 cm^{-1}.[12] All of these are in the range of stretching modes. Since there are only two Raman-active stretching modes in O_h symmetry, Smith[12] has suggested that O_h symmetry appears to be excluded for XeF_6 because of the three Raman shifts observed by Begun. However, this observation is not conclusive, since other hexafluoride molecules, which have O_h symmetry in the vapor, have D_{4h} symmetry in the solid and two of the bands observed by Begun may arise from a splitting of ν_2 in the solid due to crystal packing. Neutron diffraction studies with the solid suggest a very complex structure for the solid with the xenon atoms present in tetrameric groups,[31] so that vibrational spectra of solid XeF_6 may give quite different results from the vapor molecule.

Table XIII

Vibrational Frequencies

	O_h + electronic	XeF_4	C_1	TeF_6
ν_1(1)R	645	(543)	655 (1)	701
ν_2(2)R	580	(502)	651 (1) 582 (1)	674
ν_3(3)IR	616		616 (2) 520 (1)	752
ν_4(3)IR	243	(291)	323 (3)	325
ν_5(3)R	240	(235)	323 (3)	313
ν_6(3)I	180	(232)	200 (3)	195

The infrared spectrum of XeF_6 (part of which was shown in Figure 2) is presently quite incomplete and appears to differ qualitatively from that of the other hexafluoride molecules. (A further reason given by Smith to suggest a lower symmetry than O_h.[12]) In particular, the band at 616 cm^{-1}, which is identified with ν_3, is much broader than the corresponding band for other hexafluoride molecules, and the band at 520 cm^{-1} (and possibly at 565 cm^{-1}) does not correspond to any feature found in the infrared spectrum of other hexafluorides. Two weaker bands at 1100 and 1230 cm^{-1} have also been observed in the infrared spectrum of XeF_6,[12,26] and these could be the prominent binary transitions ($\nu_1 + \nu_3$) and ($\nu_2 + \nu_3$) that are observed for other hexafluoride molecules.[30] However, if the band at 1100 cm^{-1} is assigned as ($\nu_2 + \nu_3$), the value of ν_2 that one obtains, 484 cm^{-1}, is much lower than any observed Raman frequency. At the present time we appear to have a reasonable idea of the frequency of the stretching modes in XeF_6, but no information at all about the bending modes.

Goodman[32] has suggested that some of the features observed in the infrared spectrum of XeF_6 may be due to electronic transitions. Based on a molecular

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(26) H. H. Claassen, ref 2, pp 304–305.

(27) L. L. Lohr, Jr., and W. N. Lipscomb, ref 2, p 347; *J. Am. Chem. Soc.*, **85**, 240 (1963).

(28) E. A. Boudreaux, ref 2, p 354.

(29) R. J. Gillespie, ref 2, p 333.

(30) B. Weinstock and G. L. Goodman, *Advan. Chem. Phys.*, **9**, 169 (1965).

(31) P. A. Agron, C. K. Johnson, and H. A. Levy, *Inorg. Nucl. Chem. Letters*, **1**, 145 (1965).

(32) G. L. Goodman, Symposium on Inorganic Fluorine Chemistry, Argonne National Laboratory, Sept 1963.

orbital model in O_h symmetry, he derived the symmetry of the three lowest lying electronic levels above a nondegenerate ground state and assigned as their energies (with degeneracies in parentheses): 520 (1), 1000 (3), and 1900 (5) cm^{-1}. The first model that we tested was based on these assignments suggested by Goodman. The final vibrational assignments that we arrived at after fitting to the equilibrium constant data are given in the second column of Table XIII. A surprising thing about the bending frequencies that we obtained in this analysis is that they are only a few wavenumbers different from the original estimates we made for them. The original estimates were taken as an average of the corresponding frequencies for the three hexafluoride molecules with two nonbonding electrons, RuF_6 ($4d^2$), OsF_6 ($5d^2$), and PuF_6 ($5f^2$).[30] However, as will be seen shortly, this striking correspondence is probably entirely fortuitous.

We made similar fits of the equilibrium data to a number of other models. These included, without electronic contributions: O_h, D_{4h}, C_{5v}, D_{2h}, and C_1 symmetry. The frequencies derived for C_1 symmetry, which is a completely distorted structure without any element of symmetry, are given in the fourth column of Table XIII. This model is suggested by Gillespie's considerations,[29] although two possibilities he suggests would have symmetry numbers of 2 and 3. Of course, none of the vibrations is degenerate and the frequencies listed as degenerate are regarded as average values. It is of interest to note that these average values derived for the bending frequencies of XeF_6 in C_1 symmetry are nearly identical with those of TeF_6[30] (last column in Table XIII). The frequencies of the corresponding vibrational modes of XeF_4[21] are also listed in Table XIII for comparison.

None of the models tested gave as good a fit to the experimental equilibrium constant data as the two-constant equation (eq 18). The equation derived for C_1 symmetry is

$$\log k_6 = 4312.05/T + 1.1557 \log T - 11.4066 \quad (19)$$

and the equilibrium constants calculated from this equation are listed in the fifth column of Table XII. The entropy fit, $\Delta S°(\text{exptl}) - \Delta S°(\text{calcd})$, for eq 19 using the C_1 vibrational frequencies listed in Table XIII is given in the last column of Table XII. The values of $\Delta H°_0$ calculated for eq 17 are given in the next to last column. The value of $\Delta H°_0 = -17{,}930$ cal $mole^{-1}$ (using the C_1 model for XeF_6) for eq 17 is taken as the best value of $\Delta H°_0$ for this equilibrium. The value of $-\Delta H°_0$ that we obtain increases with increasing symmetry for XeF_6. For O_h symmetry, including the electronic states suggested by Goodman, $\Delta H°_0 = -19{,}410$ cal $mole^{-1}$. The average deviation of ± 16 cal $mole^{-1}$ given for $\Delta H°_0$ in Table XII is an indication of the reliability of the equilibrium constant data. However, the absolute uncertainty of $\Delta H°_0$ is probably of the order of 300 cal $mole^{-1}$.

The equilibrium constants calculated from eq 19 (C_1 symmetry) all deviate slightly more from the experimental data than do the values calculated for the two-constant equation (eq 18). However, these differences are hardly significant. For the models of XeF_6 with higher symmetry number, this trend continues, the deviations becoming larger the higher the symmetry number assigned to XeF_6. For the O_h model including the low-lying electronic states, the deviations from the experimental equilibrium constants are the greatest, being about twice those between eq 18 and the experimental data.

While this analysis cannot decide which model for XeF_6 is best, the trend favors low symmetry for XeF_6, and we have therefore used the C_1 model for XeF_6 to extrapolate our data to 298.15°K. The small differences arise, of course, from the $\Delta C_p°$ term, B, in the equilibrium constant equation. For the two-constant equation $\Delta C_p°$ is equal to zero. If we arbitrarily fit the experimental data to a three-constant equation (where we reproduce the experimental data almost precisely), $\Delta C_p°$ is -1.13 cal deg^{-1} $mole^{-1}$

$$\log k_6 = 3447.12/T - 2.253 \log T - 0.48888 \quad (20)$$

For the C_1 model, $\Delta C_p°$ is 0.58 cal deg^{-1} $mole^{-1}$, and for O_h, with the electronic contributions, $\Delta C_p°$ is 1.31 cal deg^{-1} $mole^{-1}$.

The most significant point of this analysis may arise when the entropy of XeF_6 is obtained from low-temperature heat capacity measurements. This work is currently underway.[33] The values derived for $S°$ of XeF_6 at 298.15°K using the different models and eq 18 and 20 are listed in Table XIV. Although the differences among the models are not large, the over-all differences derived are greater than the expected uncertainty of the heat capacity determinations.

Since this analysis was completed two reports of electron diffraction studies with XeF_6 vapor have been published.[34, 35] Although the complete structure of XeF_6 has not been determined, both authors rule out a highly symmetrical structure for XeF_6, which result agrees with the tentative conclusion we had drawn from the equilibrium constant data. Bartell, *et al.*,[34] derived the average value of the Xe–F distance in XeF_6 to be 1.90 A, which differs from the value of 1.95 A that was used in our calculations. This change from 1.95 to 1.90 A for the bond distance reduces the rotational contribution to the entropy by 0.15 cal deg^{-1} $mole^{-1}$. To compensate for this one nondegenerate vibrational mode of 323 cm^{-1} (Table XIII) must be reduced to 298 cm^{-1}. However, the extrapolated value of $S°$ for XeF_6 at 298.15°K given in Table XIV is reduced by only 0.02 cal deg^{-1} $mole^{-1}$ and the value derived for $\Delta H°_0$ given in Table XII is increased by only 30 cal $mole^{-1}$. Since these changes are so small, the analysis was not repeated using the new value of the average Xe–F distance in XeF_6.

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(33) J. G. Malm, F. Schreiner, and D. W. Osborne, *Inorg. Nucl. Chem. Letters*, **1**, 97 (1965).

(34) L. S. Bartell, R. M. Gavin, Jr., H. B. Thompson, and C. L. Chernick, *J. Chem. Phys.*, **43**, 2547 (1965).

(35) K. Hedberg, S. H. Peterson, R. R. Ryan, and B. Weinstock, *ibid.*, **44**, 1726 (1966).

TABLE XIV

$S°$ OF XeF_6 (CAL DEG^{-1} MOLE^{-1}) AT 298.15°K FOR VARIOUS MOLECULAR MODELS

Symmetry	Symmetry no.	$S°$
Eq 20	. . .	91.87
Eq 18	. . .	88.84
C_1	1	87.72
D_{2h}	4	87.39
C_{5v}	5	87.53
D_{4h}	8	87.31
O_h	24	86.96
O_h[a]	24	85.70

[a] Includes $S°$(electronic) = 0.78.

Heats of Formation and Bond Energies.—The heats of formation of XeF_2, XeF_4, and XeF_6 vapor at 298.15°K and the average bond energy for each of these molecules are listed in Table XV. The heats of formation of XeF_2 and XeF_4 vapor obtained from our work were taken from the data in Tables VIII and XI, respectively. For XeF_6, we extrapolated our experimental value to 298.15°K using the C_1 model. However, there is no significant difference in extrapolation among the various models because the change in $\Delta H_f°$ with temperature is small, amounting to 0.5 kcal mole^{-1} for the temperature range involved here.

TABLE XV

HEATS OF FORMATION (298.15°K) AND AVERAGE BOND ENERGIES

Molecule	Investigator	$-\Delta H_f°$(g), kcal mole^{-1}	Bond energy, kcal
XeF_2	This work	25.9	31.0
	S.F.	37 ± 10	39 ± 10
XeF_4	This work	51.5	30.9
	S.F.	53 ± 5	32 ± 2
	G.W.	48	30
	S.P.	57.6	32.8
XeF_6	This work	70.4	29.7
	S.P.	82.9	32.3

The values reported by Svec and Flesch[36] (S.F.) were obtained from mass spectrometric appearance potentials with vapor samples at an estimated source temperature of 150°. Gunn and Williamson[37] (G.W.) derived their value from calorimetric measurements of the heat of reaction of solid XeF_4 with aqueous iodide solutions, using 15.3 kcal mole^{-1} for the heat of sublimation of XeF_4.[25] They actually reported −45 kcal mole^{-1}, but the value (−48) given in Table XV is taken from a revision of their result[3] using a new value for the heat of formation of HF.[38] Stein and Plurien[39] (S.P.) obtained their results from isothermal calorimetry at 120–130° of the reduction of XeF_4 and XeF_6 with hydrogen. Their values given in Table XV are also corrected for the new heat of formation of HF.[40]

The average bond energies that we derived were calculated using our values of $\Delta H°_0$ for the several equilibria and the value of 36.71 kcal mole^{-1} for $\Delta H°_0$ of dissociation of F_2.[41] We find that the average bond energies of XeF_2 and XeF_4 are nearly identical, but the bond energy decreases a small amount for XeF_6. The average energy for forming the last two bonds in XeF_6 is 27.3 kcal compared to the average bond energy of 30.9 kcal in XeF_4.

A surprising feature of Table XV is the large discrepancy between the two values of $\Delta H_f°$ of XeF_4 obtained calorimetrically. One normally expects a relatively high degree of precision in calorimetric measurements, so that the discrepancy must be related to the complexity of the systems studied and to the possible presence of significant amounts of impurities in the samples studied. In the spirit of the Argonne Symposium much of the material presented was of a preliminary nature and this may also be a factor. The differences between Stein and Plurien's values for XeF_4 and XeF_6 and our values also appear to be outside the expected limit of error. It is not usual to expect equilibrium constant data to give more reliable values for enthalpy changes than direct calorimetry. However, for XeF_4 and XeF_6, the precision of the $\Delta H°_0$ values is always good regardless of the frequency fit for XeF_4 or the model used for XeF_6, and the absolute uncertainty is not greater than a few tenths of a kilocalorie. It therefore appears possible that the values of the heats of formation derived from our data are the most reliable ones at the present time. For XeF_2 our data are less complete. Although Svec and Flesch's heat of formation for XeF_4 is in excellent agreement with our value, their value for XeF_2 is much higher. Pitzer[42] has suggested that the heat of formation of XeF_2 should lie between −25 and −48 kcal mole^{-1}, which are the respective heats of formation of ClF_3 and BrF_3 from their monofluorides. Svec and Flesch's value of −37 kcal mole^{-1} is nearly the average of these values. Our present value of −25.9 kcal mole^{-1} for the heat of formation of XeF_2 agrees better with Pitzer's prediction than our preliminary value of −19.4 kcal mole^{-1},[2] but still is much closer to the value for ClF_3 than to the average. However, in view of the large uncertainty of ±10 kcal assigned by Svec and Flesch to their value for XeF_2, our value may be the better one to use at the present time. Additionally, using Svec and Flesch's values, we derive 26.4 kcal as the average bond energy of the second pair of bonds in XeF_4, which appears to be too low.

Summary and Conclusions

The equilibrium constant studies reported here have established that only three binary xenon fluorides, XeF_2, XeF_4, and XeF_6, exist in significant quantities at equilibrium in the range 250–500° and up to 500 atm of F_2. Previous reports of the possible existence of XeF_5 and XeF_8 can be ruled out on the basis of these

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(36) H. J. Svec and G. D. Flesch, *Science*, **142**, 954 (1963).

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(41) G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Co., New York, N. Y., 1961, pp 178–179.

(42) K. S. Pitzer, *Science*, **139**, 414 (1963).

experiments. Thermodynamic functions for the formation of the three binary fluorides have been derived from the equilibrium constant data, and a correlation of the temperature dependence of the equilibrium constants with molecular data has been made by least-squares analysis. The average bond energies are found to be nearly identical for XeF_2 and XeF_4 at 31 kcal, while the last two bonds in XeF_6 can be taken as 3.6 kcal weaker. Previously reported bond energies for these molecules gave a more irregular pattern.

The reliability of the data can be judged in terms of the constancy of the values of $\Delta H°_0$. For the k_4 data (eq 13), $\Delta H°_0 = 24{,}850 \pm 90$ cal mole^{-1}. There were not sufficient measurements to make a similar assessment of the reliability of $\Delta H°_0$ for k_2. The values derived for the two missing vibrational frequencies of XeF_4 are $\nu_4 = 237$ and $\nu_7 = 250$ cm^{-1}. Their average value of 246 cm^{-1} is probably good to ± 10 cm^{-1}. Claassen's[23] value of $\nu_4 = 232$ cm^{-1} derived from force constant calculations is in agreement, but his value of $\nu_7 = 183$ cm^{-1} is significantly different from our derived value. The value of $S° = 75.6$ cal deg^{-1} mole^{-1} at 298.16°K that we calculate for XeF_4 from the molecular data agrees with the experimental value of 75.3 cal deg^{-1} mole^{-1}.

Statistically there is not a significant difference in fit to the equilibrium data among all the models tested for XeF_6. However, the fit becomes progressively poorer with increasing symmetry number, being poorest when low-lying electronic states are included. One can only infer from this that our data favor a symmetry lower than O_h for XeF_6. Our analysis may be useful when $S°$ for XeF_6 is derived from calorimetric data because significantly different values of $S°$ are obtained for the different models upon extrapolation from the range of our measurements to room temperature.

To derive $\Delta H°_0$ for eq 17 from the k_6 data we have used a model with a symmetry number of 1 and obtain $17{,}930 \pm 20$ cal mole^{-1}. From the change of $\Delta H°_0$ with model we estimate the absolute uncertainty to be ± 300 cal mole^{-1}. It is interesting to note that the bending frequencies derived in C_1 symmetry for XeF_6 are very similar in magnitude to those of TeF_6.

The recent electron-diffraction studies reported by Bartell, *et al.*,[34] and by Hedberg, *et al.*,[35] with XeF_6 appear to rule out O_h symmetry. Presently the structures suggested by Gillespie,[29] which have a symmetry number of 2 or 3, are the most reasonable possibilities. Blinc, *et al.*,[43] report a diamagnetic susceptibility for XeF_6 of -45×10^{-6} cm^3 mole^{-1}, which is what would be expected from the diamagnetism of the electrons alone. If there were low-lying electronic states one would expect XeF_6 to exhibit at least a small temperature-independent paramagnetism. For example, the same authors report that PtF_6, which has a nondegenerate ground state but low-lying electronic states,[44] has a temperature-independent paramagnetism of $+812 \times 10^{-6}$ cm^3 mole^{-1}. These recent observations thus appear to agree with the related inferences that can be drawn from our data.

While evidence is mounting in favor of Gillespie's prediction of an unsymmetrical structure for XeF_6, a fundamental question remains to be answered. Molecular orbital theory appears to favor O_h symmetry for XeF_6, but only for the particular models tested.[27,28] These tests have neglected the possible influence of the s electrons in determining the structure of XeF_6, because of the success of this approximation in explaining the structures of XeF_2 and XeF_4.[42,45] It remains to be demonstrated whether or not molecular orbital theory will still favor O_h symmetry if the energy of the s electrons is taken to be closer to that of the p electrons.

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The π System of Binuclear Copper(II) and Chromium(II) Acetates

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Previous work on the electronic structure of copper acetate is briefly reviewed. Evidence is presented for the charge-transfer character of the anomalous band at 3700 A in copper acetate. Although a definite assignment is difficult, even with very detailed calculations, chemical evidence suggests that the transition may be a local symmetry-forbidden $np_\pi \rightarrow \sigma^*(x^2 - y^2)$ excitation. The electronic spectrum of binuclear chromium(II) acetate is discussed qualitatively.

Introduction

The origin of band II ($\sim$28,000 cm^{-1}) in binuclear copper(II) acetate (*cf.* Figure 1) has been a topic of considerable interest, judging by the number of papers published and the many differing and conflicting assignments put forward. Originally, Tsuchida and Yamada,[1,2] from single-crystal spectral studies, sug-

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(1) R. Tsuchida and S. Yamada, *Nature*, **176**, 1171 (1955).

(2) R. Tsuchida, H. Nakamura, and S. Yamada, *ibid.*, **178**, 1192 (1956).