

distribution data may be applied to the data shown in Fig. 1 because the teeth used in all of our studies underwent essentially the same amount of attrition.

A comparison of the strontium-90 content of incisor crowns from children who were breast-fed for 6 weeks or more after birth and for children who were bottle-fed is shown in Table 2. For all of the samples analyzed, the average time of breast feeding was 25 weeks. During 1951 and 1952 the strontium-90 content of incisor crowns of breast-fed children was lower than but not significantly different from that found for bottle-fed children. However, in succeeding years, between 1953 and 1956, when the strontium-90 content of the teeth was increasing at a rapid rate, the teeth of breast-fed children contained 25 percent less strontium-90 than comparable bottle-fed children. Since 70 percent of the tooth crown is formed *in utero* and under the influence of the placental barrier, the small differences found between breast- and bottle-fed children suggests that the teeth of bottle-fed children accumulate small amounts of additional strontium-90 by exchange from the diet.

Although bone strontium-90 levels were not measured in our study, it is possible to compare the values for teeth with values obtained by other investigators for bone. Kulp (6) found that strontium-90 levels in the bones of nine North American children 1 to 2 years old for 1957-58 averaged 1.8 pc of Sr^{90} per gram of Ca; for German children during the first year of life in 1958 the value was 2.1 pc of Sr^{90} per gram of Ca. These values are only slightly lower than the value of 2.56 ± 0.11 pc (standard error) found in four samples of incisor teeth from St. Louis children born during 1957 and may be assumed to be comparable within the analytical error of the estimates. Kulp has also estimated that the peak value in bones of 1-year-old children during 1958-59 would be 2.5 pc of Sr^{90} per gram of Ca, a value which is in accord with our data for teeth. Further comparison of bone values for children 0 to 4 years old, corrected to the approximate time of birth, with our values for teeth are shown in Table 2 for the years 1951-1957. The bone levels represent average values, for various bones of the body may vary in strontium-90 content (see 7).

Our data suggest that human teeth are useful as an index of strontium-90 accumulation during the time the teeth are formed and that the tooth strontium-90 content would represent the maximum cumulative body burden attainable if dietary strontium-90 remains at a constant level during and after the time the teeth are formed (8).

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Xenon Tetrafluoride: Heat of Formation

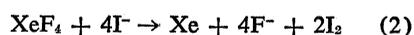
Abstract. *Calorimetric measurements of the heat of reaction of xenon tetrafluoride with aqueous iodide solution give -60 kilocalories per mole for the standard heat of formation, or an average thermochemical bond energy of about 31 kilocalories.*

Heats of formation of chemical compounds are a fundamental measure of stability and bond strength. There appear to have been thus far no such measurements reported for any of the rare-gas compounds; we have accordingly measured the heat of reaction of xenon tetrafluoride with aqueous potassium iodide solution to derive its heat of formation.

Xenon tetrafluoride was prepared in a flow system (1). Weighed samples (112 to 193 mg) were reacted with 380 ml of degassed water containing 0.0190 mole of KI and 0.00038 mole of HCl in a sealed calorimeter (2) fabricated of tantalum. Under these conditions the XeF_4 is quantitatively reduced, partly by oxidizing water (3),

$$\text{XeF}_4 + 2\text{H}_2\text{O} \rightarrow \text{Xe} + 4\text{HF} + \text{O}_2 \quad (1)$$

but mostly by oxidizing iodide (4),



The xenon and oxygen were pumped off after the run, separated, and measured in a gas buret. The amounts of iodine and fluoride in the solution were determined by titration with thiosulfate and thorium nitrate, respectively. The

amount of xenon in all cases was 99.0 percent of the theoretical. From 5 to 10 percent of the XeF_4 followed the reaction of Eq. 1. The total amount of oxygen plus iodine was about 95 percent of the theoretical, the total fluoride about 98 percent; however, there was some evidence that iodine and fluoride were being lost by slow reaction with the calorimeter vessel.

There were four runs; the observed heats of reaction ranged from -188.8 to -193.0 kcal per mole of XeF_4 . Corrections were applied for the heat of solution of that fraction of the xenon which was dissolved in the solution. Equilibrium constants for the dissociation of HF and the formation of I_3^- from I_2 and I^- were used to calculate the concentrations of individual species for each run; the ratio, F^- to HF ranged from 4.0 to 6.1 and that of I_3^- to I_2 from 27.1 to 31.6. From the values in the literature (5) for the heats of formation of the products and the other reactants, the standard heat of formation of crystalline XeF_4 was then calculated individually from each run; results were -60.2, -60.7, -59.6, and -60.0 kcal per mole.

The analytical data and known characteristics of the preparative method do not rule out the possibility of some contamination of the sample with XeF₂ or, less likely, XeF₆. From an estimated heat of formation for XeF₂ (6), it may be calculated that the presence of 5 percent XeF₂ in the samples would make the reaction heat low by 5 kcal, and the correct heat of formation of XeF₄ would then be -55 instead of -60 kcal per mole.

An estimate of 10 kcal per mole for the heat of sublimation of XeF₄ gives -50 kcal per mole for the standard heat of formation of gaseous (g) XeF₄. This is consistent with Pitzer's suggestion (6) that this value should be smaller than the known heat of reaction, -105.6 kcal per mole, for fluorination of BrF to BrF_{5(g)}. From the well-established value of 37 kcal per mole for the heat of dissociation of F₂ (7), the heat of formation of XeF_{4(g)} from the gaseous atoms is -124 kcal per mole and the average thermochemical bond

energy, $E(\text{Xe}-\text{F})$, is 31 kcal. This is lower than average bond energies in halogens and interhalogen compounds, but the molecule is stabilized since xenon has no tendency to dimerize (8).

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Xenon Tetrafluoride: Fluorine-19 High-Resolution Magnetic Resonance Spectrum

Abstract. *The F¹⁹ spectrum of XeF₄ dissolved in anhydrous hydrogen fluoride has been observed at two frequencies, yielding a F¹⁹ chemical shift of 175 parts per million to lower field than the solvent and a Xe¹²⁹-F¹⁹ spin-spin coupling constant, confirmed by double irradiation, of 3860 cycles per second. Absence of fast F¹⁹ chemical exchange and collapse of the Xe¹³¹-F¹⁹ coupling by quadrupole relaxation may be inferred from the spectrum.*

The work of Bartlett and others on the syntheses of compounds of rare gases (1) has led to considerable speculation as to the nature of bonding in these substances (2). To shed further light on this question, we have examined the F¹⁹ magnetic resonance spectrum of XeF₄ dissolved in anhydrous hydrogen fluoride.

Spectra were obtained with a Varian high-resolution ensemble, with fixed frequencies of 56.44 and 15.00 Mcy/sec and 10-mm nonspinning probe inserts. The spectrum consists of two weaker lines symmetrically split about a stronger center line which is shifted 175.0 ± 1.5 parts per million downfield from the solvent; the field-independent splitting between the outer lines is 3860 ± 20 cy/sec.

Of the naturally occurring isotopes of xenon, Xe¹²⁹ and Xe¹³¹ have nonzero spins and might, in the absence of chemical exchange, be expected to

show observable interactions with the F¹⁹ nuclei.

Xenon-131 has a spin of 3/2 and a moderately large quadrupole moment, so that a rapid averaging of nuclear spin eigenstates via quadrupole relaxation is possible, provided the intramolecular fields are of lower symmetry than tetrahedral. The observed relative intensities of the outer lines to the center line correspond within a few percent to the isotopic ratio of the 26 percent abundant Xe¹²⁹ (spin = 1/2), which suggests that the Xe¹³¹ splitting is collapsed, as might be expected if the compound in solution retains the square planar structure reported for the solid (3). The observed coupling to Xe¹²⁹ requires, moreover, that F¹⁹ exchange occur at a rate slow with respect to the coupling constant in angular frequency units; and the line widths indicate an average lifetime for fluorine attached to xenon of at least 1 second.

The above interpretation of Xe¹²⁹-F¹⁹ coupling is unequivocally shown by the perturbations of the doublet lines when a second radiofrequency is introduced in the vicinity of the Xe¹²⁹ resonance frequency. From such experiments we can infer the presence of four fluorine atoms in the molecule and calculate a Xe¹²⁹ chemical shift of about -5800 parts per million from atomic xenon.

From the results given above, we can draw some preliminary conclusions about the bonding in XeF₄. The F¹⁹ chemical shift is comparable with that of the F-X bonds in such more or less analogous compounds as BrF₃, IF₅, and TeF₆, among others (4). The Xe¹²⁹-F¹⁹ coupling constant of 3860 ± 20 cy/sec, for which corresponding comparisons are unavailable, seems somewhat large. The coupling constants in PF₃ (P³¹-F¹⁹) (5) and in NaSbF₆ (Sb¹²¹-F¹⁹) (6) are 1400 and 1940 cy/sec respectively. A much larger coupling constant of about 12 kcy has, however, been reported in TIF (TI²⁰⁵-F¹⁹) (7).

The XeF₄ was obtained from Peninsular Chem Research. The solution used was prepared by dissolving a small amount of resublimed XeF₄ in about 2 ml of anhydrous HF. It appears remarkably stable, the spectra remaining unchanged after several days.

A more complete discussion of the F¹⁹ and Xe¹²⁹ chemical shifts and coupling constants in XeF₄ is in preparation (8).

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