RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

June 1965

U. D. C. 546.295 : 546.296

COMPOUNDS OF ELEMENTS OF GROUP 0

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I. INTRODUCTION

In a brief review published a short while ago [1] the first papers on compounds of elements of Group 0 of Mendeleev's Periodic System were considered. The production of a complex of xenon and platinum hexafluoride, $XePtF_6$, [2] of xenon tetrafluoride XeF_4, [3-5] and of a radon fluoride of unknown composition [6] was described. Brief mention was also made of the production of xenon difluoride XeF_2 [7,8] and xenon hexafluoride XeF_6, [9,10] some information was given about the chemical and physical properties of these substances, and the first attempts at a theoretical explanation of the formation of chemical bonds by the atoms of the Group 0 elements [11,12] were discussed.

The first successful investigation stimulated a further, quite intensive development of work in this direction, and in a comparatively short time the experimental and theoretical material has become so voluminous that it seems opportune to attempt to give a more complete review of the present state of the investigations in the field of compounds of the Group 0 elements.

In both the Russian and foreign press a series of articles has appeared already, devoted to complete or partial reviews, sometimes popular in nature [13-31]; however, these articles do not illuminate in sufficient detail all the available material.

The present review covers the literature available to the author up to 1 October 1964. It is expedient to start by considering the compounds of xenon, since the overwhelming majority of studies are devoted to them and at present they are the most thoroughly investigated.

II. COMPOUNDS OF XENON

A. Fluorides

1. Xenon difluoride. Several methods for obtaining xenon difluoride XeF_2 have been described. Smith [8] synthesised XeF_2 by the reaction of gaseous xenon (partial pressure 60 mmHg) and fluorine (240 mmHg) in a nickel circulating system at 400° or above. Weeks and coworkers [32] obtained XeF_2 by irradiation of a mixture of fluorine and xenon with ultraviolet light from a high-pressure mercury lamp. Mixtures with F_2 : Xe molar ratios from 0.91 to 5.20 were used, circulated in a nickel apparatus with sapphire

windows at room temperature and a pressure of 890–1030 mmHg. The xenon difluoride was condensed in a trap at -78°C; under these conditions pure XeF_2 is obtained, but without a trap XeF_4 is also formed[33]. Further photochemical reaction of fluorine with XeF_2 leads to the formation of XeF_4. The quantum yield of XeF_2 is 0.3–0.7 but is somewhat less if the pressure is raised, especially the fluorine pressure. The following mechanism is proposed[33] for the photochemical formation of XeF_2:

$$F_2+h\nu \rightarrow 2F,$$
$$2F+F_2 \rightarrow 2F_2,$$
$$2F+Xe \rightarrow F_2+Xe,$$
$$F+Xe+F_2 \rightarrow XeF+F_2,$$
$$F+Xe+Xe \rightarrow XeF+Xe,$$
$$XeF+F \rightarrow XeF_2,$$
$$XeF+XeF \rightarrow XeF_2+Xe,$$
$$XeF+XeF \rightarrow 2Xe+F_2.$$

Xenon difluoride is also formed in the irradiation of xenon–fluorine mixtures by γ-rays from ^{60}Co or by high-energy electrons in nickel apparatus[34]. At room temperature and above, mixtures of XeF_2 and XeF_4 are formed, but at -35°C only XeF_2 is obtained.

A method by which pure XeF_2 can be obtained in yields of ~100 mg h^{-1} was described in detail by Hoppe and coworkers[35]. They passed an electric discharge from an induction coil through mixtures of xenon and fluorine with Xe : F_2 molar ratios from 1 : 1 to 1 : 3, at room temperature; XeF_2 was condensed on a cold finger at -78°C. The apparatus used is shown schematically in Fig. 1. Xenon from cylinder *1* and fluorine, vaporised from container *2* containing thoroughly purified liquid fluorine, is admitted into reaction vessel *3*, into which pass electrodes from the induction coil, through ground joints. The XeF_2 formed in the reaction is condensed on cold finger *4*, cooled by a mixture of alcohol and solid carbon dioxide, and occasionally shaken off into ampoule *5* for weighing.

Khutoretskii and Shpanskii[36] proposed a simple method of synthesising XeF_2; they showed that it is formed from the elements at ordinary temperature and increased pressure, with liberation of heat (~40–60 kcal $mole^{-1}$) and sometimes even explosively. The experiments were made in nickel, stainless steel, or Monel vessels; fluorine was introduced first into the reactor to a pressure of 18 atm, then xenon was added to a pressure of 35 atm; reaction was almost instantaneous.

A somewhat different method, not employing elemental fluorine, was used by Milligan and Sears[37], who obtained pure XeF_2 by passing a high-potential discharge through an

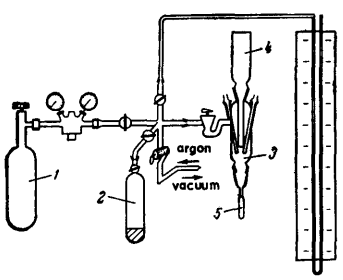


Fig. 1. Apparatus for preparing xenon difluoride[35].



Fig. 2. Crystals of xenon difluoride (a millimetre scale is shown below).

approximately equimolar mixture of xenon and carbon tetrafluoride in a Pyrex glass vessel cooled with a mixture of solid carbon dioxide and acetone, then distilling and recrystallising the reaction products.

The XeF_2 in the experiments described above was identified mass-spectrometrically and by chemical analysis.

Xenon difluoride is a colourless solid with vapour pressure 3.8 mmHg at 25°C and 318 mmHg at 100°C.[8,38] It forms excellent gleaming crystals, which grow in a few hours to millimetre dimensions (Fig. 2). The crystals exhibit double refraction. Solid XeF_2 melts at ~140°C and can be supercooled to 50°C without solidification[38]. At room temperature XeF_2 is stable and can be kept in nickel or quartz vessels for a few months[8]. In sealed glass ampoules, XeF_2 can be kept at the temperature of solid carbon dioxide for a long time, but at room temperature, even in the dark, it slowly decomposes, possibly as a result of reaction with the glass[35].

Xenon difluoride has a sharp nauseating odour[35]. It reacts vigorously with methanol and slowly with water[35]. It decomposes in solutions of alkalis (NaOH) and dilute acids (H_2SO_4) but the reactions are not particularly violent. Iodine is liberated by the action of XeF_2 on an acidified solution of potassium iodide or on moist potassium iodide–starch paper. Decomposition of XeF_2 takes place even in kerosene, redistilled and dried over metallic sodium[35]. XeF_2 dissolves in anhydrous hydrogen fluoride without decomposition; the solubility at 25°C is ~10 moles XeF_2 in 1000 g HF.[39] Hydrogen at 400°C completely reduces XeF_2 to elemental xenon and hydrogen fluoride[15].

Appelman and Malm[40] investigated the chemical properties of aqueous solutions of XeF_2 and the ultraviolet absorption spectra of such solutions. Xenon difluoride forms colourless, slowly hydrolysed aqueous solutions in which the XeF_2 is probably present as undissociated molecules, which do not form complex anions with fluoride ions. This, follows, firstly, from the low solubility of XeF_2 in water (~0.15 M at 0°C), and secondly, from the similarity of the spectra shown in Fig. 3 for an aqueous solution of XeF_2 at ~5°C and for gaseous XeF_2 at 30°C.[40,41]

The distribution coefficient of XeF_2 between water and carbon tetrachloride is 2.3 and does not change significantly in 1 M $HClO_4$ or in 4 M KHF_2. XeF_2 solution is a strong oxidant, which rapidly oxidises HCl to Cl_2, iodate to periodate, Ce^{III} to Ce^{IV}, Co^{II} to Co^{III}, and Ag^{I} to Ag^{II}. The redox potential of the Xe–XeF_2 system in an acid medium is 2.2 V. The half-decomposition life of XeF_2 dissolved in water is ~7 h at 0°C, in 1 M $HClO_4$ it falls to ~5 h, and in 30% HF to ~3 h. When XeF_2 solution is made alkaline, it rapidly becomes yellow and the solution decomposes; it was suggested[40] that the yellowing is due to the formation of an oxygen compound of xenon(II).

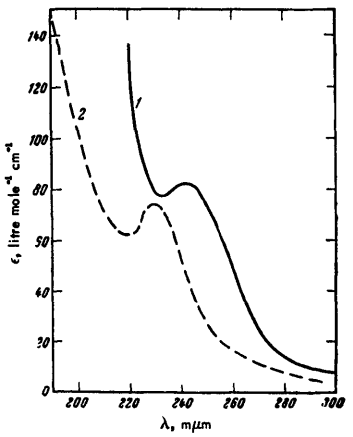


Fig. 3. Ultraviolet absorption spectrum of xenon difluoride: 1) aqueous solution at ~5°C;[40] 2) gas at 30°C.[41]

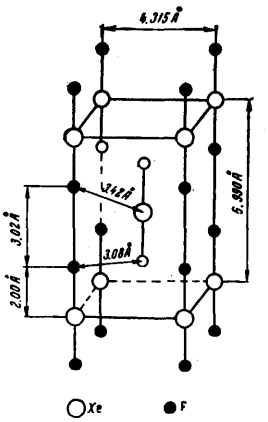


Fig. 4. Crystal structure of xenon difluoride according to neutron diffraction analysis[46].

Xenon difluoride is diamagnetic[35]; its molar magnetic susceptibility is $\chi_M = (40-50) \times 10^{-6}$. The heat of sublimation of crystalline XeF_2 is 12.3 ± 0.2 kcal mole^{-1},[42] and was determined from the temperature dependence of the intensity of the spectral bands in the vacuum ultraviolet region of gaseous XeF_2 in thermal equilibrium with the crystals[43]. The standard heat of formation of gaseous XeF_2, calculated from mass-spectroscopic data, is 37 ± 10 kcal × × mole^{-1},[44] which gives a mean energy of 39 ± 10 kcal × × mole^{-1} for the Xe–F bond in XeF_2.

The structure of XeF_2 has been studied by X-ray diffraction[45] and neutron diffraction[46] methods. The X-ray studies indicated that XeF_2 is tetragonal and has space group $I4/mmm$; the lattice parameters are: a = 4.315 ± ± 0.003, c = 6.990 ± 0.004 Å. The density calculated for two formula units in the unit cell is 4.32 g cm^{-3}. The molecule has a linear configuration F–Xe–F and the Xe–F distance is 2.14 ± 0.14 Å.

The neutron diffraction results confirmed these facts, by showing that XeF_2 has a body-centred tetragonal lattice (space group $I4/mmm$) of parallel, linear, symmetrical F–Xe–F molecules (Fig. 4). The Xe–F distance is 2.00 ± ± 0.01 Å. Each fluorine atom is associated with another fluorine atom at a distance of 3.02 Å and four fluorines at a distance of 3.08 Å. The least intermolecular Xe–F distance is 3.64 Å.

The infrared spectrum of gaseous XeF_2 [8,38] shows two intense bands: at 555 and 213.2 cm^{-1}. The first, without a Q-branch, relates to the antisymmetric stretching vibration ν_3, and the second, with a distinct Q-branch, to the ν_2 bending vibration. A third band, at 1070 cm^{-1}, is considered to be a weak $\nu_1 + \nu_3$ combination, including the infrared-inactive band of symmetrical stretching vibrations, ν_1 = 515 cm^{-1}.

The XeF_2 spectrum is characteristic of a symmetrical linear molecule. The Xe–F interatomic distance, calculated from the P–R spacing for ν_3 of 16 cm^{-1} (the maxima of the P- and R-branches are at 566 and 550 cm^{-1}, respectively), is ~1.7 Å. The force constants have been determined: k_r (the constant for the principal stretching vibration) is 2.85, k_{rr} (the constant of stretching interaction) 0.11, and k_δ/l^2 (the constant of bending vibrations)

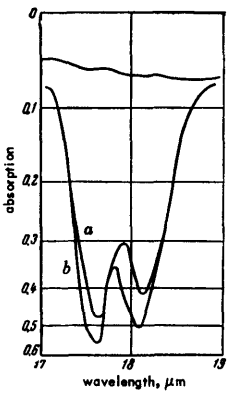


Fig. 5. Infrared spectrum of gaseous xenon difluoride[47]: *a*) pure XeF_2; *b*) $XeF_2 + F_2$ (~0.7 kgf cm^{-2}).

0.19 mdyn Å^{-1}; these values enabled the structure of the XeF_2 molecule to be settled (see p. 419).

The main points of the above picture were confirmed by Milligan and Sears[37], who also observed a very weak band at 520 cm^{-1}, probably ν_1.

An investigation of the effect of fluorine pressure on the infrared spectrum of XeF_2 [47] gave a slightly more accurate P–R spacing, 14.2 ± 0.2 cm^{-1}, which corresponds to the Xe–F distance of 1.9 Å. The more accurate force constants k_r and k_{rr} are 2.82 and 0.15 mdyn Å^{-1} respectively. Fig. 5 shows the infrared spectrum of gaseous XeF_2, according to Smith[47].

The Raman spectrum of solid XeF_2 [38] has lines at 108 and 497 cm^{-1}. The first is probably a libration frequency, but the second is ν_1. Lines at 548 and 509 cm^{-1} are evidently due to the impurity XeF_4.

Investigation of the spectrum of gaseous XeF_2 in the far ultraviolet region[43] gave information about the excited electronic levels of the molecule and this was used in

deciding the structure of the XeF_2 molecule (see p. 420). Kuznetsov and coworkers[48] investigated the spectrum from a high-frequency discharge through XeF_2 vapour; the bands found belonged to XeF_2 and XeF molecules.

Nuclear magnetic resonance has also been used in studying XeF_2, the investigation being made in anhydrous hydrogen fluoride[49,50] and in the solid state[50]. At room temperature XeF_2 enters into exchange with the solvent, but at -19.5°C this exchange is so slow that the measurements are completely feasible. Fig. 6 shows the magnetic resonance spectrum[49] of XeF_2 in HF at -20°C and at a frequency of 56.422 MHz. The chemical shift of ^{19}F in XeF_2 (for a solution in anhydrous HF) is 629 parts per million relative to F_2 [50] and 2.3 parts per million relative to HF[50]; the latter quantity at -20°C is also reported[49] to be 3.3 parts per million. The $^{129}Xe-^{19}F$ coupling constant for XeF_2 in HF is 5600 Hz [50] or 5690 Hz.[49] The impossibility of observing the $^{131}Xe-^{19}F$ coupling follows from the electrical asymmetry of the XeF_2 structure. The results of the nuclear magnetic resonance investigation of XeF_2 in HF confirmed that the XeF_2 is present in solution mainly as undissociated molecules.

The shielding constant for solid XeF_2 is 612 parts per million (relative to F_2) and the width of the resonance line is ~6.0 G.[50] The results of the nuclear magnetic resonance studies enable a number of views about the electron density distribution in the XeF_2 molecule and about the structure of this molecule to be ruled out. The Mössbauer effect in solid XeF_2 has also been studied[51,52].

2. Xenon tetrafluoride. A detailed description of the preparation of xenon tetrafluoride by heating a mixture of xenon and fluorine[3,5] was given in the previous review[1], which also included some information about the physical and chemical properties of XeF_4.

Another method, which also looks quite promising for the future preparative studies in the field of Group 0 compounds (see pp. 413 and 417) was employed by Kirshenbaum and his coworkers[53,54], who subjected a mixture of xenon and fluorine to the action of an electric discharge. They used an apparatus similar to that employed earlier for the synthesis of the oxygen fluorides O_3F_2 and O_4F_2 [55-57] (Fig. 7). The diameter of the reactor was 6.5 cm and the distance between the electrodes (dia. 2 cm) 7.5 cm. The mixture of gases with $Xe : F_2 = 1 : 2$ (by volume) was passed at a rate of 136 $cm^3\ h^{-1}$ (under standard conditions) into the reaction vessel cooled to -78°C, and was quantitatively converted into XeF_4. The discharge was varied from

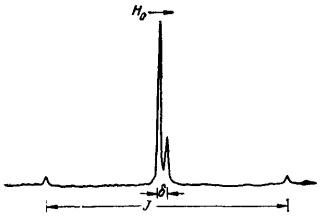


Fig. 6. Magnetic resonance spectrum with high resolution of ^{19}F in xenon difluoride at -20°C and frequency 56.422 MHz.[49] The chemical shift of ^{19}F relative to $H^{19}F$ is denoted by δ and the spin–spin coupling constant of $^{19}F-^{129}Xe$ is denoted *J*.

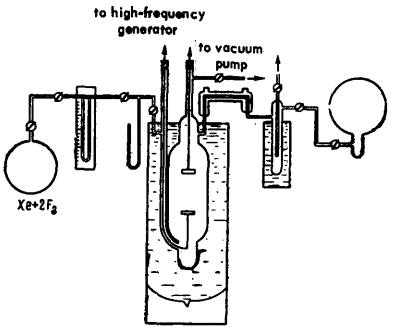


Fig. 7. Apparatus for preparing the fluorides of the Group 0 elements by the electric discharge method[54].

1100 V and 31 mA to 2800 V, 15 mA. In addition to the well-known methods for analysing the reaction products, a new method of determining xenon was employed, based on the quantitative reaction of xenon tetrafluoride with an excess of mercury:

$$XeF_4+4Hg\rightarrow Xe+2Hg_2F_2.$$

Schumacher and Schaefer[58] obtained XeF_4 in 97% yield (on Xe) from a mixture of $Xe + 3F_2$, which was circulated in an apparatus (Fig. 8) having a main section heated to 560°C and consisting of a Monel tube furnace packed with pieces of nickel sheet. Up to 20 g XeF_4 were obtained in 2 h.

A radiation method has also been used to synthesis XeF_4.[59] A mixture of xenon and fluorine in a stainless steel reactor was irradiated with a beam of electrons of energy 1.6 MeV and the reaction products were identified by their infrared spectra, which showed that XeF_4 and XeF_2 were formed.

The formation of XeF_4 (and xenon oxide fluorides) was observed in the reaction of xenon with OF_2 in an electric discharge at pressures of 3–62 mmHg and in a nickel tube at 400°C and initial pressure ~3.5 atm.[60]

In addition to the chemical properties of xenon tetrafluoride reviewed earlier[1] qualitative investigations[58] have

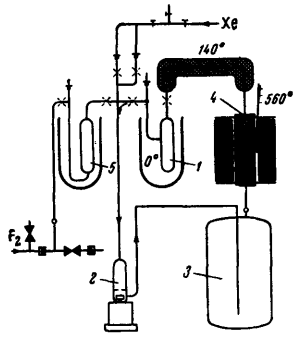


Fig. 8. Apparatus for preparing xenon tetrafluoride by a circulation method[58]:
1) trap at 0°C; 2) Teflon pump; 3) cylinder capacity 4.4 litres; 4) Monel tube furnace packed with nickel sheet; 5) trap.

shown that XeF_4 slowly attacks glass with formation of SiF_4 and O_2; when enclosed in aluminium foil it does not detonate under impact, although mixtures of XeF_4 with sugar or sulphur explode like mixtures of these substances with $KClO_3$. On being put on paper or cotton wool, dry XeF_4 explodes on heating; XeF_4 moistened in air instantly chars paper, which often also ignites spontaneously. Xenon tetrafluoride oxidises, on heating, metallic platinum to PtF_4, and possibly to PtF_6. XeF_4 dissolves in water, glacial acetic acid, concentrated nitric and sulphuric acids, and reacts with these solvents in doing so. In the reaction of XeF_4 with CH_3CO_2H or $(CH_3CO)_2O$, a crystalline substance is formed, which the authors[58] think may by xenon acetate. Cyclopentadiene, tetrahydrofuran, dioxan, and ethanol ignite under the action of XeF_4; the mixture of vapours often explodes. Acetone does not react immediately with XeF_4, but after some time the mixture froths up and the XeF_4 dissolves. Petroleum slowly dissolves XeF_4, with darkening. In carbon disulphide, carbon tetrachloride, dimethylformamide, diethyl ether, and cyclohexane, XeF_4 is insoluble, and it does not react with these substances. XeF_4 fumes in air, being hydrolysed to $Xe(OH)_4$. The formation of this compound, which vigorously explodes on being heated to 30–40°C in a vacuum, was noted a little earlier by Bartlett and Rao[61]; according to these authors $Xe(OH)_4$ (or $XeO_2.2H_2O$) is obtained in the hydrolysis of XeF_4 by water in an evacuated quartz vessel.

Xenon tetrafluoride dissolves rapidly in potassium iodide solution, with quantitative liberation of xenon[5]:

$$XeF_4+4I^-\rightarrow Xe+2I_2+4F^-.$$

The results of an investigation of the hydrolysis of XeF_4 in acid, alkali, and neutral media are not completely reproducible owing to the heterogeneous nature of this reaction. The experimental $Xe:O_2$ ratio found in the reaction products is not 1 : 1, thus indicating a departure from the simple reaction:

$$XeF_4+2H_2O\rightarrow Xe+4HF+O_2.$$

In the hydrolysis of XeF_4 in acid and neutral media the yields of xenon and oxygen do not exceed 50 and 70% respectively[62,63]; in 6 M NaOH the yield in each instance is almost quantitative, but the results in 1 M NaOH are the same as in acid and neutral media[63]. Evidently XeF_4 disproportionates in solution with the formation of xenon and a soluble compound of xenon(VI). Evaporation of the solution formed by the acid hydrolysis of XeF_4 led to the formation of the oxide XeO_3 [62] (see p. 414).

The reaction of XeF_4 with SF_4 leads to the formation of SF_6 and elemental xenon; with O_2F_2, XeF_6 is formed[58]. The reactions of XeF_4 with SbF_5 and TaF_5 give the compounds $XeF_2.2SbF_5$ and $XeF_2.2TaF_5$ [64] (see p. 411); the same compounds are formed in the reaction of XeF_2 with the corresponding pentabromides. Xenon tetrafluoride does not react with BF_3, NaF, or KF, up to 200°C.[64,65] However, according to Schumacher and Schaefer[58], XeF_4 and BF_3 form a violet addition product, stable below -100°C.

Xenon tetrafluoride is diamagnetic: the molar magnetic susceptibility at room temperature is -50.6×10^{-6}, but below 240°K the diamagnetism of XeF_4 begins, according to Slivnik and coworkers[66], to decrease with fall in temperature. A very close value for the susceptibility, $(-56\pm5)\times10^{-6}$ was found by other authors[67]. Careful measurements of the susceptibility of pure specimens of XeF_4 between 77° and 293°K showed, however, that the diamagnetism of XeF_4 is independent of temperature in this range; the molar susceptibility of xenon tetrafluoride is $(-53\pm5)\times10^{-6}$; the deviation does not exceed the limits of experimental error[68].

Boudreaux[69] made a theoretical calculation of the magnetic susceptibility of XeF_4 in the MO–LCAO approximation, paying special attention to the high-frequency elements of the paramagnetic part of the susceptibility and obtained results which agreed with the experimental data and also confirmed his assumptions concerning the scheme of molecular orbitals[79] (see p. 420).

The problem of the thermodynamic properties of xenon tetrafluoride has received much attention. XeF_4 has a high melting point, ~114°C.[15] The heat of sublimation of solid XeF_4, determined (just as that for XeF_2) from the temperature dependence of the intensity of the spectral bands in the vacuum ultraviolet region of gaseous XeF_4 in thermal equilibrium with crystals[43], was found to be 15.3 ± 0.2 kcal mole^{-1}.[42]

The heat of formation of solid XeF_4 was calculated from the calorimetrically measured heat of reaction of XeF_4 with an acidified aqueous solution of potassium iodide[71]. The value found for the standard heat of formation of crystalline XeF_4 was -60 kcal mole^{-1}, from which the calculated mean energy of the Xe–F bond is 30 kcal. Using the method of reducing XeF_4 with hydrogen by the reaction:

$$XeF_4(gas)+2H_2(gas)\rightarrow Xe(gas)+4HF(gas),$$

in an isothermal calorimeter at 120–130°C, preliminary values were found for the heat of formation of gaseous XeF_4 and the Xe–F bond energy, -55 kcal mole^{-1} and +32 kcal respectively[72]. The standard heat of formation of gaseous XeF_4, calculated from the mass spectrometric result, is -53 ± 5 kcal mole^{-1},[44] which gives 32 ± 2 kcal for the mean energy of the Xe–F bond.

The heat capacity of solid XeF_4 was measured in the temperature range from 20°K to room temperature in an adiabatic calorimeter[73,74]. The preliminary value found for the standard entropy of formation of XeF_4 was $\Delta S^\circ = -102.5$ e.u., which, together with the heat of formation[71], gives $\Delta G^\circ = -29.4$ kcal mole^{-1}.

The form of the curve of the temperature dependence of heat capacity of XeF_4 (Fig. 9) is the same as for molecular crystals, for example, C_6H_6, CO_2, or CH_4. The heat capacity of XeF_4 at 298°K is ~28 cal mole^{-1} deg^{-1}; the theoretical heat capacity of a molecular crystal of five atoms with six degrees of freedom is ~30 cal mole^{-1}deg^{-1}.

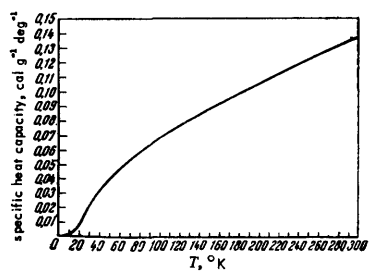


Fig. 9. Curve for the temperature dependence of the specific heat capacity of xenon tetrafluoride[74].



Fig. 10. Crystals of xenon tetrafluoride.

Judging from the heat capacity curve, XeF_4 does not undergo phase transformations in the temperature range studied.

From the results on vibrational spectra and structure of XeF_4, the thermodynamic functions of XeF_4 have been calculated for the range from 50° to 2000°K.[75]

Structural investigations on xenon tetrafluoride have employed X-ray diffraction[45,76-78] and neutron diffraction[79] with single crystals of XeF_4 (Fig. 10). The X-ray study[77] showed that XeF_4 is monoclinic, space group $P2_1/n$. The lattice parameters of XeF_4 are: $a = 5.050$, $b = 5.922$, $c = 5.771$ Å, $\beta = 99.6°$. The density calculated for two formula units in the unit cell is 4.04 g cm^{-3}; this agrees with the pyknometric determination[80].

The Xe–F distances are 1.90 and 1.92 Å, the F–Xe–F valency angles are 89.7° and 90.3°. The XeF_4 molecule has a square planar configuration with F–F distances of 2.69 and 2.71 Å. The shortest distance between two neighbouring molecules is 3.02 Å.

Neutron diffraction investigation[79] confirmed and somewhat refined the X-ray data. According to the neutron diffraction results, the Xe–F(1) and Xe–F(2) distances are 1.951 and 1.954 Å respectively; the F(1)–Xe–F(2) angle is 90.0 ± 0.1° (Fig. 11). Fig. 12 shows the position of the XeF_4 molecules in the crystal.

In a preliminary X-ray structural investigation of XeF_4 the existence of yet another polymorphic modification of

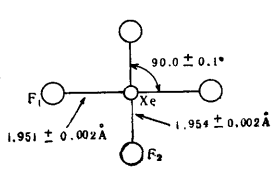


Fig. 11. Crystal structure of xenon tetrafluoride[79].

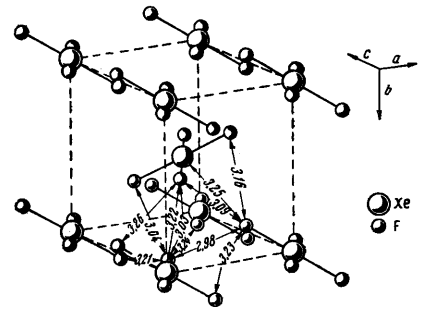


Fig. 12. Crystal structure of xenon tetrafluoride[79].

XeF_4 was suggested[76]. Subsequently it was shown[81,82] that this "modification" was really a molecular compound, $XeF_2.XeF_4$. The following parameters were found for this compound, which has the space group $P2_1/c$: $a = 6.64$, $b = 7.33$, $c = 6.40$ Å, $\beta = 92°40'$; for four formula units in the unit cell the density is 4.02 g cm^{-3}. In this compound the XeF_2 and XeF_4 molecules almost completely retain their usual configuration. The least intermolecular Xe–F distance is close to the distances in the XeF_2 and XeF_4 structures and the least intermolecular F–F distance (2.87 Å), although somewhat less than in these structures, nevertheless corresponds to the uncombined fluorine atoms. The absence of structural indications of the existence of strong bonds between the molecules supports the treatment of $XeF_2.XeF_4$ as a molecular compound.

Gaseous XeF_4 has been studied by electron diffraction[83]. The results showed that in the gaseous state the XeF_4 molecule has a square planar configuration with Xe–F distance of 1.94 Å.

The vibrational spectra of XeF_4 (the infrared spectrum of the gas and the Raman spectrum of the solid) were studied in detail by Claassen and coworkers[84], Figs. 13 and 14 show the spectra and a comparison of the frequencies is given in Table 1.

The results obtained show — in agreement with the structural data — that the XeF_4 molecule has a square planar configuration (symmetry D_{4h}). From the Q–R spacing for ν_2, 11 ± 1 cm^{-1}, the Xe–F interatomic distance was evaluated, 1.85 ± 0.2 Å. The force constants were determined: stretching vibrations, 3.00 mdyn Å^{-1}; stretching interaction between bonds at right angles,

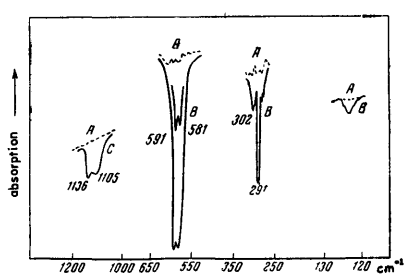


Fig. 13. Infrared spectrum of gaseous xenon tetrafluoride[84]: *A*) background; *B*) optical path 10 cm; *C*) optical path 60 cm.

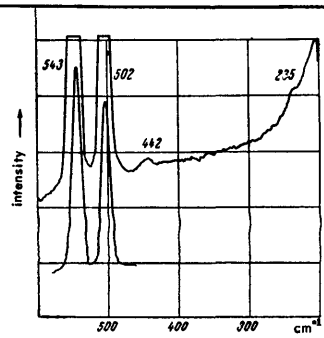


Fig. 14. Raman spectrum of solid xenon tetrafluoride[84].

TABLE 1. Assignment of the frequencies in the vibrational spectra of XeF_4.[84]

	a_{1g}	ν_1	RS	543 cm^{-1} (v.s.)
	a_{2u}	ν_2	IR	291 cm^{-1} (s.)
	b_{1g}	ν_3	RS	235 cm^{-1} (w.)
	b_{1u}	ν_4	inactive	221 cm^{-1} (?)
	b_{2g}	ν_5	RS	502 cm^{-1} (v.s.)
	e_u	ν_6	IR	586 cm^{-1} (v.s.)
	e_u	ν_7	IR	123 cm^{-1} (?)
		$\nu_5+\nu_6$	IR	1105 cm^{-1} (w.)
		$\nu_1+\nu_6$	IR	1136 cm^{-1} (w.)

Note. The following abbreviations are used in the table: IR = infrared spectrum of gaseous XeF_4; RS = Raman spectrum of solid XeF_4; v.s. = very strong; s. = strong; w. = weak intensity of band.

The 442 cm^{-1} band in the Raman spectrum is considered as comprising $2\nu_4$; hence the value 221 cm^{-1} is taken for ν_4.

0.12 mdyn $Å^{-1}$; stretching interaction between oppositely situated bonds, ~0.06 mdyn $Å^{-1}$; the values found were comparable with the corresponding quantities for the XeF_2 [8,38] and PuF_6 [85] molecules.

The investigation of the spectrum of gaseous XeF_4 in the far ultraviolet region[86] made it possible to obtain information about the excited electronic levels of the molecule and these results could be used for assigning the structure of XeF_4 (see p. 420). Fig. 15 gives the spectrum.

Nuclear magnetic resonance has also been used for investigating XeF_4. The first measurements of the resonance of ^{19}F in solid XeF_4, made over a wide range of temperatures[87] showed — in accordance with static magnetic measurements[66], a change in the form of the spectrum near 273°K. However, somewhat later these authors refuted their own results[88] and showed that the

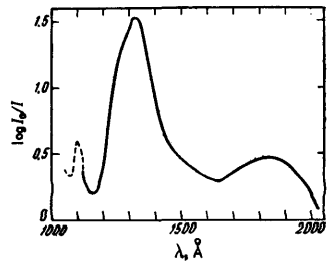


Fig. 15. Spectrum of xenon tetrafluoride in the far ultraviolet region[86].

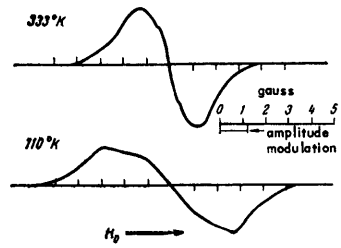


Fig. 16. Nuclear magnetic resonance spectrum of fluorine in xenon tetrafluoride at the frequency 29 MHz.[88]

form of the line was unchanged throughout the whole temperature range investigated (Fig. 16). The asymmetry of the XeF_4 spectra is ascribed to the anisotropy of the chemical shift of fluorine[66], and this problem received detailed study[88-93]. The shielding constant for solid XeF_4 was 482 parts per million (relative to F_2) and the line width ~3.8 G.[50]

Measurements of the magnetic resonance of ^{19}F in XeF_4 were also made in anhydrous HF.[49,50,94] In the spectrum there was a strong central line with a chemical shift of 175 parts per million relative to HF[49,94] and 454 parts per million relative to F_2.[50] Two weak lines on either side of the main line relate to the $^{129}Xe-^{19}F$ coupling. The coupling constant is 3860 Hz. As also in the case of XeF_2, the $^{131}Xe-^{19}F$ coupling does not appear in the spectrum; this shows the asymmetry surrounding the xenon nucleus and provides a basis for assuming[50] that the square planar structure of the XeF_4 molecule is also retained in solution. As for XeF_2, the xenon tetrafluoride is present in solution in HF mainly as undissociated molecules[50].

The information obtained from nuclear magnetic resonance spectra enabled some conclusions to be drawn about the electron density distribution and the structure of the XeF_4 molecule. The Mössbauer effect for solid XeF_4 was also investigated[51,52]. $^{131}XeF_4$ shows the Szillard-Chalmers effect[95], unlike the clathrate compounds of xenon, in which it is known that xenon does not form chemical bonds. In γ-irradiation at 77°K with single-crystal XeF_4, electron paramagnetic resonance studies showed the existence of an entrapped XeF radical; the spectrum of this radical was interpreted[96,97].

3. Xenon hexafluoride. To prepare xenon hexafluoride XeF_6 mixtures of xenon with a large excess of fluorine (Xe : F_2 ratios from 1 : 4 to 1 : 20) were heated to 300–700°C

at pressures up to 200 atm in nickel or stainless steel reactors[9,10,98,99]. Xenon hexafluoride is also formed on passing an electric discharge[54] through a 1 : 3 Xe : F_2 mixture at -78°C. The specimens of XeF_6 obtained by these methods were not completely pure and contained more or less appreciable amounts of XeF_4, XeF_2, and $XeOF_4$ impurities. Sheft and coworkers[100] proposed a method for obtaining pure crystals of XeF_6 based on the fact that unlike the other xenon fluorides and oxide fluorides XeF_6 forms a molecular compound with sodium fluoride; this offers the possibility of effectively separating the impurities.

Xenon hexafluoride at room temperature is a colourless crystalline material, m.p. 47.7° ± 0.2°C.[100] Solid XeF_6 becomes yellow at 43–43.5°C, and on melting it gives a yellow liquid, but on cooling and solidifying it becomes colourless again[9,100]. The vapour pressure of solid XeF_6 is ~7 mmHg at 0°C and 30 mmHg at 25°C; XeF_6 vapour is pale yellow-grey. XeF_6 dissolves in anhydrous HF, the solubility being ~10 moles XeF_6 in 1000 g HF at 25°C; the yellow solutions are decolorised on cooling[39]. Unlike the analogous solutions of XeF_2 and XeF_4, solutions of XeF_6 in HF exhibit high electrical conductivity (for example, the molar conductance of 0.02 M XeF_6 is 147 Ω^{-1} cm^{-1})[39]; it has been suggested that on dissociation XeF_5^+ and HF_2^- ions are formed[15].

With hydrogen at room or slightly higher temperatures, XeF_6 is reduced to elemental xenon[9]; mercury at 100°C has the same effect[10]. XeF_6 can be kept for a long period in nickel or poly(chlorotrifluoroethylene) vessels but it reacts with quartz at room temperature to form xenon oxide tetrafluoride $XeOF_4$.[9,101] The reaction of XeF_6 with BF_3 or AsF_5 at room temperature leads to the formation of the addition products $XeF_6.BF_3$ and $XeF_6.AsF_5$[102] (see p. 412).

Several important results were obtained in studying the hydrolysis of XeF_6. Dudley and coworkers[99] showed that when XeF_6 reacts with water a solution exhibiting strong oxidising properties is formed. The reaction of this solution with KI solution leads to the quantitative release of xenon. On this basis it was concluded[99] that xenic acid $Xe(OH)_6$ is formed in the solution. The alkaline hydrolysis of XeF_6 leads to the formation of pale yellow solutions, from which stable precipitates of salts of xenic acid are deposited[63,103-106] (see p. 415). Xenon trioxide XeO_3 (see p. 414) was obtained by the slow hydrolysis of XeF_6 with water vapour at room temperature[107] and $XeOF_4$ is formed in incomplete hydrolysis[108] (see p. 412).

Sheft and Hyman[109] studied the exchange of ^{19}F between XeF_6 and gaseous fluorine: the rate of exchange (at XeF_6 concentration of 0.02 M and 150°C) is a linear function of the fluorine concentration, and on extrapolation the straight line passes through the origin. The results were interpreted as showing the association of XeF_6 with a molecule of F_2.

Xenon hexafluoride is thermodynamically stable. The reduction of XeF_6 by hydrogen according to the reaction:

$$XeF_6(gas) + 3H_2(gas) \rightarrow Xe(gas) + 6HF(gas),$$

in an isothermal calorimeter at 120–130°C was used to find preliminary values of the heat of formation of XeF_6 and the energy of the Xe–F bond, -79 kcal $mole^{-1}$ and 31 kcal respectively[72]. Experimental results on the vapour pressure of solid XeF_6 were used to derive the vapour pressure equation:

$$\log P_{mm} = 8.155 - 1900/T,$$

from whence the heat of sublimation of XeF_6 is found to be 9.15 kcal $mole^{-1}$.[54]

The crystal structure and configuration of the XeF_6 molecule have not yet been established. The X-ray and electron diffraction studies are hindered by the relatively high vapour pressure of XeF_6 and its reactivity with ordinary capillary materials. Possibly X-ray diffraction studies at low temperatures have a better prospect. Preliminary electron diffraction data[110] are incompatible with the symmetry of the structure of the gaseous molecule.

No light has been cast on the problem of the structure of XeF_6 by the investigation of its vibrational spectra[9,10,47,111], which could not be sufficiently fully studied owing to experimental difficulties. In the infrared spectra of XeF_6 vapour there are bands at 520, 565, 612, 1100, and 1230 cm^{-1}, and in the Raman spectrum of solid XeF_6 lines at 582, 635, and 655 cm^{-1}. A solution of XeF_6 in anhydrous HF showed Raman lines at 620 cm^{-1}. The bands of the infrared spectrum have an unusual shape and are anomalously broad. The lines of the Raman spectrum lie in the stretching vibration region.

In view of the impossibility of a reliable allocation of frequencies, the XeF_6 spectra do not offer sufficient basis for establishing the structure of the molecule. The principal question under discussion is whether the XeF_6 structure is a right octahedron with symmetry O_h, similar to other hexafluorides[112], or whether it exhibits lower symmetry. This problem is not devoid of theoretical interest also (see p. 420).

The nuclear magnetic resonance of fluorine in XeF_6 was investigated in anhydrous hydrogen fluoride[49,50], and also in the solid and liquid states[50]. In anhydrous HF the rate of exchange of XeF_6 with the solvent is so high that only a single broad line is observed in the spectrum. The value of the chemical shift depends considerably on the XeF_6 concentration in the solution. On reducing the temperature from 25°C to -13°C the width of the resonance line decreases by ~40%. An attempt to resolve the lines of XeF_6 and HF by cooling to solid carbon dioxide temperature did not succeed; attempts to find a solvent with which XeF_6 would not react were equally unsuccessful[50].

The shielding constant for solid XeF_6 is 310 parts per million (relative to F_2) and for the liquid, 309 parts per million. The width of the resonance lines of solid and

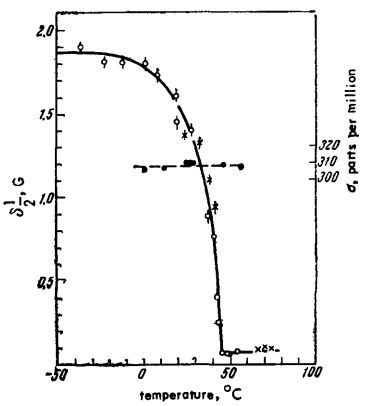


Fig. 17. Effect of temperature on the nuclear magnetic resonance spectrum of ^{19}F in solid xenon hexafluoride[50].

liquid XeF_6 are ~ 1.9 and ~ 0.14 G respectively. The temperature dependence of the shielding constant and of the line width in the nuclear magnetic resonance spectrum of ^{19}F in solid XeF_6 is shown in Fig. 17.

4. Other xenon fluorides. By heating a gaseous mixture with the molar ratio $Xe : F_2 = 1 : 16$ at 620°C and 200 atm a yellow substance was obtained whose analysis showed a higher concentration of fluorine than that corresponding to the formula XeF_6.[113,114]

After cooling to -78°C the excess of fluorine was evacuated through a trap at liquid nitrogen temperature. In the trap there condensed a yellow substance with a vapour pressure considerably less than that of fluorine, since it remained in the trap even after prolonged evacuation with a mercury diffusion pump.

Analysis of the material, by direct determination of fluorine and finding the xenon by difference, gave an atomic ratio of F : Xe equal to 7.9 ± 0.3 and 8.1 ± 0.1, which closely corresponds to xenon octafluoride XeF_8.

In order to trace in greater detail the path of the synthesis the pressure of a reaction mixture with $Xe : F_2 = 1 : 20$ was measured continuously on heating it from 20° to 620°C. The measurements showed clearly that the quantity of combined fluorine exceeds that required for the formation of XeF_6. The F : Xe ratio calculated from the pressure measurements was 6.5; the authors[113,114] assume that a mixture of 75% XeF_6 + 25% XeF_8 was formed.

At room temperature in a sealed glass ampoule the substance obtained is a pale yellow gas which is decolorised in ~ 5 min and attacks the glass. At liquid nitrogen temperature the pale yellow gas is condensed with formation of a yellow solid. In a dilute sodium hydroxide solution the substance is hydrolysed with formation of a yellow solution; the colour is stable for a few hours.

Mass spectrometric studies did not enable the product to be identified although it was suggested earlier[115] that the mass spectrograms obtained indicate the existence of higher fluorides of xenon up to XeF_8.

It is interesting to compare the above results with those obtained in investigating the kinetics of the exchange of ^{19}F between XeF_6 and gaseous fluorine[109]. As noted above (see p. 410), these results show the association of XeF_6 with a molecule of F_2. A careful study of equilibrium in the xenon–fluorine system[116] gave no indication of the formation of xenon fluorides higher than XeF_6.

The same investigation enabled the authors[116] to propose the existence of xenon pentafluoride XeF_5. A band at 520 cm^{-1} in the infrared spectrum of XeF_6 was also initially ascribed to XeF_5; however, this band was observed in the spectrum of pure XeF_6.

As noted above, when XeF_4 single crystals are irradiated with ^{60}Co γ-rays at -195°C, there is a blue coloration. The electron paramagnetic resonance spectrum of the irradiated crystal has a hyperfine structure, indicating that the xenon atom is bonded with only one fluorine atom, and consequently that the radical XeF is formed[96,97].

In the mass-spectrometric study of XeF_2 and XeF_4[117,118] a series of fragments (XeF^+, Xe_2F^+, $Xe_2F_2^+$, $Xe_2F_3^+$, $Xe_2F_5^+$, $Xe_2F_7^+$) were observed, evidently formed in the spectrometer as a result of ionic-molecular association.

Experiments on the reaction of xenon with strong oxidants[119] are also of interest; they lead mainly to the formation of XeF_2, but give no indication of the production of any other fluorides.

5. Complex fluorides of xenon. As is well-known[1], the first chemical compound of xenon which was prepared was the complex $XePtF_6$.[2] Subsequently similar compounds were obtained with ruthenium[3] and rhodium[120,121].

A more detailed study of the reactions of xenon with PtF_6,[120] made in glass, quartz, and nickel vessels, showed that the products obtained have the composition $Xe(PtF_6)_x$, where x is between 1 and 2. The infrared spectra of these compounds have bands at 652 and 550 cm^{-1}, and the spectra for different composition cannot be distinguished.

The complexes of xenon with PtF_6 are yellow in thin layers and dark red in bulk. On heating to 115°C the solid becomes vitreous but does not melt below 165°C, at which temperature it decomposes, with formation of XeF_4 and a brick-red diamagnetic powder with a composition close to $XePt_2F_{10}$.[120] The X-ray diagrams of a product of composition $XePtF_6$ do not give a diffraction picture and products with greater values of x give complex X-ray diagrams.

The reaction of $XePtF_6$ with rubidium fluoride in iodine pentafluoride gave $RbPtF_6$ containing platinum(V) but reaction of $Xe(PtF_6)_2$ with caesium fluoride under the same conditions gave $CsPtF_6$. These reactions were thought[120] to confirm that $XePtF_6$ and $Xe(PtF_6)_2$ contain platinum(V) and that consequently the first compound should be formulated as $Xe^+[PtF_6]^-$ (this also agrees with the similarity of the infrared spectra of $XePtF_6$, $KPtF_6$ and O_2PtF_6) and the second as either a mixture of $XePtF_6$ and PtF_5, formed by the reaction:

$$Xe + 2PtF_6 \rightarrow XeF_2 + PtF_5,$$

or as a complex containing platinum(V) and xenon(II).

As for the compound $XePt_2F_{10}$ formed in the pyrolysis of $Xe(PtF_6)_{1.8}$, its reaction with CsF in iodine pentafluoride gives Cs_2PtF_6, with platinum(IV). The X-ray diagram of $XePt_2F_{10}$ is complex but does not contain lines which can be ascribed to xenon tetrafluoride, therefore this substance cannot be considered a mixture of $XePtF_6$ and XeF_4.

The complex of xenon with RhF_6 is characterised by a much closer approach to the 1 : 1 stoichiometric ratio than for that with PtF_6.

The formation of products close in composition to $Xe(PtF_6)_2$ in the explosion produced on passing a current through a platinum wire in an atmosphere of fluorine and xenon has been established[122,123].

When XeF_4 is dissolved in liquid antimony(V) fluoride, a gas is evolved and a greenish solution is formed, from which a precipitate of a yellow diamagnetic complex $XeF_2 . 2SbF_5$, m.p. 63°C, separates; it sublimes in a vacuum at 60°C. The same compound is formed in the reaction between XeF_2 and SbF_5. A straw-yellow complex, $XeF_2 . 2TaF_5$, m.p. 81°C is obtained by the action of TaF_5 on XeF_4; the X-ray powder diagrams of the two complexes indicate their structural similarity. The diamagnetism of $XeF_2 . 2SbF_5$ indicates the formation of a covalent compound of xenon(II) of the type $F_5SbFXeFSbF_5$.[64] XeF_4 does not react with BF_3 even on heating to 200°C,[64,65] however, from other results[58], XeF_4 and BF_3 form a violet addition product, stable at a temperature below -100°C.

The action of a glow discharge (6500–7000 V) on a mixture of gaseous xenon and fluorine (molar ratio 2 : 1) in a

glass vessel at -78°C and a pressure below 10 mmHg leads to the formation on the walls of the vessel of a white crystalline substance, stable at -78°C, but decomposing on warming to room temperature, with formation of Xe and SiF_4.[124] Analysis of the substance showed the composition $Xe_{2.3}SiF_{5.8}$. Similar experiments with a mixture of xenon with fluorine and SiF_4 in the molar ratio 2 : 1 : 1 gave a product with the atomic ratio Xe : Si = 2.2 : 1. It was concluded from these results that a complex Xe_2SiF_6 is formed, whose structure can be expressed by the formula $(Xe^+)_2SiF_6^{2-}$.

The analogous reaction of xenon with platinum pentafluoride and fluorine gives a solid which is white to yellow, unstable at room temperature and containing — according to the mass spectrometric and infrared spectroscopic analyses of the decomposition products — xenon and platinum pentafluoride[124].

By heating 0.153 moles SbF_5, 0.0435 moles Xe, and 0.0410 moles F_2 in a nickel bomb at 250°C for 12 h, a pale yellow solid was obtained which reacts vigorously with water, xenon being liberated. This compound, which is given the composition $XeSbF_6$ [124] does not sublime below 100°C, unlike the other complex with SbF_5.

Selig[102] established the formation of addition products of XeF_6 and BF_3 and of XeF_6 and AsF_5. At room temperature, BF_3 and XeF_6 give the compound $XeF_6.BF_3$, which is a white solid, melting at 90°C to a pale yellow viscous liquid. At 20°C the vapour pressure of this addition compound is less than 1 mmHg, but it can be sublimed at this temperature and pressure. The infrared spectrum of solid $XeF_6.BF_3$ at -195°C is complex, but has a broad band with centre close to 1025 cm^{-1}, characteristic for the BF_4^- ion. The infrared spectrum of the vapour of the addition compound has bands characteristic of BF_3 and XeF_6; this signifies partial dissociation in the vapour phase.

The reaction of XeF_6 and AsF_5 at room temperature also gives a 1 : 1 addition compound — a white solid which does not sublime in a vacuum at room temperature. The Raman spectra of solid $XeF_6.BF_3$ and $XeF_6.AsF_5$ have maxima at 612 and 620 cm^{-1} respectively; it is interesting to note that a solution of XeF_6 in anhydrous hydrogen fluoride also gives a maximum in the Raman spectrum at 620 cm^{-1}.[39]

The reactivity of the addition products of XeF_6 is comparable with that of XeF_6 itself. These substances are extremely hygroscopic and although they can be stored in nickel vessels, they react with Pyrex glass. By analogy with the complex $XeF_2.2SbF_5$ (see p. 411), a covalent structure has been proposed for $XeF_6.BF_3$ and $XeF_6.AsF_5$, although an ionic structure of the type $(XeF_5)^+(AsF_6)^-$ cannot be ruled out.

B. Oxide Fluorides

1. Xenon oxide tetrafluoride. The first indications of the possible existence of xenon oxide tetrafluoride $XeOF_4$ were obtained in the mass-spectrometric investigation of XeF_4.[115,117] Then the formation of $XeOF_4$ was established in the reaction of XeF_6 with quartz[9,101] and as a result of the slow hydrolysis of XeF_6.[101,108]

For the preparation of $XeOF_4$ by the first method[101], XeF_6 was condensed in a quartz vessel, this was sealed and then heated to ~50°C. The liquid XeF_6 reacted with the SiO_2 thus:

$$2\,XeF_6+SiO_2 \rightarrow 2\,XeOF_4+SiF_4.$$

The vessel was cooled to -78°C and the SiF_4 evacuated, leaving a colourless liquid in the vessel. In prolonged reaction, a white crystalline precipitate was formed in addition to the liquid; the precipitate was subsequently identified as XeO_3.[107] Evidently the reaction proceeds stepwise:

$$2\,XeOF_4+SiO_2 \rightarrow 2XeO_2F_2+SiF_4,$$

$$2XeO_2F_2+SiO_2 \rightarrow 2XeO_3+SiF_4.$$

Smith[108] obtained $XeOF_4$ in the circulating system which he employed for the synthesis of XeF_2 (without the heater zone) by the action of air saturated with water vapour, on XeF_6 at room temperature. After removing unreacted XeF_6 and hydrogen fluoride the yield of $XeOF_4$ was ~80%. In a somewhat different method[101] a known weight of XeF_6 was hydrolysed with the accurately calculated quantity of water in accordance with the equation:

$$XeF_6+H_2O \rightarrow XeOF_4+2HF$$

Xenon hexafluoride was condensed in a small nickel vessel at liquid nitrogen temperature, and water in a glass vessel. The two vessels were evacuated to a pressure of 10^{-4} mmHg, the water was transferred into a nickel vessel and the latter warmed to room temperature; during this the XeF_6 and H_2O were completely converted into the vapour phase and under these conditions there was hydrolysis. After purifying the $XeOF_4$, it was analysed, using the method of reduction by hydrogen:

$$XeOF_4+3H_2 \rightarrow Xe+H_2O+4HF.$$

An analysis was also made by mass spectroscopy.

Xenon oxide tetrafluoride is a colourless liquid stable at room temperature and can be kept in a nickel vessel for several days. It freezes at -41°C.[108] It is reported[101] that its melting point, measured in a sealed quartz capillary, is -28°C. The vapour pressure of $XeOF_4$ is ~8 mmHg at 0°C and ~29 mmHg at 23°C.[101]

The infrared spectrum of $XeOF_4$ vapour and the Raman spectrum of liquid $XeOF_4$ were studied by Smith[47,108] and by Claassen and coworkers[125]. The spectra are shown in Figs. 18 and 19, and the allocation of the frequencies according to Claassen and coworkers[125] in Table 2 (Smith's results[47,108] are only slightly different).

These results support a $XeOF_4$ structure with symmetry C_{4v}. The vibrational spectra of $XeOF_4$ and BrF_5 [126]

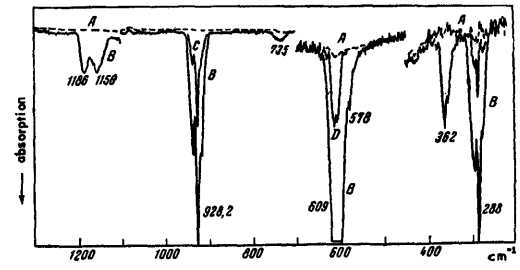


Fig. 18. Infrared spectrum of gaseous $XeOF_4$.[125] Optical path 10 cm: *A*) background; *B*) pressure of 30 mmHg; *C*) pressure of 2 mmHg; *D*) pressure of 1 mmHg.

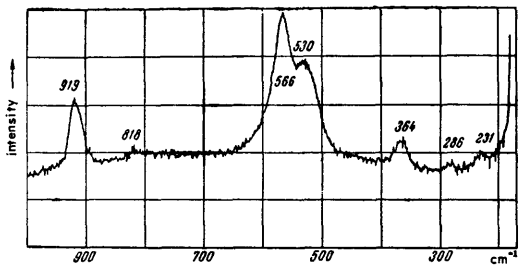
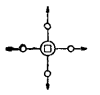
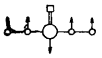
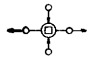
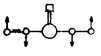
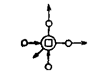
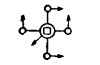


Fig. 19. Raman spectrum of liquid $XeOF_4$.[125]

TABLE 2. Assignment of the frequencies in the vibrational spectra of $XeOF_4$.[125]

	a_1	ν_1	RS, p IR	919 cm^{-1} (s.) 928 cm^{-1} (s.)
	a_1	ν_2	RS, p IR	566 cm^{-1} (v.s.) 578 cm^{-1} (v.s.)?
	a_1	ν_3	RS IR	286 cm^{-1} (v.s.) 288 cm^{-1} (s.)
	b_1	ν_4	RS	231 cm^{-1} (w.)
	b_2	ν_5	RS	530 cm^{-1} (s.)
	b_2	ν_6	RS	not observed
	e	ν_7	RS IR	not observed 609 cm^{-1} (v.s.)
	e	ν_8	RS IR	364 cm^{-1} (w.) 362 cm^{-1} (s.)
	c	ν_9	RS IR	161 cm^{-1} (v.w.) not observed
		$\nu_2+\nu_7$	IR	1186 cm^{-1} (w.)
		$2\nu_3$	IR	1156 cm^{-1} (w.)
		$2\nu_8$ and/or $\nu_7+\nu_9$ and/or $\nu_5+\nu_6$	IR	735 cm^{-1} (w.)
		$\nu_3+\nu_5$	RS	818 cm^{-1} (w.)

Note. The following abbreviations are used in the table: IR = infrared spectrum of gaseous $XeOF_4$; RS = Raman spectrum of liquid $XeOF_4$; p. = polarised; v.s. = very strong; s. = strong; w. = weak; v.w. = very weak intensity of band.

are very similar, and on this basis it was concluded[47,108] that the structures of these compounds are similar; consequently $XeOF_4$ has been given[47,108] the structure of a square pyramid with an atom of oxygen at the apex and the xenon atom is close to the plane of the four fluorine atoms.

The force constants for $XeOF_4$ were calculated[47,108] for idealised valency angles of 90°, and the values found (mdyn $Å^{-1}$) were: Xe–F stretching vibration, 3.20; Xe–O stretching vibration, 7.10; stretching interaction for Xe–F bonds at right angles, 0.12; stretching interaction for Xe–F bonds at 180°, 0.15. The high value of the constant for the stretching vibration of the Xe–O bond indicates that it possesses appreciable double-bond character.

The nuclear magnetic resonance spectra of ^{19}F and ^{129}Xe in $XeOF_4$ were investigated for liquid $XeOF_4$ [50] and for solutions of $XeOF_4$ in anhydrous hydrogen fluoride[49,127]. The triplet structure of the spectrum of liquid $XeOF_4$, consisting of a central line and a symmetrical doublet, agrees with the structure proposed on the basis of the spectral results. The doublet corresponds to the $^{129}Xe-^{19}F$ interaction; the coupling constant of which is 1086 Hz. The shielding constant is 326 parts per million (relative to F_2).[50] The double resonance spectra of ^{19}F and ^{129}Xe in a solution in anhydrous hydrogen fluoride has been recorded; as for liquid $XeOF_4$, the ^{19}F spectrum confirms the views about the equivalency of the four fluorine atoms. The chemical shift of ^{19}F is 292 parts per million and that of ^{129}Xe is 5511 parts per million (relative to HF). The constant of the $^{129}Xe-^{19}F$ interaction is 1163 Hz.[49,127]

2. Other oxide fluorides. Mass spectrometric investigations[117,118] showed the possibility of the existence of other oxide fluorides of xenon in addition to $XeOF_4$. The oxide fluoride XeO_2F_2 was obtained by slow, controlled hydrolysis of XeF_6 with subsequent careful separation of the reaction products[118]. The compound was identified mass-spectrometrically[118]. The authors[118] suggested that the hydrolysis of XeF_6 proceeds thus:

$$XeF_6+H_2O \rightarrow XeOF_4+2HF,$$
$$XeOF_4+H_2O \rightarrow XeO_2F_2+2HF,$$
$$XeO_2F_2+H_2O \rightarrow XeO_3+2HF.$$

The action of fluorine on xenon at 250–400°C in a flow system, using oxygen or air as carrier gas gave XeF_2 plus a little of a more volatile fraction with m.p. 90°C, b.p. ~115°C; in preliminary experiments this fraction was identified as $XeOF_2$.[64]

The oxide fluoride $XeOF_2$ was also prepared by passing an electric discharge through a 1 : 1 mixture of xenon and OF_2 at 195°K.[54] Fig. 7 (p. 406) shows the apparatus in which the experiments were made, the pressure in the reaction vessel was 3–62 mmHg and the discharge current was varied between 12 and 32 mA, and the potential between 1200 and 3600 V. The colourless crystals, whose analysis led to the formula $XeOF_2$, were stable at room temperature.

Heating a 1 : 1 mixture of xenon and OF_2 at 300–400°C led to the formation of colourless transparent crystals stable at room temperature and which readily sublime and grow to more than 2 mm. Analysis of the crystals gave the empirical formula $Xe_{1.2}O_{1.1}F_{3.0}$, close to the formula $XeOF_3$.[54] It is not clear whether this substance is an individual compound.

C. Oxygen compounds

1. Xenon trioxide. Xenon trioxide XeO_3, as noted above, is formed as a result of the neutral or acid hydrolysis of XeF_4,[62,128] in the prolonged action of XeF_6 on quartz[107] and in the slow hydrolysis of XeF_6 by water vapour[107].

The hydrolysis of XeF_4 in alkaline, neutral, and acid media was studied by Williamson and Koch[128], who showed that in the last two stages hydrated XeO_3 (the degree of

hydration was not found) is formed in the solution and on evaporating the solution at room temperature over barium oxide, colourless crystals are deposited. Analysis of these crystals, carried out by determining the atomic ratio O : Xe in their decomposition products, led to the formula XeO_3. The hydrolysis evidently proceeds according to the equation [104]:

$$3XeF_4+6H_2O\rightarrow XeO_3+2Xe+1{,}5O_2+12HF.$$

The mechanism of this reaction can be represented thus [63,104]:

$$2XeF_4+6H_2O \rightarrow 2XeO+XeO_4+12HF,$$
$$2XeO \rightarrow 2Xe+O_2,$$
$$XeO_4 \rightarrow XeO_3+0.5O_2.$$

No one has yet succeeded in establishing the existence of XeO, although a band spectrum observed in the electric discharge was ascribed to this molecule [129]. As regards XeO_4, this compound has been obtained and identified [130,131] (see next section).

As a result of the slow hydrolysis of XeF_6 at room temperature in the vapour phase, carried out analogously to that described above for $XeOF_4$ (see p. 412), colourless acicular crystals of XeO_3 were formed directly [107]. The hydrolysis follows the equation:

$$XeF_6+3H_2O \rightarrow XeO_3+6HF.$$

Xenon trioxide is a colourless involatile crystalline substance. Crystals of XeO_3 are strongly hygroscopic and so explosive that there is a great hazard in working with them. XeO_3 explodes on rubbing, compression, even on slight heating, and also in contact with cellulose-containing materials; explosions also occur near aqueous solutions. Crystals of XeO_3 are considerably less stable under conditions of even very slight humidity than in a dry atmosphere. Because of the risk of explosion (XeO_3 is comparable with trinitrotoluene as regards the force of explosion), working with quantities of XeO_3 exceeding 50 mg is not recommended [107]. A few hundred milligrammes of XeO_3 are sufficient to blow a hole in a Teflon plate 1 cm thick, or to rupture a desiccator [128]. It was noted [128] that preparations of XeO_3 obtained by hydrolysis of XeF_4 are more stable as regards detonation if the hydrolysis is performed with distilled water in the presence of traces of sulphuric acid (for example, 10 ml H_2O + 4 μl 1 M H_2SO_4 per 1 g XeF_4).

The chemical properties of solid XeO_3 have been little studied [107]. At a humidity greater than 25% crystals of XeO_3 start to deliquesce, bubbles appear in the liquid formed, and the XeO_3 is decomposed. When the deliquescing crystals of XeO_3 are in contact with copper, the liquid becomes pink and after drying a little dark residue is left. With nickel, a green residue remains. On adding XeO_3 to dilute ammonia and drying the solution a precipitate soluble in water is formed, whose infrared spectrum shows the presence of the NH_4^+ ion and of another ion absorbing at 790 cm^{-1}. This observation could be reproduced only once since usually XeO_3 exploded even in direct proximity to the solution.

Aqueous solutions of XeO_3 were investigated by Willamson and Koch [128,132] and also by Appelman and Malm [104,106]. The solubility of XeO_3 in water exceeds 2 M. [104] Measurements of Raman spectra of such solutions provide a basis for assuming that the dissolved substance is present in solution mainly as the molecule XeO_3, [104] but the degree and character of hydration were not established. The chemistry of aqueous solutions of xenon(VI) and xenon(VIII) compounds are considered in detail in the section dealing with xenic acids and their salts (see p. 415).

To determine the heat of formation of XeO_3 we measured the heat of explosion of XeO_3 calorimetrically [133]. The standard heat of formation of XeO_3 was found to be 96 ± 2 kcal $mole^{-1}$. The energy of the Xe–O bond in XeO_3 can be evaluated only approximately [143]; it is evidently considerably less than the energy of the Xe–F bond.

The crystal structure of XeO_3 was investigated by X-ray diffraction on single crystals [134,135]. Xenon trioxide is orthorhombic with parameters a = 6.163 ± 0.008, b = 8.115 ± ± 0.010, c = 5.234 ± 0.008 Å; space group $P2_12_12_1$; the density calculated for four formulae units in the unit cell is 4.55 g cm^{-3}. The XeO_3 molecule has the trigonal pyramid configuration; the distances and valency angles are shown in Fig. 20. The least O–O distance between different XeO_3 molecules is 2.91 Å, the remaining distances exceed 3.02 Å. Each xenon atom has, as well as the nearest atoms of oxygen, three neighbouring oxygen atoms of adjacent molecules at distances of 2.80, 2.89, and 2.90 Å. It was noted that the crystal structure of XeO_3 closely resembles that of HIO_3.

The explosibility of XeO_3 did not permit the Raman spectrum of this molecule to be investigated. Only the infrared spectrum of a thin film of XeO_3 in polyethylene could be recorded [47]. Absorption bands were observed in the 800 and 300 cm^{-1} regions and the principal frequencies were assigned by analogy with ClO_3^-, BrO_3^-, and IO_3^- ions: $\nu_1(a)$ 770 cm^{-1}, $\nu_2(a)$ 311 cm^{-1}, $\nu_3(e)$ 820 cm^{-1}, and $\nu_4(e)$ 298 cm^{-1}. The force constant of the principal stretching vibration (5.66 mdyn $Å^{-1}$) shows the considerable degree of double-bond character of the xenon–oxygen bond in XeO_3.

2. Xenon tetroxide. The existence of xenon tetroxide XeO_4 was first established by the mass-spectrometric analysis of the gas liberated during the reaction of sodium perxenate with concentrated sulphuric acid [130]. Then XeO_4 was obtained in quantities up to 100 mg by the reaction of sulphuric acid with sodium or barium perxenate in a glass U-tube [131]. As a result of the reaction a pale yellow substance condensed in a glass trap cooled by liquid nitrogen, and after its purification by sublimation its analysis indicated the formula XeO_4. It was analysed by determining the Xe : O_2 ratio in the decomposition products; these were identified by mass spectrometry.

Better yields of XeO_4 (34%) were obtained when the reaction was slow; the most satisfactory results were given by

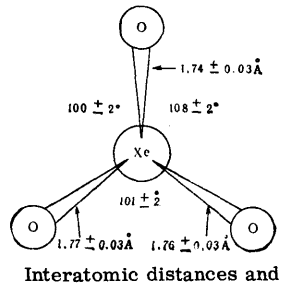


Fig. 20. Interatomic distances and valence angles of the XeO_3 molecule according to the X-ray diffraction data [134].

slow addition of the salt (preferably barium perxenate) to the acid cooled to -5°C.

The vapour pressure of XeO_4 is 3 mmHg at -35°, 10 mmHg at -16°, and 25 mmHg at 0°C. The specimen could be heated to 0°C only in rare instances; usually the substance decomposed (sometimes with explosion) before reaching this temperature, xenon and oxygen being formed.

Gaseous XeO_4 is relatively stable at room temperature also. This enabled its infrared spectrum to be studied (Fig. 21). The two intense bands were found to belong to XeO_4 and the weaker bands (marked X in Fig. 21) are obviously due to impurities. The frequencies corresponding to the maxima of the *P*-, *Q*-, and *R*-branches are: 298, 305.7, 314, and 870, 877, 885 cm^{-1}. In the infrared spectrum of XeO_4 only two frequencies are active: 877 (ν_3) and 305.7 (ν_4); the frequencies ν_1 and ν_2 are inactive. This circumstance and also the triplet structure of both bands, equally also the close similarity of the spectra of XeO_4 and IO_4^- provide a basis for assuming that the XeO_4 molecule has a tetrahedral structure and symmetry T_d, which had been predicted[136] even before the discovery of this compound. From the *Q*–*R* spacing, 16 cm^{-1}, the approximate length of the Xe–O bond in XeO_4 was found to be 1.6 Å.

3. Xenic acids, xenates, and perxenates. On the basis of the results of studies of the hydrolysis of XeF_4 and XeF_6 in acid, neutral, and alkaline media, conclusions have been drawn concerning the existence in solution under known conditions of unstable xenic acids: H_6XeO_6 with sexivalent xenon, and H_4XeO_6 with octovalent xenon. The salts of these acids were separated and named respectively xenates (Xe^{VI}) and perxenates (Xe^{VIII}).

Closely connected with the work on the isolation and study of salts of xenic acids is the investigation of the chemistry of aqueous solutions of Xe^{VI} and Xe^{VIII} compounds. Study of the chemical properties of solutions of XeO_3 showed[128] that even dilute solutions exhibit strong oxidising properties. Table 3 gives some qualitative results.

Koch and Williamson[132] investigated the kinetics of the reaction of aqueous XeO_3 with bromide and iodide ions. The reaction follows the equation:

$$XeO_3 \cdot aq + 6H^+ + 9X^- \rightarrow Xe + 3H_2O + 3X_3^- \ (X = Br, I).$$

From the experimental results curves were constructed of the dependence of the optical density on time, the order of the reaction was determined, and the activation energy was found.

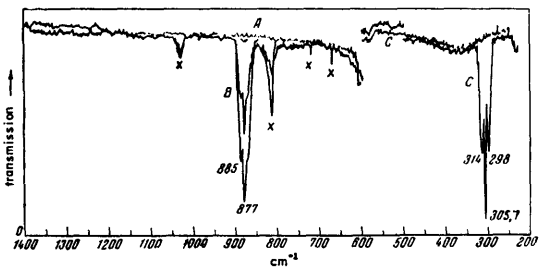


Fig. 21. Infrared spectrum of gaseous XeO_4:[131] *A*) background; *B*) optical path 10 cm, pressure unknown; *C*) optical path 10 cm, pressure 8 mmHg.

TABLE 3. Chemical reactions of XeO_3.aq.[128]

Reagent	pH	Product	
NH_3	6 M NH_4OH	presumably N_2	very vigorous
Excess of I^-	7 or less	I_3^-	rapid
3% H_2O_2	neutral	O_2	very vigorous
Excess of Br^-	1 or less	Br_2	slow
Fe^{2+}	neutral	Fe^{3+}	rapid
Hg	1 M H_2SO_4	Hg_2SO_4	rapid

Appelman and Malm[104], and also Appelman[106] made detailed studies of the chemical properties of solutions of compounds of xenon(VI) and xenon(VIII) using chemical analysis, cryoscopy, conductometry, pH measurement, and spectrophotometry in the ultraviolet region. During this investigation they isolated and characterised several salts of xenic acids.

Solutions of Xe^{VI} are strong oxidants, and there is simultaneous reduction of xenon to the elemental form. Iodide is oxidised by a Xe^{VI} solution to iodine very rapidly in acid solution, but rather slowly at pH > 7, and bromide is rapidly converted into bromine in 1 M HBr, but considerably more slowly at lower H^+ and Br^- concentrations. The Cl^- ion is oxidised to Cl_2 slowly in 2 M HCl, more rapidly in 3 M HCl, and very rapidly in 6 M HCl. Acid solutions of Mn^{2+} are oxidised to MnO_2 in a few hours and after 1–2 d MnO_4^- is formed. In 2 M $HClO_4$, iodine is very slowly converted into iodate. The rate of this reaction is considerably greater in 6 M $HClO_4$; at this concentration of the acid XeO_3.aq very slowly oxidises bromine to bromate.

The ultraviolet absorption spectra of Xe^{VI} solutions, according to Appelman and Malm's results[104], differ considerably from those given by Williamson and Koch[128]; the reason for the difference is not clear. On the basis of the pH dependence of the ultraviolet spectra and also the pH titration of XeO_3 solutions by alkali, it was concluded[104] that there is the equilibrium:

$$HXeO_4^- \rightleftarrows XeO_3 + OH^-.$$

with an equilibrium constant of $(6.7 \pm 0.5) \times 10^{-4}$ at 25°C. Possibly, however, ions of the type $H_5XeO_6^-$ are formed and also unchanged XeO_3 molecules with attached OH^- ions, for example, $XeO_3.OH^-$.[104] XeO_3 does not exhibit noticeable basic properties[104].

In the hydrolysis of XeF_6 by the action of 2.5 M sodium hydroxide, a solution of Xe^{VI} is formed instantaneously, which then undergoes slow disproportionation accompanied by deposition of a perxenate precipitate; the overall equation is:

$$2XeF_6 + 4Na^+ + 16OH^- \rightarrow Na_4XeO_6 + Xe + O_2 + 12F^- + 8H_2O.$$

The rate of this reaction is different in different experiments (the half-decomposition period varies from 2 to 20 h) and is greater than the disproportionation rate for pure XeO_3 in alkaline solution; it has been suggested[104] that the reaction is catalysed by impurities. However, the results of experiments on the disproportionation of solutions with XeO_3 concentrations < 0.0003 M in 1–4 M KOH previously treated with ozone to destroy reducing impurities were also non-reproducible.

In the dissolution of Na_4XeO_6 in water a strongly alkaline solution is produced (0.0036 M solution has, for example, pH 11.61 at 24°C):

$$Na_4XeO_6+H_2O \rightarrow HXeO_6^{3-}+OH^-+4Na^+.$$

An aqueous solution of Xe^{VIII} slowly liberates oxygen and is converted into Xe^{VI} solution; the rate of this process increases as the pH is reduced and at pH 7 the decomposition is almost instantaneous. The strong and rapid oxidising action of Xe^{VIII} solutions is accompanied by the reduction of Xe^{VIII} to Xe^{VI}. Xe^{VIII} solutions oxidise iodide to iodine very rapidly even in 1 M solution of a base; bromide is almost instantaneously oxidised to bromine at pH 9 and less, and chloride is converted into chlorine in dilute acid. The rapid oxidation of Co^{II} into Co^{III} and iodate into periodate takes place both in acid and in alkaline solution.

The results of studying the dependence of ultraviolet spectra of Xe^{VIII} solutions on pH and also the results of pH titrations are explained essentially by the equilibria [104,106]:

$$HXeO_6^{3-}+H^+ \rightleftarrows H_2XeO_6^{2-},$$

$$H_2XeO_6^{2-}+H^+ \rightleftarrows H_3XeO_6^-,$$

$$H_3XeO_6^- \rightarrow HXeO_4^-+0.5O_2+H_2O,$$

$$HXeO_4^-+H^+ \rightarrow XeO_3+H_2O.$$

The equilibrium constant of the reaction:

$$HXeO_6^{3-}+H_2O \rightarrow H_2XeO_6^{2-}+OH^-,$$

is $(2.4 \pm 0.5) \times 10^{-4}$.

The results obtained in investigating solutions of Xe^{VI} and Xe^{VIII} permitted an evaluation of the redox potentials [104]; the results can be expressed by the following schemes:

Acids

$$Xe—1.8—XeO_3—3.0—H_4XeO_6,$$

Bases

$$Xe—0.9—HXeO_4^-—0.9—HXeO_6^-.$$

The oxidising properties of xenic acid H_6XeO_6 with respect to a series of vicinal diols and organic alcohols was investigated qualitatively by Jaselskis and Vas [137]. The difference in oxidising action of xenic and iodic acids, which exhibit similar redox potentials, is attributed by these authors to the absence from aqueous solutions of stable oxidation states of xenon below Xe^{VI}. This conclusion agrees with the results of an investigation of the polarographic reduction of xenic acid [138]. The reduction of $XeO_3.xH_2O$ at a dropping mercury electrode proceeds in a single stage to xenon; the half-wave potential changes from -0.10 to -0.360 V relative to the Hg_2SO_4–Hg electrode, in the pH interval from 4.60 to 8.00. Sodium perxenate in alkaline solution is also reduced in a single stage; the half-wave potential changes from -0.21 to -0.31 V relative to the same electrode, in the pH interval from 10.1 to 11.3. [139]

The nuclear magnetic resonance spectrum of ^{17}O in H_6XeO_6 solution obtained by hydrolysis of XeF_6 showed a single line of width 420 Hz with chemical shift 278 ± 2 parts per million relative to water. The chemical shift which is close to that found earlier for perchloric acid and also for bromate, chlorate, and perchlorate ions, indicates that the xenon–oxygen bond in H_6XeO_6 possesses some double-bond nature [140].

As already noted repeatedly, Xe^{VIII} deposits precipitates of stable perxenates — salts of the acid H_4XeO_6 — which in many instances have been isolated and investigated.

Malm and coworkers [63] made the first experiments on the preparation of sodium perxenate. To a weighed portion of XeF_6, sublimed into a Pyrex glass vessel at a temperature close to that of liquid nitrogen, a large excess of 2 M NaOH was slowly added, the mixture was heated to room temperature, diluted with an equal quantity of water, and kept for about a day. The initial yellow colour of the solution gradually paled and a white precipitate came down; its analysis led to the formula intermediate between $Na_4XeO_6.2H_2O$ and $Na_6XeO_7.H_2O$. The yield of the product reached 80%. The substance obtained was completely stable, could be kept without change at room temperature and was decomposed with liberation of xenon and oxygen above 300°C, by which temperature the salt had not melted. The solubility of the dry salt in water at 25°C was 7 g litre^{-1}.

Further investigations [104] showed that this product contained sodium fluoride as an impurity. Purer preparations were obtained by ozonisation of a solution of XeO_3 in 1 M NaOH. The precipitation of sodium perxenate takes place in this almost quantitatively. The solubility of sodium perxenate in water is 0.025 M at room temperature, which permits the excess of base to be readily washed from the precipitate. The substance obtained is a white crystalline powder of composition Na_4XeO_6, containing from 0.6 to 6 molecules of crystallisation water per 1 g-atom Xe, depending on the conditions of drying, and a little sodium carbonate. Sodium perxenate is completely stable at room temperature, is dehydrated to the anhydrous salt at ~100°C and decomposes vigorously at 360°C. [141]

The reaction of 0.2 M $Ba(OH)_2$ with 0.007 M XeO_3 followed by drying in a stream of nitrogen, grinding and repeat drying in a vacuum over magnesium perchlorate gave a white stable product of empirical composition $Ba_2XeO_6.1.5H_2O.0.05BaCO_3$. As with the sodium salt, barium perxenate is stable at room temperature and is decomposed at ~300°C. [141] It is almost insoluble in water; at room temperature a saturated solution has a total concentration of only 2.3×10^{-5} M. [104]

Potassium perxenate could not be obtained by hydrolysis of XeF_6 with KOH solution, by disproportionation of a solution of Xe^{VI} in KOH and by ozonisation of a solution of Xe^{VI} in KOH; a salt $K_4XeO_6.2XeO_3$ was isolated [104]. However, $K_4XeO_6.9H_2O$ was obtained by the action of a little solid potassium permanganate on concentrated KOH solution, holding the solution at 70°C for 3 d (until the colour disappeared) and adding xenic acid (obtained by dissolving XeO_3) at 0°C in a vacuum [142].

Yellow uranyl and lead perxenates and black silver perxenate were obtained by the action of solid sodium perxenate on aqueous solutions of uranyl, lead, and silver nitrates [143]. Furthermore, there are reports of the preparation of calcium, lithium, and caesium perxenates [144].

The attempts of Appelman and Malm [104] to obtain barium xenate were unsuccessful, but Kirshenbaum and Grosse [105] prepared it and also reported the results of preliminary experiments on the preparation of the sodium and potassium salts of xenic acids.

The initial preparations of H_6XeO_6 were obtained by slow hydrolysis of XeF_4 or xenon oxide fluorides with water at 0°C. Removal of HF was effected by shaking the solution with a small excess of $CaCO_3$ or $Ca(OH)_2$ at 0°C; CaF_2 was formed, which was readily removed from the reaction zone. Solutions of H_6XeO_6 can be kept at temperatures from -20° to -30°C without decomposition for a few weeks [105].

On adding a solution of 3 moles $Ba(OH)_2$ to 1 mole H_6XeO_6 at 0°C a white amorphous precipitate was obtained, whose analysis gave the formula Ba_3XeO_6.[105] The yield of Ba_3XeO_6 reached almost 100% when the solution of the base was added rapidly enough to prevent decomposition of the acid.

Barium xenate is very poorly soluble in water: 0.25 g × × litre^{-1} at 20°C. At room temperature Ba_3XeO_6 is completely stable; slow decomposition starts at 125° and ends at 250°C. The decomposition of Ba_3XeO_6 follows the reaction:

$$Ba_3XeO_6 \rightarrow 3BaO+Xe+1.5O_2.$$

Sodium and potassium xenates have also been obtained[105], but have not been characterised completely. These salts are also stable at room temperature for at least a few months.

With the aim of determining the structure and configuration of the perxenate ion X-ray diffraction investigations have been made of $Na_4XeO_6.6H_2O$,[145] $Na_4XeO_6.8H_2O$,[146] and $K_4XeO_6.9H_2O$.[142] The results showed that these perxenates are orthorhombic and that the XeO_6^{4-} ion has the configuration of a regular octahedron: the mean Xe–O distance is 1.84 Å in $Na_4XeO_6.6H_2O$, 1.875 Å in $Na_4XeO_6.8H_2O$, and 1.86 Å in $K_4XeO_6.9H_2O$.

The investigation of the infrared spectra of the sodium, uranyl, lead, and silver perxenates[143] showed that all these compounds have an intense absorption band in the region 650–680 cm^{-1}, the position of which is independent of the nature of the cation. This band is related to the principal vibration of the XeO_6 octahedral group, which agrees with the results of the structural investigation.

The structural and spectrographic information and equally the results of studies of the Mössbauer effect in sodium perxenate[51,52], have been used to judge the structure of the perxenate ion.

The first investigation of the physiological action of compounds of Group 0 elements was made using sodium perxenate as example, by Finkel and coworkers[147]. They studied the metabolic and toxicological effects of injections of an aqueous solution of sodium perxenate on mice. It was established that sodium perxenate is of average toxicity in intravenous injection; the lethal does lie between 15 and 30 mg kg^{-1}. The perxenate introduced is rapidly reduced to elemental xenon, the bulk of which is lost from the body a few minutes after injection.

III. COMPOUNDS OF RADON AND KRYPTON

A. Radon Fluorides

The production of a stable radon fluoride of unknown composition[6] was described in the previous review[1]. In addition, there are indications of a volatile radon hexafluoride[148], which has still not been confirmed.

B. Krypton Compounds

1. Krypton tetrafluoride. After the preparation of compounds of xenon and radon, the natural interest concerned the problem of the possibility of preparing compounds of other Group 0 elements, above all those of krypton.

Experiments on the reaction of krypton with platinum and ruthenium hexafluoride on heating to 50°C were unsuccessful[121]. Attempts to prepare krypton fluorides by the reaction of gaseous krypton and fluorine at 400–500°C in a nickel vessel and also by irradiating mixtures of these gases with ultraviolet light at -60°C were also unfruitful[32].

Krypton tetrafluoride KrF_4 was obtained[54,149] by the action of an electric discharge on a mixture of krypton and fluorine. The experimental method was the same as was used in preparing xenon tetrafluoride (see p. 406). A 1 : 2 mixture (by volume) of krypton and fluorine was passed at 7–12 mmHg and at a rate of 125 cm^3 h^{-1} (s.t.p.) into a reactor cooled to -188°C by a mixture of liquid oxygen and nitrogen; the current was 24–37 mA and the potential 700–2200 V. The krypton tetrafluoride, whose yield reached 100% in isolated experiments, was deposited on the glass walls of the reactor as a white solid. After removing the unreacted krypton and fluorine by evacuation at -78°C, (as well as silicon tetrafluoride and oxygen), the KrF_4 was sublimed at -30° to -40°C into a glass vessel in which was dry powdered KF (as a getter for HF).

Krypton tetrafluoride forms colourless transparent crystals (Fig. 22). Thermally, KrF_4 is less stable than XeF_4, but at -78°C it can be kept without decomposition for several weeks. At 20° in a poly(chlorotrifluoroethylene) vessel with copper taps, KrF_4 slowly decomposes; it decomposes rapidly by the reaction:

$$KrF_4 \rightarrow Kr+2F_2,$$

at 60°C; the method of analysing KrF_4 is based on this reaction.

The temperature dependence of the vapour pressure of KrF_4 is expressed by the equation:

$$\log P_{mm} = 8.531 - 1930/T.$$

Fig. 23 shows the corresponding curve together with the vapour pressure curve of XeF_6 (see p. 410) for comparison. The heat of sublimation of KrF_4 is found to be 8840 ± ± 300 cal mole^{-1} by extrapolating to the sublimation temperature (at 760 mmHg), ~70°C.

The physical properties of KrF_4 have been insufficiently studied†. The ions KrF^+ and Kr^+ have been observed in

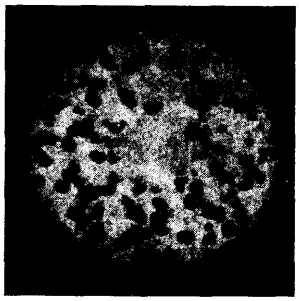


Fig. 22. Crystals of xenon tetrafluoride.

† The reader may like to consult F. Schreiner, J. G. Malm, and J. C. Hindman, J. Amer. Chem. Soc., 87, 25 (1965) who show that the preparation believed to yield KrF_4 actually gives KrF_2 (Ed. of Translation).

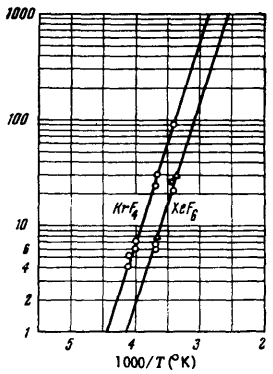


Fig. 23. Vapour pressure curves for KrF_4 [149] and XeF_6. [54]

the mass spectrum of KrF_4. [150] In the nuclear magnetic resonance spectrum of ^{19}F in krypton tetrafluoride dissolved in anhydrous HF a single ^{19}F resonance line was observed [151], with a chemical shift of 254 parts per million with respect to HF. On the basis of the nuclear resonance spectrum it was concluded [151] that the fluorine atoms in KrF_4 are equivalent and that exchange with the solvent does not take place to any significant extent. The absence of hyperfine structure obviously indicates a planar or pyramidal structure for the KrF_4 molecule.

2. Krypton difluoride. The first successful experiments on the preparation of krypton difluoride KrF_2 [152,153] employed the matrix-isolation technique [154]. A gaseous mixture with a molar ratio $F_2 : Kr : Ar = 1 : 70 : 220$ was slowly precipitated on a caesium fluoride window at 20°K. After recording the infrared spectrum of a specimen it was irradiated with the focussed light of a medium-pressure mercury lamp and the infrared spectrum again recorded. After it had been irradiated for 3 h a specimen gave an infrared spectrum with two absorption bands: at 580 cm^{-1} (half-width ~3.5 cm^{-1}, optical density 0.19) and at 236 cm^{-1} (optical density 0.04).

For the confirmation of the assignment of these bands to krypton difluoride, photolysis experiments were made under the same conditions with mixtures of fluorine and argon and of fluorine, xenon, and argon. In the first case there was no absorption, and in the second the spectrum showed the formation of XeF_2 and a trace of XeF_4.

The bands at 580 and 236 cm^{-1} in the infrared spectrum of KrF_2 belong respectively to the asymmetric stretching vibration ν_3 and the bending vibration ν_4 of a linear symmetric molecule. The values calculated for the force constants ($k_\gamma - k_{\gamma\gamma} = 2.59$; $k_\gamma + k_{\gamma\gamma} = 2.91$; $k_\delta/l^2 = 0.21$ mdyn $Å^{-1}$) were close to those found for XeF_2 (see p. 405)‡.

The preparation of KrF_2 in amounts of ~100 mg was brought about by subjecting a mixture of krypton and fluorine to a beam of electrons with energy 150 MeV at -150°C in a nickel vessel [155]. When the reaction had finished, the unreacted krypton and fluorine were evacuated and the KrF_2 was frozen out in a quartz trap at solid carbon dioxide or liquid air temperatures. At these temperatures KrF_2 is a fine white powder. KrF_2 sublimes under gentle heating without noticeable decomposition; in one experiment a colourless crystal measuring ~1 mm was obtained. This crystal did not change appreciably in 5 min at room temperature, and then suddenly decomposed with a small explosion.

The composition of the specimens was determined by decomposing them with mercury and analysing the decomposition products. Difficulties were encountered in measuring the vapour pressure of KrF_2, owing to the instability of this compound, but it was established that at -40°C the vapour pressure is 1.5–2 mmHg. [155]

An X-ray investigation of KrF_2 showed [156] that krypton difluoride is tetragonal with parameters $a = 6.533$ and $c = 5.831$ Å; the density for four formula units in the unit cell is 3.24 g cm^{-3}. It was noted that KrF_2 is not isostructural with XeF_2. Because crystals of KrF_2 decompose appreciably on irradiation, the X-ray diagrams were insufficiently sharp.

3. The complex of krypton difluoride with antimony pentafluoride. During the interaction of KrF_2 with antimony pentafluoride at -20°C in glass or poly(chlorotrifluoroethylene) vessels a white crystalline substance, whose analysis led to the formula $KrF_2.2SbF_5$, was formed [157]. It dissolves in an excess of SbF_5 at room temperature with the formation of a transparent, pale yellow solution, from which, after evacuation of the solvent at 25°C, the original complex separated again.

The complex $KrF_2.2SbF_5$ is considerably more stable and much less volatile than the initial krypton difluoride. It melts at ~50°C, but in the liquid state it decomposes rapidly with the formation of SbF_5, krypton, and fluorine. As might have been expected, the complex is exceptionally reactive and ignites organic materials with explosion. Solutions of the complex in antimony pentafluoride decompose slowly at 25°C; they are also quite reactive and attack poly(chlorotrifluoroethylene). The hydrolysis of the complex in a base or weak acid leads to the formation of not only krypton and oxygen, but also considerable amounts of OF_2. In the infrared spectrum of $KrF_2.2SbF_5$ a strong characteristic band was observed at 813 cm^{-1} and another strong, but badly resolved band in the region 600–700 cm^{-1}.

Preliminary experiments also showed that KrF_2 combines with AsF_5 at -78°C, but the addition product formed is very unstable and could not be isolated [157].

4. Kryptic acid and its barium salt. The hydrolysis of KrF_4 at room temperature proceeds almost quantitatively by the equation:

$$KrF_4 + 2H_2O \rightarrow Kr + O_2 + 4HF.$$

However, when hydrolysis takes place slowly at temperatures from -30° to -40°C the aqueous solution formed contains a very slight trace of a compound which exhibits oxidising properties and releases iodine from an acidified iodide solution. As careful experiments on the hydrolysis of KrF_4 with ice at -30°C showed [158], the solution after hydrolysis then contains 2–3 mole % kryptic acid, which oxidises potassium iodide solution by the reaction:

$$KrO_3 \cdot xH_2O + 6KI + 6HCl \rightarrow Kr + 3I_2 + 6KCl + (3+x)\,H_2O.$$

‡ The reader should refer to H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, J. Chem. Phys., 42, 1229 (1965) (Ed. of Translation).

The question of the valency of krypton in this acid, and consequently the formula of the acid, is still open.

To prepare the barium salt of kryptic acid[158], KrF_4 was hydrolysed at 0–5°C by $Ba(OH)_2$ solution. During the reaction gas was evolved and a white precipitate separated; it contained BaF_2 and barium kryptate. The precipitate was filtered off, washed with small portions of ice water, and dried at 0°C. The dry preparation is stable at room temperature, starts to decompose at ~50°C, and decomposes completely at 200°C. The results of chemical and mass spectrometric analyses of the gases evolved during the preparation, and also of the decomposition products of barium kryptate, agree with the formula $BaKrO_4$; the decomposition of the kryptate proceeds thus:

$$BaKrO_4 \rightarrow BaO + Kr + 1.5O_2,$$

and the reaction with acidified KI solution:

$$BaKrO_4 + 8HCl + 6KI \rightarrow BaCl_2 + 6KCl + 3I_2 + Kr + 4H_2O.$$

The yield of $BaKrO_4$ is ~7% , and the product contains BaF_2 ~ 95, $BaKrO_4$ ~ 5%. On the basis of studies of the salts of xenic and kryptic acids it is suggested that xenon and krypton may exist in nature not only in the atmosphere but also in hydrothermal minerals and in the oceans[105,158].

IV. THE CHEMICAL BONDS IN COMPOUNDS OF THE ELEMENTS OF GROUP 0

The first attempts at a theoretical description of the chemical bonds in the compounds of the elements of Group 0, made even before the discovery of these compounds, were those of Pauling[159] and Pimentel[160], who used the methods of valency bonds[159] and molecular orbitals[160]. Today, when as a result of the preparation of several compounds of xenon and krypton and the investigation of their chemical and physical properties it is already possible to make some generalisation about the experimental material, a considerable number of theoretical studies have appeared which are devoted to explaining the structure and the nature of the chemical bonds in these compounds[11,12,38,47,136,161-184].

Allen's model[11], based on calculation of the correlation effects in pairs of electrons with antiparallel spins was developed to some extent in the later work of Allen himself[161] and also in Michels' work[162]. However, this model was subjected to serious criticism by Coulson[163], in his review of the theories of the chemical bond in compounds of the elements of Group 0. Nevertheless it must be stated that with the aid of the correlation model the linear configuration of the XeF_2 molecule and the square planar structure of the XeF_4 molecule were first explained successfully.

The valency bond method with allowance for the hybridisation with participation of the *d* electrons of xenon was used by Allen and Horrocks[12] to explain the linear and square structures of XeF_4 and XeF_4 and to predict the configuration of certain (then as yet unobtained) xenon oxide fluorides. In a somewhat altered form this approach, together with the use of molecular orbitals (MO) was employed by Bersohn[164]. Gillespie[136] has made the most detailed application of the valence bond method to the compounds of xenon and the other elements of Group 0; with a view to explaining and predicting the configuration of the known and still unknown molecules and also to evaluate the bond lengths in these molecules by comparison with the interhalogen compounds. According to Gillespie, eight of the electrons of the outer shell of the Xe atom and one electron of each F atom (or two electrons of an O atom) form pairs, which either form bonds between the atoms or exist as lone pairs. The form of the molecule is eventually determined by the degree and character of the electrostatic repulsion of unshared pairs, of ordinary Xe–F bonds and of Xe=O double bonds. For example, the distribution of ten electrons (two ordinary bonds and three unshared pairs) in XeF_2, 12 electrons (four ordinary bonds and two unshared pairs) in XeF_4, and 14 electrons (four ordinary bonds, one double bond, and one unshared pair) in $XeOF_4$ leads to the known structures of these molecules. This theory predicts a distorted octahedral structure for XeF_6. The interatomic distances Xe–F in XeF_2 and XeF_4, and Xe–O in XeO_3, which were estimated, agree well with the experimental values.

Smith[38,47] came to analogous conclusions, reducing to a minimum the part played by ionic bonds in xenon fluorides, on the basis of an analysis of the vibrational spectra. Smith showed that for XeF_2 and XeF_4 the ratio of the constant valency interaction to a constant principal valence vibration is considerably less than for the ICl_2^- ion, the bonds in which are considered to be essentially ionic[185,186] and on this basis it was concluded that covalent bonds with participation of *d* orbitals play an extremely important part in xenon fluorides. According to this view, the structure of XeF_6 cannot be octahedral. Smith rejects the consideration of the bond in XeF_2 from the standpoint of the resonance of the $F-Xe^+F^-$ and F^-Xe^+-F structures, but Coulson[163], in considering this possibility in greater detail, concluded that it leads to a charge distribution in agreement with the experimental results.

The MO method, in which delocalised MO are constructed from the atomic 5*p* orbital of xenon and the 2*p* orbital of fluorine (without any participation of the *d* orbital), was employed by Rundle[165], using his earlier proposal to treat the structure of the interhalogen compounds with the aid of three-centre four-electron bonds. For example, for the XeF_2 molecule three MO's are obtained: bonding, non-bonding, and antibonding, in which the first two are occupied by pairs of electrons. In XeF_4 there are two choices of such orbitals, and in XeF_6 three. In accordance with this the XeF_6 molecule is given an octahedral structure. By comparing XeF_4 with IF_5, Rundle evaluated some thermodynamic and structural characteristics of XeF_4 and these values agreed satisfactorily with the experimental data.

Rundle's ideas have been developed further in subsequent studies[166-174] in some of which[167-173] there is a more quantitative approach. The calculations of Lohr and Lipscomb[170,171] by the MO–LCAO method, in which the MO were constructed with allowance for the 2*s* and 2*p* orbitals of fluorine and the 4*d*, 5*s*, and 5*p* orbitals of xenon, showed that the 4*d* electrons of xenon played a very small part in the bonds. According to Lohr and Lipscomb[171] KrF_4 should be stable but ArF_4 unstable; in both cases the calculations were carried out assuming a square planar structure for the molecule.

Hinze and Pitzer[167] also concluded that there was hardly any participation of the *d* orbitals in the bond formation. Jortner and coworkers[168,169] using the same model in principle, as Rundle, employed the semiempirical MO–LCAO method and concluded that the bond in xenon fluorides is described with the aid of delocalised MO's, which are formed by a combination of the 5*p* σ orbitals of xenon and the 2*p* σ orbitals of fluorine. The results of the authors'

theoretical calculations[168,169] were compared with spectroscopic data for XeF_2 and XeF_4 in the far ultraviolet region[43,86] and also the results of determinations of the heats of sublimation of these fluorides[42]. The experimental results agree with the proposed model; comparison of theoretical and experimental data led the authors[168,169] to conclude that the essential contribution to the stability of crystalline XeF_2 and XeF_4 is provided by electrostatic interaction, due to the transfer of charge from the xenon atom to the fluorine atoms. The ionic character of the halides of the Group 0 elements also follows from Waters and Gray's calculations[172], made within the framework of the simple MO method.

Some authors have used the MO method with allowance for the *d* orbitals of xenon. Boudreaux[70] studied the 5*p*, 5*d*, 6*s*, and 6*p* orbitals of xenon and the 2*p* orbitals of fluorine and showed that the bond in XeF_4 has mainly a *p* character, but partially *d* and *s* character. The results of his calculations of the magnetic susceptibility of XeF_4 [69] agree with the experimental results and confirm his proposed model. The scheme of MO's proposed by Israéli[175,176] was also constructed with allowance for the *d* orbitals of xenon. In this case qualitative consideration led to agreement with the experimental results on the geometrical configuration of the xenon fluorides.

Nesbet[177] proposed that the bond in the xenon fluorides is similar to the mechanism of indirect exchange in the antiferromagnetic oxides of type MnO. Nesbet's ideas and conclusions were criticised by Allen[161].

The work of Bilham and Linnett[178] was devoted to the approximate calculation of XeF_2 by the valency bond method with allowance for four electrons and the island $F^+Xe^{2+}F^+$. The wave functions of the molecule are constructed from the $2p_z$ orbitals of two fluorine atoms and one $5p_z$ orbital of a xenon atom in the assumed linear structure of the molecule. Calculations for XeF_6, made by the MO–LCAO method, led to an octahedral structure for this molecule[179]. The electronic structure of the kryptates and xenates was considered by Urch[180]. The ion XeO_6^{4-}, in all probability, exhibits octahedral symmetry. In this problem there is no difference between the MO method and the valency bond method.

The above ideas were subject to some criticism both from theoretical positions and also by comparison with experimental results[110,163,181,183]. Coulson[163] discussed the merits and deficiencies of the various models and came to a conclusion that the correlation model[11] and the models using the hybridisation of the *d* electrons[12] (in this case the excitation energy of the electrons to the *d* level is too high) were inapplicable; Coulson considered that both the MO theory and the valence bond theory with allowance for resonance in the structure (see p. 419) are suitable for describing the chemical bonds in the compounds of the Group 0 elements. Both these theories give a charge distribution of $F^{-\frac{1}{2}}-Xe^{+1}-F^{-\frac{1}{2}}$ for XeF_2; in XeF_4 and XeF_6 the charge migration is somewhat less. Such a charge distribution agrees with the results derived from investigations of the nuclear magnetic resonance[49,50,91–94,187,188].

Hemmerlich[181] and Noyes[183] consider the most acceptable treatment from the position of the theory of three-centre four-electron MO.[165,169] This theory well explains the spatial configuration of the compounds of xenon and gives interatomic distances in these compounds which agree satisfactorily with the experimental values. The considerable degree of ionicity of the bonds in the xenon fluorides, resulting from this consideration, also agrees with the experimental results. Thus the essential role of ionic bonds in xenon fluorides is demonstrated by the chemical shifts measured by the nuclear magnetic resonance method (Fig. 24); for XeF_4 this is also apparent from the asymmetry of the resonance lines (see p. 409). The results of a study of the Mössbauer effect in the xenon fluorides[51,52], the heats of sublimation of XeF_2 and XeF_4,[42,168,169], and certain other physical and chemical properties of xenon compounds have also been interpreted from this viewpoint.

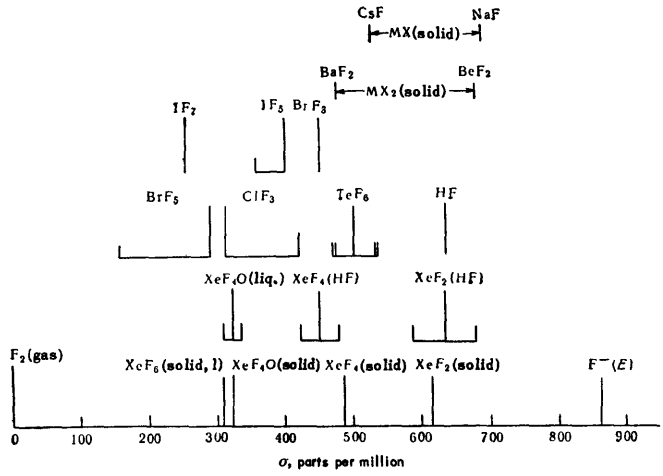


Fig. 24. Shielding constants σ for some fluorides[50].

Consideration by the valence bond method also gave a series of results agreeing with the experimental data[136]. In general, in most instances the MO theory and the valence bond theory lead to the same configuration and this agrees with experiment. The essential difference between the methods considered occurs, however, in the case of XeF_6. For this molecule the valence bond theory leads to a non-octahedral structure, whereas consideration by the MO method leads to regular octahedral structure. Unfortunately the experimental results have still not made possible the solution of this question.

Each of the theories has, naturally, its merits and its drawbacks; Coulson[163], for example, notes that the valence bond theory is simpler and more graphic, but states that the MO method is more suitable for considering different electron transitions. The most important conclusion, which can be drawn on the basis of the theoretical discussions, is the absence of a necessity to postulate any new type of bond for the compounds of the Group 0 elements and the possiblity of a semiquantitative explanation of the experimental facts with the assistance of existing theoretical concepts.

V. SOME THERMODYNAMIC CONSIDERATIONS

One of the most astonishing experimental facts revealed in the process of investigating xenon compounds, was the thermodynamic stability of many of these compounds. The standard heat of formation of gaseous XeF_2 is -37 ± 10 kcal × × $mole^{-1}$.[44] Evaluation of this value for solid XeF_2 from spectrographic data led to the value -20 kcal $mole^{-1}$,[116] but Hoppe[189], as the result of a comparison of the bond

energies of the xenon fluorides and the halogen fluorides, concluded that it should be greater. For XeF_4, ΔH° = = -60 kcal mole^{-1},[71] and ΔG° = -29.4 kcal mole^{-1}. For XeF_5, ΔH° = -79 kcal mole^{-1}.[72] The xenon oxides, however, are thermodynamically unstable.

Some investigators attempted, by more or less complex calculations, to evaluate the thermodynamic stability of Group 0 element compounds not yet obtained and so to decide the question of the possibility of obtaining these or other compounds. Waters and Gray[172] calculated by the simple MO method, the energy of formation from the elements and the energy of dissociation of the halides of the Group 0 elements. They found the following values (in kcal mole^{-1}) for the dissociation energy: XeF_4 123.1, KrF_4 23.5, ArF_4 -30.7, NeF_4 -507.1, $XeCl_4$ -50.9, $KrCl_4$ -137.4, XeF_2 11.1, KrF_2 -5.3, $XeCl_2$ -42.9. Bartlett[18,190] started principally from a comparison of the mean bond energies of the compounds of the Group 0 elements with other halides and oxides. He evaluated the mean bond energy (in kcal): $KrF_2 \sim 30$, $KrF_4 \sim 19$, $KrF_6 \sim 18$, and $XeCl_4 \sim 10$, and concluded that the first three were exothermic and the fourth endothermic.

Although the results of all the calculations demonstrate sufficiently convincingly the thermodynamic instability of the compounds of even argon, Pimentel and Spratley[173,191] consider that the existence of a helium fluoride HeF_2 is possible; these authors calculated the infrared spectrum of the hypothetical molecule HeF_2 and considered possible methods for obtaining HeF_2 based on the β discharge of tritium nuclei, the irradiation of lithium fluoride with slow neutrons and the bombardment of metal fluorides with α particles[191]. Noyes[183] briefly considered various possibilities for the formation of still unknown compounds of Group 0 elements and proposed for these elements the group name "aerogens".

VI. POSSIBLE APPLICATIONS

The interest in the compounds of the elements of Group 0 is obviously not due solely to their theoretical importance. It must be supposed that such broad development in the investigations also had some practical aims. Unfortunately this question has only been touched upon and then in very few works.

The question of the potential applications of the compounds of Group 0 elements has received the most detailed consideration in the article by Pomeroy[192]. He noted the important part played by the xenon isotopes ^{133}Xe and especially ^{135}Xe, which exhibits a very large cross-section for the capture of thermal neutrons ($> 10^6$ barns) in industrial nuclear energy and briefly considered the possiblity of using them as solid, and not gaseous compounds. On the other hand, there is the interesting possibility of recovering radioactive xenon and krypton, formed in the operation of a nuclear reactor, as fluorides or other compounds of low volatility.

The xenon fluorides can serve as "stores" of xenon and fluorine; it is possible that they will show promise as oxidants for rocket fuels[14,192]. The regeneration of xenon from its fluorides, particularly the complex ones, can prove to be a good method of obtaining pure xenon. The possibility of an analogous use of krypton fluorides is not excluded, although their instability can create obvious difficulties.

The xenon oxides very easily detonate and are highly explosive; it is possible that their ability to explode without leaving traces of solid substances can be utilised[14,192].

Compounds of xenon, especially the xenates and perxenates, may find many uses as oxidants in carrying out various processes[192].

Finally, it can be suggested that if the radon fluorides prove to be involatile they will find wider application in radiation therapy than gaseous radon, the use of which sometimes is hazardous[14].

Undoubtedly in the very near future a profitable use will be found for the compounds of the elements of Group 0. Even now for inorganic chemistry the immense value of the discovery and study of these substances is completely indisputable, and it is possible, finally, to visualise a further wide development of manifold investigations in this interesting and promising field.

NOTE ADDED IN PROOF

Whilst this article was in the press several papers dealing with the compounds of the elements of Group 0 were published; they include both reviews[193-201] and original work[202-210].

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THE CHEMISTRY OF DECABORANE AND ITS DERIVATIVES

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1. INTRODUCTION

Decaborane† is one of the most interesting representatives of the boron hydrides, information about which before the nineteen-fifties was restricted to Stock's unique monograph [1].

After World War II, in connection with the vigorous development of reaction propulsion for aviation there arose the need to devise a more effective aviation fuel than hydrocarbons. The high calorific value of boron hydrides served as an impetus to the intensive investigation of the chemistry of decaborane, the most stable boron hydride. In view of the complex constitution of decaborane the establishment of its structure was the first task.

This problem was solved by the combined forces of a large group of physicists and chemists.

This review surveys all the main literature on the chemistry of decaborane and also that on the structure and reactivity of its stable derivatives — anions of the $B_{10}H_{10}^{2-}$ type, barenes (carboranes), etc.

† Strictly, decaborane(14), according to the nomenclature recommended in the Preliminary Report of the Advisory Committee presented at the 125th Meeting of the American Chemical Society, 25th March, 1954. This nomenclature has been used where possible in this translation (Ed. of Translation).