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Compounds of the Noble Gases

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The results of investigations of the physical and chemical properties of compounds of the noble gases and their structure, stability, and reactivity are given; the principal methods of synthesis are considered. Special attention is paid to the latest achievements in this field—to investigations of complexes, derivatives of xenon fluorides and oxo-acids, xenon hexafluoride, and the study of the electronic structure. Non-empirical methods of calculation on the bonding in noble gas compounds are discussed and their results are compared with experimental results obtained with the aid of photoelectronic and X-ray electronic spectroscopy. Possible practical uses of the compounds of the noble gases are considered on the basis of the material presented. There is a bibliography of 400 references.

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I. INTRODUCTION

The development of the new field of inorganic chemistry—compounds of the noble gases—which began not much more than ten years ago is still continuing, although the direction and nature of the investigations has undergone certain changes. Whereas in the first two years after the discovery of this new class of substances (1962–1964) there appeared many papers dealing with their preparation and preliminary study, subsequent years are distinguished by a broadening and simultaneous deepening of the investigations, by the isolation of a series of new, previously unknown compounds, and also by continuation on a more complete basis of the theoretical comprehension of new experimental results. A significant increase in the importance of the work of Soviet scientists is also characteristic for this period of time.

The studies of the first two years were reflected in a review[1] published in 1965. It is now opportune to systematise the many new experimental and theoretical results to create a complete picture of the present state of investigations of the compounds of the noble gases. The present review has this aim and deals with the literature available to the authors in January 1974.

During the years which have elapsed since the first review was published[1] there have appeared several publications[2-12] which treat in more or less detail the particular aspects of the problem being considered. Of these, we think that of Dyatkina[2] merits special attention, in which a detailed analysis is given of all investigations of the nature of the chemical bond in compounds of the noble gases, and also the reviews of Malm and Appelman[3], Holloway[4], and Jha[5]. Because of this, in the present review greater attention is paid to papers published after 1969.

For brevity and also with the aim of simplifying the exposition, the molecular constants and physical properties of the most studied compounds of xenon and krypton are given in Tables 3 and 5, and in the text are given only those data which require explanation or serve for subsequent discussion.

II. XENON COMPOUNDS

A. XENON FLUORIDES

1. The Fluorine–Xenon System

The fluorine–xenon system has been investigated[13] over a wide range of temperature and pressures. The processes taking place in this system are described by the following consecutive-concurrent reactions:

$$Xe + F_2 \rightleftarrows XeF_2;\ K_2 = [XeF_2]/[Xe][F_2];$$
$$XeF_2 + F_2 \rightleftarrows XeF_4;\ K_4 = [XeF_4]/[XeF_2][F_2];\ K_4^* = [XeF_4]/[Xe][F]^2;$$
$$XeF_4 + F_2 \rightleftarrows XeF_6;\ K_6 = [XeF_6]/[XeF_4][F_2].$$

Table 1 gives experimental and calculated (in parentheses) equilibrium constants.

The equilibrium constants showed[16] that XeF_2 and XeF_6 can be easily obtained in the pure form, whereas there are no conditions which would ensure that the XeF_4 concentration in the equilibrium mixture exceeds 91 vol.%. At an initial molar ratio of $Xe : F_2 \geq 1.4$ the equilibrium mixture consists almost solely of the excess of xenon and XeF_2. In every instance the equilibrium is reached rather rapidly above 250°C. The optimal conditions of synthesis of the pure xenon fluorides at various temperatures have been determined[17].

An investigation of equilibria in the fluorine–xenon system showed[13] that a xenon fluoride with the ratio $F:Xe > 6$ does not exist even under conditions of high pressures (500 atm, 250°C). Other work[18] agrees with this result and also refutes a previous report[19] of the synthesis of xenon octafluoride.

Table 1. Equilibrium constants of the reactions for the formation of xenon fluorides[13].

Equilibrium constant	25°	250°	300°	350°	400°	500°
K_2	$(1.23\cdot10^{13})$	$(8.8\cdot10^{4})$	$(1.02\cdot10^{4})$	(1670)	(360)	29.8
K_2[14]	$(7.23\cdot10^{12})$	—	$(7.74\cdot10^{3})$		(285±49)	—
K_4'[15]	$(1.65\cdot10^{24})$	$(1.1\cdot10^{8})$	$(1.49\cdot10^{6})$	$(4.14\cdot10^{4})$	$(1.98\cdot10^{3})$	(14.4)
K_4	$(1.35\cdot10^{11})$	1431	154.9	27.22	4.857	0.5020
K_6	$(8.2\cdot10^{5})$	0.9435	0.2112	0.05582	0.01822	—

The reaction rate in the fluorine–xenon system depends on the diameter of the reaction vessel and the state of its surface[16]. The reactions for the formation of the xenon fluorides are mainly heterogeneous and take place on the fluorinated walls of the reaction vessels or at the surface of certain metal fluorides, for example, CoF_3, NiF_2, or CaF_2. The catalytic influence of these fluorides was investigated[20] at 300–450°C and pressures of 1.5–2.0 atm and is tentatively explained by the formation of the complexes $XeF_6.CoF_3$, $XeF_6.NiF_2$, etc. The existence of such compounds was confirmed[21] by the investigation of interaction in XeF_6–metal fluoride systems: $XeF_6.2CrF_2$, $XeF_6.CoF_2$, and $XeF_6.2FeF_2$ were prepared. Slivnik and coworkers[22,23] investigated the catalytic influence of highly disperse nickel and magnesium fluorides on the reaction between xenon and fluorine (1 : 10) and found that at 120°C XeF_2 is almost the only product in the presence of MgF_2, whereas in the presence of NiF_2 the only reaction product is XeF_6 even at the molar ratio $F:Xe = 5$. Chromium, vanadium, and manganese fluorides also exert a catalytic influence[24].

The catalytic formation of XeF_2 on heated metals has been investigated[25]. This process is catalysed only by metals which form ionic fluorides, for example, Ni, Pd, Co, Cu, Al. Investigation of the adsorption of xenon in the presence of fluorine on nickel and palladium[26] suggested that the stage determining the rate of catalytic formation of XeF_2[25] is the desorption of XeF_2 from the metal surface.

2. Xenon Difluoride

a. Methods of Preparation

Most of the papers on the preparation of noble gas compounds belong to the first period of investigation[1]. No method new in principle has originated in recent years.

Almost pure XeF_2 can be obtained by the interaction of xenon and fluorine ($Xe:F_2 = 1.3–2.0$) in the temperature range 400–500°C at pressures of 0.5–27 atm.[27,28] XeF_2 can also be prepared in a cylindrical flow reactor filled with a nickel packing with a contact surface of 0.2 m^2, when heated to 600°C and at a total pressure of 650 mmHg.[29] XeF_2 is formed in good yield in a mixture of xenon and fluorine (1 : 1 by volume) subjected to a glow discharge[30]. The yield of XeF_2 increases with the rate of flow of the mixture through the reactor.

XeF_2 of high purity has been prepared photochemically[31–34]. Small quantities of XeF_2 can be obtained in quartz or Pyrex vessels by irradiation of mixtures of xenon and fluorine (600–1000 mmHg, $Xe:F_2 = 1:1$) with daylight. However, when the conversion reaches 60% the xenon difluoride begins to be contaminated with the tetrafluoride[33]. The irradiation of a mixture of xenon and fluorine with the light from a high-pressure mercury lamp is recommended[35,36] as a convenient method of obtaining pure XeF_2. The photochemical interaction of xenon with OF_2 leads to the formation of XeF_2.[31]

Xenon difluoride is obtained in 98% yield by the reaction of xenon with an excess of O_2F_2[37] at −118°C and O_4F_2.[38] The reaction of xenon with fluorine in the gaseous and condensed phases under the action of protons with energies of 10 MeV at temperatures from −78° to −180°C can be used for the synthesis of XeF_2.[39] XeF_2 is also formed by the reaction of xenon with fluorine in shock waves[40] at 1100°C.

b. Physical Properties of XeF_2

The vapour pressure of XeF_2 in the temperature range 0–115°C is expressed by the equation[41]

$$\lg P_{mmHg} = -3057.67/T - 1.23521 \lg T + 13{,}969736.$$

The density of liquid XeF_2 in the temperature range 115 to 90°C is given by the expression[42]:

$$\rho_{g\,cm^{-3}} = 3.641 - 3.96\cdot10^{-3}\,t.$$

The heat capacity of XeF_2 was measured[14] by an adiabatic method in the temperature range from −268° to 77°K.

The standard enthalpies of formation of XeF_2, and also XeF_4 and XeF_6, obtained by different methods[13,43–45] are somewhat different. Johnson and coworkers[45] consider the results of the calorimetric investigation of the reaction of solid XeF_n with phosphorus(III) fluoride to be the most reliable.

As an extension of the earlier[1] spectroscopic investigations, the infrared, Raman, and ultraviolet spectra of gaseous and solid XeF_2 have been studied. The high-resolution infrared spectrum of gaseous XeF_2 was investigated in the range of the ν_3 vibrations (544–574 cm^{-1}).[46] An analysis of the spectrum led to the following molecular constants: $\nu_0 = 560.101\ cm^{-1}$, $B_0 = 0.11350\ cm^{-1}$, $\alpha_3 = 3.31\times10^{-4}$, $X_{23} = -1.44\ cm^{-1}$. The B_0 found was used to calculate the bond length $r(Xe–F) = 1.997 \pm 0.0015$ Å.

The laser Raman spectrum of XeF_2 has been obtained and interpreted[47]. The very interesting band at 514.5 cm^{-1} has been assigned to the ν_1 symmetric stretching vibration. The agreement with the predicted $\nu_1 = 515\ cm^{-1}$ (from the composite band $\nu_1 + \nu_3$ at 1070 cm^{-1} in the infrared spectrum of XeF_3)[48] shows the very low anharmonicity of the vibrations of the XeF_2 molecule.

The investigation of the spectra of gaseous and solid (−193°C) XeF_2 in the far ultraviolet range (50–160 eV)[49] enabled information to be obtained about the excited electronic levels of the molecule and to assign the absorption lines in the range 61–73 eV on the basis of a semi-empirical calculation.

Radioelectronic[50,51] and photoelectronic spectroscopy[52–54] have played a large part in the study of the structure of noble gas compounds, especially XeF_2. The results for XeF_2 obtained by these methods are discussed in Chapter V.

NMR and EPR methods have also been used for studying XeF_2. In ^{19}F NMR the variation of the second moment of the rigid XeF_2 lattice with the external magnetic field has been measured [55]. The magnetic screening parameters do not agree with the results of semiempirical calculation [56]. The EPR of γ-irradiated XeF_2 were investigated at 77°K. [57] The spectrum obtained was assigned to the XeF radical; the parameters of the spin-hamiltonian of XeF in the XeF_2 and XeF_4 lattices [58] differ slightly. In connection with the EPR results it is interesting to note that the hypothetical formation of XeF in the gas phase [40, 59-61] has still not been confirmed experimentally [62]. A calculation by the SCF MO method showed that the $^2\Sigma^+$ and $^2\Pi$ states of XeF are repulsive and the XeF radical should not exist in the gas phase in the free state [63].

The deflection of an XeF_2 molecular beam in a heterogeneous electric field has been studied [64]. The results obtained confirmed the structure $D_{\infty h}$ for this molecule. The emission spectrum of a Xe + BF_3 (NaF, LiF) mixture in a microwave discharge [65] is characterised by the existence of two groups of bands of different intensity, assigned to XeF_2: 3510, 2635 and 3080, 2355 Å.

c. Chemical Properties

Behaviour of XeF_2 in Non-Aqueous Solvents

Xenon difluoride dissolves in BrF_3, [66] BrF_5, [67] HF, [68] IF_5, [69] SO_2, [69] and CH_3CN. [70] The solubility of XeF_2 in IF_5 reaches 1538 g per 1000 g IF_5. [71] Different opinions [72-74] have been expressed about the behaviour of XeF_2 in IF_5. The most complete picture of the interaction in the IF_5–XeF_2 system was obtained in investigating the equilibrium diagram [71,75] (Fig. 1). Fig. 1*b* shows the so-called "transitional" equilibrium diagram obtained at temperatures up to 80°C. At 80°C the irreversible conversion of the unstable solvates $XeF_2.nIF_5$ (n = 1.5–9) into $XeF_2.IF_5$ takes place. An attempt [76] to reproduce the earlier results [72-74] led to the production of only $XeF_2.IF_5$, which according to spectroscopic, Raman, and X-ray diffraction results is a molecular compound [76]. $XeF_2.IF_5$ is tetragonal with parameters a = 7.65, b = 10.94 Å, space group $I4/m$. The structure (Fig. 2) shows the existence of the discrete molecules XeF_2 ($D_{\infty h}$) and IF_5 (C_{4v}). [77]

The maximal solubility of XeF_2 in BrF_5 is 1893 g per 1000 g bromine pentafluoride [78]. Xenon difluoride dissolves readily in anhydrous HF; at −2°C the solubility is 6.38 moles XeF_2 per 1000 g HF and increases with the temperature. The enthalpy of dissolution is 2.5 kcal $mole^{-1}$. The investigation of the electrical conductivity of such solutions, their Raman spectra, and ^{19}F NMR led to a conclusion about the solubility of XeF_2, in molecular form, in HF. [68] The solubility of XeF_2 in 3HF.NOF is unusually high [79]: 73.25 wt.% at 16.8°C.

Xenon difluoride is slightly soluble in Mo and W hexafluorides. According to DTA results [80], the unstable compounds $XeF_2.MoF_6$ and $XeF_2.WF_6$ are formed in the WF_6–XeF_2 and MoF_6–XeF_2 systems.

The solubility of XeF_2 in acetonitrile at 0°C is 16.8 g and that at 21°C 32.0 g per 100 cm^3 solvent [70]. Xenon difluoride is oxidised at the boiling point of acetonitrile [69]. XeF_2 dissolves in dimethyl sulphoxide (DMSO) and pyridine but not in liquid ammonia [69]. XeF_2 forms the complex $XeF_2.2Bipy$ with bipyridyl [72].

The behaviour of XeF_2 in various solvents was investigated by infrared spectroscopy [81]. A shift in the frequency of the vibrations of the Xe–F bond into the longer-wave range with increase in the donor strength of the solvent was noted and this can be regarded as qualitative indication of the weakening of this bond.

The XeF_2–XeF_6 system has a simple eutectic [82].

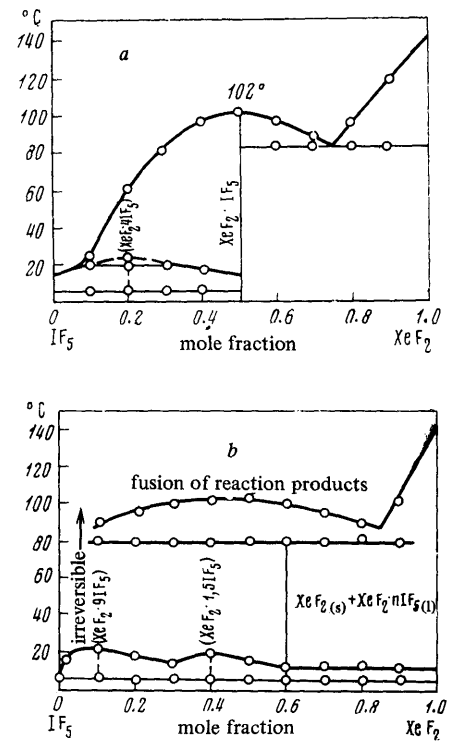


Figure 1. *a*) Equilibrium diagram of the IF_5–XeF_2 system; *b*) "transitional" equilibrium diagram of the IF_5–XeF_2 system.

Redox Reactions of XeF_2

It would seem that in redox fluorination reactions XeF_2 from both the thermodynamic and kinetic viewpoints does not compete with such powerful fluorinating agents as molecular fluorine, oxygen fluorides, certain halogen fluorides, etc. However, this "kinetic inertness" is the merit of XeF_2 and simplifies the practice of oxidising fluorinations.

DTA has shown [83] that at moderate temperatures XeF_2 reacts with many elements: with Mo at −11°, W (21°), Te (16°), S (27°), P (−10°), Ge (−12°), Si (16°), Nb (6°), Ta (22°), Sb (33°), Sn and Ti (28°), etc. In all these reactions higher fluorides of the corresponding elements are formed. XeF_2 reacts with elemental bromine and iodine with the formation of BrF_3 and IF_5. On the basis of the results of an investigation of the reactions of XeF_2, of the calculations of the free energies of the corresponding processes, and also of the relative reactivities of the halogen fluorides [84] a series for the relative fluorooxidising capability of XeF_2 has been compiled [83]:

$$ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > XeF_2 > IF_5 > BrF\ .$$

The high fluorinating activity of XeF_2 also appears in reactions with WO_3 (27°), U_3O_8 (67°), Nb_2O_5 (49°), V_2O_5 (26°), KBr (21°), KI (12°), KIO_3 (47°), and $NaBrO_3$ (41°), as a result of which higher fluorides, $KBrF_4$, KIF_6, and $NaBrO_2F_2$ are formed[88]. Solid XeF_2 reacts at 20°C with ICl and ICl_3 with the formation of IF_5.[85] Chromium(V) fluoride fluorinates XeF_2 to XeF_4 at 120°C, and at 60°C a mixture of $XeCr_2F_{10}$ and XeF_4 is formed[86].

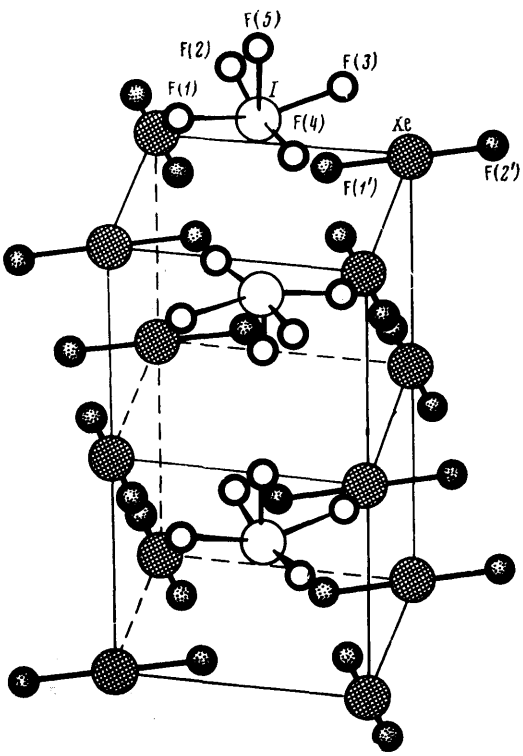


Figure 2. Crystal structure of $XeF_2.IF_5$.

A qualitative investigation of the oxidising power of xenon fluorides was carried out in the case of their interaction with UF_4.[87] The greatest rate of fluorination is observed with XeF_6.

Xenon difluoride is used as fluorinating agent for obtaining the higher fluorides of the rare-earth elements (r.e.e.). When mixtures of XeF_2 and TbF_3 are heated to 300–350°C, TbF_4 is formed[88,89]. The reaction of XeF_2 with the fluoro-complexes of tervalent r.e.e. can be used to obtain compounds of Ce^{IV}, Pr^{IV}, and Tb^{IV} of composition Cs_8LnF_7.[90]

The oxidising reactions of XeF_2 in solutions of non-aqueous solvents are interesting. In acetonitrile, the reactions of XeF_2 with I_2, SO_2, and SO_3 take place with the formation of IF_5, SO_2F_2, and $S_2O_6F_2$ respectively[67]. The reactions are catalysed appreciably by traces of HF and BF_3, which is probably linked with the formation of the cations XeF^+ and $Xe_2F_3^+$ in the solutions[67]. The catalytic influence of certain fluoro-acids on the formation of BrF_3 was investigated[83]; the rate constants observed are characterised by the catalytic activity of certain fluoro-acids in the reactions of XeF_2 with Br_2 in BrF_3 solutions (s^{-1}) at 19°C: 0.0081 (XeF_2), 0.016 ($XeF_2 + TaF_5$), and 0.045 ($XeF_2 + SbF_5$). The order of increase of the rate constants $BrF_3 < TaF_5 < SbF_5$ ($k_{BrF_3} : k_{TaF_5} : k_{SbF_5} = 1:2:6$) agrees with the relative acceptor capability of these fluorides[91]. The reaction of XeF_2 with the oxides of As, P, and Sb in BrF_3 leads to the formation of AsF_5, PF_5, and SbF_5.[66] In the presence of AsF_5, BF_3, PF_5, or TiF_4, xenon difluoride decomposes acetonitrile[92].

Solutions of XeF_2 in CCl_4 are stable up to the boiling point of CCl_4.[93] In the presence of traces of Group V element halides, XeF_2 reacts with CCl_4 with the formation of Freons, SiF_4, Xe, and Cl_2. The reaction of XeF_2 with $SiCl_4$, $TiCl_4$, and $SnCl_4$ leads to the formation of tetrafluorides[93]; when there is an excess of XeF_2 the compounds $2XeF_4.MF_4$ (M = Sn or Ti) are formed. $2XeF_2.ZrF_4$ and $2XeF_2.HfF_4$ are formed in the direct interaction of the fluorides[93].

In HF solutions xenon difluoride reacts with $Re_2(CO)_{10}$ with the formation of ReF_5.[94] Tungsten and molybdenum carbonyl fluorides can be obtained analogously[95]. Marshall and Peacock[96] reported the production of Re, Mo, Ru, and Os carbonyl fluorides by the reaction of XeF_2 with carbonyls and carbonyl chlorides of the corresponding metals. They also obtained the double carbonyl fluorides $Mo(CO)_3F_2.MoF_5$, $Re(CO)_5F.ReF_5$ of tungsten, osmium, iridium, and rhodium[97].

Reactions of XeF_2 in Aqueous Solutions

Xenon difluoride dissolves readily in water but the solutions are unstable[98]. The solubility of XeF_2 in the molecular form has been shown by the ultraviolet spectra[99] and electrical conductivity[100,101] of its aqueous solutions.

The hydrolysis of XeF_2 is a first-order reaction, the rate constant in pure water being 2.8×10^{-5} s^{-1} at 0° and 25×10^{-5} s^{-1} at 25°C.[102] The activation energy of hydrolysis is 18.4 kcal $mole^{-1}$.[103] The rate constant for the hydrolysis of XeF_2 in 0.01 M $HClO_4$ is 42×10^{-5} s^{-1} at 25°; the activation energy is 20.2 kcal $mole^{-1}$.[104] The rate of hydrolysis of XeF_2 in water is minimal in the range pH 4–9.[105] The hydrolysis is strongly catalysed by bases, the anions F^-, NO_3^-, HCO_3^-, CO_3^{2-}, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, and by the cations Th^{4+}, Al^{3+}, La^{3+}, and Be^{2+}.[104,105] The rate of hydrolysis of XeF_2 also increases with the concentration of HF in the solution[106]. The results obtained in investigating the hydrolysis of XeF_2 in neutral aqueous solutions are explained[104] by the reactions:

$$XeF_2 + H_2O \rightarrow XeO + 2HF;\ XeO + H_2O \rightarrow$$

$$\rightarrow Xe + H_2O_2;\ H_2O_2 + XeF_2 \rightarrow Xe + 2HF + O_2,$$

which have also found experimental confirmation[104,107].

Aqueous solutions of XeF_2 exhibit a pronounced oxidising ability. The redox potential of the XeF_2/Xe couple in acidic medium $XeF_{2(aq)} + 2H^+_{(aq)} + 2e^- = Xe_{(g)} + 2HF_{(aq)}$ is estimated[3] to be 2.64 V ($\Delta G^\circ_{298}XeF_{2(aq)} = -20.35$ kcal $mole^{-1}$). Other results[108] obtained by use of the Powell and Latimer equation for aqueous solutions of non-electrolytes, give $E^\circ_{(XeF_2/Xe)} = 2.3$ V. The bromate ion was oxidised by XeF_2 in aqueous solutions, which enabled previously unknown perbromates to be synthesised, in particularly $RbBrO_4$.[109] Xenon difluoride also oxidises iodates and chlorates[110–112]. In alkaline solutions, XeF_2 oxidises astatides to perastatate[113], Np^V and Np^{VI} to Np^{VII}.[108,114]

Reactions of XeF_2 with Organic Compounds

The use of elemental fluorine in organic chemistry is very limited and requires a special technique [115]. The use of other fluorinating agents, such as HF, certain metal fluorides, or interhalogen compounds, while allowing fluoro-substituted compounds to be obtained, results in low yields and poor selectivity. Xenon fluorides, and XeF_2 in particular, have been investigated recently as promising fluorinating agents.

Xenon difluoride reacts with an excess of benzene in CCl_4 in the presence of small quantities of HF with the formation of fluorobenzene [116] (68% yield on the benzene); with substituted benzenes in CCl_4 or CH_2Cl_2 the corresponding fluorobenzenes are formed [117]. These investigations [116,117] showed that the use of XeF_2 gives a possibility of changing the Balz–Schiemann reaction for obtaining fluorinated aromatic compounds. The conversion is effected in a single stage, which is an advantage in comparison with the usual three-stage process [115].

An investigation of the reactions of XeF_2 with benzene and its derivatives by an EPR method allowed the formation of intermediate *para*-substituted radical-cations of the polyphenyls $R(C_6H_4)_2R^+$, where R is Cl, CH_3, F, or $F-C_6H_4-C_6H_4$, to be established [118]. On this basis it was concluded that XeF_2 initiates the generation of radical-cations, in particular from compounds with a relatively high oxidation potential. The results obtained are explained satisfactorily within the framework of a mechanism [119] which postulates the formation of an intermediate complex and a radical-cation.

Xenon difluoride reacts with 1,1-diphenylethylene in the presence of HF and CF_3CO_2H as catalysts with the formation of 1,2-difluoro-1,1-diphenylethanes (yield 65–95%). [120] Aromatic compounds are fluorinated not just in solutions; XeF_2 readily replaces hydrogen in benzene and its derivatives in the gas phase [121] at 100–200°C. Pentafluorophenyl peroxide has been isolated [122] by the reaction of XeF_2 with pentafluorophenol in acetonitrile. Ethylene reacts with XeF_2 with the formation of 1,2-di- and 1,1,2-trifluoroethanes with yields of 35 and 20% respectively [123]. XeF_2 reacts with propene with the formation of a multicomponent mixture of volatile substances. Propyne resists the action of XeF_2; only after 100 days at room temperature is 2,2-difluoropropane formed (33% yield) [123].

In acetonitrile, XeF_2 reacts with certain organometallic compounds containing Si–Si, Si–H, Si–C (allyl), or Si–O bonds [124]. With chlorine-containing compounds the following substitutions take place:

$$2\,R_3SiCl + XeF_2 \rightarrow 2\,R_3SiF + Cl_2 + Xe\ [R = CH_3,\ C_2H_5,\ R_3 = C_6H_5(CH_3)_2]\ ,$$

$$R_3SiHCl \xrightarrow{XeF_2} R_3SiHF \xrightarrow{Cl_2} R_3SiClF \xrightarrow{XeF_2} R_3SiF_2\ [R_3 = C_6H_5(CH_3)]\ .$$

An effective oxyacylation of benzene is effected in the presence of XeF_2. [125] Oxyacylation was studied by the example of the reactions of benzene with toluic acid, benzoic acid and its nitro- and fluoro-derivatives; the corresponding phenyl benzoates are formed:

$$RCOOH + C_6H_6 + XeF_2 \rightarrow RCOOC_6H_5 + Xe + 2HF\ .$$

The activation energy of the oxybenzoylation of benzene in the presence of XeF_2 is 16 kcal mole^{-1}. [126] The yield of esters is 50–70%. In the absence of benzene the carboxylic acids in the RCOOH + XeF_2 + CCl_4 mixture undergoes decarboxylation with the formation of hydrocarbons and their fluoro-derivatives.

Xenon difluoride participates in solvolysis with alcohols; reaction with C_1–C_4 primary aliphatic alcohols leads to the formation of aldehydes [127]. The rate constants for the oxidation decrease with increase in the length of the carbon chain. The direct fluorination of pyridine by xenon difluoride in the gas phase at 100°C leads to rapid polymerisation of pyridine [128]. In the fluorination of liquid pyridine, 2-, 2-, and 4-monofluoro-derivatives are formed in 10% yield (on XeF_2), which then are also polymerised. The fluorination of 2-fluoropyridine allows all the disubstituted products to be synthesised, mainly the 2,5-difluoro-isomer [128].

3. Xenon Tetrafluoride

The principal methods of synthesis of XeF_4 were described in the previous review [1]. Xenon tetrafluoride can be obtained by thermal, photochemical [33], and radiation [39] methods, and also by the action of a glow discharge. The synthesis of comparatively pure XeF_4 can be effected at 400°C and a total pressure of the mixture of xenon and fluoride of 7 atm ($Xe : F_2 = 1 : 5$). [129] After an hour the yield of XeF_4 reaches 90%. The purification of XeF_4 from the impurities XeF_2 and XeF_6 is effected on metal fluorides, owing to the differing abilities of the xenon fluorides for complex formation [91,130]. XeF_4 is also purified effectively by gas–liquid chromatography [131–133]. This method is recommended as a preparative method for the synthesis of the pure individual fluorides of Xe and for their quantitative analysis [132,133].

Xenon tetrafluoride readily sublimes at room temperature. The vapour pressure over solid XeF_4 is represented by the equation [41]:

$$\lg P_{mmHg} = -3226.21/T - 0.43434\ \lg T + 12.301738\ \ (2-117^\circ)\ .$$

The density of supercooled liquid XeF_4 is described by the equation [42]:

$$\rho(g\ cm^{-3}) = 3.500 - 4.05\ 10^{-3}\ t\ \ (110-50^\circ)\ .$$

The heat capacity of XeF_4 has been measured [15] in the range 5–350°K. The laser Raman spectrum [47] of gaseous XeF_4 has been interpreted and compared with the Raman spectrum of solid XeF_4. As a result of a study of the spectra of gaseous and solid (–193°C) XeF_4 in the far ultraviolet range (50–160 eV) [49] information has been obtained about the excited electronic levels of this molecule and the absorption lines in the range 61–73 eV have been assigned on the basis of a semiempirical calculation.

Brundle and coworkers [53] investigated the photoelectronic spectrum of XeF_4 with a high resolution by use of HeI and HeII radiation. The electron-impact excitation method was also used for studying XeF_4. [134]

The ^{19}F NMR method was used to study the variation of the second moment of XeF_4 with temperature and the external magnetic field for a rigid lattice and for higher temperatures, when the molecular motion leads to some narrowing of the absorption lines [135]. The magnetic screening parameters found do not agree with the results of a semiempirical calculation [56]. The results of an investigation of the deflection of an XeF_4 molecular beam in a non-homogeneous electric field [64] confirmed that the structure of this molecule was D_{4h}.

Xenon tetrafluoride dissolves in anhydrous HF [68] and in liquid NOF.3HF. [79] The results of an investigation of the electrical conductivity of the XeF_4 solutions and of their ^{19}F NMR spectra show the solubility of XeF_4 in the molecular form in HF, [68] NOF.3HF, [79] and IF_5. [136] The results obtained by various investigators [69,137] for solutions of XeF_4 in IF_5 disagree. The most reliable results are those of Sladky and Bartlett [76], who found that specially

purified XeF_4 dissolves readily in IF_5 without any reaction even in the presence of AsF_5.

Xenon tetrafluoride reacts[69] with NH_3, AsF_3, CCl_2F–$CClF_2$, C_6H_5N, CH_3CN, and $(CH_3)_2SO$ with the formation of the same products as for XeF_2, but the oxidising properties of XeF_4 in these reactions is more clearly expressed. With perfluoropropene, XeF_4 forms perfluoropropane; 1,2-di and 1,1,2-tri-fluoroethane are formed with ethylene; cyclohexane is fluorinated to fluorocyclohexane. With aromatic compounds, XeF_4 takes part in substitutions[123]: benzene is fluorinated to fluorobenzene; toluene to *o*-, *m*-, and *p*-fluorotoluenes, fluorobenzene to the *o*-, *m*-, and *p*-difluorobenzenes, hexafluorobenzene to perfluorocyclohexane, perfluoro-1,4-cyclohexadiene, and perfluoro-1,3-cyclohexadiene. Unlike those of XeF_2, the reactions of XeF_4 take place in the absence of a catalyst[123].

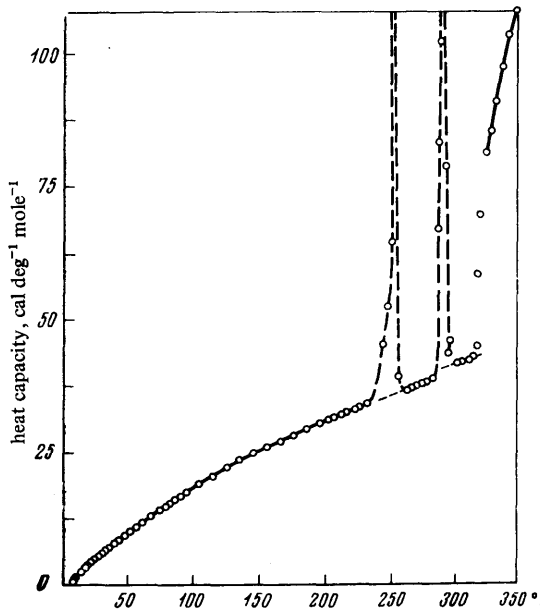


Figure 3. Temperature dependence of the molar heat capacity of xenon hexafluoride.

As a result of the hydrolysis of XeF_4, solutions of XeO_3 are obtained[98,138]:

$$3XeF_4+6H_2O\rightarrow XeO_3+2Xe+{}^3/_2O_2+12HF.$$

Owing to the extremely violent nature of the reaction, the hydrolysis was carried out[139,140] by the slow addition of water to XeF_4 cooled by liquid nitrogen followed by heating the "frozen" mixture.

An attempt to use XeF_4 for obtaining solutions of Pu^{VIII} from Pu^{VII} was unsuccessful[141]. Testing for sensitivity to shock and detonation stability showed that XeF_4 is not an explosion hazard[142]. However, it often explodes when mixed with substances of organic origin.

4. Xenon Hexafluoride

Xenon hexafluoride can be obtained by heating a mixture of xenon and fluorine (1 : 10 or 1 : 20) at 200–300 °C for 15–17 h and a total pressure of 30–50 atm.[17,143] XeF_4 is removed most effectively on sodium fluoride[1]. XeF_6 can also be obtained by a radiation method[39].

The density of XeF_6 was measured[144] over a wide range of temperatures. An equation was derived for the temperature dependence of the molar volume of XeF_6. The following analytical expressions were found[144] for the vapour pressure of XeF_6:

$$\lg P_{mmHg} = -3313.5/T + 12.5923, \quad \text{(from -19° to 18.65°C)};$$

$$\lg P_{mmHg} = -3093.9/T + 11.8397, \quad \text{(from 18.65° to 49.23°C)};$$

$$\lg P_{mmHg} = -6170.88/T - 23.67815 \lg T + 80.77778, \quad \text{(from 49.38° to 76.85°C)}.$$

The second virial coefficient is determined by the relation[144]: $B = -1.143 \times 10^8 T^{-2}$ cm^3 mole^{-1}. The relatively small B (−955 cm^3 mole^{-1} at 73 °C) shows the monomericity of XeF_6 in the gas phase; this agrees with the results of measurements of the vapour density of XeF_6 at 73 °C and 494 mmHg,[144] and at 25 °C and 15 mmHg.[13] Another picture is observed in liquid xenon hexafluoride. In the range from the melting point of XeF_6 (49.48°) to 100 °C the Raman spectra[145] and heat capacities[144] as well as the unusually high entropy of vaporisation at the boiling point clearly show either polymerisation or a high degree of association in the liquid.

Table 2. Crystalline modifications of XeF_6.[149]

Phase and temp. limits of existence, °C	Characteristics of the crystal lattice							
	a	*b*	*c*	angle, deg	*Z*	ρ_{calc}, g cm^{-3}	space group	structural element
Monoclinic, from 49.48 to 18.65	9.33	10.96	8.95	β 91.9	2	3.56	$P2_1/m$ or $P2_1$	2 tetrameric rings of XeF_5^+ groups and F^-
Orthorhombic from 18.65 to −19.35	17.01	12.04	8.57	—	16	3.71	$Pnma$	4 tetrameric rings of XeF_5^+ groups and F^-
Monoclinic below −19.35	16.80	23.93	16.95	α 90.7	64	3.825	$P2_1/b$	16 tetrameric rings of XeF_5^+ groups and F^-
Cubic from −180 to 49.48	25.06	—	—	—	144	3.73	$Fm3c$	24 tetrameric and 8 hexameric rings of XeF_5^+ groups and F^-

The heat capacity of XeF_6 was investigated[144] in the temperature range 5–350 °K. Fig. 3 shows the variation of the molar heat capacity of XeF_6 with temperature. The distinct maxima are due to phase transformations in the solid state. Investigations[146–151] of the crystal structure of XeF_6 made by X-ray diffraction and neutron diffraction methods, confirmed the polymorphism of this compound and the existence of four crystalline modifications (Table 2).

The structure of the cubic phase of XeF_4 has been studied in most detail[147,151]. An X-ray diffraction examination of a single crystal was made at 93 °K. The main structural elements are XeF_5^+ tetragonal pyramide, the five vertices of which are occupied by fluorine atoms. The pyramids are connected with one another by bridges of fluoride ions into tetrameric and hexameric rings (Fig. 4) which are found in the structure in right and left forms; there are for the hexameric rings an ordered, and for the tetrameric rings a disordered, alternation of enantiomorphic forms. The polymeric rings are three-dimensional and also have an almost spherical form.

The tetramer (Fig. 4*a*) is an eight-membered ring consisting of four XeF_5^+ ions and four F^- ions. In the XeF_5^+ ion the interatomic distances are (the F atoms at the vertices are denoted F*a*, and those in the basal plane F*b*): Xe–F*a* = 1.83 Å, Xe–F*b* (mean) = 1.84 Å, F*a*–F*b* (mean) = 2.29 Å, F*b*–F*b* (mean) = 2.54 Å. The mean angles are: F*a*–Xe–F*b* = 77.2°, F*b*–Xe–F*b* = 87.2°. The bridging F^- is 2.23 Å from one Xe and 2.60 Å from the other; the angle in the bridge is 120.7°.

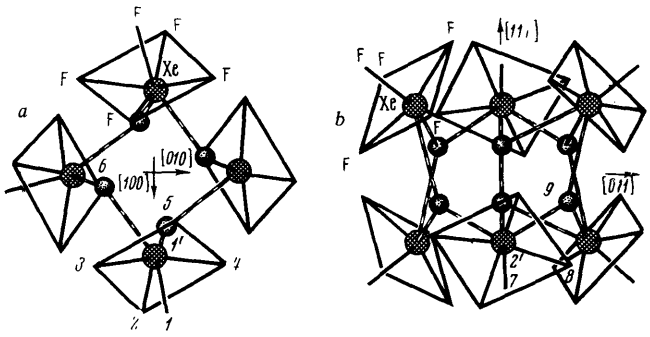


Figure 4. *a*) Structure of the tetrameric rings in the crystal lattice of xenon hexafluoride; *b*) structure of the hexameric rings in the XeF_6 crystal lattice.

The hexamer (Fig. 4*b*) is a twelve-membered ring of six XeF_5^+ ions and six F^- ions. In the XeF_5^+ the distances are: Xe–F*a* = 1.75 Å, Xe–F*b* = 1.88 Å, F*a*–F*b* = 2.33 Å, F*b*–F*b* = 2.62 Å. The angles are: F*a*–Xe–F*b* = 80.0°, F*b*–Xe–F*b* = 88.3°. The bridging F^- are 2.56 Å from each of the Xe; the angle in the bridge is 118.8°.

The polymeric nature of xenon hexafluoride in condensed phases does not allow the structure of the XeF_6 molecule to be found by investigations of, for example, crystal structure, as has been done for XeF_2 and XeF_4. The problem of the structure of XeF_6 is therefore still the subject of discussion and its solution must evidently be sought in an investigation of the gas phase, where the XeF_6 molecules are monomeric.

As even the first investigations of the vibrational spectra showed[1], XeF_6 differs from all the known hexafluorides and evidently exhibits a symmetry other than octahedral. Interest in the structure of XeF_6 has also been aroused by the fact that the first calculation made within the framework of the valence-bond theory predicted a non-octahedral structure for the then still hypothetical XeF_6 molecule, whereas in accordance with a semiempirical calculation by the MO method O_h symmetry is preferable for XeF_6.[1] In discussing these results, Dyatkina[2] suggested that the success of the valence-bond theory in this instance was only apparent, since certain arbitrary assumptions were made in the calculation.

In attempting to explain this difference and also the earlier experimental results, Goodman (see Holloway[5]) advanced a hypothesis according to which these results are completely compatible with the ground state O_h and a low-lying triplet state ^3T_u which can be thermally populated at room temperature. However, measurements of the magnetic susceptibility of XeF_6 showed[152,153] temperature-independent diamagnetism; this signifies that over the entire range of temperatures studied (that is, in the condensed phases) the ^3T_u state is not occupied. An investigation of the deflection of a molecular beam in a non-homogeneous magnetic field[154] led to the same conclusion extended to the gas phase.

An investigation of the deflection of a molecular beam of XeF_6 in a non-homogeneous electric field[64] showed that XeF_6 has a structure with a symmetry-forbidden dipole moment.

After the first electron diffraction investigations[155,156] which showed, as did theoretical results[157,158], that XeF_6 did not have octahedral symmetry, Gavin and Bartell[160] made a careful electron diffraction investigation of gaseous XeF_6 and thoroughly discussed the results in conjunction with the accumulated experimental and theoretical data[159,161].

The results of the investigations[160] seemed incompatible with a regular octahedral configuration for the XeF_6 molecule, in which there are independent normal vibrations. Some asymmetry of the radial distribution in the region of the Xe–F bonds shows the existence of non-equivalent bonds; the mean length of the Xe–F bond is 1.890 Å. The mean square amplitude of the vibrations for non-bonded fluorine atoms l(F...F) = 0.07 Å is somewhat less than l(Xe–F) = 0.08 Å. According to Bartell and Gavin[160,161], the electron diffraction results show either distortion of an octahedral configuration with displacement of the fluorine atoms towards a configuration with C_{3v} or (less probably) C_{2v} symmetry, or that in the XeF_6 molecule there exists an inversion motion (combination of deformation vibrations t_{1u} of very large amplitude and t_{1g}) with a minimum energy at the configuration with symmetry O_h. Theoretical consideration[159,161] showed that in the XeF_6 molecule there can exist conditions under which there appears a pseudo Jahn-Teller effect, brought about by distortion of the O_h configuration as a result of the deformation vibration of type t_{1u} (see Dyatkina[2]).

The results of early investigations of the vibrational spectra of XeF_6[1,162] were discussed by Glass[163] who drew the conclusion that the ground state of gaseous XeF_6 has symmetry O_h but unusual electronic properties affect the width of the bands.

On the basis of a simplified electronic model of XeF_6 derived to explain the "anomalies" of the electronic isomerism hypothesis, Goodman[164] concluded that gaseous XeF_6 at normal temperature is a mixture of three isomers differing in electronic states and geometric configurations (Fig. 5). In addition to the ground state $^1A_{1g}$ (O_h) in the lowest positions, there are also $^3A_{2u}$ (D_3d), and ^3Eu (D_3d) excited states, 450 and 1200 cm^{-1} respectively away from the ground state, due to the Jahn–Teller effect.

The results of an extensive spectroscopic investigation made by Claassen and coworkers[165] were interpreted in the spirit of Goodman's hypothesis. They measured the spectra of gaseous XeF_6 in the visible and ultraviolet ranges, the Raman spectra in the range from the boiling point of XeF_6 (76°C) to 150°C, the infrared spectrum and Raman spectrum in an argon matrix at 4°K, and also reproduced the earlier measurements[162] of the infrared spectrum of gaseous XeF_6.

According to Clarassen and coworkers[165], the temperature dependence of the spectra in the visible and ultraviolet regions confirms Goodman's hypothesis. Using results obtained at 298.1°, 323.6°, and 365.6°K, and the statistical weights of the three isomers calculated according to Goodman, three spectral curves were constructed

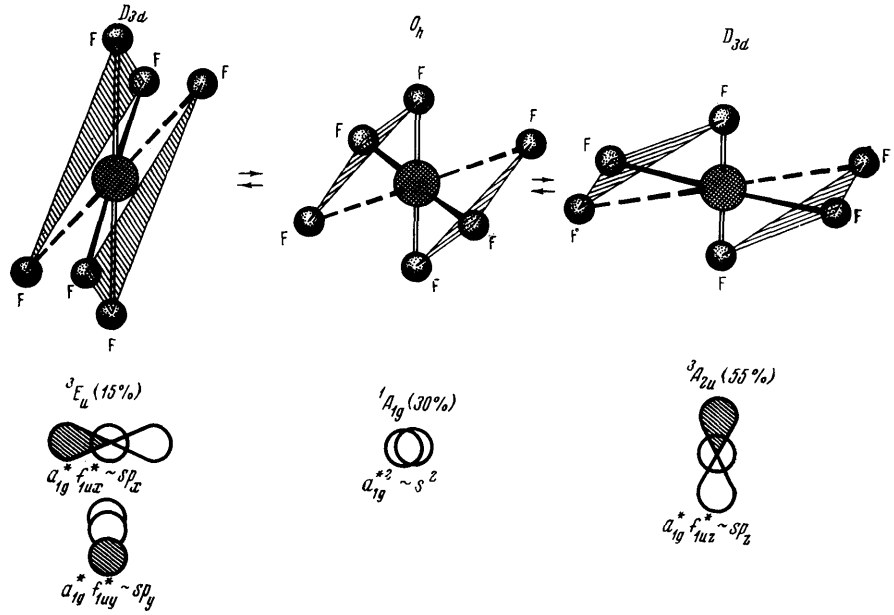


Figure 5. Electronic isomers of xenon hexafluoride; in parentheses, the statistical weights of the isomers.

in this way a spectrum measured at each of these temperatures was resolved into three temperature-independent spectra. The frequencies in these spectra were not assigned in this paper [165].

On the basis of the laser Raman spectra and their temperature dependence it was concluded that gaseous XeF_6 consists of two or more species, the relative concentration of which is a function of temperature. The interpretation of the infrared and Raman spectra, based on the hypothesis of electronic isomerism, led to a satisfactory (in the opinion of these investigators [165]) assignment of the bands to transitions in the isomers or between the isomers.

Mention has been made of the significant influence of preliminary heat treatment of the specimen on the infrared [165,166] and Raman [165] spectra of matrix-isolated XeF_6 molecules. The question of solid-state pseudorotation has been discussed [167].

The dependence of the second moment of polycrystalline XeF_6 on temperature and the external field has been studied by the ^{19}F NMR method [168]. The values found for the magnetic screening parameters are comparable with the corresponding values for UF_6, PuF_6, OsF_6, PtF_6, and MoF_6.

The solubility of XeF_6 in anhydrous HF also shows an anomaly in comparison with other hexafluorides [169]. At room temperature the solubility (moles per 1000 g HF) is: MoF_6 1.50, WF_6 3.14, UF_6 0.49, ReF_6 1.75, OsF_6 0.97, XeF_6 8.6. The results of the measurements of electrical conductivity and of the Raman spectra of solutions show that all the above hexafluorides except XeF_6 dissolve in the molecular form. The anomalously high electrical conductivity of XeF_6 in HF shows strong ionic dissociation in the solution. The solubility of XeF_6 in BrF_5 is ~11 moles per 1000 g BrF_5 at 25°C. [170]

Hydrolysis of XeF_6 takes place with the formation of xenon trioxide [98]:

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

Hydrolysis can be effected most simply and safely by using argon or helium as carrier [171,172] and also at liquid nitrogen temperature.

5. Complexes of Xenon Fluorides

After the years which have elapsed since the discovery of noble gas compounds, there have been considerable developments in investigations of the interaction of these compounds, especially xenon fluorides, with fluoro-acids and fluoro-bases.

The SbF_5–XeF_2 system has been investigated in detail [173]. Fig. 6 shows the equilibrium diagram of this system. The considerable supercooling (up to 100 deg) of the specimens in composition range 0.1–0.3 mole fraction XeF_2 is due [75] to the formation of XeF and XeF^+. The presence of an EPR spectrum of solutions of $XeF_2.2SbF_5$ in SbF_5 can be confirmation of the occurrence of this type of process [174].

The TaF_5–XeF_2, [175] NbF_5–XeF_2, [175] and VF_5–XeF_2 [176] binary systems have been investigated. In the TaF_5–XeF_2 system $XeF_2.TaF_5$ and $XeF_2.2TaF_5$ are formed, in the XeF_2–NbF_5 system only $XeF_2.2NbF_5$, and in the VF_5–XeF_2 system only $XeF_2.VF_5$. [176,177] The production of $XeF_2.NbF_5$ has also been reported [178].

The UF_6–XeF_2 system [179] consists of mixture with unrestricted mutual solubility of the components in the liquid state and with the crystallisation of $XeF_2.UF_6$ without formation of solid solutions. The degree of dissociation of $XeF_2.UF_6$ in the region of the melting point (120°C) does not exceed 20%. The pressure for the dissociation into constituent components is determined by the relation [180]:

$$\lg P_{mmHg} = 9.30 - 2171/T \quad (20\text{–}100°C).$$

The enthalpy of dissociation of $XeF_2.UF_6$ is independent of temperature (18.6 kcal mole^{-1}); the enthalpy of fusion is −3.5 kcal mole^{-1}.

$XeF_2.RuF_5$, $2XeF_2.RuF_5$, $XeF_2.2RuF_5$, $XeF_2.IrF_5$, $2XeF_2.IrF_5$, $XeF_2.2IrF_5$, $XeF_2.PtF_5$, $XeF_2.OsF_5$, $2XeF_2.OsF_5$, and $2XeF_2.AsF_5$ have been isolated[130] from solutions of XeF_2 and the noble metal pentafluoride in BrF_5. A report[34] of the formation of stable $XeF_2.AsF_5$ was not confirmed subsequently[130]. $XeF_2.OsF_5$ also decomposes[130] at 20°C; with the formation of osmium hexafluoride:

$$3(XeF_2 \cdot OsF_5) \rightarrow 2XeF_2 \cdot OsF_5 + 2OsF_6 + Xe.$$

Bartlett regards this reaction as an intermolecular reaction with the transfer of an electron and the intermediate formation of the XeF radical in the solid phase.

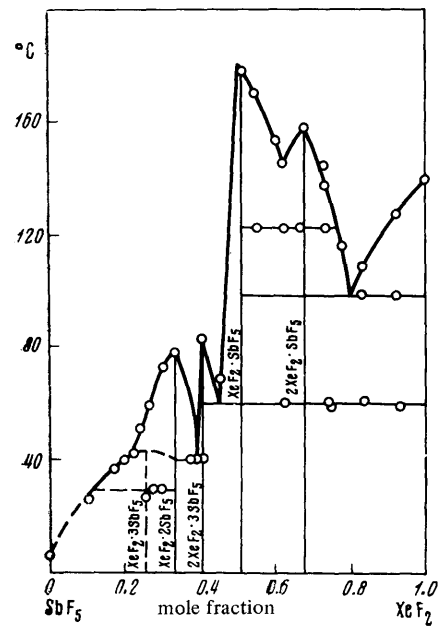


Figure 6. The equilibrium diagram of the SbF_5–XeF_2 system.

The reaction of XeF_2 with MnF_2 leads to the formation of the paramagnetic complex $XeMnF_6$ with an effective magnetic moment[181] of 3.86 μ_B, which shows that Mn is quadrivalent in the compound.

Xenon tetrafluoride reacts in BrF_3 solutions with PBr_5, As_2O_3, and Sb_2O_3 with the formation of the corresponding pentafluorides[182]. Only recently it was found reliably that XeF_4 reacts with fluoro-acids: $XeF_4.2SbF_5$[183] and $XeF_4.SbF_5$[184] are formed during the dissolution of XeF_4 in SbF_5 at 50°C.

When XeF_6 is reduced with uranium tetrafluoride, in addition to XeF_4 and UF_6, $XeF_6.UF_5$ is also obtained[185,186]. This compound can be made also by mixing XeF_6 and UF_5. The magnetic susceptibility of $XeF_6.UF_5$ obeys the Curie–Weiss law in the temperature range from −183° to 17°C, the Weiss constant being 55° and the effective magnetic moment 1.57 μ_B, which confirms that uranium is quinquevalent in the complex.

$XePtF_{11}$ and Xe_2PtF_{17} are formed[187] in the F_2–PtF_5–Xe system at a fluorine pressure of 80 atm and 180–220°C. The magnetic susceptibility of $XePtF_{11}$ obeys the Curie–Weiss law in the temperature range from −183° to 18°C; the Weiss constant is 35° and the effective magnetic moment of $XePtF_{11}$ is 1.97 μ_B.[187]

Under conditions most favourable for the formation of XeF_6, fluorination at 400°C of a mixture of AuF_3 and XeF_2 in the molar ratio 1:6 gave[188] a gold(V) complex $2XeF_6.AuF_5$; this shows that XeF_6 facilitates the stabilisation of the higher degrees of oxidation of the elements. $XeF_6.CrF_4$ was obtained[189] by the reaction of a considerable excess of XeF_6 with CrF_2 at 120°C. The oxidation of Cr^{II} to Cr^{IV} was confirmed by magnetic susceptibility measurements: the effective magnetic moment was 2.76 μ_B. The formation of $XeF_6.CrF_4$ by the reaction of XeF_6 with CrF_5 was also reported[189], although considering the known properties of XeF_6 and CrF_5, the reduction of Cr^V is difficult to explain.

In reactions with alkali metal fluorides[190], NOF,[191] and NO_2F[4,192] xenon hexafluoride acts as a fluoro-acid; in these reactions M_2XeF_8 (M = Cs, Rb, K, Na) and $MXeF_7$ (M = Cs or Rb), $2NOF.XeF_6$ and $NO_2F.XeF_6$ are formed. An X-ray diffraction investigation[193] of $2NOF.XeF_6$ showed the presence in the crystal lattice of the groups NO^+ and XeF_8^{2-}; $a = 8.914$, $b = 5.945$, $c = 12.83$ Å, $\rho_{calc} = 3.354$ g cm^{-3}, $Z = 4$, space group *Pnma*. Fig. 7 shows the structure of XeF_8^{2-}.

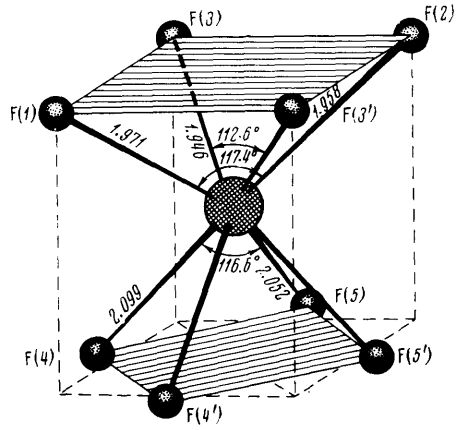


Figure 7. Structure of the XeF_8^{2-} anion in the $2NOF.XeF_6$ crystal lattice.

Reactions of the xenon fluorides in which they act as fluoro-bases (donors of fluoride ions) are interesting. Up till now the following complexes of xenon difluoride have been prepared: $2XeF_2.MF_4$ (M = Sn,[83] Ti,[83,194] Zr,[93] Pd,[195] Mn,[181]), $4XeF_2.PdF_4$,[195] $3XeF_2.PdF_4$,[195] $XeF_2.PdF_4$,[195] $XeF_2.2PdF_4$,[195] $XeF_2.MF_5$ (where M = As,[130] Sb,[173] Ta,[175,178] Nb,[178] V,[177] I,[71,76] Os,[130,178] Ir,[178] Pt,[130] Ru[130]), $XeF_2.2MF_5$ (M = Sb,[173] Ta, Nb,[175,178] Br,[78] Ir, Ru[130]), $2XeF_2.MF_5$ (M = As,[34,130] Sb,[173] Os,[130,178] Ir, Ru[130]), $XeF_2.MF_6$ (M = U,[179] Mo, W[80]), $XeF_2.XeF$,[196,197] $XeF_2.XeOF_4$;[198] xenon tetrafluoride: $XeF_4.SbF_5$,[184] $XeF_4.2SbF_5$;[183,184] xenon hexafluoride: $2XeF_6.MF_4$ (M = Ge,[199] Sn,[200] Pd[195]), $4XeF_6.MF_4$ (M = Ge,[199] Sn,[200] Pd,[195] Mn[201]), XeF_6MF_4 (M = Ge,[199] Pd,[195] Cr[189]), $XeF_6.MF_5$ (M = As,[91,200] Sb,[170] Ir,[190] Ta,[201] Ru,[91] Pt,[187] U[185]), and $2XeF_6.MF_5$ (M = P,[202] As,[91,202] V,[203] Ta,[201] Pt,[187] Au[188]); the ability of the xenon fluorides to supply fluoride ions decreases in the order[91]: $XeF_6 > XeF_2 > XeF_4$.

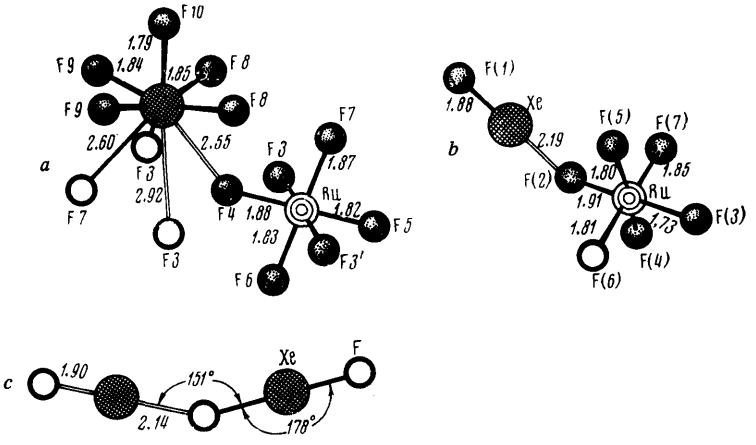


Figure 8. Crystal structure of the complexes of the xenon fluorides: *a*) $XeF_5^+RuF_6^-$; *c*) $Xe_2F_3^+$ in $2XeF_2.AsF_5$.

X-Ray diffraction and spectroscopic investigations of several xenon fluoro-complexes have enabled an understanding of their structure to be approached.

Peacock and coworkers [204] made an X-ray structural diffraction investigation of $XeF_2.2SbF_5$ and although they formally represented the complex in an ionic form ($XeF^+Sb_2F_{11}^-$) they attributed covalent character to the bonds in it. Bartlett and coworkers' X-ray diffraction investigation [205] of $2XeF_2.AsF_5$ led to the opposite conclusion: the structure of $2XeF_2.AsF_5$ is constructed from $Xe_2F_3^+$ cations and AsF_6^- anions. As Fig. 8 shows, the $Xe_2F_3^+$ cation has a planar V-shaped configuration with bridging fluorine atoms.

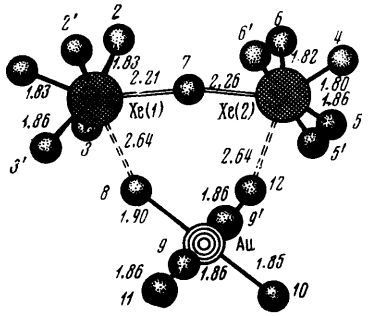


Figure 9. Crystal structure of $Xe_2F_{11}^+AuF_6^-$.

Bartlett and coworkers [130] investigated the Raman spectra of the compounds of XeF_2 with noble metal pentafluorides and calculated the normal vibrations of $XeF_2.IrF_5$ for strong and weak interactions of the XeF^+ and IrF_6^- ions. On the basis of a comparison of calculated and experimental frequencies for the ionic and bridging models they concluded it was possible to describe the compounds $XeF_2.MF_5$ and $XeF_2.2MF_5$ within the framework of the ionic model. An approximate calculation of $XeF_2.SbF_5$ using the frequencies of the Sb–F stretching vibrations of the $SbF_5SO_3F^-$ anion and the "frequency" formulae for a linear triatomic asymmetric molecule also showed that an ionic structure corresponds to the best agreement of the observed and calculated spectra [206]. Infringement of the selection rules for molecules with symmetry O_h, which is observed in the vibrational spectra of xenon fluoro-complexes cannot alter the correctness of ideas about the ionic structure of the compounds and is tentatively explained by a reduction in the symmetry of the anion in the crystal lattice [180,207]. X-Ray diffraction investigations confirmed the conclusion about the ionic structure of these substances.

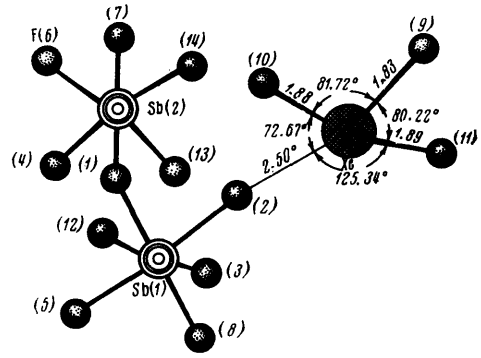


Figure 10. Crystal structure of $XeF_3^+Sb_2F_{11}^-$.

In addition to the molecular constants of the simple xenon compounds, Table 3 gives experimental values of the vibrational frequencies of the cations of certain fluoro-complexes of xenon. Table 4 gives the crystallographic properties of these compounds. Figs. 8–10 show the structures of typical compounds.

Table 3. Molecular constants of xenon compounds.

Compound, reference	Symmetry	Vibrational wavenumbers (Ref.208) and their assignment		Bond length, Å		Force constant	
		ν^{**}_{Xe-F}	δ^{**}_{F}	Xe—F	Xe—O	K^{**}_{F}	K^{**}_{O}
XeF_2[47] *	$D_{\infty h}$	Ram(g)—514,5 (ν_1); IR(g)—555 (ν_3)	Ram(g)—213,2 (2) (ν_2)	1.98		2.694	
XeF^+ $(XeF^+SbF_6^-)$[209-211]	$C_{\infty v}$	Ram(s) —615,617; IR(s) —615; Ram(s) —337,388 (Xe . . .F);	Ram(s) —141,180 (F—Xe . . .F)	1.84		3.68	
$XeF^+(XeF^+IrF_6^-)$[130]		Ram(s) —608,602		1.88		3.59	
$XeF^+(FXeOSO_2F)$[211]		Ram(s) —539,532,527	Ram(s) —239 (OXeF)	1.94	2.15	2.85	
$XeF^+(2XeF^+SnF_6^{2-})$[212]		IR(s) —585				3.35	
$Xe_2F_3^+$ $(Xe_2F_3^+SbF_6^-)$[209-211]	C_{2v}	Ram(s) —582.591,420 (Xe . . .F); IR(s) —617,584,572,440 (Xe . . .F)	Ram(s) —161,171,179,255 (F—Xe...F)	1.90			
XeF_4[47]	D_{4h}	Ram(g)—591,3 (ν_1); 524 (ν_5) IR(g) —586 (2) (ν_6)	Ram(g)—218 (ν_3); IR(g)—291 (ν_2); 161 (2) (ν_7)	1.94		2.829	
$XeF_3^+(XeF_3^+SbF_6^-)$[213]	C_{2v}	Ram(s) —645,613,569	Ram(s) —290,275 (F—Xe . . .F)	1.83—1.88			
		IR(g) —619 (f_{1u}); IR(s) —624 (f_{1u})					
	O_h	Ram(g)—613 (a_{1g}), 509 (e_g)	IR(s) —252 (f_{2u})	1.75—1.88			
XeF_6[165]	D_{3d} ($^3A_{2u}$)	IR(s) —630 (a_{2u}), 506 (e_u) Ram(g)—582 (a_{1g}), 509 (e_g)	IR(s) —302 (e_u), 326 (a_{2u}) Ram(g)—69 (e_g), 102 (a_{1g})				
	D_{3d} (^3E_u)	IR(g) —599 (a_{2u}), 520 (e_u) Ram(g)—582 (a_{1g}), 509 (e_g)	IR(s) —352 (a_{2u}), 365 (e_u)				
$XeF_5^+(XeF_5^+SbF_6^-)$[170]		IR(s) —582,550,420					
$XeF_5^+(XeF_5^+BF_4^-)$[184]	C_{4v}	Ram(s) —650—680,585—630,600—640, 640—670		1.80—1.85			
$Xe_2F_{11}^+(Xe_2F_{11}^+AuF_6^-)$[188]		Ram(s) —661,600,593,400	Ram(s) —356,290,111,58	1.80—1.86			
		form of spectrum	ν^{**}_{Xe-F}	ν^{**}_{Xe-O}	δ^{**}_{F}	δ^{**}_{O}				
$XeOF_2$[139,208]	C_{2v}	IR(s)	520.490	747	213(2)	(327)	1.95	1.76		
XeO_2F_2[214]	C_{2v}	IR(s) Ram(s)	585(ν_8) 537(ν_2)	848(ν_1).905(ν_6) 850(ν_1).882(ν_6)	317(ν_9) 315(ν_9)224(ν_5) 205(ν_4)	324(ν_7) 350(ν_3)	1.93	1.75		
$XeO_2F^+(XeO_2F^+Sb_2F_{11}^-)$[215]		Ram(s)	595	865.924						
XeO_3F_2[216]	D_{3h}	Ram,IR(s) Ram(s)	567.4(ν_2)	894(2)(ν_5)	318(2)(ν_6); (190)(2)(ν_7)	361(2)(ν_8)	(1.91)	(1.73)	2.69	6.67
		IR(s)	631.7(ν_3)	806.7(ν_1)	375.4(ν_4)				3.112	6.245
$XeOF_4$[47]	C_{4v}	IR,Ram(g)	609(2)(ν_7) 576.9(ν_2)	926.3(ν_1)	285.9(ν_3)219(ν_6) 161(2)(ν_9)	362(2)(ν_8)	1.90	1.71	2.964	6.672
		Ram(g)	543(ν_5)	225(ν_4)						
$XeF_2 \cdot XeOF_4$[198]		Ram(s)	494(XeF_2),573, 532	903	254,188,125	378				
$XeOF_3^+(XeOF_3^+SbF_6^-)$[213]	C_{2v}	Ram(s)	633,621,583	944		365.341 (O—Xe—F)	1.86	1.70		
XeO_3	C_{3v}	IR(g)		833(2)(ν_3).780(ν_1)		344(ν_2)317(2)(ν_4)		1.76		5.66
$XeO_3F^-(KXeO_3F)$[217]	C_{3v}	IR,Ram(s)	257(ν_3)	781(ν_1).822(2)(ν_4)	222(2)(ν_6) (O—Xe—F)	358(ν_2).315(2)(ν_5)	2.36	1.75—1.79		5.48
XeO_4[218,219]	T_d	IR(g) Ram(s)		879.2(3)(ν_3) 867(3)(ν_3);767(ν_1)		305.7(3)(ν_4) 303(3)(ν_1); 277(2)(ν_2)		1.736		6.28 6.40

Note. *The Raman spectra of the complexes of XeF_2 were investigated in Refs. 130, 206, 209, and 211; the infrared spectra in Refs. 206, 209, 210, and 220; **ν and δ are stretching and deformation vibrations respectively; K is the force constant of the main stretching vibration; the following abbreviations are used in the Table: IR(g) and IR(s), the infrared spectra of the gaseous and solid substances; Ram(g) and Ram(s) the Raman spectra of the gaseous and solid substances respectively. The numbers in parentheses show the degree of degeneracy of the vibrations.

From Table 3, clearly in compounds which contain the XeF^+ cation the frequency of the vibration of the Xe–F terminal bond is shifted to the long-wave part of the spectrum. This shift is explained with semiempirical calculation by the simple LCAO MO method[212], which led to the following series of energies of the xenon–fluorine bond (in kcal mole^{-1}): XeF^+ (~ 50) > XeF_2 (~ 30) > XeF (< 10); consequently for an ionic compound the frequency of the vibration of the Xe–F bond should be higher than for XeF_2, which is also observed experimentally. Since the frequency of the vibrations of the Xe–F bond depends directly on the strength of the fluoro-acid, it can serve as a criterion of the relative acceptor capability of fluoro-acids in reactions with XeF_2:[212]

$$(Sb_2F_{10}) > SbF_5 > (Ir_2F_{10}) > PtF_5 > IrF_5 > (Ta_2F_{10}) > RuF_5 > Ta_{...} > (Nb_2F_{10}) > TiF_4 > SnF_4 > SO_3F > CF_3COO > IF_5.$$

Rüdiger and Meinert[226] showed the possibility of using the MO method in the Hückel approximation for bonding calculations on the complexes of XeF_2 and obtained satisfactory correspondence of the experimental and calculated results for the salts XeF^+ and $Xe_2F_3^+$.

Table 4. Some properties of the complexes of xenon fluorides.

Compound	Method of preparation	M.p., °C	Lattice (°C)	Characteristics							Structure	Reference
				a	*b*	*c*	angle β, deg	*Z*	ρ_{calc}, g cm^{-3}	space group		
$XeF_2 \cdot RuF_5$	XeF_2+RuF_5, 120°	110—111	monoclinic	7.991	11.086	7.250	90.68	4	3.78	$P2_1/n$	$XeF^+RuF_6^-$	221
$XeF_2 \cdot 2SbF_5$	XeF_2+SbF_5	79—80	monoclinic	8.07	9.55	7.33	105.8	2	3.69	$P2_1$	$XeF^+Sb_2F_{11}^-$	204
$XeF_2 \cdot IF_5$	XeF_2+IF_5	102	tetragonal	7.65	—	10.94	—	4	4.06	$I4/m$	$XeF_2 \cdot IF_5$	77
$XeF_2 \cdot XeF_4$	XeF_2+XeF_4		monoclinic	6.64	7.33	6.40	92.40	4	4.02	$P2_1/c$	$XeF_2 \cdot XeF_4$	197
$XeF_2 \cdot XeOF_4$	XeF_2+XeOF_4	29	tetragonal	7.56	—	11.36	—	4	—	$I4/m$	$XeF_2 \cdot XeOF_4$	198
		99—100	monoclinic (20)	15.443	8.678	20.888	90.13	12	—	$I2/a$		
$2XeF_2 \cdot AsF_5$	XeF_2+AsF_5 (in BrF_5)		trigonal (50)	8.68	—	10.70	—	3	—		$Xe_2F_3^+AsF_6^-$	198
$XeF_4 \cdot SbF_5$	$(XeF_4 \cdot 2SbF_5)+XeF_4$	109—113	monoclinic	5.50	15.50	8.95	102.9	4	3.81		$XeF_3^+SbF_6^-$	213
$XeF_4 \cdot 2SbF_5$	XeF_4+SbF_5	81—83	triclinic	8.237	9.984	8.004	112.59 (α)72.54 (γ)117.05	2	3.98	$P\bar{1}$	$XeF^+Sb_2F_{11}^-$	222
$XeF_6 \cdot RuF_5$	$(XeF_6 \cdot RuF_5)+F_2$, 350°C		orthorhombic	16.771	8.206	5.617	—	4	3.79	$Pnma$	$XeF_5^+RuF_6^-$	221
$XeF_6 \cdot PtF_5$	$Xe+F_2+PtF_5$, 200°	100	orthorhombic	8.16	16.81	5.73	—	4	4.52	$Pmns$	$XeF_5^+PtF_6^-$	223
$XeF_6 \cdot AsF_5$	XeF_6+AsF_5 (in BrF_5)	—	monoclinic	5.886	16.564	8.051	91.57	4	—	$P2_1/c$	$XeF_5^+AsF_6^-$	198
$XeF_6 \cdot UF_5$	XeF_6+UF_5	—	orthorhombic	9.39	19.86	8.41	—	8	4.70	$Pcca$		186
$2XeF_6 \cdot AsF_5$	XeF_6+AsF_5	—	monoclinic	15.63	8.96	8.37	91.5	4	—		$Xe_2F_{11}^+AsF_6^-$	198
$2XeF_6 \cdot AuF_5$	$XeF_2+AuF_3+F_2$, 400°	145—150	orthorhombic	9.115	8.542	15.726	—	4	4.24	$Pnma$	$Xe_2F_{11}^+AuF_6^-$	224
$2XeF_6 \cdot PdF_4$		—	orthorhombic	9.346	12.786	9.397	—	4	3.91	$Pca2_1$	$[XeF_5^+]_2[PdF_6^{2-}]$	225
		65	monoclinic (20)	15.436	6.846	17.241	93.12	4	—	$C2/c$		
$2XeF_6 \cdot XeF_2 \cdot 2AsF_5$	$XeF_6+AsF_5+XeF_2$, 85°		monoclinic (40)	16.82	7.00	15.40	95.30	4	—		$XeF_2 \cdot 2[XeF_5^+AsF_6^-]$	198

B. Oxygen-containing Compounds of Xenon

1. Xenon Oxide Fluorides

Xenon oxide tetrafluoride can be obtained by controlled hydrolysis of XeF_6 or by reaction of XeF_6 with silicon dioxide[1,98]; XeF_6 is removed on sodium fluoride.

At room temperature $XeOF_4$ is a colourless transparent liquid. The density of liquid $XeOF_4$ is given by the relation[227]:

$$\rho \text{ g cm}^{-3} = 3.168 - 0.0032\ t\ .$$

The similarity of the Raman spectra of $XeOF_4$ and of a solution of $XeOF_4$ in HF indicated[228] that $XeOF_4$ dissolves in molecular form in HF. A study of the change in the form of the peak of the Xe–O stretching vibration with dilution of the solution of $XeOF_4$ in HF suggested molecular association in liquid $XeOF_4$.[229]

The physical properties of $XeOF_4$ were studied rather thoroughly even at an early stage of the investigations[1] and are given in Table 5. The square pyramidal structure (Table 3) is confirmed by the microwave spectrum[233], according to which the Xe–O and Xe–F distances in the $XeOF_4$ molecule are respectively equal to 1.703 and 1.900 Å and the angle O–Xe–F is 91.8°. The results of an electron diffraction investigation[234] of gaseous $XeOF_4$ led to the following values: r(Xe–O) = 1.7109 Å, r(Xe–F) = 1.9010 Å, and the angle O–Xe–F = 91°. The agreement between the two methods is satisfactory.

The Raman spectra of gaseous[47] and liquid[235] $XeOF_4$ were obtained. The infrared and Raman spectra of $XeOF_4$ were interpreted[47] (Table 3).

The ^{17}O NMR spectrum of $XeOF_4$[236] has the form of a triplet with an intense central peak of width 130 Hz and two symmetric side peaks of width 110 Hz. An analysis of the intensities showed that the side lines are due to the interaction of ^{17}O with ^{129}Xe and the main line to the interaction of ^{17}O with the remaining xenon isotopes. The ^{17}O chemical shift (relative to $H_2{}^{17}O$) is 313 p.p.m. The spin–spin coupling constant ($^{129}Xe-{}^{17}O$) is 629 Hz. Investigations of the ^{19}F NMR spectrum for $XeOF_4$ have continued[237,238]. The relaxation times were measured in the temperature range from −56° to 85°C and the presence of molecular association in liquid $XeOF_4$ was concluded. The high-resolution ^{19}F NMR spectrum[237] is characterised by an intense central line and a doublet with a spin–spin coupling ($^{129}Xe-{}^{19}F$) constant of 1124 Hz. The chemical shift at 25° is 100.27 p.p.m. (relative to CCl_3F).[237]

The interaction of $XeOF_4$ with alkali : metal fluorides leads to the formation of $3KF.XeOF_4$, $3RbF.XeOF_4$, and $CsF.XeOF_4$,[227] which decompose when heated. With NOF, $NOF.XeOF_4$ is formed[227]. With fluoro-acids, $XeOF_4$ forms the unstable $2XeOF_4.AsF_5$,[229] $2XeOF_4.VF_5$,[229] $XeOF_4.SbF_5$,[213,229] and $XeOF_4.2SbF_5$.[213,227] From the Raman spectrum[229], $2XeOF_4.VF_5$ is a molecular compound. The presence of ^{19}F NMR peaks and their position in the spectrum of solutions of $XeOF_4.2SbF_5$ in SbF_5 shows the presence in the solutions of the cation $XeOF_3^+$, in which the electron pair and the F atom occupy an equatorial position of the trigonal bipyramid and two other F atoms are located axially[215]. The chemical shifts at 5° are −195.1 p.p.m. ($F_{eq}-{}^{129}Xe$) and −147.1 p.p.m. ($F_{ax}-{}^{129}Xe$) relative to CCl_3F. The coupling constants ($^{129}Xe-{}^{19}F$) are 938 Hz (F_{eq}) and 434 Hz (F_{ax}). The ionic structure of $XeOF_4.SbF_5$ and $XeOF_4.2SbF_5$ is confirmed by their Raman spectra[213,215] and by X-ray diffraction investigations[213,222] (Tables 3 and 4).

Xenon dioxide difluoride XeO_2F_2 is formed in the interaction of XeO_3 with $XeOF_4$ or with XeF_6.[239] Removal of impurities is most effectively brought about by distillation. XeO_2F_2 forms colourless crystals which melt at 30.8°C to give a colourless liquid. XeO_2F_2 is more stable than XeO_3, but like XeO_3 is explosive; in moist air

Table 5. Physical properties of compounds of xenon and krypton.

Property	XeF_2	XeF_4	XeF_6	$XeOF_4$	XeO_3	KrF_2
Molecular weight	169.2968	207.2936	245.2904	223.2930	179.2982	121.7968
Melting point, °C	129.0 [41]	117.0 [41]	49.48 [144] 75.57(b.p.)	−46.2 [227]	—	(77) [10]
Vapour pressure, mmHg	4.55(25°) [41]	2.55(25°) [41] 95.28(77°)	28.9(25°) [144]	28(0°) [227]	—	31.0(0°) [10] 96(20°) [10]
Density, g cm^{-3}	4.32(25°) [42]		3.411(24.4°) [144] 3.229(50.3°)	3.11(22.5°) [227]	—	—
Critical parameters (Ref.42)						
temperature, °C	358	339	—	—	—	—
pressure, atm	92	69.5				
density, g cm^{-3}	1.14	1.10				
Solubility, moles per 1000 g						
H_2O	0.15(0°) [1,3]	XeO_3 is formed	XeO_3 is formed	XeO_3 is formed	>2 [1,3]	0.04(2°) [10]
HF	9.88(30°) [68]	0.18(20°) [68]	8.6(20°) [169]	—		16.0(20°) [230]
BrF_5	11.2(20°) [78]	—	~11(20°) [170]	—	—	16.5(20°) [10]
Electrical conductivity, Ω^{-1} cm^{-1}	—	—	$1.45\cdot10^{-6}$(50°) [3]	$1.03\cdot10^{-5}$(24°) [227]	—	—
Electrical conductivity in HF, Ω^{-1} cm^{-1}	—	—	$3.52\cdot10^{-3}$(0.02M) [1]	$1.0\cdot10^{-5}$(24°) [227]	—	—
Dielectric constant	—	—	4.10(55°) [1,3]	24.6 [217]	—	—
Thermodynamic properties:						
ΔH°_{298}(g), kcal $mole^{-1}$	−25.58 [45]	−49.28 [45]	−66.99 [45]	(−6) [3]	96 [1,2]	14.4 [231]
S°_{298}(g), cal deg^{-1} $mole^{-1}$	62.01 [208]	77.05 [208]	89.38 [208]	81.45 [208]	69.09 [208]	60.65 [232]
C°_{p298}(g), cal deg^{-1} $mole^{-1}$	12.94 [208]	21.45 [208]	30.15 [208]	24.87 [208]	14.89 [208]	12.96 [232]
ΔG°_{298}(g), kcal $mole^{-1}$	−17.54 [45]	−31.40 [45]	−38.46 [45]	—		22.1 [10]
$<D^\circ(Xe-F)>$, kcal $mole^{-1}$	31.62 [45]	31.15 [45]	29.94 [45]	—	(27) [1,3](Xe—O)	11.7 [231]
ΔH°_{298}(s), kcal $mole^{-1}$	−38.90 [45]	−63.84 [45]	−80.82 [45]	—	—	5.2 [10]
ΔG°_{298}(s), kcal $mole^{-1}$	−20.58 [45]	−34.77 [45]	−40.40 [45]	—	—	—
ΔH(fus.), kcal $mole^{-1}$			1.37 [144]	—	—	—
ΔH(subl.), kcal $mole^{-1}$	13.32 [41]	14.56 [41]	14.13 [45]	—	—	9.2 [10]
Crystal structure (Ref.1):						
—lattice	tetragonal	monoclinic			orthorhombic	tetragonal
—parameters: *a*, Å	4.315	5.050	cf. Table 2	—	6.183	6.533
b, Å		5.922	—	—	8.115	—
c, Å	6.990	5.771, β=99.6°	—	—	5.234	5.831
ρ_{calc}, g cm^{-3}	4.32(*Z*=2)	4.04(*Z*=2)	—		4.55 (*Z*=4)	3.24 (*Z*=2)
—space group	*I4/mmm*	$P2_1/n$	—	—	$P2_12_12_1$	—
—bond length, Å	2.00	1.951;1.954	—	—	1.74—1.77	—
Molar magnetic susceptibility (20°C) (Ref.1)	$-(40-50)\cdot10^{-6}$	$-50.6\cdot10^{-6}$	$-76.9\cdot10^{-6}$ [152]	—		diamagnetic
Dipole moment (Refs.1,3)	0.5	<0.03	<0.03	0.65	—	—

The following abbreviations are used in the Table: (g) gaseous state of the substance, (s) solid (crystalline) state of the substance.

it is rapidly hydrolysed to XeO_3. When XeO_2F_2 reacts with XeF_6, $XeOF_4$ is formed [239]. The standard enthalpy of formation of XeO_2F_2 (g) [240] was estimated as 56 kcal $mole^{-1}$.

The Raman spectra of liquid and solid XeO_2F_2 and the infrared spectrum of solid XeO_2F_2 in an argon matrix at 4°K were investigated [214]. It was concluded that the XeO_2F_2 molecules are monomeric in the liquid and possibly the solid phases. According to the vibrational spectra, the XeO_2F_2 molecule has a pseudopyramidal structure of C_{2v} symmetry (Table 3). The normal vibrations of XeO_2F_2 and SO_2F_2, CrO_2F_2, and SeO_2F_2 were compared and it was shown that the frequencies of monotypical vibrations are arranged in a series in accordance with the mass of the central atom [214].

The molecular structure and symmetry of XeO_2F_2 were investigated by neutron diffraction on single crystals [241]. It was found that the XeO_2F_2 structure is orthorhombic, with parameters $a = 6.443$, $b = 6.288$, $c = 8.312$ Å, $Z = 4$, $\rho_{calc} = 4.10$ g cm^{-3}. The structure consists of dimeric layers of XeO_2F_2 molecules linked by weak Xe...O bridges.

The ^{19}F NMR spectrum for XeO_2F_2 and also that for XeO_2F_2–$XeOF_4$ mixtures (1 : 1) have been obtained [237]. The XeO_2F_2 spectrum is characterised by a single peak accompanied by a doublet from the spin–spin coupling ($^{19}F-^{129}Xe$) with constant 1178 Hz. The chemical shift is 105.10 p.p.m. in relation to CCl_3F. Throughout the entire range of temperatures studied (16–70°C) significant broadening of the lines was not observed.

The compound $XeO_2F_2.2SbF_5$ has been prepared [215]. The ^{19}F NMR spectrum of a solution of $XeO_2F_2.2SbF_5$ in SbF_5 shows the formation in the solution of the cation XeO_2F^+, the structure of which is analogous to the isoelectronic XeO_3—a trigonal bipyramid [215]. The chemical shift at 5° is −199.4 p.p.m. relative to CCl_3F; the spin–spin coupling constant ($^{129}Xe-^{19}F$) is 79.7 Hz. The presence of the XeO_2F^+ cation in $XeO_2F_2.2SbF_5$ is confirmed by the Raman spectrum [215] (Table 3).

Xenon trioxide difluoride XeO_3F_2 was isolated in the reaction of XeF_6 with Na_4XeO_6 at room temperature [242]; it was identified by the mass spectrum. The volatility of XeO_3F_2 is comparable with that of XeO_4 but less than that of XeO_2F_2. The infrared and Raman spectra of XeO_3F_2 in an argon matrix at 4°K were investigated [216] (Table 3).

Xenon dioxide tetrafluoride XeO_2F_4 is formed by the reaction [243]:

$$XeO_3F_2+XeF_6\rightarrow XeOF_4+XeO_2F_4\,.$$

Xenon oxide hexafluoride $XeOF_6$ could not be isolated but its compound $XeOF_5^+Sb_2F_{11}^-$ was obtained [184] by the reaction of $KrF^+Sb_2F_{11}^-$ with $XeOF_4$ at −10°C.

2. Xenon Trioxide

The behaviour of XeO_3 in aqueous solutions was discussed in detail by Malm and Appelman [3], and that in non-aqueous solutions by Jaselskis [11].

The method for obtaining pure aqueous solutions of XeO_3 [140] is the hydrolysis of XeF_6 with the subsequent precipitation of fluoride ion with magnesium oxide,

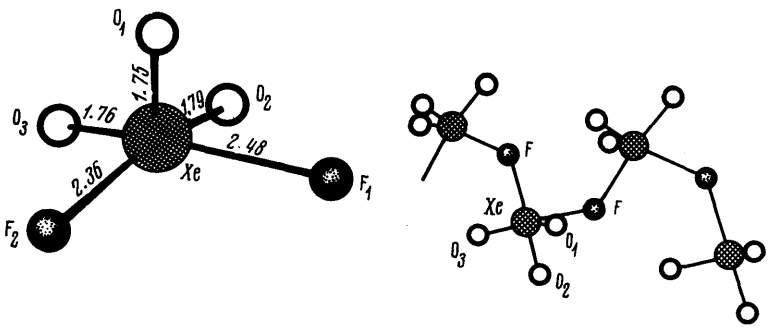


Figure 11. Structure of the XeO_3F^- anion in the $nK^+(XeO_3F^-)_n$ crystal lattice.

removal of Mg^{2+} ions by the action of zirconium phosphate and trace amounts of fluoride ions with the aid of ZrO_2.

Crystalline colourless XeO_3 can be obtained by the evaporation of aqueous solutions of XeO_3 at room temperature[244]; XeO_3 sublimes at 70°C and decomposes under these conditions; in amounts exceeding 20 mg gaseous XeO_3 partly explodes. According to other results[245], the thermal decomposition of XeO_3 starts at 40°C and proceeds without explosion. The properties of XeO_3 are given in Table 5.

The thermodynamic properties of aqueous XeO_3 have been studied[246]. The standard enthalpy of formation $\Delta H^\circ_{298}(XeO_3 \infty H_2O)$ is 99.94 kcal mole^{-1}. The value $\Delta G^\circ_{298}XeO_{3(aq)} = 120.8$ kcal mole^{-1} was used to calculate the redox potential of the couple XeO_3/Xe in acid medium and $HXeO_4^-/Xe$ in alkaline medium:

$$XeO_{3(aq)} + 6H^+_{(aq)} + 6e^- = Xe_{(g)} + 3H_2O,$$

$$HXeO_{4(aq)}^- + 3H_2O + 6e^- = Xe_{(g)} + 7OH^-,$$

equal respectively to 2.10 and 1.24 V.

The kinetics of decomposition of XeO_3 in a neutral aqueous solution has been studied[247]. The variation of the optical density of solutions of XeO_3 with time has been plotted. It has been shown that the decomposition of XeO_3 is described by a first-order equation up to high degrees of conversion. The rate constant is independent of the concentration of the solution in the range 1.01×10^{-3}–3.30×10^{-3} M. The Arrhenius relation has the form:

$$k = 10^{13,4\pm1,1} \cdot \exp(-28\,100 \pm 1900/RT).$$

The results of an investigation[247] of the kinetics of decomposition of XeO_3 in aqueous solutions can be regarded as a quantitative measure of the stability of these solutions As the pH is increased, the stability of the XeO_3 solutions falls[3]. γ-Radiolysis of the aqueous solutions of XeO_3 at room temperature leads to decomposition of XeO_3 into Xe and O_2.[248] The radiation-chemical yield increases with the XeO_3 concentration[249,250]. The possible mechanism of γ-radiolysis has been discussed[249,250].

Aqueous solutions of XeO_3 readily oxidise H_2O_2 to O_2,[251] Pu^{III} to Pu^{IV} in 2 M $HClO_4$,[252,253] Np^V to Np^{VI} in 2 M $HClO_4$,[254] Np^{VI} to Np^{VII} in 1 M KOH[255] and 10–11 M KOH.[108] Many organic compounds, for example, primary and secondary aliphatic alcohols,[256,257] benzyl alcohol,[257,258] benzaldehyde,[258] diphenylmethanol,[257] etc., are decomposed in aqueous solutions of XeO_3 with the formation of CO_2. XeO_3 reacts with t-butyl alcohol only in the presence of transition metal ions, with the formation of Bu^tOXeO_3K. $.Bu^tOH$.[259] In alkaline solutions XeO_3 epoxidises alkenes by electrophilic attack at the double bond[260]. Carboxylic acids are decomposed to CO_2.[261]

3. Xenates and Perxenates

The fluoroxenates $RbF.XeO_3$ and $CsF.XeO_3$ crystallise on the evaporation of a 0.5 M aqueous solution of XeO_3 (containing HF) after its neutralisation to pH 4 by the corresponding hydroxides[262]. $CsF.XeO_3$ can also be made by atmospheric hydrolysis of $CsF.XeF_6$[261] or $CsF.XeOF_4$.[227] Potassium fluoroxenate is formed in the evaporation of a mixture of a 0.5 M solution of XeO_3 and 1 M solution of KOH.[262] The fluoroxenates mentioned are comparatively stable; their decomposition starts to become appreciable above 260°C.[262] $CsCl.XeO_3$ can be obtained[263] by mixing aqueous solutions of XeO_3 and CsCl; unstable $CsBr.XeO_3$ has been isolated[262] from saturated solutions of CsBr at pH 9 and 0°C. The stability of the halogenoxenates falls with increase in the mass of the halogen[262]: $CsF.XeO_3 > CsCl.XeO_3 > CsBr.XeO_3$.

The halogenoxenates are much more stable than XeO_3, which does not agree with the view[227] that they are molecular compounds. Actually, X-ray diffraction investigations[264] showed that the crystal structure of $KF.XeO_3$ is constructed from infinite XeO_3 chains connected by bridging fluorine atoms in such a manner that each link acquires a negative charge, XeO_3F^-. As Fig. 11 shows, the anion has a polymeric structure and the links are connected by potassium ions. Consequently, the correct structural formula of potassium fluoroxenate is $nK^+(XeO_3F^-)_n$. The orthorhombic lattice of $KF.XeO_3$ has the parameters a = 7.354, b = 6.811, c = 8.815 Å, ρ_{calc} = 3.835 g cm^{-3}, Z = 4, space group $Pn2_1a$.[264] The ionic structure of the halogenoxenates has been confirmed by the results of an investigation[217] of the infrared and Raman spectra of $MXeO_3F$ (M = K, Rb, or Cs) and $MXeO_3Cl.MCl$ (M = Rb or Cs), which agree most satisfactorily with C_{3v} symmetry for XeO_3F^-.

Cs, Rb, K, and Na xenates of composition $MHXeO_4$ crystallise from solutions of XeO_3 when the corresponding hydroxides are added[265]. They are all stable up to 150 to 160°C, tend to detonate, and decompose slowly in aqueous solutions. An investigation[266] of the Raman spectra of aqueous 1.1 M solutions of $NaHXeO_4$ showed the presence of $HXeO_4^-$ in them.

In the ozonisation of aqueous solutions of XeO_3 and KOH the stable salt of sexivalent and octivalent xenon is isolated—$K_4XeO_6.2XeO_3$,[267] which tends to denotate and decomposes above 200°C by the reaction:

$$K_4XeO_6 \cdot 2XeO_3 \rightarrow K_4XeO_6 + 2Xe + 3O_2.$$

On the basis of the results of investigations of the thermal stability, infrared spectra, and an X-ray diffraction analysis of $K_4XeO_6.2XeO_3$, it was concluded[267] that in this

compound the XeO_3 molecules are coordinated (by means of two bridging oxygen atoms) to the central group—octahedral perxenate, in such a manner that $K_4Xe_3O_{12}$ is formed.

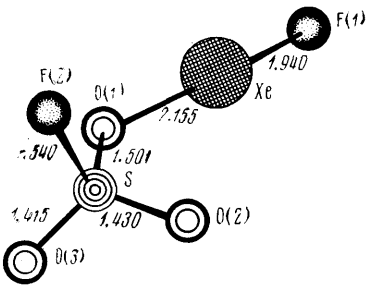


Figure 12. Molecular structure of $FXeOSO_2F$.

The salts of xenon(VIII), the perxenates, are formed in solutions of strong bases in the hydrolysis of XeF_6, the disproportionation of XeO_3, and in ozonation of XeO_3 solutions. Appelman thinks[268] that the ozonation of XeO_3 in 1–2 M alkali is the most effective. Some perxenates, for example, $Na_4XeO_6 . 2.5NaF$, can also be obtained, but in smaller yield, by the hydrolysis of XeF_4 in alkaline solutions[269]. An investigation of the Raman spectra of aqueous solutions of perxenates[266] shows the high concentration of symmetric, evidently octahedral, anions:

$$HXeO_6^{3-} + OH^- \rightleftarrows XeO_6^{4-} + H_2O.$$

Methods of making $Na_4XeO_6.nH_2O$ (n = 2, 4, or 6) of high purity have been developed[270], involving the hydrolysis of mixtures of XeF_4 and XeF_2 in alkaline solutions. The thermal stability of $Na_4XeO_6.6H_2O$ has been investigated[271]. The following parameters of its hexagonal lattice have been found[272] for Na_4XeO_6 by X-ray diffraction: a = 5.63, c = 16.00 Å. At the basis of the structure lies cubic close packing of O atoms with distribution of the Na and Xe atoms in octahedra; here the $Na_2XeO_6^{2-}$ layer lies parallel to the plane bc with distance between them 6.25 Å. Lithium perxenate of composition $Li_4XeO_6.nH_2O$ where $0.6 < n < 2$,[273] is less stable than sodium perxenate.

The rare-earth elements (r.e.e.) form dipole perxenates. In the general instance, the r.e.e. and yttrium form complex salts[270,274] $M_nLn_m(XeO_6)_l.xH_2O$, where M is an alkali metal, Ln is Ho, Eu, Dy, Pr, La, Nd, or Y, with $2 < x < 4$. Analogous compounds are obtained for Th^{IV}, U^{VI}, Np^{VI}, and Pu^{VI}.[275] The compound $3(UO_2)_2XeO_6 . 5Na_4XeO_6.nH_2O$, which is stable up to 100°C and is slowly hydrolysed in water, has also been synthesised. Np^{VI} perxenate decomposes spontaneously with the formation of Np^{VII}.[275] Americium perxenate $Am_4(XeO_6)_3.4OH_2O$ is precipitated from basic solutions of Am^{III}.[276] Cobalt[277], barium and strontium[278], copper, lead, silver, nickel, tin, and zinc[3] perxenates have also been obtained. Their properties have not been studied. In aqueous solutions the perxenates are strong oxidants[3].

4. Xenon Tetroxide

Xenon tetroxide XeO_4 is formed in the reaction of perxenates with sulphuric acid at room temperature, for example[1]:

$$Ba_2XeO_6 + 2H_2SO_4 \rightarrow XeO_4 + 2BaSO_4 + 2H_2O.$$

The standard enthalpy of formation of XeO_4 is 153.5 kcal $mole^{-1}$, which corresponds to a mean thermochemical bond energy of 21.1 kcal $mole^{-1}$.[279]

The molecular structure of gaseous XeO_4 has been determined by electron diffraction[280]; the tetrahedral configuration of the molecule (symmetry Td) has been confirmed; the interatomic distances are: r(Xe–O) = 1.736 Å, r(O...O) = 2.832 Å, and the mean square amplitudes of the vibrations are: l(Xe–O) = 0.046 Å, l(O...O) = 0.086 Å. The results obtained for the bond lengths led Gundersen and coworkers[280] to the conclusion that the bond between xenon and oxygen had considerable double bond character, although the amplitudes of the vibrations are more characteristic of a single bond.

The vibrational spectra of XeO_4 were investigated by Yeranos[281] (infrared spectrum), Huston and Claassen[218] (Raman spectrum), and McDowell and Asprey[219] (infrared and Raman). Table 3 gives the vibrational wavenumbers of XeO_4. The frequencies in the laser Raman spectra of gaseous and solid XeO_4 have been assigned[218] and with the aid of a force field Urey and Bradley calculated the force constants. Unlike most of the tetrahedral molecules and ions studied[282], in XeO_4 the force constant for the interaction of non-bonded atoms is negative (–0.18 mdyn $Å^{-1}$). McDowell and Asprey[219] studied the infrared and Raman spectra of gaseous XeO_4^{16} and XeO_4^{18} and showed the existence of a difference between the force fields of XeO_4 on the one hand and OsO_4,[283] and RuO_4[284] on the other. The negative sign of the coupling constant of non-bonded atoms shows, in complete agreement with Huston and Claassen's work[218], a significant difference between the nature of the bonds in XeO_4 and in the tetroxides of the noble metals.

5. Derivatives of Xenon Fluorides and Oxides

Xenon forms comparatively stable compounds only with the most electronegative elements—fluorine and oxygen. The concept of electronegativity played a positive part in the prediction of the possibility of the formation of compounds with groups more electronegative than fluorine and oxygen.

When XeF_2 reacts with stoichiometric amounts of fluorosulphonic or perchloric acids below –60°C colourless crystalline substances are formed: $FXeSO_3F$, $Xe(SO_3F)_2$, $FXeClO_4$, $Xe(ClO_4)_2$.[285,286] $FXeSO_3F$ melts at 36.6°C to a yellow-green liquid and decomposes on melting:

$$2FXeSO_3F \rightarrow XeF_2 + S_2O_6F_2 + Xe.$$

The reactions of $FXeSO_3F$ are accompanied by the release of xenon. The $FXeSO_3F$ structure consists of discrete $FXeOSO_2F$ molecules (Fig. 12), in which the Xe atom is coordinated linearly with F and O atoms of a distorted tetrahedral fluorosulpho-group[287]. $FXeSO_3F$ has an orthorhombic lattice with parameters a = 9.88, b = 10.00, c = 10.13 Å, Z = 8, ρ_{calc} = 3.30 g cm^{-3}, space group $Pbca$. $Xe(SO_3F)_2$ melts at 43–45° to a yellow liquid, which slowly decomposes[285,286]:

$$Xe(SO_3F)_2 \rightarrow S_2O_6F_2 + Xe.$$

Preliminary investigation[286] of the crystal structure of $Xe(SO_3F)_2$ showed that the crystals are monoclinic with $a = 7.94$, $b = 13.7$, $c = 6.84$ Å, $\beta = 96°$. $FXeClO_4$ melts sharply at 16.5°C with decomposition; $Xe(ClO_4)_2$ melts at 0°C. Xe, O_2, and Cl_2O_7 have been observed[286] in the decomposition products of $FXeClO_4$ and $Xe(ClO_4)_2$.

The reaction of XeF_2 with $HOTeF_5$ leads to the formation of $FXeOTeF_5$ and $Xe(OTeF_5)_2$.[288-291] These compounds decompose above 150°C with the formation of $F_5TeOTeF_5$. The compound $Xe(OTeF_5)_2$ is orthorhombic with the lattice parameters $a = 9.83$, $b = 8.73$, $c = 12.97$ Å, $Z = 4$, $\rho_{calc} = 3.64$ g cm^{-3}, space group *Cmca*.[289] Like the noble gas fluorides, $FXeOTeF_5$ acts as a fluoride-ion donor with the formation[288,292] of $[F_5TeOXe]^+[AsF_6^-]$, is a weaker fluorobase than XeF_6 and XeF_2, but a stronger one than XeF_4. When XeF_2 reacts with $HOSeF_5$, $FXeOSeF_5$ and $Xe(OSeF_5)_2$ are formed[293,294]; their properties are reminiscent of xenon pentafluoro-orthotellurates. The thermal decomposition of these compounds starts at 100°C and leads to the formation of $F_5SeOSeF_5$.

XeF_2 forms $FXeOC(O)CF_3$ and $Xe[OC(O)CF_3]_2$ with trifluoroacetic acid at −24°C; they are pale yellow solid substances which explode when heated above 25°C and detonate under impact[290,295,296]. In addition to the above compounds, the following have been obtained: $FXeOSO_2CF_3$ and $FXeOSO_2CH_3$,[286] and $F_5TeOXeOSeF_5$,[294] which exists in equilibrium with $Xe(OTeF_5)_2$ and $Xe(OSeF_5)_2$, $FXeOPOF_2$ and $Xe(OPOF_2)_2$ are formed by the reaction of XeF_2 with $P_2O_3F_4$ in trichlorofluoromethane at −40°C and are stable up to 20°C.[297]

Investigation of the infrared and Raman spectra of derivatives of XeF_2 in oxo-acids[286-293] gave certain information about the nature of the bonds in the compounds obtained. Comparison of the vibrational frequencies of the Xe–F bond in these compounds and in XeF_2 led to the conclusion that the bonds of the Xe atoms with the ligands in all the compounds are similar[286]. This agrees with the results of the X-ray diffraction investigation of $FXeOSO_2F$:[287] the length of the Xe–F terminal bond in $FXeOSO_2F$ (1.94 Å) is close to the Xe–F distances in XeF_2 (2.01 Å), $Xe_2F_3^+$ (1.90 Å), $FXeFRuF_5$ (1.88 Å), and $FXeFSb_2F_{10}$ (1.84 Å).

The compounds listed are thermodynamically and thermally unstable. There are two points of view concerning the mechanism of their decomposition: according to one of these[286] the decomposition proceeds through the intermediate formation of the free radicals SO_3F and XeF; according to the other[298], the decomposition of $FXeOSO_2F$ takes place through the intermediate formation of XeF_2 and SO_3. Recently published results of experimental investigations of certain products of the reactions of XeF_2 with oxo-acids show the formation of rather stable free radicals during the course of their decomposition. Thus, in the EPR spectra of the yellow solutions of $FXeOPOF_2$ in CCl_4 a line of width 67 G with *g*-factor of 2.0067 is found[297]. This fact, just like the nature of the ultraviolet spectra of such solutions[297], has been interpreted as a sign of the formation of free radicals (evidently, PO_2F_2) in the decomposition of $FXeOPOF_2$ and $Xe(OPOF_2)_2$. The EPR method was also used for studying[294] the intermediate products of the photochemical decomposition of $Xe(OTeF_5)_2$ and $Xe(OSeF_5)_2$; the investigation was made in the solid state and in hexafluoroethane at −150°C. Lines with half-width 10.2 G, *g*-factor 2.00 were observed in the spectra of both solid substances. The appearance of the EPR signals is explained[294] by the formation of the free radicals $OSeF_5$ and $OTeF_5$.

The interaction of $FXeSO_3F$ with AsF_5, SbF_5, and RuF_5 did not lead, as expected[286], to the formation of salts containing the cation $(XeSO_3F)^+$; however, the complex $[(FXe)_2O_2S(O)F]^+[AsF_6]^-$, which decomposes above 60°C, was obtained[286] by the reaction of $FXeSO_3F$ with XeF_2 and AsF_5. An analysis of the Raman spectra of $[(FXe)_2O_2S(O)F]^+[AsF_6]^-$ and $[(FXe)_2F]^+[AsF_6]^-$ showed similar Xe–F bonds in these cations and confirmed the structure given[286].

Xenon tetrafluoride and hexafluoride are also capable of the formation of compounds with oxo-acids[299]. $FXeOSO_2F$ and $Xe(OSO_2F)_2$ are formed in the reaction of XeF_4 with $HOSO_2F$ in the temperature range from −22° to 5°C; under analogous conditions XeF_6 forms the colourless crystalline substance F_5XeOSO_2F, which melts above 73°C with decomposition[298]. The results of the measurement of the ^{19}F NMR spectrum of F_5XeOSO_2F, in HSO_3F at −60° show the existence in the solutions of the cation F_5Xe^+ ($FXeF_4^+$).[298] The data of the NMR spectrum: chemical shift (relative to HSO_3F) −188 p.p.m. (F_{ax}) and −68.9 p.p.m. (F_{eq}), (^{129}Xe–^{19}F) coupling constants 1377 Hz (F_{ax}) and 170 Hz (F_{eq}), agree with the results of earlier investigations[215] of the ^{19}F NMR for XeF_5^+. The ionic structure of F_5XeSO_3F is also confirmed by the Raman spectrum[298], the intense polarised bands at 650 and 595 cm^{-1} in which were assigned[300] to ν(Xe–F) and $\nu_{sym}(XeF_4)$ in XeF_5^+.

C. Other Xenon Compounds

Xenon dichloride $XeCl_2$ can be obtained: (a) by passing a high-frequency discharge (25 MHz, 150–350 mA) through a mixture of xenon, fluorine, and $SiCl_4$ or CCl_4 at −78°C.[300] It is suggested that the XeF_2 formed initially undergoes an exchange reaction with the halogen from the $SiCl_4$ (or CCl_4) with the formation of $XeCl_2$. It was shown later that an exchange reaction actually occurs in solutions of XeF_2 in CCl_4 under the action of ultraviolet radiation[301]; (b) by the action of a microwave discharge in a mixture of xenon and chlorine in the molar ratio 25:1 with subsequent rapid withdrawal of the reaction products into a zone cooled to 4°K;[302] (c) in the β-decay reaction[303]: $^{129}ICl_2^- \rightarrow {}^{129}XeCl_2$; (d) by the reaction of xenon with chlorine at high pressure and room temperature for several days[304] (Malm and Appelman think[3] that under the experimental conditions[304] unstable clathrates of xenon are formed, and not $XeCl_2$).

Xenon dichloride is a colourless crystalline substance which can be stored in sealed glass ampoules for long periods, which sublimes under reduced pressure at room temperature and decomposes in a high vacuum or when heated to 80°C.[300] The calculated standard enthalpy of formation ΔH°_{298} $XeCl_2$ (g) is 27 kcal mole^{-1},[286], which corresponds to a thermochemical bond energy of 15 to 16 kcal mole^{-1}.

In the infrared[302] and Raman[305] spectra of matrix-isolated $XeCl_2$ at 4°K bands with maxima at 319 and 253 cm^{-1} respectively are observed. These experimental wavenumbers agree with those calculated for a linear symmetric molecule (symmetry $D_{\infty h}$). The force constant of the Xe–Cl bond is 1.34 mdyn Å^{-1}.[304] The Mössbauer effect in solid $XeCl_2$ at 4.2°K was investigated[303]. The quadrupole splitting is 28.20 mm s^{-1}, the isomer shift 0.17 mm s^{-1} (relative to atomic xenon). The formal charge on each chlorine atom is 0.5.

Xenon tetrachloride $XeCl_4$ was identified by the Mössbauer spectrum as the product of the β-decomposition of ^{129}I introduced into $KICl_4$: $^{129}ICl_4^- \rightarrow {}^{129}XeCl_4$.[303] The quadrupole splitting in $XeCl_4$ is 25.62 mm s^{-1}, the isomer

shift 0.25 mm s^{-1}. The results of the investigation confirm the square planar configuration for $XeCl_4$. The charge on the central xenon atom in $XeCl_4$ is 1.9.

The negative ion $XeCl^-$ is formed as a result of the occurrence in the gas phase at a pressure of 10^{-4} mmHg of the ion-molecular reaction $Xe + CoCl^-$.[306] The energy of the dissociation of $XeCl^-$ into Xe and Cl^- is less than 10 kcal $mole^{-1}$.

Xenon dibromide $XeBr_2$, which is formed in the β-decay of ^{129}I in $KIBr_2$, was identified from the Mössbauer spectrum[307]. The outer ones of the three intense, sharply resolved lines are regarded as an $XeBr_2$ doublet with quadrupole splitting 22.2 mm s^{-1}. The formal charge on the bromine atoms in $XeBr_2$ is 0.41.[307]

Attempts to synthesise xenon chloride fluorides were unsuccessful[308,309]. The existence of $FXeBF_2$[310] has not yet been confirmed. The stable ion CH_3Xe^+ is formed in the interaction of xenon with CH_3FH^+ in the gas phase[311].

D. Radiochemistry of Xenon Compounds

The synthesis of xenon fluorides containing ^{133m}Xe or other radioactive isotopes can be effected from the elements by traditional methods, and also by the irradiation of xenon fluorides with neutral fluxes in a nuclear reactor[1,3]. The xenon fluorides are then used for obtaining oxygen compounds of xenon[274]. The retention of radioactive xenon in the initial XeF_2 and XeF_4 when they are irradiated in neutron fluxes (10^{12}–10^{13} n cm^{-2} s^{-1}) reaches 98% in XeF_4 and 93% in XeF_2,[312] that of radioactive fluorine is 100% in XeF_2 and 90% in XeF_4.[313] In the isomeric transformation of ^{135m}Xe in XeF_2 in organic solvents, ^{133}Xe is released in the elemental state to the extent of 95%.[314] The effectiveness of such processes for XeF_4 in aqueous solutions of XeO_3 is 50%.[315]

The distribution of iodine among the chemical species in the process of capture of an electron $^{125}Xe \rightarrow {}^{125}I$ in H_2O, XeF_2, and XeF_4 has been studied. It has been found that 95% of the ^{125}I is found in the form IO_4^- and 5% in the form IO_3^-. These investigations[316] allowed a method to be developed for obtaining ^{125}I without a carrier, which enabled preparations in the form of NaI with a specific activity exceeding 100 mC ml^{-1} to be obtained. The irradiation with an integral neutron flux of 2.5×10^{19}–5.1×10^{19} of a matrix target, for which XeF_2 was used, leads to the formation of a final product with a yield of 26–43 mC per g XeF_2.[317]

The chemical changes in the β-decay of iodine isotopes in the composition in iodates and periodates are regarded as an effective method of investigating the processes of formation of the xenon fluorides[318]. For example, the yield of chemically bound xenon in the decay of the isotopes ^{131}I, ^{133}I, ^{135}I in periodates reaches 45–85% in crystals and 70% in H_2O, 0.001 M H_2SO_4, and 1 M HNO_3.[319,320] The yield of combined xenon in the decay of isotopes in the alkali metal iodates varies from 10% (Cs, Rb, K) to 43.8% (Na) and 62.2% (Li) in 0.001 M H_2SO_4 and amounts to only 0.3% (K, Na) in 2 M NaOH.[321] An analysis of the results obtained allowed a complex relation to be found between the yield of chemically bound xenon and the valence of the iodine in the compounds, the state of these compounds (solution or crystal), the nature of the cation, the conditions of storage, the presence or absence of carriers, etc.[319–321] XeO_3 is formed in these processes. Xenon trioxide is also the only form of combined xenon in the β-decay of ^{131}I in I_2O_5 (yield 27%) and HIO_4 (yield 44%).[322] The processes for the formation of oxygen compounds of xenon in the β-decay of iodine and some of their properties have been discussed[323,324]. It has also been shown that XeO_3 is formed in aqueous solutions in the β-decay of ^{131}Xe in the composition of $C_6H_5IO_2$.[325] Several methods have been proposed for the separation of radioactive XeO_3 from the parent compounds by use of ion-exchange and thin-layer chromatography[326–329].

The possibility of the formation of xenon compounds under natural conditions as a result of the occurrence of nuclear processes has been examined[330]. The Szillard–Chalmers effect in dissolved XeO_3 has been investigated[331]. The retention of radioactive xenon amounts to 3%. It was found that the factor of enrichment of the xenon radioactive isotopes in the gas phase varies with the period of irradiation. Investigations[332,333] of processes of β-decay of ^{131}I or ^{133}I in C_6H_5I, $(C_6H_5)_2ICIO_4$, and other iodonium salts showed the formation of chemically bound xenon in an involatile form and it was concluded that $C_6H_5Xe^+$ is formed. The yield of onium compounds depends on the nature of the anion present, and the stabilising ability in relation to $C_6H_5Xe^+$ decreases in the order:

$$ClO_4^- > BF_4^- > SO_4^{2-} > NO_3^- > Cl^-.$$

III. KRYPTON COMPOUNDS†

Krypton difluoride is formed by the action of an electric discharge (15–20 mA, 3000–4000 V) on a mixture of krypton and fluorine with the molar ratio 1.1 : 1 at a total pressure of 20 mmHg.[230] The variation of the yield of KrF_2 with the parameters of the electric discharge, the pressures of krypton and fluorine, and the geometry and the temperatures of the walls of the discharge tube was investigated[334]. The synthesis of KrF_2 in an electric discharge can also be brought about in a metallic reactor at a wall temperature of −196°C, pressure of the gas mixture 4–20 mmHg, molar ratio $F_2 : Kr = 5 : 1$, current 20–30 mA, potential 500–1000 V.[335]

Gaseous krypton and fluorine react readily, with the formation of KrF_2 under the action of protons with energies of 10 MeV or α-particles with energies of 40 MeV at −140°C.[39] The radiation-chemical yield is 1.0–1.5, depending upon the temperature. A photochemical reaction is effected in the $Kr-F_2$ and $Kr-OF_2$ systems at room temperature[336]: the yield of KrF_2 in these experiments is insignificant.

At room temperature krypton difluoride is a colourless crystalline substance; it sublimes below 0°C. The vapour pressure in the temperature range from −30° to +25°C is described by the equation[337]:

$$\lg P_{mmHg} = 8.814 - 2000/T.$$

The physical properties of KrF_2 are given in Table 5.

The kinetics of thermal decomposition of gaseous KrF_2 were studied in the temperature range 20–100°C and at KrF_2 pressures of 5–70 mmHg.[338] The variation of the homogeneous decomposition of KrF_2 with temperature (60–100°C) is expressed by the equation:

$$k_{(hom)} = 2 \cdot 10^{13} \exp(-23\,800/RT)\,s^{-1}.$$

In the general instance, the activation energy of the thermal decomposition of KrF_2 varies from 10.2 kcal $mole^{-1}$ (20°C) to 23.8 kcal $mole^{-1}$ (60–100°C).

†See Prusakov and Sokolov's review[10] for a more detailed account of the papers published up to 1971.

The ions KrF^+ and Kr^+ with appearance potentials of 13.21 ± 0.25 and 13.71 ± 0.20 eV respectively have been observed[335] in the mass spectrum of KrF_2. The emission spectrum of KrF_2 in the ultraviolet range has been investigated[65]. The infrared and Raman spectra of gaseous KrF_2 have been obtained and interpreted[339] and have confirmed that the symmetry of this molecule is $D_{\infty}h$. The force constants were found to be: f_r = 2.46, f_{rr} = −0.20, f_{α} = 0.21 mdyn Å^{-1}. The negative force constant for the interaction between the bonds f_{rr} = −0.20 mdyn Å^{-1} and also the absence of Fermi resonance between the frequencies ν_1 and $2\nu_2$ were discussed[339–342]. The asymmetric stretching vibration ν_3 in the infrared spectrum of $^{86}KrF_2$ was studied[343] further with a resolution of 0.08 cm^{-1}. Two alternative assignments were proposed and two corresponding sets of constants were obtained. The most probable, in the opinion of Murchison and coworkers[343], set gives ν_0 = 589.889, B_0 = 0.126 26, B' = 0.125 75, D_0 = D' = 7.8 × 10^{-8} cm. Hence r(Kr–F) = 1.875 ± 0.002 Å (or 1.876 ± 0.002 Å). The spectrum of solid KrF_2 (400 to 1000 cm^{-1})[170] at 77 °K is characterised by sharply expressed maxima at 520, 536, and 573 cm^{-1}. It has been suggested that KrF_2 is polymerised in the solid state. The band at 573 cm^{-1} is assigned to the Kr–F (ν_3) stretching vibration of the monomeric molecule, the remaining bands to the polymeric species of KrF_2. Electron diffraction investigations of gaseous KrF_2 confirmed the linear symmetry structure of the molecule[344]. The mean interatomic distances are r(Kr–F) = 1.889 and r(F...F) = 3.781 Å.

The ^{19}F NMR spectrum of KrF_2 in anhydrous HF was investigated[230]. The two fluorine atoms in KrF_2 were found to be equivalent. Exchange by the fluorine atoms between HF and KrF_2 was not noted even at 25 °C. From the Mössbauer spectrum of $^{83}KrF_2$ the quadrupole coupling constant was found to be 130 mm s^{-1} and the ratio of the quadrupole moments of the excited and ground states (1.70), and the isomeric shift (in relation to atomic krypton) (1.50 mm s^{-1}) were found[345]. The formal charge on the krypton atom in KrF_2 is 1.06. High-resolution photoelectronic spectra were obtained for KrF_2 in He–I and He–II radiation[346,347].

The BrF_5–KrF_2 system was studied by the DTA method[348]. The complexes $KrF_2.SbF_5$, $KrF_2.2SbF_5$, $KrF_2.TaF_5$, $KrF_2.2TaF_5$, $KrF_2.2NbF_5$, $2KrF_2.SnF_4$, and $2KrF_2.TiF_4$ have been isolated[10,337] from solutions of KrF_2 in anhydrous HF and BrF_5. The stability of the complexes of KrF_2 in non-aqueous solvents is much lower than that in the solid state, owing to the chemical reaction of these compounds with the solvents. Investigations of the infrared spectra[10] enabled ionic structures to be suggested for these compounds which were also confirmed by measurements of the Raman spectra of $KrF_2.2SbF_5$, $KrF_2.TaF_5$, $KrF_2.2TaF_5$, $KrF_2.2NbF_5$, and BrF_5 at −196 °C.[349] The stretching vibration Kr–F (KrF^+) in the Raman spectra[349] is characterised by doublet and even triplet absorption bands 620 and 623 cm^{-1} in $KrF^+Sb_2F_{11}^-$, 599 and 604 cm^{-1} in $KrF^+TaF_6^-$, 600 and 609 cm^{-1} in $KrF^+Nb_2F_{11}^-$, and 597, 605, and 613 cm^{-1} in $KrF^+Nb_2F_{11}^-$. The stretching vibration Kr–F in KrF^+ corresponds to the band at 622 cm^{-1} in the infrared spectrum[170] of $KrF^+SbF_6^-$.

$2KrF_2.SbF_5$ was synthesised in BrF_5 solutions at −40 °C; it is stable at the synthesis temperature[350] and decomposes in a dynamic vacuum at −30 °C with the formation of $KrF_2.SbF_5$, which is stable at room temperature. The Raman spectra of these compounds were investigated[349]. The bands at 627 and 619 cm^{-1} in $KrF_2.SbF_5$ were assigned to the KrF^+ vibration; the bands at 595 and 607 cm^{-1} in $2KrF_2.SbF_5$ to the principal stretching vibrations of the $Kr_2F_3^+$ cation. Gillespie and Schrobilgen[351] obtained $KrF_2.MF_5$ (M = As, Pt), $2KrF_2.AsF_5$, and $(KrF_3^+MF_6^-)_n KrF_2$ (M = As, Sb) and confirmed the existence of $KrF_2.SbF_5$ and $2KrF_2.SbF_5$. The compound $KrF_2.PtF_5$ was prepared by the reaction of KrF_2 and PtF_6 at 0 °C. The Raman spectra of these compounds were studied[351] and the ^{19}F NMR in $KrF_2.SbF_5$ at −40 °C and in $2KrF_2.SbF_5$ at −66 °C was measured in anhydrous HF and BrF_5. The results show the existence of the cations KrF^+ and $Kr_2F_3^+$ in the solutions. In the NMR spectrum of $KrF^+SbF_6^-$ a singlet line with a chemical shift of 22.6 p.p.m. relative to CCl_3F (−55.6 p.p.m. for KrF_2 in HF) is observed. The NMR spectrum of a solution of KrF_2 and SbF_5 with molar ratio 2:1 is assigned to the AX_2 type, which suggests a

Table 6. Change in free energy (enthalpy) in the reactions of certain gaseous inorganic fluorides.

Initial substance	$-\Delta G^0_{298}$ EF_n ($-\Delta H^0_{298}$) kcal mole^{-1}	Reaction product	$-\Delta G^0_{298}$ EF_{n+2} ($-\Delta H^0_{298}$) kcal mole^{-1}	$-\Delta G_{298}EF_{n+2}$($-\Delta H_{298}$), kcal mole^{-1}								
				F_2	$OF_2^{(2)}$(to O_2)	$O_2F_2^{(2)}$	N_2F_2 (to N_2)	XeF_2	XeF_4 (to XeF_2)	XeF_6 (to XeF_4)	KrF_2	RuF_6^* (to RuF_5)
ClF	13.8 (13.9)	ClF_3	29.5 (37.8)	15.7	(19.5)	28.4	50.7	—1.8	1.8	8.6	37.8	(32.9)
ClF_3	29.5 (37.8)	ClF_5	35.8 (57.7)	6.3	(15.5)	19.0	41.3	—11.2	—7.6	—0.8	28.4	(28.9)
BrF_3	55.2 (64.8)	BrF_5	84.4 (106.2)	29.2	(37.0)	41.9	64.2	11.7	15.3	22.1	51.3	(50.4)
XeF_2	17.5 (25 6)	XeF_4	31.4 (49.3)	13.9	(19.3)	26.6	48.9	—	—	6.8	36.0	(32.7)
XeF_4	31.4 (49.3)	XeF_6	38.5 (66.7)	7.1	(13.0)	19.8	42.1	—	—	—	29.2	(26.4)
UF_4	424.6 (443.4)	UF_5	458.7 (485.2)	34.1	(39.6)	40.5	51.6	25.4	27.1	30.6	45.1	(46.3)
UF_5	458.7 (485.2)	UF_6	492.0 (511.0)	33.3	(23.6)	39.7	50.8	24.6	26.0	29.8	44.3	(30.3)
UF_4	424.6 (443.4)	UF_6	492.0 (511.0)	67.4	(63.2)	80.2	102.4	49.9	53.2	60.4	89.5	(76.6)
N_2F_4[1]	—18.7 (2)	NF_3	21.4 (31.6)	61.5	(56.8)	74.2	96.5	44.0	47.6	54.4	83.6	(70.2)
NOF	12.1 (15.8)	NOF_3	(32)	(16.2)	(11.8)	(20.9)	(41.8)	(—9.4)	(—7.5)	(—1.2)	(30.6)	(25.2)
Rn	—	RnF_2	(57.4*)	(57.4)	(53.0)	(62.1)	(92.4)	(31.8)	(33.7)	(40.0)	(71.8)	(66.4)

Notes. (1) The reaction of N_2F_4 proceeds through the formation of NF_2 radicals, for which the addition of fluorine with formation of NF_3 is energetically more favourable.

(2) In the reactions of OF_2 the radicals OF and F participate, in those of O_2F_2, the radicals O_2F and F.

(3) The relatively low fluoro-oxidising ability of N_2F_2 (according to the experimental results) is due to kinetic restraints.

*Estimated values.

V-shaped structure for $Kr_2F_3^+$ with fluorine bridging atom[351]. The ^{19}F chemical shifts are −19.0 p.p.m. (A) and −73.6 p.p.m. (X_2). The coupling constant ($^{19}F_A-^{19}F_X$) is 351 Hz, close to that found for $Xe_2F_3^+$ (308 Hz).[351] In the Raman spectrum of $Kr_2F_3^+$, bands are observed at 603 and 594 cm^{-1}, 555 and 456 cm^{-1}; the results are interpreted[351] in terms of the asymmetric structure $FKr^+...FKrF$.

$XeF_6.SbF_5$ was isolated from a solution of KrF_2, SbF_5, and XeF_6 (1 : 1 : 1) in BrF_5 at 0°C, showing that the donor properties of XeF_6 are stronger than those of KrF_2; this is also confirmed by XeF_6 replacing KrF_2 in its complexes[170]. Xenon difluoride is also a better fluoride-ion donor than KrF_2. The molecular complex $KrF_2.XeF_6$ has also been obtained[170]; it is a colourless crystalline substance with m.p. 41°C and a vapour pressure of 11 mmHg at 20°C. The molecular nature of the complex was established by measurements of the infrared spectrum.

Taken together, the properties of KrF_2 suggest that KrF_2 as a fluoro-oxidant surpasses such strong fluorinating agents as F_2, oxygen fluorides, and halogen fluorides, and is only slightly worse than atomic fluorine (see Table 6). The complexes of KrF_2 are also strong oxidants. For example, in solutions of bromine pentafluoride KrF^+ ($KrF_2.nSbF_5$) readily oxidises IF_5 to IF_6^+, $XeOF_4$ to $XeOF_5^+$,[184] and BrF_5 to BrF_6^+.[351]

Previous papers (cf. Neiding[1]) have discussed the preparation and study of krypton tetrafluoride, and also the formation during its low-temperature hydrolysis of kryptic acid and its barium salt. These results were not confirmed subsequently. Furthermore, mass-spectrometric measurements and investigations of the vibrational spectra and ^{19}F NMR spectra of the products of the reaction of krypton with fluorine in a glow discharge showed that the identification of the reaction product as krypton tetrafluoride is erroneous.

Mössbauer spectroscopy was used to observe the chemically bound states of krypton[352] formed during electron capture in ^{83}Kr. The Mössbauer spectra of ^{83}Kr in solid matrices are characterised by broad lines, which suggests a different degree of chemical bonding[345,352,353]. In an investigation[353] of the products of the β-decay of ^{83m}Br in $KBrO_3$ a resonance line 2 mm s^{-1} broad is observed in the spectrum and is assigned to the bond of ^{83m}Kr with oxygen. These results were confirmed by measurements of the Mössbauer spectra of the products of the β-decay of ^{83}Se ($^{83}Se \rightarrow {}^{83}Br \rightarrow {}^{83}Kr$) in Se, SeO_2, and $(NH_4)_2SeO_4$.[354]

IV. RADON COMPOUNDS

The preparation and identification of radon compounds is extremely difficult owing to the high activity of the most stable radon isotope ^{222}Rn ($\tau_{1/2}$ = 3.8 d.) Therefore information about radon compounds is only qualitative.

It has been reported[355] that radon is oxidised in aqueous solutions by certain oxidants, in particular H_2O_2, $KMnO_4$, and $K_2S_2O_8$. Subsequent investigations[356] showed that under the conditions of the experiment[355] the radon is held mechanically in the solid phase. The formation of significant amounts of oxygen-containing compounds of radon is also not observed[357] in the α-decay of ^{226}Ra.

Vasilescu[358] estimated $\Delta H^\circ_{298}RnF_n$ (g). After some refining of these values, the following quantities are obtained: $\Delta H^\circ_{298}RnF_2$ (g) = −57.4 kcal $mole^{-1}$ (mean energy of the Rn–F bond 46.5 kcal $mole^{-1}$), $\Delta H^\circ_{298}RnF_4$ (g) = −81.1 kcal $mole^{-1}$ (39.1), $\Delta H^\circ_{298}RnF_6$ (g) = −98.5 kcal $mole^{-1}$ (35.2).

Radon fluorides are formed in the reaction of elemental radon with ClF_3, KrF_2, and XeF_n at room temperature[359], with O_2F_2 at −100°C, or under the action of α-radiation in liquid fluorine or solid ClF_3 at −196°.[359] The products of these reactions were not identified. Radon fluoride of a definite composition is isolated by distillation with XeF_6 from the reaction products of mixtures of xenon and radon with fluorine at 300°C and 100 atm.[359] The formation of RnF_2 and RnF_4 has also been reported[360].

The oxidation of gamma amounts of radon was effected in BrF_3, BrF_5, and ClF_3 solutions[361]. The formation of RnF_2 was suggested. Radon can also be oxidised by the action of ClF, ClF_5, BrF, IF_7, or NiF_6^{2-} (in HF) in the temperature range from −195° to +25°C.[362] Experiments on the electrolysis of solutions of oxidised radon in BrF_3 (potential difference 18–50 V, current 50 mA) showed that the Rn is concentrated only in the near-cathode region without reduction. On this basis the existence in the solutions of the cations RnF^+ or Rn^{2+} (products of the dissociation of RnF_2) was suggested. The coprecipitation of radon fluoride with the molecular compound of XeF_2 and IF_5 was studied[363] to find the chemical composition of the radon in BrF_3–IF_5 solutions. The results show that the most probable product of the reaction Rn + XeF_2 (XeF_4) is RnF_2. Involatile radon compounds are formed in the reaction of radon with ClF_2SbF_6, BrF_2SbF_6, $BrF_4Sb_2F_{11}$, $If_4(SbF_6)_3$, or BrF_2BiF_6 at 25°C.[364] $KBrF_4$, $CsBrF_6$, $KClF_4$, $RbClF_4$, and BrF_2TaF_6 are less effective. It is suggested that the reaction leads to the formation of complexes of the type $RnF^+MF_6^-$ or $RnF^+M_2F_{11}^-$ and radon difluoride[364].

Vasilescu[358] discussed the possibility of obtaining various compounds of radon and their expected stability. Stein[365] discussed problems of radon chemistry in detail.

V. ELECTRONIC STRUCTURE OF COMPOUNDS OF THE NOBLE GASES

In her extremely thorough critical review[2] Dyatkina examined the main theoretical studies in this field published in the period 1963–1968 and compared the theoretical with the experimental results. Dyatkina came to the general conclusion "that the main reason for the formation of these compounds is the establishment of delocalised molecular orbitals and the specific characteristics of the molecular orbitals—their energies and atomic orbital coefficients—determine the properties of the molecules".[2]

Without any pretension to the completeness and depth of exposition present in Dyatkina's review[2] we will examine the most recent theoretical publications on the compounds of the noble gases.

First let us briefly examine the attempt of Mitchell[366–369] to prove by use of the valence bond method the significant role of the atomic *d*-orbitals (5*d* for Xe, 4*d* for Kr) in the formation of bonds in the halides of these elements. Mitchell calculated the excitation energy of three valence states of the Xe atom in hybridisations with participation of the 5*s*-, 5*p*-, and 5*d*-orbitals and with the aid of the method of Hartley, Lennard-Jones, and Pople evaluated the energies of the valence structures Hal–Xe–Hal, $Hal-Xe^+Hal^-$, and $Hal^-Xe^{2+}Hal^-$ (the first structure is based on the assumption of the hybridisation of the 5*s*- and $5d_{z^2}$-orbitals of Xe) for XeF_2 and $XeCl_2$.[368] The first structure seemed the most stable and on this basis Mitchell concluded that the 5*d*-orbitals of Xe participate in the formation of XeF_2 and $XeCl_2$, assuming that the high excitation energy is compensated by the gain in the bond

energy. Somewhat later, Catton and Mitchell[368] made a refined calculation of XeF_2 by the valence bond method and found that the structures based on the participation of the Xe $5d_{z^2}$-orbitals contribute ~ 69% to the complete wave function, whereas the contribution of the resonance structures which include only the $5p_z$-orbital totals only ~ 16%. Developing these ideas, the same investigators[369] calculated the energies of various valence structures in KrF_2, XeF_2, $XeCl_2$, and also in the hypothetical molecules ArF_2, $ArCl_2$, and $KrCl_2$. The calculations showed that in every instance (except ArF_2) the minimal energies are exhibited by the structure Hal–X–Hal. On this basis Catton and Mitchell concluded that the greater part is played by a valence scheme based on the promotion of p-electrons to a d-AO and the hybridisation of pd-AO; here the high excitation energy in the free atoms is compensated by the influence of the ligands on the AO atoms, greater for the fluorides than for the chlorides. The role of the Hal–X–Hal structure increases, according to the calculation, in the order Ar < Kr < Xe. Finally, in the most recent paper in this series[367] Mitchell has suggested the participation of the Xe $4f$- and $6s$-orbitals in the formation of xenon hexafluoride and he related the participation of the $4f$-orbitals to Bartell and Gavin's views (discussed above) on the structure of XeF_6.

Table 7. Correlation of the calculated[373] and experimental[53,374] values of the ionisation potentials of XeF_n (in eV).

XeF_2			XeF_4			XeF_6		
MO	$-0,92\varepsilon$	vertical IP	MO	$-0,92\varepsilon$	vertical IP	MO	$-0,92\varepsilon$	vertical IP
$10\ \sigma_g$	11.79	13.65	$10\ a_{1g}$	11.7	13.1	$8\ a_{1g}$	10.8	12.5
$5\ \pi_u$	12.51	12.42*	$5\ a_{1g}$	13.9	13.4	$5\ e_g$	17.2	15.2
		12.89	$5\ b_{1g}$	15.2	14.5	$1\ t_{1g}$	17.6	16.0
$3\ \pi_g$	14.71	14.35	$1\ a_{2g}$	15.8	15.1	$7\ t_{2u}$	18.0	(16.5)
		15.60*	$7\ e_u$	16.2	(15.4)	$1\ t_{2u}$	18.1	(17.1)
$4\ \pi_u$	15.92	16.00	$1\ b_{2u}$	16.5	15.8	$3\ t_{2g}$	18.8	17.7
$6\ \sigma_u$	16.93	17.35	$3\ e_g$	16.6	(16.0)	$6\ t_{1u}$	22.3	20.0
$9\ \sigma_g$	25.24	22.5	$3\ b_{2g}$	16.8	16.3	$7\ a_{1g}$	29.2	21.0
			$4\ a_{2u}$	19.0	17.9			
			$6\ e_u$	19.6	18.4			
			$9\ a_{1g}$	27.4	19.8			

*Doublet structure, due to spin–orbital coupling.

Before turning to the consideration of non-empirical calculations, we note the method proposed by Andreev for the determination of the conformation of the molecules of XeF_2, KrF_2,[370] and XeF_4[371] by the combined use of the theory of the interaction of bonding and unshared electron pairs and the maximal overlap criterion. The same investigator[372] considered the electronic structure of XeF_3 and XeF_3^+, having used the Wolfsberg–Helmholz method with allowance only for $p\sigma$-AO. According to the calculation, the most stable configuration for XeF_3 has C_{2v} symmetry, but for XeF_3^+ there are alternatives in the choice of a stable geometry—D_{3h} or C_{2v} are the most probable.

Basch and coworkers[373] made non-empirical calculations for XeF_2, XeF_4, and XeF_6, using Roothaan's complete SCF MO method with a basis set of gaussian functions including the $1s$-, $2s$-, $3s$-, $4s$-, $5s$-, $2p$-, $3p$-, $4p$-, $5p$-, $3d$-, and $4d$-AO of xenon, and the $1s$-, $2s$-, and $2p$-AO of fluorine (all the AO were checked by calculation of the orbital and total bond energies). The total and orbital energies were calculated and the composition of the valence MO was found. An analysis of the populations after Mulliken was made for the individual AO and the overlap populations were also found.

The photoelectron spectra of XeF_2 were investigated almost simultaneously by Brundle and coworkers[374] and by Brehm and coworkers[52]. The ionisation potentials found in the two studies agree and differ little from those obtained by the photon collision method[54] and by photoionisation mass spectrometry[44]. The photoelectron spectra of XeF_4 and XeF_6, investigated by Brundle and coworkers[53], led to ionisation potentials close to those found by photoionisation mass-spectrometry[44]. The assignment, proposed on the basis of these results[53,373,374], of the vertical ionisation potentials to ionisation from MO_5 and a comparison of the experimental results with the calculated orbital energies multiplied by 0.92 (a factor introduced by Brundle and coworkers[53] to correct for the approximations of the Koopmans theorem) are given in Table 7. Fig. 13 gives the corresponding correlation diagram.

The effective charges on the xenon atoms were evaluated in the calculation[373] and are +1.304, +2.455, and +3.458 for XeF_2, XeF_4, and XeF_6 for a comparatively constant charge on the fluorine atoms (−0.652, −0.614, and −0.576). Between the calculated effective charges and the quantities estimated on the basis of EPR[58] and NMR[375,376] investigations, Mössbauer spectra[303], and X-ray electronic spectra[50,51] there are significant differences; the reasons for these have been discussed[58].

Basch and coworkers[373] used the results of their non-empirical calculation of the xenon fluorides for a detailed interpretation of the electronic spectra of XeF_2 and XeF_4 on the basis of the experimental results of Jortner and coworkers (cf. Dyatkina's review[2]). They also calculated and tabulated certain one-electron properties of the molecules of the xenon fluorides: the mean values of magnetic screening tensor of the xenon and fluorine nuclei, the quadrupole moments of XeF_2 and XeF_4, the components of the field gradient at the xenon and fluorine nuclei[373].

A regular octahedral structure was chosen for XeF_6 in the calculation[373]. Such an approximation must reflect on the accuracy of the results obtained since in reality the XeF_6 molecule does not maintain strictly O_h symmetry. Unfortunately, later investigations of the electronic structure of XeF_6 made by the wave scattering method with statistical allowance for the exchange interactions[377] was also based on the adoption of O_h symmetry for this molecule. In this work[377] the orbital energies were calculated within the framework of the ideas of half-occupied spin-orbitals, since Koopmans' theorem is inapplicable in a statistical calculation of exchange interactions. When the factor 0.92 is not used, the results of the calculations by scattered waves method[377] give better agreement with experiment.

Three non-empirical calculations were made[378–380] for the krypton fluorides (KrF_2, KrF, and KrF^+). The calculations for KrF and KrF^+ were made by the SCF MO method with a large basis set of functions of the Slater type[380]. The potential curve for KrF was calculated by assuming the ground state $^2\Sigma^+$ (in agreement with EPR results[381]), and that for KrF^+ the state $^1\Sigma^+$. The curve for KrF, like that for XeF, is repulsive, since these molecules can exist in the gas phase solely owing to van-der-Waals interaction. The dissociation energy found for the molecular ion KrF^+ was $D_0 = 1.90$ eV, which agrees with the experimental $D_0 \geq 1.58$ eV.[382] The calculated spectroscopic constants of KrF^+ are also in good agreement

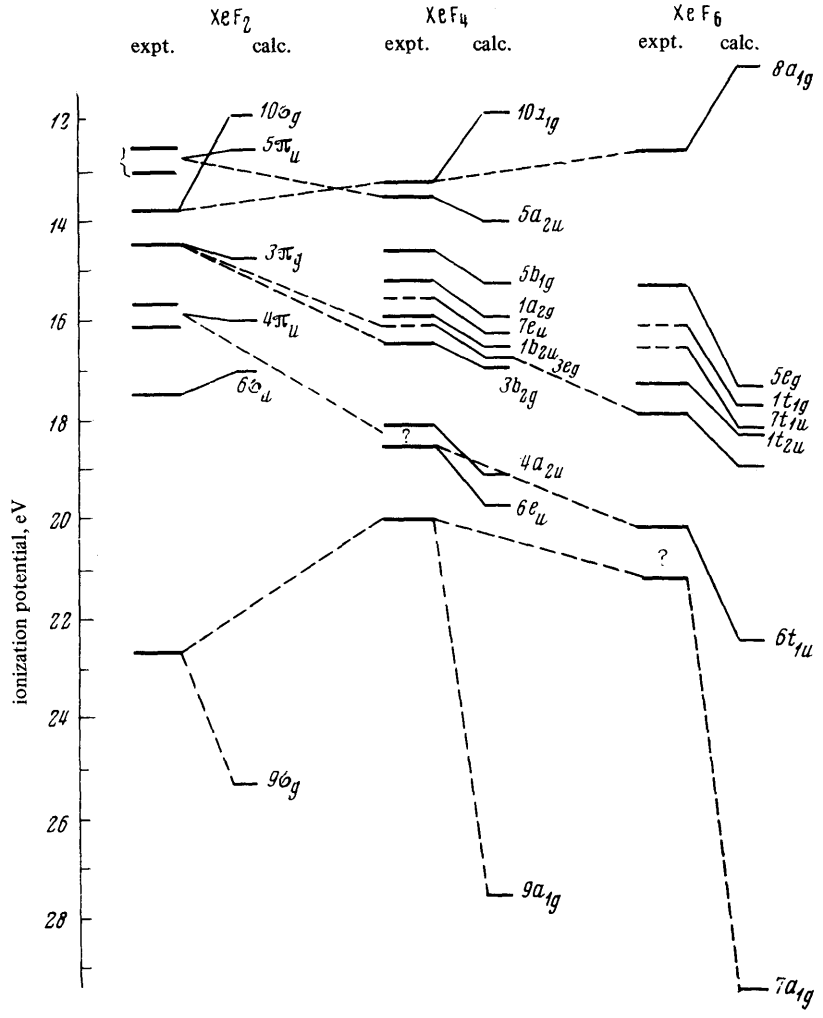


Figure 13. Diagram of the molecular orbitals of xenon fluorides.

with experiment, in particular the theoretical wavenumber of the stretching vibration (621 cm^{-1}) is close to that found from the Raman spectrum for $KrF^+Sb_2F_{11}^-$.[184]

Concerning the problem of the role of the "higher" AO's in the formation of bonds in noble gas compound (the role of the polarisation functions (4*d* and 4*f* for Kr and 3*d* and 4*f* for F) has been evaluated[380]. In KrF the inclusion of the polarisation functions decreases the total energy by only 0.0044 a.u., in KrF^+ by 0.0388 a.u. In the first non-empirical calculation for KrF_2, the main aim of which was the explanation of the role of the 4*d*-orbitals of Kr, the SCF MO method was used with a minimal set of Slater-type functions[378]. From the results of this work there follows the need for the inclusion in the basis of the Kr 4*d*-functions, but a calculation made with a broadened basis set[379] showed insufficient justification for this assertion.

Bagus and coworkers[379] made a complete calculation of KrF_2 by the SCF MO method using an extended basis set of Slater-type functions with allowance for configuration interaction. The potential curve found with 993-configuration wave function corresponds to the bound state of KrF_2 in relation to three atoms infinitely removed from one another. The calculated Kr–F distance, found to be 1.907 Å, and the dissociation energy, 0.39 eV, are comparable with the experimental results (respectively 1.88 ± 0.01 Å and 1.013 eV). On the potential curve there is a barrier at r(Kr–F) = 2.42 Å of height 0.22 eV in relation to the total energy of the disconnected atoms. The electric field gradient at the Kr nucleus near to the minimum of the potential curve is close to the value calculated by the SCF method for the Kr^+ ion and falls rapidly to zero close to the maximum of the potential curve. These results show that the Kr–F bond is ionic at the equilibrium distance and covalent at greater distances, which agrees with Coulson's views[340].

To investigate the role of the polarisation functions (4*d* and 4*f* Kr, 3*d* and 4*f* F), a series of calculations was

made[379] with various basis sets and it was shown that the role of the Kr 4*d*-AO is significantly less than that found from the previous calculation[378]. A compilation of the theoretical results[378,379] with high-resolution photoelectron spectra of KrF_2,[346,383] are given in Table 8 and Fig. 14 (on which results for XeF_2 are given for comparison).

Table 8.

MO	-0.92ε (Ref.378)	-0.92ε (Ref.379)	Vertical IP (Refs.346, 383)	MO	-0.92ε (Ref.378)	-0.92ε (Ref.379)	Vertical IP (Refs.346, 383)
$8\sigma_g$	7.9	14.71	13.90	$3\pi_u$	15.0	19.36	16.92
$4\pi_u$	10.5	15.43	13.34* 13.47	$5\sigma_u$	16.1	20.85	17.7
$2\pi_g$	12.6	17.64	14.37	$7\sigma_g$	29.0	33.75	23.0

*Doublet due to spin–orbital coupling.

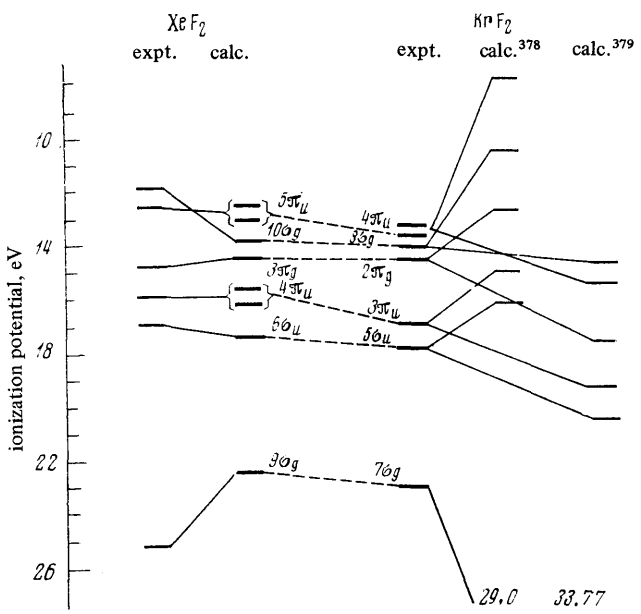


Figure 14. Diagram of the molecular orbitals of the lower fluorides of xenon and krypton.

The xenon oxide fluorides have been examined theoretically in only one paper, published comparatively recently[383]. The electronic structures of $XeOF_2$, XeO_2F_2, and $XeOF_4$ were calculated within the framework of the semiempirical modified Wolfsberg–Helmholz method. The results obtained by Gillespie using the method of localised electron pairs (see Dyatkina[2]) formed the basis of a comparison of the electronic and geometric structures of the oxide fluorides. The energies and populations of the MO were found on the basis of the nodal structure of the upper occupied MO and the geometric structure of the xenon oxide fluorides was predicted.

According to the prediction, the $XeOF_2$ molecule should have C_{2v} symmetry with an O–Xe–F angle less than 90°. For XeO_2F_2 the O–Xe–O angle should be less than 120°, and the F–Xe–F angle (at the side of both O atoms) less than 180°. For $XeOF_4$, C_{4v} symmetry was obtained with O–Xe–F angle greater than 90°. In all three molecules the Xe–O bond should be shorter than Xe–F.

When Hsu and coworkers' paper[383] appeared experimental results were known only for $XeOF_4$. They[383] cited only Martins and Wilson's study of the microwave spectrum[233] and did not consider a later electron diffraction investigation[234]. As for XeO_2F_2, a detailed electron diffraction investigation of this molecule appeared recently[241]. Theoretical calculations give qualitative agreement with experimental results for both XeO_2F_2 and $XeOF_4$. For the former the O–Xe–O angle is 105.7° and the Fe–X–F angle is 174.7°; the Xe–O and Xe–F distances are 1.714 and 1.889 Å respectively[241]; in the second instance the O–Xe–F angle is 91.9° and the Xe–O and Xe–F bonds are respectively 1.711 and 1.901 Å.[234]

VI. POSSIBILITY OF THE EXISTENCE OF COMPOUNDS OF THE NOBLE GASES LIGHTER THAN KRYPTON

An approximate evaluation of the possibility of obtaining some compounds of argon and their stability led Ferreria[384] to a conclusion about the similarity in stability of the Ar–F and Kr–F bonds and even of the greater stability of the Ar–O bond compared with Kr–O. However, an estimate of the enthalpy of formation of the hypothetical $ArF_2(g)$, made by extrapolation of the values of ΔH°_{298} along the series (RnF_2)–XeF_2–KrF_2–$[ArF_2]$ and on the basis of the ionisation potentials of the noble gases, leads to a negative bond energy in ArF_2. Some calculations show the possibility of the existence of HeF_2;[385] the results of other theoretical calculations[386,387], made by the SCF LCAO MO and valence bond methods show that for all forms of the geometry of HeF_2 an unstable repulsive state is characteristic. The potential curves for the processes of formation of HeF^+ and HeF, NeF, NeF_2, and NeO also do not have a minimum[388].

Liebman and Allen[389] undertook calculations for ArF^+ and ArO by the SCF LCAO MO method and showed that the $^1\Sigma\sigma^2\pi^4\pi^{*4}$ state should be rather stable and be characterised by the equilibrium distance r_e = 1.8 Å and dissociation energy $D_e \simeq 70$ kcal mole^{-1}. On the basis of these results they suggested the possibility of the synthesis of $ArF^+PtF_6^-$ by the reaction of argon with fluorine in the presence of platinum hexafluoride. Berkowitz and Chupka[390] reported that ArF^+ ($^1\Sigma\pi^4$) is formed in the ion-molecular reactions $F_2^+ + Ar$ and $Ar^+ + F_2$. On the basis of a simple analysis of the exothermic reaction

$$F_2^+ + Ar \rightarrow ArF^+ + F$$

they concluded that $D_0(ArF^+) \geqslant 38$ kcal mole^{-1}. Analogous reactions of F_2^+ with neon and helium were not observed even at high collison energies. Liebman and Allen[391] used the SCF LCAO MO method to calculate the potential curves for the lowest electronic states of HeF^+, NeF^+, HeN^+, and NeN^+ and made an analysis of the possibility of the synthesis and stability of these cations. Unlike earlier investigations[388], these calculations showed the rather high stability of the states $^1\Sigma\pi^4$ HeF^+ (r_e = 1.33 Å, $D_e \simeq$ 33 kcal mole^{-1}) and $^1\Sigma\pi^{*4}$ NaF^+ (re = 1.65 Å, $D_e \simeq$ 30 kcal mole^{-1}). It was suggested[391] that the stabilisation of these states can be effected by bonding in $HeF^+SbF_6^-$ and $NeF^+SbF_6^-$ by the reaction of He and Ne with fluorine (in the presence of SbF_5 or PtF_6) at high temperatures and pressures. Liebman and Allen[392] also showed that although

some of the states HeN^+, NeN^+, HeO^+, ArO^+, and NeO^+ are sufficiently stable and should be observed in ion-molecular reactions, the existence of the corresponding crystalline salts is improbable. On the basis of an SCF LCAO MO calculation of the potential surfaces of HeB^+, NeB^+, and ArB^+ the same investigators[393] concluded that the bound states of these ions were absent unlike the $^1\Sigma$ XeB^+ state, the bond energy of which is estimated to be 10–20 kcal $mole^{-1}$.

VII. POSSIBLE USES OF COMPOUNDS OF THE NOBLE GASES

The interest of the wide circle of investigators in the chemistry of the noble gases is not limited to the theoretical value of this problem. The considerable experimental and theoretical material on the compounds of the noble gases which has now accumulated allows the question of their practical use to be examined.

The investigation of the compounds of the noble gases is of prime importance in connection with the need for solving one of the most important problems of the protection of the environment—the collection of radioactive krypton and xenon—the gaseous products fission of uranium in nuclear reactors. The electrical power of atomic power stations now amounts to ~ 3% of the total power of all power stations. However, even in the next decade the position will change radically and the fraction of atomic power stations to the total production of electric energy will increase considerably. The development of atomic energy is responsible for the need for the reprocessing of large amounts of spent fuel elements of nuclear reactors. In the operation of nuclear reactors and the chemical reprocessing of irradiated nuclear fuel the removal of gaseous fission products is very complex, especially ^{85}Kr (half-life 10.76 years) and ^{133}Xe (9.27 days). This problem is still more complicated because of the future development of fast neutron reactors owing to the increased yield of fission products.

The successful development of noble gas chemistry opens new pathways for the utilisation of radioactive noble gases—in the form of their chemical compounds. The first success has already been achieved. This, it was shown recently[394] that when it reacts with O_2SbF_6 xenon is bonded in the solid involatile compound $XeF^+Sb_2F_{11}^-$. In five experiments with ^{133}Xe on a column of dia. 5.5 × length 65 mm. packed with O_2SbF_6 almost 100% bonding of the xenon from the air at 23–25°C was achieved (^{133}Xe from 2 to 10 mC $litre^{-1}$ mean flow rate 13 ml min^{-1}). It has been proposed to use the analogous reaction with radon for purifying the atmosphere in uranium mines[394]. The oxidation of radon and xenon can be effected also with the aid of K_3NiF_6, K_2NiF_6, Cs_2CoF_6, K_3CuF_6, $CsAgF_4$, Cs_2AgF_6, etc.[395–397] Radioactive xenon and radon are oxidised at 25°C by the action of N_2FSbF_6, but $N_2F_3Sb_2F_{11}$ oxidises only radon at 25–100°C.[398]

The most complex tasks in the problem of the removal of radioactive noble gases is the bonding of ^{85}Kr, since krypton forms only compounds that are comparatively unstable under ordinary conditions, their stability decreasing still further under the action of ionising radiations. In addition, the problems of the chemical bonding of krypton is further complicated by the high oxidising ability of krypton compounds, which is due to the need for obtaining inorganic fluoro-oxidants capable of oxidising krypton. Stein[394] notes that the replacement of the O_2^+ cations in O_2SbF_6 by a cation of greater oxidising ability can yield reagents capable of spontaneous reaction with krypton with the formation of $KrF^+Sb_2F_{11}^-$. On the basis of theoretical calculations[395] salts with the N_2F^+ cation can be regarded as potential oxidants for bonding ^{85}Kr.

Hence the problem of the chemical removal of radioactive xenon and krypton is closely connected with the fluoro-oxidising properties of the compounds of these elements. Naturally, use of the compounds of the noble gases as fluoro-oxidants is of independent interest. Table 6 gives the values of ΔG_{298} (ΔH_{298}) of the reactions of certain inorganic fluoro-oxidants with halogen fluorides, uranium tetrafluoride, nitrogen compounds, and radon. Comparison of the calculated and known experimental results suggests that the reactivity of the fluoro-oxidants correlates with their dissociation energies ($EF_n - EF_{n-} + 2F$) and on this basis the fluoro-oxidants can be arranged in the following series:

$$KrF_2 > O_2F_2 > RuF_6 > F_2 \approx N_2F_2 > XeF_6 > ClF_5 \approx XeF_4 > XeF_2.$$

Complexes of inorganic fluorides, the fluoro-oxidising ability of which is somewhat greater than that of the initial compounds, can also be regarded as potential fluoro-oxidants.

The noble gas fluorides and oxides of the noble gases are powerful oxidants in aqueous solutions of acids and bases. The redox potentials of the xenon compounds[3] are given below:

$$\begin{array}{l} \text{acid } Xe \xrightarrow{2{,}12\,V} XeO_{3(aq)} \xrightarrow{2.36\,V} H_4XeO_6 \\ \qquad\quad \big| \xrightarrow{2{,}36\,V\,(2{,}64)} XeF_{2(aq)} \\ \text{base } Xe \xrightarrow{1.26\,V} HXeO_4^- \xrightarrow{0.95\,V} HXeO_6^{3-}. \end{array}$$

The oxidising ability of these compounds is not less than that of ozone. XeO_3 can also find a use as an effective oxidant in organic solvents[11].

The use of labelled xenon compounds is of importance for medical-biological investigations. Rapid methods for making periodates and perbromates labelled with short-lived isotopes[391–321] can be successfully developed on the basis of XeF_2. Methods of isolating ^{125}I without a carrier have been developed[316]. In view of their involatility, radon compounds can find a use in radiation therapy instead of gaseous radon[1].

The possibility of using XeF_2 and XeF_4 as photolytic sources of atomic fluorine for $F + H_2$ chemical lasers has been examined[399,400]. The use of xenon fluorides as initiators of polymerisations and in gas-filled incandescent lamps is known (cf. Jha[5]).

The study of the possibility of using noble gas compounds for practical purposes has only just begun, but already there is no doubt about the future possibilities of these compounds.

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