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Rhenium Fluorides

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The properties of simple and complex fluorides of rhenium have been reviewed, and the most important directions of study in the field of rhenium fluorides have been formulated.
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I. INTRODUCTION

The electronic configuration of the rhenium atom (d^5s^2) and its position in the periodic system make it unusual among transition metals. It can form compounds in which it has oxidation numbers from −1 to +7 (including zero in the carbonyls), many of which are thermally stable. Rhenium compounds have coordination numbers from 4 to 9. Rhenium is the only metal forming a stable heptafluoride. The relative similarity in the affinities of rhenium for oxygen and fluorine leads to the formation of a large number of oxide fluorides and oxofluoro-anions.

The melting point of rhenium (3190°) [1] is exceeded only by those of tungsten (3420°) [1] and carbon, and this opens up extensive possibilities for its practical application. Because of the extremely low concentration of rhenium in ores and concentrates[2,3], a special place in the technology of this metal is occupied by processes for obtaining alloys and coatings; one of the most progressive methods for producing the latter is considered to be the reduction of gaseous fluorides by hydrogen[4-7]. Dozens of papers have been devoted to the development of this method, and their examination represents an independent problem.

Thus rhenium fluorides are of interest from the viewpoints of both chemistry and technology. However, the only review summarising the properties of rhenium fluorides[8] requires supplementing and correcting.

The aim of the present review is to systematise the methods of preparation and properties of rhenium fluorides, and to outline the principal directions of study in this field.

II. SIMPLE RHENIUM FLUORIDES

Rhenium hepta-, hexa-, penta-, and tetrafluorides are known. The highest fluoride, ReF_7, was first obtained from the elements[9,10]. To isolate pure rhenium heptafluoride, the mixture of ReF_6 and ReF_7 formed by fluorinating the metal was heated at 400 °C and a fluorine pressure of ~3 atm. For this purpose, Slivnik and coworkers[11] recommended more rigorous conditions—a fluorine pressure of ~50–60 atm and a temperature of 150–500°. ReF_7 has been successfully synthesised using a solution of KrF_2 in anhydrous HF.[12] Small quantities of the heptafluoride having a low concentration of ReF_6 (~1%) can be obtained by exploding rhenium wire in an atmosphere of fluorinating reagents[13].

The physical properties of the heptafluoride are similar to those of ReF_6 and other metal hexafluorides (Table 1).[14] The high-temperature modification of ReF_7 is cubic, with lattice parameters 6.26 Å at 25° and 6.14 Å at −90°.[14,17] There is no published information on the low-temperature modification. The vapour pressure of ReF_7 is given by the equations[10,14]:

$$\lg p, [\text{atm}] = 10.1624 - 1.4703 \lg T - 2205.8/T \quad (258.68 \leqslant T \leqslant 321.45\ \text{K})$$
$$\lg p, [\text{atm}] = -24.4643 + 9.90825 \lg T - 244.28/T \quad (321.45 \leqslant T \leqslant 347.76\ \text{K}).$$

Table 1. Physical properties of ReF_7 and ReF_6.[10,14]

Parameter	Value	
	ReF_7	ReF_6
Melting point, °C	48.3±0.1	18.5±0.1
Boiling point, °C	73.7±0.2	33.7±0.1
Temperature of phase transformation, °C	−110	−3.45±0.10
Heat of formation in the gaseous state at 298.2 K, kcal mole^{-1}	−337±3[16]	−324±3[16]
Heat of the phase transformation, kcal mole^{-1}	—	2.02±0.01
Heat of fusion, kcal mole^{-1}	1.3±0.2	1.09±0.01
Heat of volatilisation, kcal mole^{-1}	7.6±0.2	6.76±0.05
Heat capacity of the gas at 298.2 K, cal mole^{-1} K^{-1}	31.6±0.3	28.6±0.3
Entropy of the gas at 298.2 K, cal mole^{-1} K^{-1}	84.7*	86.9±0.5
Density of the crystal, g cm^{-3}	4.32 (cubic)	4.06 (cubic) 4.68 (orthorh.)
Density of the liquid, g cm^{-3}	3.65 (52° C)	3.58±0.02 (22° C)

*This value is apparently too low.

The vibrational spectra of ReF_7 (Table 2) have been interpreted with the assumption that the molecule has the pentagonal bipyramidal configuration[18]; this has been confirmed by the ^{19}F NMR spectra[19].

Vapour-phase electron diffraction has confirmed that the ReF_7 molecule belongs to the symmetry point group D_{5h},[24] and the average internuclear distance Re–F has been calculated (1.835 Å). It was also shown that this model is not completely adequate, and that the axial distances are greater than the equatorial distances, by 0.062 Å. The ReF_7 molecule has a non-zero dipole moment[25,26], which is not compatible with simple D_{5h} symmetry. Nevertheless, it is usually assumed that the distortions are small, and this

symmetry has been assumed in calculations of the force constants[22,23,27] and thermodynamic properties[14,22,23].

The photoelectron spectra of ReF_7 have been characterised[28,29], and the ionisation potentials determined. The range 14.1–17.0 eV contains bands assumed to be due to a contribution from molecular orbitals of the p_π-type; the most intense band lies at 14.6 eV.

Table 2. Vibrational wavenumbers in the spectra of ReF_7 (cm^{-1}).

Raman (gas) (Ref.20)	Infrared (gas) (Ref.20)	Raman (liquid) (Ref.21)	Raman (solution in HF) (Ref.21)	Assignment
736	—	736 v.s.*	741 v.s.	$\nu_1=\nu_2$
—	703	—	—	ν_5
645	—	650 w.	650 w.	
597	—	590 med.	594 med.	ν_8
489	—	—	488 s.	ν_{10}
—	—	385 s.	—	
352	353	351 med.	360	$\nu_4=\nu_9$
—	299	—	—	ν_7
—	217	—	—	ν_6

*Symbols: v.s. = very strong, s. = strong, med. = medium, w. = weak.
The wavenumbers ν_3 and ν_{11} were estimated as 800 cm^{-1} and 241 cm^{-1}.[23]

The chemical properties of ReF_7 have been little studied. It is hydrolysed rapidly by water to HF and $HReO_4$. ReF_7 does not react with oxygen up to 500°.[10] In the opinion of some authors[30], the reactivity of ReF_7 in redox reactions is similar to that of ReF_6. Thermodynamic calculations[31] show, however, that ReF_7 is a much stronger oxidising agent than ReF_6. This is confirmed, for example, by the fact that, at the same temperatures, ReF_7 reacts with metallic rhenium, and ReF_6 does not[10].

Attempts to obtain Re^{VII} complexes by bringing ReF_7 into contact with alkali metal fluorides under pressure were unsuccessful[10], but ReF_7 reacts with nitryl and nitrosyl fluorides to form $NOReF_8$ and NO_2ReF_8.[32] The compounds $[ReF_6]^+[SbF_6]^-$ and $[ReF_6]^+[Sb_2F_{11}]^-$ have been isolated by heating ReF_7 with antimony pentafluoride[33]. The force constants of the bond in the $[ReF_6]^+$ cation were found to be much greater than those for ReF_6 and WF_6, indicating the high electronegativity of Re^{VII}.

The solubility of ReF_7 in anhydrous HF at 25° is 0.26 mole in 1000 g HF.[21] The solutions are weakly ionised.

Rhenium hexafluoride has been much more fully characterised. It was first obtained from the elements at 120 to 125°.[34–36] It is usually formed in a mixture with ReF_7,[9] and can be purified by reducing the latter by metallic rhenium at 400°,[10] or by distilling in a stream of dry hydrogen.[37] ReF_6 can also be obtained by treating the metal with ClF_3 [38] or O_2F_2.[39]

The kinetics of the reaction of rhenium and a W–Re alloy with fluorine have been studied[40,41]. An interesting feature is that the fluorination of the metal has a much lower activation energy than the fluorination of transition metal oxides, the activation energy of which is close to 25 kcal $mole^{-1}$.[42] The thermodynamic parameters of the fluorination (from out-of-date original data) have been published[43].

The chief physical properties of ReF_6 are given in Table 1. The low-temperature orthorhombic modification of ReF_6 (VF_3 structure, space group *Pnma*) at −22° has the following lattice parameters: $a = 9.61$; $b = 8.76$; $c = 5.06$ Å; $Z = 4$. The low-temperature modification is isostructural with the cubic phase MoF_6 ($Z = 2$), and at 10 °C has lattice parameters 6.26 ± 0.02 Å.[17] The cubic crystals are glassy. The magnetic moment of ReF_6 is only 0.25 B.M. [8]

The vapour pressure of ReF_6 is given by the equations[10,14]:

$$\lg p, [\text{atm}] = 9.8264 - 2303.6/T - 0.8327 \lg T \quad (262.68 \leqslant T \leqslant 269.70\ \text{K})$$

$$\lg p, [\text{atm}] = 6.2421 - 1765.4/T - 0.1790 \lg T \quad (269.7 \leqslant T \leqslant 291.65\ \text{K})$$

$$\lg p, [\text{atm}] = 16.3273 - 1956.7/T - 3.599 \lg T \quad (291.65 \leqslant T \leqslant 321.21\ \text{K}).$$

These results[10,14] agree with earlier measurements[44]. The wavenumbers in the vibrational spectrum of ReF_6 are given in Table 3. All authors agree that ReF_6 has a regular octahedral configuration. The anomalies in the wavenumbers are attributed to the Jahn–Teller effect[50–52]. Electron diffraction measurements[53] show that the interatomic distances in the octahedron are 1.832 ± 0.004 Å. The force constants of ReF_6 have been published[54].

Table 3. Vibrational frequencies in the spectra of ReF_6 (cm^{-1}).

Infrared (gas) (Refs. 45–48)	Raman (gas) (Refs. 46–48)	Raman (soln. in HF) (Ref. 49)	Assignment	Infrared (gas) (Refs. 45–48)	Raman (gas) (Refs. 46–48)	Raman (soln. in HF) (Ref. 49)	Assignment
755	755	756	ν_1	257	257	—	ν_4
715	715	—	ν_3	246	246	249	ν_5
596	596	578	ν_2	193	193	—	ν_6

The electronic structure of ReF_6 has been described[28,29,55–59]. The photoelectron spectra have been recorded[28,29], and the ionisation potentials of WF_6 and ReF_6 correlated; the bands in the range 15.1–17.2 eV correspond to p_π-orbitals, those in the range 18.0–20.1 eV to p_σ-orbitals, and the band having a maximum at 11.43 eV is due to the additional electron of ReF_6, situated in a $2t_{2g}$-orbital.

The chemical properties of ReF_6 resemble those of other metal hexafluorides[60,61]. It is hydrolysed extremely readily, and on contact with atmospheric moisture it disproportionates to give flocculent black rhenium dioxide[62]. Traces of moisture convert ReF_6 into $ReOF_4$.[63] Hydrolysis by water is sometimes accompanied by the formation of an unstable green solution, which rapidly becomes dark and non-transparent. The green colour of the solution has been attributed to the formation of the unstable anion $ReOF_5^-$.[64]

ReF_6 is coordinatively unsaturated, and forms complexes with alkali metal fluorides[65]; it gives ionic compounds with NOF and NO_2F.[66] In the hexafluoride series, ReF_6 is intermediate between the most reactive PtF_6 and the kinetically most stable SF_6; its properties are similar to those of MoF_6.[30,61]. Like MoF_6 [67,68] and WF_6,[4,69] ReF_6 is reduced to the metal by hydrogen[4,7]. At 200°, the reaction stops when ReF_4 is formed[70,71], but at 250° in a large excess of hydrogen it gives up to 75% yield of the metal[7].

The Gibbs free energies for the reduction of ReF_6 by hydrogen and for the simultaneous reduction of ReF_6 and the higher fluorides of a series of elements of groups III–VI have been calculated[31]. The simultaneous reduction of ReF_6 with

BF_3, NbF_5, MoF_6, and WF_6 by hydrogen is probable at room temperature, and that with SiF_4, TiF_4, and TaF_5 at a temperature above 500–650 K. SO_2 reduces ReF_6; at 400° it converts ReF_6 into ReF_4.[71] Thermodynamic calculations show that many elements can reduce ReF_6 to the metal; the strongest reducing agents include Zr, Ti, and Si.[31]

ReF_6 reacts with the carbonyls of rhenium, tungsten, and molybdenum to give $ReOF_4$, and also ReF_5 in an excess of tungsten carbonyl[72]. A detailed study of the reaction of ReF_6 with $Re_2(CO)_{10}$ in liquid HF made it possible to identify two compounds, for which X-ray diffraction indicated the formulae $Re(CO)_5F.ReF_5$ and $[Re(CO)_6]^+[Re_2F_{11}]^-$.[73] The fluorination of a solution of $Re_2(CO)_{10}$ in 1,1,2-trichlorofluoroethane by xenon difluoride also gives the first of these salts[74].

In HF solution, rhenium hexafluoride is reduced by $N_2H_6F_2$ to $N_2H_6ReF_6$ and $N_2H_6(ReF_6)_2$,[75] and in solution in SO_2 and IF_5 it is reduced by alkali metal iodides to M_2ReF_6 and $MReF_6$ respectively (M = Na, K, Rb, Cs).[76,77] ReF_6 is also reduced by NO ($NOReF_6$ is formed),[66] BCl_3 ($ReCl_5$ is formed),[16] etc.[30] In IF_5 solution, elemental iodine is oxidised to I_2^+ by rhenium hexafluoride.

ReF_6 is readily soluble in anhydrous HF (1.75 mole in 1000 g HF).[49] The molar conductance of this solution is 0.70 Ω·cm·mole, and the degree of ionisation of ReF_6 in solution is ~0.2%.

Rhenium pentafluoride can be obtained together with ReF_4 and $ReOF_4$ by the reaction of tungsten carbonyl with an excess of ReF_6.[72] ReF_5 is also obtained by reducing ReF_6 by hydrogen, silicon[78], metallic tungsten or rhenium[79,80], and PF_3.[30]

Various physical properties of ReF_5 are given in Table 4. ReF_5 crystallises in the orthohombic system, with lattice parameters: $a = 5.70$; $b = 17.23$; $c = 7.67$ Å.[81]

Table 4. Physical properties of ReF_5.[14,72]

Parameter	Value
Melting point, °C	48.0
Boiling point, °C	221.3*
Heat of volatilisation, kcal mole^{-1}	12.0 (221.3 °C)
Heat capacity of the gas at 298.2 K, cal mole^{-1} K^{-1}	25
Entropy of the gas at 298.2 K, cal mole^{-1} K^{-1}	80.7
Entropy of volatilisation, cal mole^{-1} K^{-1}	24.2 (221.3 °C)
Curie–Weiss temperature, K	580

*The boiling point was determined by extrapolation, since above 180 °C ReF_5 disproportionates irreversibly to ReF_4 and ReF_6.[72]

The vapour pressure of ReF_5 is given by the equation[44]:

$$\lg p, [\text{atm}] = 9.024 - 3037/T \quad (321.15 \leqslant T \leqslant 413.15\ \text{K}) .$$

The vibrational wavenumbers of the two possible structural forms of ReF_5, and the thermodynamic properties in the temperature range 298–3200 K, have been calculated[82]. Reference works[14,83] give estimated values of S^0_{298} and C^0_p (298.2) for gaseous ReF_5 (cal mole^{-1} K^{-1}): 81 and 25, and 84.1 and 28.55 [83] respectively.

The mass spectrum of ReF_5 [84–86] has shown that it is associated in the gaseous phase, and exists as dimers and trimers at temperatures close to room temperature.

The chemical properties of ReF_5 have been little studied. It reacts with CCl_4 [72] and is hydrolysed instantly by water to give $ReO_2.2H_2O$ and the ions F^-, ReO_4^-, and ReF_6^{2-}.[8] Like ReF_6, ReF_5 is coordinatively unsaturated, but only a few fluoro-complexes of Re^V are known[8].

Rhenium tetrafluoride is obtained by reducing ReF_6 by metallic rhenium, hydrogen, or SO_2, or by the disproportionation of ReF_5.[72,79] Crystalline ReF_4 sublimes above 300°.[72]

The X-ray diffraction pattern of ReF_4 has been indexed[8] on the basis of a tetragonal cell having the parameters $a = 10.12$ Å and $c = 15.95$ Å.

Estimated values of the thermodynamic functions of gaseous ReF_4 have been published[14,82].

Rhenium tetrafluoride is readily hydrolysed by water according to the equation[8]:

$$ReF_4 + 4\,H_2O \rightarrow ReO_2 \cdot 2H_2O + 4H^+ + 4F^- .$$

The existence of fluorides of rhenium having an oxidation number less than +4 has been doubted by many workers, but Malm and Selig[10] have reported the preparation of the fluoride $ReF_{3.5}$. Other authors[13] considered that they isolated $ReF_{2.99 \pm 0.17}$ and $ReF_{2.05 \pm 0.16}$ by exploding rhenium wire in at atmosphere of SF_6 and PF_5. There are apparently no grounds for regarding these products as individual compounds.

III. RHENIUM OXIDE FLUORIDES

Possible simple oxide fluorides of rhenium(V–VII) are given in Table 5. ReO_3F, ReO_2F_3, $ReOF_5$, and $ReOF_4$ have been most reliably characterised[8]. $ReOF_3$ has also been isolated and described[72].

Table 5. Rhenium oxide fluorides.

Oxidation state of rhenium		
V	VI	VII
$ReOF_3$ (ReO_3F)	$ReOF_4$ (ReO_2F_2)	$ReOF_5$ ReO_2F_3 ReO_3F

Rhenium trioxide fluoride was first obtained by the reaction of ReO_3Cl with anhydrous HF.[87] It can also be synthesised by the reaction of $KReO_4$ with IF_5,[88] of Re_2O_7 with ReF_7,[89] and of Re_2O_7 or $KReO_4$ with an excess of anhydrous HF.[90] ReO_3F melts at 147° and boils at 164° with slight decomposition[87]. At the same time, it has been reported[89] that ReO_3F has the highest thermal stability among rhenium oxide fluorides.

The microwave spectrum of gaseous ReO_3F showed that the bond lengths are Re–O 1.692 Å and Re–F 1.859 Å, and the angle F–Re–O is 109.5°.[91] The calculated dipole moment is 0.85.

The infrared and electronic spectra of gaseous ReO_3F [92] and the Raman and NMR spectra of its solutions in anhydrous HF [90] show that the ReO_3F molecule belongs to the symmetry group C_{3v}. Thus the infrared and Raman spectra show all six vibrational wavenumbers expected for this structure[93,94]; the force constants of the ReO_3F molecule isolated in an argon matrix have been calculated. The photoelectron spectra of

gaseous ReO_3F have been recorded[28,29], and the ionisation potentials determined; the first ionisation potential is 12.37 eV. The calculated thermodynamic functions of gaseous rhenium trioxide fluoride have been published[14,95].

All that is known of the chemical properties of ReO_3F is that it is readily hydrolysed in a moist atmosphere to give HF and $HReO_4$.

Rhenium dioxide trifluoride ReO_2F_3 has been obtained (with small quantities of $ReOF_5$) by fluorinating rhenium oxides or $KReO_4$ in flow[96] and static[89] systems. It is also obtained by the action of a mixture of O_2 and F_2 on metallic rhenium[44]. Pure ReO_2F_3 can be isolated by the reaction of a mixture of Re_2O_7 and KBr (1:1) with bromine trifluoride[94]. Various physical properties of ReO_2F_3 are given in Table 6.

Table 6. Physical properties of ReO_2F_3.[8]

Parameter	Value
Melting point, °C	90
Boiling point, °C	185.4
Heat of volatilisation, kcal mole^{-1}	15.7
Entropy of volatilisation, cal mole^{-1} K^{-1}	34.3

The vapour pressure of ReO_2F_3 is given by the equation[14,44]

$$\lg p,[\text{atm}]=7.48-3437/T \quad (363\leqslant T\leqslant 443\ \text{K}) .$$

Falconer and coworkers[97] found that the ReO_2F_3 molecule is non-polar and apparently belongs to the symmetry point group D_{3h}, with the oxygen atoms in the *trans*-position. Later studies[94] showed that in the gaseous phase, ReO_2F_3 is chiefly monomeric and has a trigonal bipyramidal structure, but with the oxygen atoms in the *cis*-position (symmetry C_{2v}). A study of the dimer $(ReO_2F_3)_2$ in the gaseous phase[26] established the relatively high stability of the system, formed by two oxygen bridges. The high viscosity of ReO_2F_3 indicates association in the liquid phase[8].

The chemical properties of rhenium dioxide trifluoride have been little studied. It is stable in the glass up to the boiling point. Like other Re^{VII} oxide fluorides, it is rapidly hydrolysed to HF and $HReO_4$.

Rhenium oxide pentafluoride $ReOF_5$ is formed by the same reactions as ReO_2F_3, but is obtained in smaller yields[96]. The difference in the volatilities of ReO_2F_3 and $ReOF_5$ makes it possible to separate these substances easily by sublimation. The physical properties of $ReOF_5$ resemble those of ReF_6 and ReF_7 (Table 7).[8,14,44]

The vapour pressure is given by the equations[14,44]:

$$\lg p_s[\text{atm}]=6.700-2250/T \quad (273\leqslant T\leqslant 303\ \text{K})$$
$$\lg p_s[\text{atm}]=5.739-1958.9/T \quad (303\leqslant T\leqslant 314\ \text{K})$$
$$\lg p_s[\text{atm}]=4.846-1678.6/T \quad (314\leqslant T\leqslant 346\ \text{K}) .$$

Analysis of the NMR,[19] infrared, and Raman spectra[98,99] indicates that the $ReOF_5$ molecule belongs to the symmetry group C_{4v}. Thus for gaseous $ReOF_5$, all eleven wavenumbers required for this configuration were detected: 989.8, 738.6, 643, 309, 652, 234, 334, 713, 260, 365, and 125 cm^{-1}.

The calculated thermodynamic functions of gaseous $ReOF_5$ have been published[14]; these have been used[31] to calculate the parameters of the reduction of $ReOF_5$ by hydrogen, and it was shown that it is possible to obtain the metal at room temperature. The first ionisation potential of gaseous $ReOF_5$, determined from the photoelectronic spectrum, is 13.53 eV.[28,29]

Table 7. Physical properties of $ReOF_5$ and $ReOF_4$.[8,14]

Parameter	Value	
	$ReOF_5$	$ReOF_4$
Melting point, °C	40.8	108
Boiling point, °C	73.0	171
Temperature of phase transformation, °C	30	—
Heat of formation in the crystalline state at 298.2 K, kcal mole^{-1}	−294*	—
Heat of the phase transformation, kcal mole^{-1}	1.339	—
Heat of fusion, kcal mole^{-1}	1.220	—
Heat of volatilisation, kcal mole^{-1}	7.720	14.59
Heat of sublimation, kcal mole^{-1}	10.280**	17.82
Heat capacity of the gas at 298.2 K, cal mole^{-1} K^{-1}	28.0	21.7
Entropy of the gas at 298.2 K, cal mole^{-1} K^{-1}	85.6	78.7
Entropy of the phase transformation, cal mole^{-1} K^{-1}	3.868	—
Entropy of fusion, cal mole^{-1} K^{-1}	3.886	—
Entropy of volatilisation, cal mole^{-1} K^{-1}	22.3	32.7
Curie–Weiss temperature, K	—	307

*From published data[100].
**Value at temperatures below 30 °C; above 30 °C, the heat of sublimation is 8.940 kcal mole^{-1}.

The chemical properties of $ReOF_5$ resemble those of ReF_6;[101] at the same time, it is more readily reduced to rhenium(VI) by organic compounds, compared with ReO_2F_3, and on hydrolysis it gives HF and $HReO_4$. The reaction of $ReOF_5$ with NOF and NO_2F gives the ionic salts $NOReOF_6$ and NO_2ReOF_6.[32]

Rhenium oxide tetrafluoride can be obtained by the reactions of $W(CO)_6$ with ReF_6,[72] of ReF_6 with SiO_2,[102] of ReF_6 with ReO_3,[29] of ReF_6 with aqueous HF solution[89,102], and also by fluorinating metallic rhenium or ReO_3 at fluorine:oxygen ratios of 4:1 and 2:1 respectively[89]. Various physical properties of $ReOF_4$ are given in Table 7.

$ReOF_4$ crystals have a monoclinic lattice, space group $C2/c$.[103,104] The values of a, b, and c are 19.01, 5.57, and 14.72 Å; $\beta = 114°$, $Z = 16$; the bond lengths are Re–O 1.65 Å, Re–F(terminal) 1.86 Å, and Re–F(bridging) 1.99 Å and 2.30 Å. The calculated density is 5.28 g cm^{-3}. The magnetic moment of $ReOF_4$ agrees with that expected for Re^{VI}.[8]

The vapour pressure of $ReOF_4$ is given by the equations[44]:

$$\lg p_s[\text{atm}]=8.92-3888/T \quad (323\leqslant T\leqslant 380\ \text{K})$$
$$\lg p_s[\text{atm}]=7.21-3206/T \quad (381\leqslant T\leqslant 445\ \text{K}) .$$

The structural and spectroscopic characteristics of gaseous $ReOF_4$ have been estimated[105]; it has been assigned to the symmetry group C_{2v}, and the thermodynamic functions at 298–2000 K have been calculated on this basis[106]. Later studies[107,108] of the infrared spectra of $ReOF_4$ isolated in an argon matrix indicate that the rhenium oxide tetrafluoride molecule has C_{4v} symmetry. The corrected thermodynamic functions of $ReOF_4$ have been published[95].

Mass-spectrometric studies[89,102] showed that $ReOF_4$ is monomeric in the gaseous phase. The ionisation potentials of gaseous $ReOF_4$ have been published[29]; the first ionisation potential is 10.98 eV. Like $ReOF_5$, $ReOF_4$ can be reduced by hydrogen to the metal[31].

The chemical properties of $ReOF_4$ have been little studied. It reacts vigorously with water to give HF, $ReO_2.2H_2O$, and $HReO_4$; it reacts with CCl_4 to give $ReCl_5$.[72] In HF solution, rhenium oxide tetrafluoride is weakly ionised according to the scheme[102]:

$$ReOF_4 + 2HF \rightleftarrows H_2F^+ + ReOF_5^- .$$

At 250°, $ReOF_4$ vapour reacts slowly with Pyrex, forming black non-volatile $ReOF_3$.[72]

Rhenium oxide trifluoride is extremely hygroscopic; it crystallises in the tetragonal system with unit cell parameters $a = 8.54$ Å and $b = 8.21$ Å.[72] $ReOF_3$ dissolves in water to give a pale-blue solution. The mechanism of the process has not been established.

No reports of the existence of other oxide fluorides have been published, particularly containing rhenium having an oxidation number below +5. This is probably due to the fact that this class of compound has been little studied. At the same time it has been reported[89] that the non-volatile residues formed by the reactions of ReO_2F_3 with Si and of $ReOF_4$ with Si consist of mixtures of lower oxide fluorides of rhenium, which when heated to 500° disproportionate to give ReO_3F, which is more stable at this temperature.

IV. COMPLEX FLUORIDES AND OXIDE FLUORIDES OF RHENIUM

Fluoro-complexes of rhenium are known only for rhenium having oxidation numbers from +4 to +7. The properties of the Re^{IV} salts have been most fully studied, firstly because of their stability and relative ease of handling, and secondly because of the interest in the electronic configuration of the rhenium ion in a d^3-octahedral environment. Complex oxide fluorides are known only for rhenium(V–VII).

Hexafluororhenates(IV) can be obtained either by reducing ReF_6 by alkali metal iodides in liquid SO_2 [109] or by ion exchange from K_2ReF_6, which is formed by the hydrofluorination of hexachloro-, hexabromo-, or hexa-iodorhenates(V),[63,110] and also by treating molten KHF_2 with a $KReO_4 + KI$ mixture or K_2ReBr_6.[79]

The fluororhenates of Na^+, NH_4^+, K^+, Rb^+, and Cs^+ have the K_2GeF_6 structure; the Re–F distance in the almost regular octahedron is ~2 Å.[111,112] The magnetic moment of the crystalline salts (3.3 B.M. at 300 K) and the aqueous solutions (3.47 B.M.) is lower than the spin-only value for a regular d^3-octahedron[113].

The vibrational spectra of a number of salts show that the ReF_6^{2-} ion has D_{4h} symmetry (the force constants and mean amplitudes of the vibrations of the Re–F bond have been published[114,117]). The electronic, infrared, and Raman spectra of a single crystal of Cs_2ReF_6 [118,119] confirmed these conclusions. The ionic character and energy of the Re–X bond in ReX_6^{2-} anions (X = F, Cl, Br, I) decrease from fluorine to iodine[120,121].

Hexafluororhenates(IV) are stable to hydrolysis, and can be recrystallised from aqueous solutions. The solubility decreases from the Na^+ to the Cs^+ salts. The enthalpy of solutions of crystalline K_2ReF_6 in water, determined calorimetrically, is 15.05 kcal mole^{-1}; the calculated enthalpy of hydration of the gaseous ReF_6^{2-} anion is 239 kcal mole^{-1}.[122] Alkalies slowly decompose the ion ReF_6^{2-}, giving ReO_2; decomposition is complete in molten alkali[63]. The thermal decomposition of $(NH_4)_2ReF_6$ in air is accompanied by hydrolysis and oxidation. One of the decomposition products is NH_4ReO_4,[123] taken as ReNF by other workers[79].

Hexafluororhenates(V) are formed by reducing ReF_6 by alkali metal iodides in SO_2 or IF_5 solution[76,109]; $NOReF_6$ is obtained by bringing ReF_6 into contact with nitric oxide[66]. The reaction of Cd, Cu, and Tl with a solution of ReF_6 in acetonitrile gives the solvates $Cd(ReF_6)_2.5CH_3CN$, $CuReF_6.4CH_3CN$, and $TlReF_6.2CH_3CN$.[124] The structure of salts of the ReF_6^- anion is similar to that of the compounds MoF_6^- and WF_6^-.[125]

The anomalies in the temperature dependence of the magnetic properties of the number of hexafluororhenates(V) were attributed to antiferromagnetic interaction[76]. The infrared, Raman, and electronic spectra of the salts $M^+ReF_6^-$ indicate that the ReF_6^- anion belongs to the symmetry group O_h; the force constants of the Re–F bond have been calculated[109,126,127].

Salts of the type $M^+ReF_6^-$ react vigorously with water to give hydrated rhenium dioxide, F^-, ReO_4^-, and ReF_6^{2-};[76] like salts of the type $M_2^+ReF_6^{2-}$, however, decomposition is complete only when fused with alkali.

Fluororhenates(VI) are obtained by the reaction of ReF_6 with alkali metal fluorides. Depending on the conditions, the reactions give salts of the type $M^+ReF_7^-$ or $M_2^+ReF_8^{2-}$,[65] which differ sharply in colour, crystal form, and other properties. The salt K_2ReF_8 crystallises in the orthorhombic system, space group *Pnma*, lattice parameters $a = 8.70 \pm 0.02$ Å, $b = 5.91 \pm 0.02$ Å, $c = 12.53 \pm 0.03$ Å, pyknometric density 4.33 ± 0.03 g cm^{-3}.[128] The basic structural unit of K_2ReF_8 is the $[ReF_8]^{2-}$ anion, having the form of a twisted cube with angle of rotation 45°.[129] The Re–F distance is 1.90 ± 0.03 Å. The magnetic moment of the K^+, Rb^+, and Cl^+ salts lies in the range 1.6–1.7 B.M., and differs considerably from the low moment of ReF_6.[65] The alkali metal octafluororhenates are thermally stable[130].

The action of ReF_6 on M_2ReF_8 gives yellow salts having the composition $MReF_7$ ($M = K^+$, Rb^+, Cs^+).[65] The thermal stability of the hexafluororhenates decreases in the order $Cs^+ > Rb^+ > K^+$. Magnetic measurements[65] showed that these salts are weakly paramagnetic (0.6–0.7 B.M.).

The vibrational spectra of hepta- and octafluoro-complexes of rhenium(VI) [131] show that the MF_8^{n-} ion is a square antiprism, whereas the spectra of $RbReF_7$ and $CsReF_7$ are similar to the spectra of ReF_7 and IF_7, and the ReF_7^- anion can be assigned D_{5h} symmetry.

Hepta- and octafluororhenates(VI) are hydrolysed, with the intermediate formation of $MReOF_5$.[132] The stability to hydrolysis decreases in the order $Na^+ > K^+ > Rb^+ > Cs^+$. K_2ReF_8 dissolves in anhydrous HF with decomposition according to the equation[133]:

$$K_2ReF_8 + n\,HF \rightarrow ReF_6 + 2KF \cdot n\,HF .$$

When this solution is evaporated in a stream of dry nitrogen, ReF_6 volatilises, with the partial entrainment of HF.

As already noted, ReF_7 reacts with nitrosyl and nitryl fluorides to give the adducts $NOReF_8$ and NO_2ReF_8. The Raman spectra of the solid salts and the ^{19}F NMR spectra of their solutions in anhydrous HF show that these complexes are ionic, and that the ReF_8^- anion has D_{4d} symmetry[32].

The complex oxide fluoride of Re^V, $NH_4ReO_{1.5}F_3.H_2O$, has been obtained by the reaction of NH_4ReO_4, NH_4HF_2, and Re at 400 °C and high pressure[134]. The product crystallises in the cubic system (space group *Fm*3*m*) with parameter $a = 16.563$ Å. The calculated density (for $Z = 32$) is 3.55 g cm^{-3}, and the measured density 3.57 g cm^{-3}. The magnetic properties showed the presence of unpaired electrons, possibly due to the existence of isolated $Re_8O_{12}F_{24}$ molecules, joined by NH_4^+ bridges.

Complex oxide fluorides of Re^{VI} can be isolated by the careful hydrolysis of complex fluorides of Re^{VI}.[109,130] The hydrolysis products—salts of the type $M^+ReOF_5^-$—are soluble in methyl ethyl ketone. The oxidation number of rhenium in the caesium salt is +6, and the magnetic moment 1.40 B.M. [132] The vibrational spectra of a series of salts containing the $ReOF_5^-$ anion showed that it has C_{4v} symmetry; the force constants were also calculated[109].

Complex oxide fluorides of Re^{VII}, which can be regarded as derivatives of ReO_3F, ReO_2F_3, and $ReOF_5$, are also known. The first of these ($M_2ReO_3F_3$ and $MReO_2F_4$) are obtained by the action of IF_5 and BrF_3 [135,136] on alkali and alkaline earth metal perrhenates. In addition, ReO_3F complexes of the type $ReO_3F.2DMF$ and $[(CH_3)_4N]ReO_3F_3$ [137] have been isolated, and their infrared spectra studied. The vibrational spectra of $K_2ReO_3F_3$ and $KReO_2F_4$ have been studied[109], and the force constants of both anions have been calculated assuming C_{2v} symmetry.

The only known derivatives of $ReOF_5$ are the ionic complexes $NOReOF_6$ and NO_2ReOF_6, formed by the reaction of $ReOF_5$ with NOF and NO_2F. The $ReOF_6^-$ anion has C_{5v} symmetry[32].

Conductometric titration of $KReO_4$ solutions in hydrofluoric acid[138] showed the formation of the ionic complex $[ReO_4F]^{2-}$. Attempts to isolate the fluoro-complexes of K^+, $Co(NH_3)_6^{3+}$, and $[Co(en)_3]^{3+}$ were unsuccessful. A later study of the ReO_4^-–HF–H_2O system[139] showed the formation of the anionic complexes $[ReO_3(OH)F_2]^{2-}$ at an F^- ion concentration of 0.05–0.26 M, and $[ReO_2(OH)(HF_2^-)_3]^-$ at 0.5–5.3 M, with stability constants $\lg \beta_2 = 4.8 \pm 0.4$ and $\lg \beta_3 = 2.8 \pm 0.4$ respectively.

The synthesis of $H_2[ReOF_5]$ in HF solution has been reported[140]. The electronic spectra of the systems $ReOF_5^{2-}$–H_2SO_4–HF and Re^{VII}–H_2SO_4–HF showed that $[ReOF_5]^-$ ions are formed in solution in the first case, and rhenium(VII) complexes in the second.

V. CONCLUSION

As expected, the physicochemical properties of rhenium fluorides to a large extent resemble those of molybdenum fluorides. The hexafluorides of the two elements show extremely similar chemical and thermodynamic properties[30]. The oxide tetrafluorides have similar melting points and boiling points (108° and 171° for $ReOF_4$, and 97.2° and 186° for $MoOF_4$).[14] The oxide tetrafluorides are polymerised in the crystalline state[104,141] and partly in the vapour. The properties of rhenium dioxide difluoride, which has not yet been obtained, are probably similar to those of molybdenum dioxide difluoride. The pentafluorides also have similar melting points and boiling points (48.0° and 221° for ReF_5, and 67° and 214° for MoF_5),[14] and also tend to polymerise in the liquid and even in the vapour[93].

The extremely limited amount of experimental data for rhenium tetrafluoride and more particularly rhenium trifluoride makes a reliable comparison difficult, but there are grounds for assuming that in this case, analogies with the corresponding molybdenum fluorides will be observed.

Definite similarities are observed in the methods of synthesis and chemical and physicochemical properties of the fluoro- and oxofluoro-complexes of rhenium and molybdenum[61], although in this case also it is difficult to make an exhaustive comparison, because of the limited amount of data for fluoroderivatives of rhenium.

The main difference between rhenium fluorides and oxide fluorides and the analogous molybdenum compounds is the higher reactivity of the rhenium derivatives. Rhenium fluorides are much more sensitive to hydrolysis, and are more readily reduced by hydrogen, organic compounds, and many metals.

Moreover, rhenium, unlike molybdenum, forms compounds in which it has an oxidation number of +7, and this extends considerably the range of fluorides and oxide fluorides formed.

An important problem in the chemistry of rhenium fluorides is the development of reliable methods of synthesis giving sufficiently pure products.

Table 8. Methods of preparing higher fluorides and oxide fluorides of rhenium.

Rhenium fluoride	Starting material	Reagent	Conditions of reaction	Side products	Refs.
ReF_7	Re	F_2	400 °C, 2–3 atm	—	9, 10
ReF_7	Re	F_2	150–500 °C, 50–60 atm	—	11
ReF_7	Re	SF_6	exploding Re wire	~1% ReF_6, SF_4	13
ReF_7	Re	soln. of KrF_2 in HF	20 °C, 1 atm	Kr	12
ReF_6	Re	F_2	120–125 °C, 1 atm	ReF_7	9, 10, 34–36
ReF_6	Re	F_2	150 °C, 1 atm	ReF_7	40, 41
ReF_6	Re	ClF_3	300 °C, 1 atm	—	38
ReF_6	Re	O_2F_2	< 100 °C	—	39
ReO_3F	ReO_3Cl	HF	80 °C, 1 atm	HCl	87
ReO_3F	$KReO_4$	IF_5	100 °C, 1 atm	IO_2F, KF	88
ReO_3F	Re_2O_7	ReF_7	Re_2O_7:ReF_7 = 4.6:1*; 150 °C, > 1 atm, 20 h	ReO_2F_3, lower oxide fluorides	89
ReO_3F	Re_2O_7	ReF_7	Re_2O_7:ReF_7 = 3.6:1; 150 °C, > 1 atm, 20 h	—	89
ReO_2F_3	Re_2O_7	BrF_3	Re_2O_7:KBr = 1:1 excess of BrF_3, 20 → 140 °C, vacuum**	Br_2O_2	94
ReO_2F_3	ReO_2	F_2	100–300 °C, 1 atm	$ReOF_5$, O_2	96
ReO_2F_3	ReO_2	F_2	ReO_2:Fe_2 = 1:2; 400 °C > 1 atm	$ReOF_5$, O_2	89
ReO_2F_3	ReO_3	F_2	ReO_3:Fe_2 = 1:1; 200 °C, > 1 atm	$ReOF_5$, O_2	89
ReO_2F_3	Re_2O_7	F_2	ReO_7:F_2 = 1:4; 200 °C, > 1 atm, 65 h	O_2	89
ReO_2F_3	$KReO_4$	F_2	300 °C, > 1 atm	$ReOF_5$, O_2, KF	96
ReO_2F_3	$KReO_4$	F_2	traces of SiO_2, 350 °C, 1 atm	$ReOF_5$, O_2, KF	89
ReO_2F_3	Re	F_2+O_2	> 25% O_2, 100 °C, 1 atm	$ReOF_5$, ReF_6	96
$ReOF_5$	ReO_2	F_2	100–300 °C, 1 atm	ReO_2F_3, O_2	96
$ReOF_5$	$KReO_4$	F_2	300 °C, 1 atm	ReO_2F_3, O_2, KF	96
$ReOF_5$	Re	F_2+O_2	25% O_2, 100 °C, 1 atm	ReO_2F_3, ReF_6	96
$ReOF_5$	$ReOF_4$	F_2	50% excess of F_2, 300 °C, > 1 atm	—	89
$ReOF_5$	ReO_2	F_2	10% excess of F_2, 250 °C, 12 h, > 1 atm	12 и ReF_6, O_2	89, 99
$ReOF_5$	ReO_3	F_2	200 °C, > 1 atm, 17 h	ReO_2F_3, O_2	89
$ReOF_4$	ReF_6	$Re_2(CO)_{10}$	excess of ReF_6, 20 °C, 1 atm	lower fluorides, CO	72
$ReOF_4$	ReF_6	$W(CO)_6$	large excess of ReF_6, 20 °C, 1 atm	CO, WF_6, ReF_4	72
$ReOF_4$	ReF_6	$W(CO)_6$	small excess of ReF_6, 20 °C, 1 atm	CO, WF_6, ReF_4, ReF_5	72
$ReOF_4$	ReF_6	$M(CO)_6$	20 °C, 1 atm	lower fluorides	72
$ReOF_4$	ReF_6	SiO_2	ReF_6:SiO_2 = 2:1; 20 °C, 1 atm	CO, ReF_5, MoF_5 SiF_4	102
$ReOF_4$	ReF_6	H_2O	traces of H_2O in HF, ReF_6:H_2O = 1:1	—	89
$ReOF_4$	Re	Fe_2+O_2	F_2:O_2 = 4:1; 300 °C, > 1 atm, 17 h	—	89
$ReOF_4$	ReO_3	F_2	F_2:ReO_3 = 2:1; 200 °C, > 1 atm	—	89
$ReOF_4$	ReF_6	B_2O_3	ReF_6:B_2O_3:3:1, 1 atm	BF_3	152

*Here and subsequently, the molar ratio is given.
**Heating from 20 °C to 140 °C.

An analysis of methods for obtaining higher fluorides and oxide fluorides of rhenium (Table 8) shows that these methods require improvement. Thus the preparation of ReF_7 requires the use of fluorine under pressure, and the only reagent which makes it possible to carry out the synthesis at low temperature and atmospheric pressure is KrF_2. Available published data indicate that even more effective methods of obtaining rhenium heptafluoride may be developed by fluorination using atomic fluorine and by using catalysts[142,143].

Existing methods for synthesising ReF_6 from the elements are simple and satisfactory. Here, however, the main problem of the purification of the starting materials and products is still unsolved; even traces of oxygen in the metal or fluorine lead to the contamination of ReF_6 by oxide fluorides.

Of the methods for synthesising ReO_3F, the best yield with a low concentration of impurities is given by the reaction between ReF_7 and Re_2O_7 (1:3.6).[89]

ReO_2F_3 and $ReOF_5$ are most simply obtained in a mixture by the reactions of oxides of rhenium[89,96] or the metal[96] with a mixture of fluorine and oxygen. The improvement of the synthesis of these individual oxide fluorides will involve the development of effective methods of separation.

The synthesis of $ReOF_4$ using metal carbonyls[72] is complicated, and gives a low yield of the main product, which is difficult to purify. Methods for preparing $ReOF_4$ by fluorinating the metal and ReO_3 are simpler[89], but in this case the product contains impurities which are difficult to remove. The purest oxide tetrafluoride can be obtained by the careful hydrolysis of ReF_6.[89,102] Here, the complexity of the method is associated with the need to observe carefully the reagent ratio and the reaction conditions. The optimum method may be the reaction of B_2O_3 with a slight excess of ReF_6.[152]

The synthesis of lower fluorides and oxide fluorides of rhenium (Table 9) involves the reduction of the higher fluorides by carbonyls, metals, and hydrogen, and also by sulphur dioxide and phosphorus trifluoride. Many transition metals (for example Zr, Ti, etc.) can also be used as reducing agents. Thermodynamic calculations[31] show, however, that many of these reagents can reduce the higher fluorides and oxide fluorides of rhenium to the metal, and this may give mixtures difficult to separate.

Table 9. Methods of preparing lower fluorides and oxide fluorides of rhenium.

Rhenium fluoride	Starting material	Reagent	Conditions of reaction	Side products	Refs.
ReF_5	ReF_6	$W(CO)_6$	small excess of ReF_6, 20 °C, 1 atm	$ReOF_4$, WF_6, ReF_4	72
ReF_5	ReF_6 in WF_6	$W(CO)_6$	small excess of ReF_6, large excess of WF_6, 20 °C, 1 atm	ReF_4, lower fluorides	72
ReF_5	ReF_6	$Mo(CO)_6$	20 °C, 1 atm	$ReOF_4$, MoF_5	72
ReF_5	ReF_6 in HF	Si	20 °C, 1 atm	SiF_4	77
ReF_5	ReF_6 in HF	H_2	20 °C, 3.5 atm	—	77
ReF_5	ReF_6	W	600 °C, < 1 atm	—	80
ReF_5	ReF_6	Re	600 °C, 1 atm	—	80
ReF_5	ReF_6	PF_3	<20 °C, 1 atm	PF_5	30
ReF_4	ReF_6	$W(CO)_6$	large excess of ReF_6, 20 °C, 1 atm	$ReOF_4$, WF_6	72
ReF_4	ReF_6	$W(CO)_6$	small excess of ReF_6, 20 °C, 1 atm	$ReOF_4$, WF_6, ReF_5	72
ReF_4	ReF_6 in WF_6	$W(CO)_6$	small excess of ReF_6, large excess of WF_6, 20 °C, 1 atm	ReF_5	72
ReF_4	ReF_6	Re	400 °C, 1 atm	—	79
ReF_4	ReF_6	SO_2	400 °C, 1 atm	SF_6, O_2	71
ReF_4	ReF_5 in HF	Si	20 °C, 1 atm	SiF_4	77
ReF_4	ReF_6 in HF	Si	20 °C, 1 atm	SiF_4	77
ReF_4	ReF_6	H_2	200 °C, 1 atm	HF	70, 71
ReF_4	ReF_5 in HF	H_2	20 °C, 3.5 atm	HF	77
ReF_4	ReF_6 in HF	H_2	20 °C, 3.5 atm	ReF_5	77
ReF_4	ReF_5	—	240 °C, 1 atm	ReF_6	72
$ReOF_3$	$ReOF_4$	SiO_2	250 °C, 1 atm	SiF_4, O_2	72

In general, the lower fluorides of rhenium have been much less extensively studied than the analogous compounds of molybdenum and tungsten. Thus molybdenum fluorides have been studied by Opalovskii and Khaldoyanidi[61], and the lower fluorides of molybdenum and tungsten by Pervov[144–150], whereas rhenium fluorides have not been studied.

The data in Table 10 indicate that methods for the synthesis of fluoro-complexes of rhenium are insufficiently developed. The synthesis of rhenium complexes is based on reactions of three types—the combination of a rhenium fluoride with the fluoride ion, oxidation–reduction, and partial replacement of oxygen by fluorine in the starting material. There is only one example of the partial hydrolysis of a fluoro-complex to give an oxofluoro-complex (Table 10). Even this group of methods, however, does not exhaust all possible ways of obtaining fluoro- and oxofluoro-derivatives of rhenium. For example, the possible hydrolysis of oxofluoro-complexes has not been carried out, although new methods of synthesis and the preparation of new substances can be expected here; the reactions of $ReOF_5$, ReO_2F_3, and ReO_3F with alkali metal fluorides in the absence of solvent and in non-aqueous solutions have not been studied.

Table 10. Methods of preparing complex fluorides and oxide fluorides of rhenium.

Complex fluoride of rhenium	Starting material	Reagent	Conditions of reaction	Side products	Refs.
$NOReF_8$	ReF_7	NOF	20° C, 1 atm	—	32
NO_2ReF_8	ReF_7	NO_2F	20° C, 1 atm	—	32
M_2ReF_8	ReF_6	MF	200° C, 1 atm	—	65
$MReF_7$	ReF_6	M_2ReF_3	20° C, 1 atm	—	65
$MReF_6$	ReF_6	MI in SO_2 or in IF_5	—60° C, 1 atm 20° C, 1 atm	M_2ReF_6, I_2	76 109
$MReF_6 \cdot n CH_3CN$	ReF_6 in CH_3CN	M *	20° C, 1 atm	—	125
M_2ReF_8	ReF_6	MI in SO_2	—60° C, 1 atm	—	109
M_2ReF_6	M_2ReX_6 **	HF	450° C, 1 atm	HX	63, 110
$KReF_6$	K_2ReBr_6	KHF_2	700° C, 1 atm	HBr	79
K_2ReF_6	$KReO_4$	KHF_2+KI	800° C, 1 atm	H_2O, I_2	79
$NOReOF_6$	$ReOF_5$	NOF	20° C 1 atm	—	32
NO_2ReOF_6	$ReOF_5$	NO_2F	20° C, 1 atm	—	32
$MReO_2F_4$	$MReO_4$	BrF_3	25° C, 1 atm	Br_2, O_2	136
$M_2ReO_3F_3$	$MReO_4$	IF_5+MF	100° C, 1 atm	IO_2F, MIO_3	135
$ReO_3F.2DMF$	R_2O_7	HF + DMF	25° C, 1 atm	H_2O	137
$[(CH_3)_4N]_2 \times ReO_3F_3$	$ReO_3F.2DMF$	$[(CH_3)_4N]F$	25° C, 1 atm	—	137
$MReOF_5$	$MReF_8$	H_2O	25° C, 1 atm	HF, MF	132
$MReOF_5$	$MReF_7$	H_2O	25° C, 1 atm	HF	109
$NH_4ReO_{1.5}F_3 \cdot H_2O$	NH_4ReO_4+Re	NH_4HF_2	400° C, 1360 atm	—	134

* M=Cd, Cu, Tl.
** X=Cl, Br, I.

Rhenium should form a larger number of fluoro-complexes than are known at present. The known crystalline compounds containing the anions ReF_8^-, $ReOF_6^-$, $ReO_2F_4^-$, $ReO_3F_3^{2-}$, ReF_8^{2-}, ReF_7^-, $ReOF_5^-$, ReF_6^-, $ReO_{1.5}F_3.H_2O^-$, and ReF_6^{2-} [32,65,76,109,132,134,135,136] apparently do not exhaust the possible complex compounds of rhenium. Their theoretical and practical importance is potentially very high, since complex fluorides might be used to separate rhenium fluorides and oxide fluorides, and to purify them and remove them from gas streams.

The detailed study of fluoro-complexes of rhenium containing organic ligands would reveal the regular features of the change in the structure of transition metal compounds.

The thermochemistry and thermodynamics of rhenium fluorides are among the unsolved problems in this field. Their solution would make possible a deeper understanding of the regular features of the change in the strength of the bonds formed by metals with fluorine with change in the position of the metals in the periodic system. The first studies in the thermochemistry of rhenium fluorides were carried out only recently[15,16,100], however, and unfortunately do not extend to complex fluorides.

Simple rhenium fluorides deserve more extensive study. Thus ReF_6 is still the only rhenium fluoride whose electronic structure has been described.

Preliminary calculations by the present authors have shown that ReF_7 can decompose with the liberation of fluorine at 500 °C. The liberation of fluorine or oxygen may be expected when rhenium(VII) oxide fluorides are heated. This is of interest, since at present, PuF_6 is the only known volatile metal fluoride decomposing with the liberation of fluorine[151].

The problems in the field of the chemistry and technology of rhenium fluorides are wider than those listed, but the latter appear to be the most important.

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