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# Sulphur Hexafluoride

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An attempt is made in the present review to arrange systematically the available data for the physicochemical and, primarily, chemical properties of sulphur hexafluoride. The inertness usually attributed to sulphur hexafluoride on the basis of early data obtained by Moissan hindered the investigation of its chemical properties. This gap is now being successfully filled. Data are presented showing that sulphur hexafluoride can serve as an effective fluorinating agent whose advantages are due to its high fluorine content, its non-toxicity, and the ease with which it can be handled. It is shown that further advances in the development of the chemistry of sulphur hexafluoride and of its practical applications depend significantly on the rate of development of research in this field.
The bibliography includes 236 references.

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## I. INTRODUCTION

Metal and non-metal hexafluorides constitute a large and interesting group of fluorine-containing compounds, a distinctive feature of which is a strikingly wide variety of chemical properties, ranging from an extremely high reactivity to the inertness characteristic of noble gases[1-11]. Despite the fact that more than half of the members of this group of compounds were discovered as early as the beginning of the present century[12-19], their active study began only from the 1940's in connection with the preparation and employment of the hexafluorides of a number of elements in certain stages of the manufacture of nuclear fuel[20-24]. The eighteen hexafluorides known at present can be divided into two groups on the basis of their chemical behaviour: non-metal hexafluorides ($SF_6$, $SeF_6$, $TeF_6$, $PoF_6$ and $XeF_6$) and metal hexafluorides ($CrF_6$, $MoF_6$, $TcF_6$, $RuF_6$, $RhF_6$, $WF_6$, $ReF_6$, $OsF_6$, $IrF_6$, $PtF_6$, $UF_6$, $NpF_6$, and $PuF_6$). Whereas the former (with the exception of $XeF_6$ and $PoF_6$) are regarded as the most inert compounds, the latter exhibit a high activity, for example in fluorination or hydrolytic reactions.

Naturally this classification is extremely arbitrary and qualitative. Thus the reactivities of xenon and polonium hexafluorides resemble those of the most reactive metal hexafluorides. There is no doubt that the hexafluorides of iodine, astatine, and radon, which are so far unknown but are possible in principle, will not be chemically inert either.

Excluding $XeF_6$ and $PoF_6$, we may note that the chemical reactivities of the known non-metal fluorides increase in the sequence $SF_6 < SeF_6 < TeF_6$. For example, sulphur hexafluoride is inert with respect to hydrolysis by water vapour up to 500°C, while $TeF_6$ is fully hydrolysed by water in 24 h.

A similar situation obtains also for the lower chalcogen fluorides (tetrafluorides). Indeed the vigorously fuming liquid $SeF_4$ corrodes glass rapidly even at room temperature, solid $TeF_4$ readily reacts with quartz, while gases $SF_4$ is completely inert with respect to the latter. The chemical reactivities of the lower chalcogen fluorides served as a basis for their use as promising fluorinating and complex-forming agents.

On passing from the highest to the lowest fluoride of the same chalcogen, the chemical reactivity increases,

which is shown particularly clearly by sulphur compounds, for which the greatest number of lower fluorides is known[25-29].

Thus the sulphur pentafluoride dimer $S_2F_{10}$ is more reactive than $SF_6$. On heating, it reacts with copper, mercury, and platinum and its reaction with iron takes place at room temperature. However, hydrolysis by water or concentrated alkalis is extremely slow. Sulphur tetrafluoride is very rapidly hydrolysed by water and sulphur fluoride (thiothionyl fluoride) $S_2F_2$ is hydrolysed even by atmospheric moisture.

Thus the above comparison shows that, among the nonmetal fluorides, sulphur hexafluoride is chemically the most inert. On the other hand, its high fluorine content (78%)—one of the most important parameters determining the effectiveness of any fluorinating agent—cannot fail to draw attention as regards the possible use of this compound in fluorination and oxidation processes, as pointed out at one time by Simons in his well known monograph[29]. The chemical inertness of $SF_6$ is an extremely arbitrary concept like the term "inert substance" in general.

The recent growth of interest in sulphur hexafluoride is due to its exceptional dielectric properties[30,31]. As data (mainly physical) accumulate, the range of practical applications of $SF_6$ is being extended, involving fields such as astronautics[32,33], electronics[34,35], refrigeration technology[36-39], meteorology[40-43], metallurgy[44,45], machine engineering[46], laser engineering[47,48], and medicine[49].

The available information about the chemical properties of sulphur hexafluoride has not changed significantly since the synthesis of this compound. A number of reviews[30,31,50], the latest of which is ten years old, contribute nothing new to the chemistry of sulphur hexafluoride compared with the information which was already available to Moissan. The gas which he isolated was very inert. Its hydrolysis by water vapour was not observed up to 500°C and it did not react with refractory glass up to the softening temperature of the latter. The gas did not react with halogens, phosphorus, arsenic, carbon, silicon, boron, copper, and silver at red heat. No reaction was observed between $SF_6$ and HCl or $NH_3$.

Sulphur hexafluoride is not acted upon by hot CuO and $PbCrO_4$ and by fused KOH. Only boiling sodium reacts rapidly and quantitatively with $SF_6$, which was used as a basis for the determination of the composition of this compound. A fairly large number of substances (large under the conditions prevailing at the time) had been tried in the reaction with $SF_6$, which enabled Moissan to characterise the hexafluoride as a chemically inert gas and to regard it as comparable to nitrogen in this sense. Thus there arose a seemingly well justified barrier, which determined the subsequent course of studies on the chemistry of this compound. Only in recent years new experimental data suggested ways of overcoming this largely psychological barrier in connection with certain advances in the chemistry of sulphur hexafluoride. A number of interesting reports dealing with the possibility of using $SF_6$ as a potential fluorinating and oxidising agent were published[51-59]. A number of studies by the authors of the review were directed to the same end[60-67]. It appears that further expansion of practical applications of sulphur hexafluoride will depend significantly on the rate of development of such investigations and therefore a survey of the accumulated data is an essential step in the development. This is why the authors of the review considered in greatest detail the advances in the investigation of the physicochemical and chemical properties of $SF_6$.

## II. THE SYNTHESIS OF SULPHUR HEXAFLUORIDE

Sulphur hexafluoride is usually synthesised by the reaction of sulphur with gaseous fluorine[68-75]:

$$S + 3F_2 = SF_6 + Q \quad .$$

Depending on the apparatus employed and the purity of the starting materials, the product contains up to 5% of impurities in the form of lower sulphur fluorides ($S_2F_2$, $SF_2$, $SF_4$, and $S_2F_{10}$), oxide fluorides ($SOF_2$, $SOF_4$, and $SO_2F_2$), and dioxide ($SO_2$) as well as impurities introduced with the fluorine (HF, $OF_2$, $CF_4$, $C_2F_6$, $N_2$, and $O_2$). The gas obtained after purification is 99.8% pure and contains $8 \times 10^{-6}$% of $SF_4 + S_2F_2$ and $15 \times 10^{-6}$% of $H_2O$, $S_2F_{10}$, HF, and the inert gases being absent[31]. It is noteworthy that this gas is physiologically completely harmless[76].

Attempts were made recently to synthesise $SF_6$ without using elemental fluorine. This was done primarily by the electrolysis of sulphur or sulphur-containing compounds ($H_2S$, $SCl_2$, $S_2Cl_2$, and $CS_2$) in anhydrous hydrogen fluoride[77-80]. The processes[81,82]

$$6MF + S + 3Cl_2 = 6MCl + SF_6$$

or

$$3MF_2 + S + 3Cl_2 = 3MCl_2 + SF_6 \quad ,$$

where M is a Group I–IV metal, and the pyrolysis of lower sulphur fluorides[83] were considered as the basis for the possible methods of synthesis. However, both of the above reactions lead to the formation of a gas with a low sulphur hexafluoride content requiring careful purification.

Thus the method of synthesising sulphur hexafluoride based on the interaction of the elements still remains the one well tested and technologically and economically viable procedure. Nevertheless the synthesis of $SF_6$ on an industrial scale without the use of elemental fluorine appears to be very promising, since the available data suggest that this procedure is quite realistic.

Although the analytical chemistry of sulphur hexafluoride has not developed adequately[83-87], we may note that gas and gas–liquid chromatography appear to be the most useful in this field. The determination of impurities by this procedure has been sufficiently well developed[88-90]. The solid carriers employed are usually silica gel, Chromosorb W, or the "Kel-F" polymer with added fluorinated liquid hydrocarbons, among which poly(chlorotrifluoroethylene) is most frequently used.

## III. PHYSICAL PROPERTIES

### The Structure and Spectra

The first convincing evidence in support of the octahedral structure of $SF_6$ was obtained in electron diffraction experiments[91,92]. Six normal vibrations may be expected for a molecule with $O_h$ symmetry, of which three [$\nu_1(A_{1g})$, $\nu_2(Eg)$, and $\nu_5(F_{2g})$] are active in the Raman spectrum and two [$\nu_3(F_{1u})$ and $\nu_4(F_{1u})$] are active in the infrared spectrum. There is also an inactive vibration in both spectra ($\nu_6$), which may be observed as a combination band. All five absorption bands of gaseous and liquid sulphur hexafluoride were discovered as early as 1934, but the refinement of their positions by using better apparatus and purer specimens is still being continued (Table 1)[93-105].

The Raman spectra of solid and gaseous sulphur hexafluoride are very similar[94], which was in fact to be expected in view of the high symmetry of the molecule.

**Table 1.** The fundamental vibrational wavenumbers of $SF_6$ ($cm^{-1}$).

| State of aggregation | $\nu_1(A_{1g})$ stretching vibration | $\nu_2(E_g)$ stretching vibration | $\nu_3(F_{1u})$ deformation vibration | $\nu_4(F_{1u})$ stretching vibration | $\nu_5(F_{2g})$ deformation vibration | $\nu_6(F_{2u})$ |
|---|---|---|---|---|---|---|
| Gaseous | 772.4<br>775<br>769.4<br>773.5 | 639.5<br>641.7 | 940<br>947<br>932<br>939<br>947<br>947.9 | 615<br>613<br>614<br>615 | 522<br>525 | 363<br>344<br>345<br>347 |

However, with the exception of the $\nu_1$ line, other lines in the spectrum of solid $SF_6$ are weak and their assignment is extremely indefinite.

The absorption spectrum of $SF_6$ in the region of ultrasoft X-rays differs strongly from the usual X-ray spectra [106,107] and has a pronounced non-hydrogen-like character.

The electronic structure of the sulphur atom has been specified as $3s^{1.64}3p^{3.50}3d^{0.19}$, which leads to an effective charge of the sulphur atom of +0.67. [108] The experimental effective charge of the sulphur atom obtained by Coulson's method [109] proved to be 2.50. [110] The latter value is more accurate, since it was determined from the $K\alpha$ emission line, which corresponds to a more realistic redistribution of the electron density of sulphur. We may note that the involvement of $d$ electrons in the formation of a chemical bond has been established also in a theoretical study of the electronic structure of $SF_6$ by the LCAO-MO SCF method [111]. A direct experimental confirmation of this finding was obtained by La Villa [112], who measured directly the probability of the $3d-2p$ transitions.

The photoelectronic spectrum of sulphur hexafluoride, obtained on excitation with 584 Å monochromatic radiation [113], shows four thresholds of increasing ionisation current (15.35, 16.71, 18.11, and 19.50 eV), three of which correspond to the formation of $SF_5^+$, probably via the reactions [114]

$$SF_6 + h\nu \rightarrow SF_6^+ + e \ ,$$
$$SF_6^+ \rightarrow SF_5^+ + F \ .$$

The mass spectrum of sulphur hexafluoride was investigated in fair detail [116-128], since studies of this kind make it possible to account for the characteristics of the behaviour of $SF_6$ as a dielectric. The ability of sulphur hexafluoride to form negative ions on irradiation with low-energy electrons [116] is of great practical interest in connection with its characteristic large electron capture cross-section [32,33,115].

The mechanism of the interaction of sulphur hexafluoride with low-energy electrons (0–2 eV) can be represented schematically by the resonance absorption (capture) of an electron with formation of a metastable ion:

$$SF_6 + e \rightleftarrows (SF_6^-)^* \ , \qquad (1)$$

the ion either dissociates (dissociative capture):

$$(SF_6^-)^* \rightarrow SF_5^- + F \ , \qquad (2)$$
$$SF_5 + F^-$$

or is stabilised by collision with an extraneous molecule:

$$(SF_6^-)^* + A \rightarrow SF_6 + A \ . \qquad (3)$$

There are also data obtained in studies on sulphur hexafluoride by NMR; $^{19}F$ NMR spectra have been recorded for both gaseous $SF_6$ and the hexafluoride fixed in the form of clathrate compounds [129-135].

## IV. PHYSICOCHEMICAL PROPERTIES

The main physical properties of sulphur hexafluoride are listed in Table 2. Under normal conditions, $SF_6$ is a colourless gas with a nearly theoretical density. On cooling to −63 °C, it condenses to a colourless solid, which may be fused under pressure. The triple point parameters are $t = -50.8$ °C and $P = 2.3$ atm. [156] The vapour pressure changes from 3.4 to 26.4 atm in the range from −40° to +30 °C. [157] At 94.30 K there is an endothermic transformation of solid $SF_6$.

The critical parameters of sulphur hexafluoride are as follows: $P_{cr} = 38.328 \pm 0.05$ kgf $cm^{-2}$, $t_{cr} = 45.560 \pm 0.05$ °C, and $v_{cr} = 198.0 \pm 0.4$ $cm^3$ $mole^{-1}$ (Makarevich and Sokolova [158]) and agree well with earlier data [36,139].

The temperature variation of the vapour pressure of $SF_6$ in the range from −30 °C to $t_{cr}$, derived by Elema [37] from experimental data [36,139,156,159], is

$$\lg P(\text{bars}) = 4.40538 - 8.47739/\theta - 3.72000/\theta^2 + 5.33334/\theta^3,$$

where $\theta = T/100$.

At the same time Mears et al. [160] obtained the following relation between the vapour pressure and temperature in the range 25–130 °C (the temperature in both equations are expressed on the Kelvin scale) using their own data and results quoted in the literature [137,139]:

$$\lg P(\text{bars}) = 4.41780 - 889.185/T - 0.56334 \times 10^{-3}T + 0.120040 \times 10^{-5}T^2.$$

The temperature variation of the density of liquid sulphur hexafluoride can be represented by a five-term equation [160]:

$$d(\text{g cm}^{-3}) = A_0 + \sum_{n=1}^{n=4} A_n(1 - T/318.80)^{n/3},$$

where $A_0 = 0.725$, $A_1 = 1.4721$, $A_2 = -0.282881$, $A_3 = 1.302590$, and $A_4 = -0.628493$. The absolute error in the determination of the density in the range from −41 ° to +42 °C does not exceed 0.1%.

The sublimation pressure of solid $SF_6$ is described by the equation

$$\lg P(\text{mmHg}) = A - B/T,$$

which is probably valid in the temperature range from 102 to 222 K (Table 3).

**Table 2.** Physical properties of sulphur hexafluoride.

| Property | Value | References |
|---|---|---|
| Melting point, °C | −50.8 | 136 |
| Sublimation temperature, °C | −63.8 (760 mmHg) | 136 |
| Critical temperature, °C | 45.642, 45.547, 45.55 | 36, 137–139 |
| Critical pressure, atm | 37.193, 37.113, 38.27, 38.15 | 36, 137–139 |
| Heat of fusion, kcal $mole^{-1}$ | 1.201, 1.1, 1.39 | 136, 140, 141 |
| Heat of sublimation, kcal $mole^{-1}$ | 5.64, 5.57, (−63.8) | 136, 141, 142 |
| Density of gas, g $litre^{-1}$ (20 °C) | 6.093 (753.5 mmHg) | 143 |
| Density of solid, g $cm^{-3}$ | 2.683 (−195°), 2.51 (−50°) | 136 |
| Density of liquid, g $cm^{-3}$ | 1.37 (20°), 1.722 (−20°), 1.787 (−39°), 1.818 (−45°), 1.878 (−50°) | 136, 138, 144, 145 |
| Critical density, g $cm^{-3}$ | 0.74, 0.73, 0.7517, 0.741 | 36, 137, 138, 146 |
| Surface tension, dyn $cm^{-1}$ | 11.63 (−50°), 8.02 (−20°) | 145, 147 |
| Viscosity of gas, $10^4$CGS units | 1.537 (22.5°), 1.871 (100°) | 148 |
| Molecular diameter, Å (from viscosity) | 4.77 | 148 |
| Thermal conductivity (of liquid), $10^5$W $cm^{-1}$ $deg^{-1}$ | 13.2 (20°), 13.6 (30 °), 14.3 (50°) | 149 |
| Thermal conductivity (of gas), $10^4$W $cm^{-1}$ $deg^{-1}$ | 1.3 (20°, 1 atm) | 150 |
| Refractive index (of liquid) | 1.170 (20°), 1.167 (25°) | 151 |
| Dielectric constant (at 27.6 °C), CGS units | 1.009191 (178 mmHg)<br>1.00123 (457 mmHg)<br>1.00034 (131 mmHg) | 152, 153 |
| Dipole moment, CGS units | $3 \cdot 10^{-20}$ | 154 |
| Velocity of sound, m $s^{-1}$ | 146.3 (30°, 750 mmHg) | 155 |
| Magnetic susceptibility, CGS units | $(-0.300 \pm 0.003) \cdot 10^{-6}$ | 142 |

## Solubility of Sulphur Hexafluoride

The behaviour of $SF_6$ in polar and non-polar solvents (Table 4) is of undoubted practical[164-167] and theoretical[168-170] interest. The solubility of sulphur hexafluoride in water ($5.5 \times 10^{-3}$ $cm^3/cm^3$ $H_2O$), determined for the first time by Friedman[171], is much lower than the solubilities of gases as helium ($9 \times 10^{-3}$), molecular nitrogen ($16 \times 10^{-3}$), xenon ($118 \times 10^{-3}$), or argon ($34 \times 10^{-3}$). The experimental entropy of solution (−50 e.u.) proved to be higher by more than 10 e.u. than the values calculated empirically[177-179]. The enthalpy of solution is also more negative than the enthalpy of condensation of $SF_6$, which is −4 kcal $mole^{-1}$.

**Table 3.** The constants $A$ and $B$ in the equation $\lg P = A - B/T$ for the sublimation pressure of sulphur hexafluoride.

| Temperature range, K | $A$ | $B$ | References |
|---|---|---|---|
| 175—222.5 | 8.711 | 1222 | 136 |
| 201—222.5 | 8.7648 | 1231.3 | 161 |
| 200.7—222.5 | 8.736 | 1224.8 | 162 |
| 102—143 | 8.9555 | 1265 | 163 |

**Table 4.** The solubilities of sulphur hexafluoride in various solvents ($t$ = 25°C, $P$ = 1 atm).

| Solvent | $10^4$ × mole fraction | References | Solvent | $10^4$ × mole fraction | References |
|---|---|---|---|---|---|
| $H_2O$ | 0.05* | 173 | $C_7F_{16}$ | 224.4 | 175 |
| HF | 1.3** | 174 | $CCl_4$ | 65.54 | 174 |
| $C_6F_6$ | 26.4 | 174 | $C_2Cl_3F_3$ | 278.6 | 174 |
| $C_6H_{12}$ | 53.91 | 174 | $CS_2$ | 9.245 | 175 |
| $n$-$C_7H_{16}$ | 100.55 | 174 | $(C_4F_9)_3N$ | 731 | 176 |
| $i$-$C_8H_{18}$ | 153.5 | 174 | $N_2H_3CH_3$ | 2.11 | 167 |
| $C_6H_5CH_3$ | 33.95 | 174 | $N_2O_4$ | 93.46 | 167 |
| $C_6H_{11}CH_3$ | 70.15 | 174 | $CH_3NO_2$ | 10.0* | 171 |

*Recalculated from data of Ashton et al.[172]
**Recalculated from data of Gillespie and Humphreys[173].

It is noteworthy that the estimates of the thermodynamic properties of solution when the solubility of the gas is so low may not be adequately reliable. The use of better apparatus (accuracy to within a mole fraction of $10^{-6}$) made it possible to obtain an expression for the temperature variation of the solubility of $SF_6$ in water, in the range 0–50°C:[172]

$$\lg X_2 = 6648.32/T + 45.2067 \lg T - 139.5793,$$

where $X_2$ is the mole fraction of $SF_6$ in water and $T$ the temperature in K.

The heat and entropy of solution of sulphur hexafluoride can be determined from the relations.

$$\Delta H_2^\circ/R = \partial \ln X_2/\partial(1/T) = -2.303 \times 6648.32 + 45.2067\,T,$$

where the entropy of solution refers to the transfer of 1 mole of gas to a hypothetical solution of unit mole fraction. The enthalpy and entropy of solution of $SF_6$ in water calculated by this formula are respectively −4.9 kcal $mole^{-1}$ and −41 cal $mole^{-1}$ $deg^{-1}$ [at 25°C].

## The Formation of Clathrate Compounds

It is interesting to note that, despite the low solubility of sulphur hexafluoride in water and other solvents, the existence of two clathrate compounds of $SF_6$ has been established: the gas hydrate $SF_6.17H_2O$ and the clathrate derivative formed by Dianin's compound with sulphur hexafluoride ($6C_8H_{20}O_2.2SF_6$).[180-184]

The gas hydrate can be obtained by slowly forcing $SF_6$ into water until the gas pressure reaches 5–6 atm. White crystals resembling snow are formed at 0°C. It was established on the basis of the $P$–$T$ phase diagram in the temperature range between −9° and 15°C that the gas hydrate of sulphur hexafluoride contains 17.02 moles of water per mole of sulphur hexafluoride at 0°C.[181] The vapour pressure at this temperature is 0.8 atm. The heats of formation of the hydrate from liquid water and ice are respectively −29.57 and 5.140 kcal $mole^{-1}$. The temperature and pressure corresponding to the coexistence of four phases (the $SF_6$ hydrate–liquid enriched in water–liquid enriched in $SF_6$–vapour) are 14°C and 20 atm.

The clathrate derivative formed by Dianin's compound[182,183] with sulphur hexafluoride can be obtained by keeping the ethanol modification of this compound, dissolved in decanol, at a 20–25 atm pressure of gaseous $SF_6$ and 130–140°C for 4–5 days. This results in the formation of a solid clathrate derivative whose composition is close to $6C_{18}H_{20}O_2.1.79SF_6$.[184] The product contains up to 13% $SF_6$, i.e. a little less than 2 moles (14.7%), probably owing to the limited solubility of sulphur hexafluoride in decanol. The melting point of the clathrate compound $6C_{18}H_{20}O_2.1.79SF_6$ is 163–165°C and its density is 1.3 g $cm^{-3}$.

It is quite evident that the capacity for the formation of clathrate compounds is not unusual for sulphur hexafluoride and the small number of examples known at present is due merely to the current state of research in this field. There is no doubt about the great promise and theoretical and practical value of the latter.

## Thermochemical Properties

The heat of formation of sulphur hexafluoride under standard conditions was determined from calorimetric measurements of the heat of combustion of sulphur in fluorine. Such measurements were made for the first time by Yost and Claassen[141], who found $\Delta H_{298}^\circ$ = −262 kcal $mole^{-1}$. A later study of a similar kind by Gross[185] yielded −288.5 ± 0.7 kcal $mole^{-1}$ as the heat of formation of $SF_6$ under standard conditions and, finally, according to O'Hare et al.[186], $\Delta H_{298}^\circ$ = −291.7 ± 0.2 kcal $mole^{-1}$. The last value is probably the most accurate, which was confirmed by redeterminations using fluorine with a lower oxygen content[185].

The heat capacity of sulphur hexafluoride was determined experimentally by Eucken and Schröder[140] up to 13 K. These results were used by Kelley and King[187] to calculate the standard entropy of formation of $SF_6$, which proved to be 70.3 ± 0.7 cal $mole^{-1}$ $deg^{-1}$, in agreement with statistical calculations of this quantity: 69.5 to 70.7 cal $mole^{-1}$ $deg^{-1}$.[186,188-191]. The small differences between the entropies calculated by the statistical method are largely due to the differences between the molecular constants and particularly the S–F bond lengths employed.

## Thermal Stability

The thermal dissociation of sulphur hexafluoride results in a gaseous mixture containing mainly the following components: S, F, $e$, $SF_6$, $SF_4$, $SF_3$, $SF_2$, SF, $S_2$, $F_2$, $S^{2+}$, $F^+$, $F^-$, and $S^-$.[192-195] Calculation of the mixture composition in the temperature range 1000–20 000 K at pressures of 1–20 atm in the dissociation range showed that

at 1000 K the mole fraction of atomic fluorine and sulphur tetrafluoride is $6 \times 10^{-6}$ and that of molecular fluorine is $1 \times 10^{-6}$. Up to 1400 K ($P = 1$–$10$ atm), the mole fraction of $SF_6$ is still close to unity (0.992). Rapid dissociation begins at 2000 K with the appearance of new species: S, $SF_2$, SF, and $S_2$. At 3000 K $SF_6$ no longer exists and the decomposition products begin to be enriched in the ions $S^+$, $F^+$, $F^-$, and $S^-$. $SF_4$ disappears at 5000 K and the remaining molecules vanish at 7500 K, the plasma consisting of electrons, sulphur, and fluorine in atomic and ionised states [195].

## V. CHEMICAL PROPERTIES

The chemical activity (reactivity of a particular compound is determined by the rate of reaction between the latter and another substance, provided of course that the process itself is thermodynamically feasible. In order to compare the reactivities of various compounds in relation to the same substance, the reaction rates compared must refer to the same stage, common to the processes under consideration occurring under comparable conditions. The isolation of the rate determining stage of the reaction and observation of the latter involve considerable difficulties, which increase on passing from homogeneous to heterogeneous systems. Therefore in practise one usually employs a systematic empirical procedure frequently based on qualitative observations. Naturally, such a procedure may be unreliable. Thus, recent studies of the chemical properties of molybdenum and tungsten hexafluorides [10,11] showed that both compounds are appreciably inert, in contrast to earlier investigations in which $MoF_6$ and $WF_6$ were regarded as vigorous fluorinating agents[29,196]. The difficulties of the empirical approach faced investigators with the necessity to establish some, at least qualitative, criteria for the prediction of the potentially possible changes in the chemical systems of the hexafluorides of several elements, since such systems are of some practical interest. One of these criteria is the thermal stability of the hexafluorides.

A comparative estimate of the thermal stabilities was made most completely and in greatest detail, using various physicochemical characteristics (the force constants of $EF_6$, the E–F bond energies, and the equilibrium constants for the dissociation reactions), by Galkin and Tumanov[2]. Table 5 presents the thermal stability series of the hexafluorides established by the authors on the assumption that the thermal stability is related to various physicochemical characteristics of the $SF_6$ molecule.

Analysis of the results led the authors to the conclusion[2] that the most objective criterion of the thermal stability of hexafluorides as a characteristic of their reactivity is apparently the thermodynamic stability constant (the reciprocal of the equilibrium constant for the dissociation reaction), characterising the partial dissociation of the hexafluorides to the corresponding tetrafluorides. The thermal stability estimated from the average E–F bond energy in $EF_6$ agrees fully with the thermodynamic estimate with the exception of $ReF_6$. The valence force constants and the interatomic distances are of the doubtful value, according to the authors, as characteristics of the chemical properties of hexafluorides.

† It was assumed that an increase in the thermal stability of the molecule entails a decrease of its reactivity [197].

Returning now to sulphur hexafluoride, it can be shown by estimating its reactivity from the thermodynamic stability constant that it is a fairly reactive substance capable of converting into the highest fluorides at any rate compounds of metals such as molybdenum, tungsten, or uranium. Indeed the conversion of $UO_2$ into $UF_6$ with the aid of sulphur hexafluoride was achieved recently [52].

On the other hand, the list of substances in relation to which sulphur hexafluoride is fairly reactive can be greatly extended if one assumes the possibility of another reaction pathway, based, for example, on the high electron affinity of $SF_6$. We may recall that sodium dissolved in the dimethyl ether of diphenylethylene glycol reduces sulphur hexafluoride even at room temperature and the reaction is apparently based on electron transfer from a diphenyl radical-ion to the $SF_6$ molecule with formation of the unstable radical-anion $SF_6^-$. [84]

**Table 5.** Variation of the thermal stabilities of hexafluorides with certain physicochemical characteristics of the molecules.

| Physicochemical characteristic of the molecule | Variation of thermal stabilities with increase of the physicochemical characteristic of the molecule |
|---|---|
| Bond energy $D_0^0$ | $UF_6 > WF_6 > NpF_6 > MoF_6 > PuF_6 > ReF_6 > TcF_6 > OsF_6 > TeF_6 > SF_6 > SeF_6 > IrF_6$ |
| Thermodynamic stability constant: $MF_6 \rightarrow M(gas) + 6F(gas)$ | $UF_6 > WF_6 > NpF_6 > MoF_6 > PuF_6 > TcF_6 > ReF_6 > OsF_6 > TeF_6 > SF_6 > SeF_6 > IrF_6$ |
| Thermodynamic stability constant: $MF_6 \rightarrow MF_4(gas) + 2F(gas)$ | $WF_6 > MoF_6 > UF_6 > SF_6 > NpF_6 > PuF_6$ |

The above considerations should be used as the starting point in the search for ways of increasing the reactivity of sulphur hexafluoride in order to use it as a fluorinating agent. This is quite feasible, since the inertness of sulphur hexafluoride can be successfully overcome by various process activation procedures, including ordinary heating.

### Reactions in an Electric Discharge

The lower sulphur fluorides ($SF_2$ and $S_2F_2$), whose reactivity is much higher than that of the initial sulphur hexafluoride, are formed under the conditions of an electric discharge [198–201].

The effect of a high-frequency electric discharge was used for preparative purposes in reactions of sulphur hexafluoride with chlorine and oxygen [202]. In the first case the process is accompanied by the formation of $SF_5Cl$, probably in accordance with the overall equation

$$SF_6 + Cl_2 \rightarrow SF_5Cl + ClF \quad .$$

The yield of $SF_5Cl$ is $1.97 \times 10^{-3}$ mole $h^{-1}$. Chlorine monofluoride (ClF) was not identified, evidently owing to its reaction with glass.

The reaction between $SF_6$ and $O_2$ (in proportions of 1.32 : 1) leads to the formation of $SOF_4$, the approximate yield of which is $0.11 \times 10^{-2}$ mole $h^{-1}$ (degree of conversion 18%) at a gas flow rate of $0.61 \times 10^{-2}$ mole $h^{-1}$. The mechanisms of the two reactions could not be determined owing to the abundance of the $SF_6$ dissociation and ionisation products formed under the influence of the electric discharge.

Reaction Accompanying the Explosion of Metallic Wires in an Atmosphere of $SF_6$

Studies on the pyrolysis of hydrocarbons under the conditions of exploding wires using sulphur hexafluoride as the inert diluent established that the latter reacts with the exploding metals even at relatively low levels of the supplied energy [56,203,204]. This results in the formation of either the corresponding metal fluoride and sulphur tetrafluoride:

$$2/n\,M + SF_6 = 2/n\,MF_n + SF_4 \qquad (4)$$

or of the metal fluoride and elemental sulphur:

$$6/n\,M + SF_6 = 6/n\,MF_n + S \ , \qquad (5)$$

where $n$ is an index corresponding to the highest degree of oxidation of the metal.

The particular reaction pathway depends on the molar ratio $SF_6$ : M. For example, the reaction with tungsten for the ratio $SF_6$ : W = 3.0 takes place in accordance with Eqn. (4). The fraction of $WF_6$ obtained by reaction (5) increases to 42% when the molar ratio of the components is 1.8. The yield of $MoF_6$ in reaction (5) involving molybdenum varies from 12 to 52% when the molar ratio $SF_6$ : Mo is reduced from 2.0 to 1.6 respectively.

The explosion of rhenium in an atmosphere of $SF_6$ leads to the formation of the volatile rhenium hexafluoride and heptafluoride. By selecting appropriate conditions, it is possible to obtain rhenium heptafluoride in which the $ReF_6$ content is minimal. Moreover the hitherto unknown involatile rhenium fluoride $ReF_3$, which cannot be obtained by direct synthesis from the elements, was formed in this reaction.

Thus sulphur hexafluoride becomes a very effective fluorinating agent under the conditions where a metal is exploded electrically. The processes investigated lead to the possibility of new syntheses of both $SF_4$ and specific metal fluorides without the use of elemental fluorine. It is interesting to note that the yield of reaction products is independent of the stoichiometry of the initial components, while the composition does depend on the latter. This makes it possible to regulate the purification of the volatile fluorides formed and it can serve as a basis for the synthesis of hitherto unknown inorganic fluorides.

The explosion of extremely small amounts of platinum or copper can initiate the above reaction between $SF_6$ and $O_2$, but the yield is lower [205,206].

The high kinetic barrier to the reaction between $SF_6$ and $O_2$ is probably due to the ability of fluorine to repel the electronegative oxygen [206]. In fact the rate of reaction can be increased appreciably in the presence of various gaseous additives (promoting agents), for example $H_2$, $Cl_2$, $Br_2$, and $CH_4$, the effectiveness of the promoting agent being inversely proportional to its electronegativity:

$$CH_4 > H_2 > Br_2 > Cl_2 \ .$$

Ion–Molecule Reactions

The $SF_6$ molecule belongs to the class of halogen-containing molecules, which are of considerable theoretical interest in connection with their characteristic large electron capture cross-sections. The radical-anion $SF_6^-$ (or $SF_5^-$) formed on interaction with electrons is very reactive with respect to a series of fluorine-containing molecules: $PF_3$ and $PF_5$, [207] $SiF_4$ and $BF_3$, [208] and $POF_3$ and $PSF_3$. [209] Thus, when a mixture of two fluorides ($SF_6$ and $AF_n$) is introduced into an ionisation chamber and bombarded with thermal electrons (0–0.2 eV), the formation of $AF_{n+1}^-$ anions may be observed in the mass spectrum:

$$AF_n + SF_6^- (SF_5^-) \rightarrow AF_{n+1}^- + SF_5 (SF_4) \ .$$

These cannot be formed independently under the given conditions ($BF_4^-$ and $SiF_5^-$ are observed in the mass spectrum only for energies in excess of 10 eV). [210,211]

Reactions on $\gamma$-Radiolysis

The high electron affinity of sulphur hexafluoride made it possible to use the latter as a specific electron acceptor in $\gamma$-radiolysis of substances [212–217], influencing in some way the composition of the final reaction products. The $\gamma$-radiolysis of water in the presence of $SF_6$, which was investigated recently, is accompanied by a high yield of $F^-$, which is formed only by the reaction between $SF_6$ and $\bar{e}$.aq. The reaction mechanism quoted above is consistent with the experimental data [212]:

$$SF_6 + \bar{e}aq \rightarrow (SF_6^{\cdot})^- \rightarrow SF_5^{\cdot} + F^- \ , \qquad (6)$$

$$SF_5^{\cdot} + 2H_2O \rightarrow OH^{\cdot} + H_3O + SF_4 + F^- \ , \qquad (7)$$

$$SF_4 + 9H_2O \rightarrow SO_3^{2-} + 6H_3O + 4F^- \ , \qquad (8)$$

$$SO_3^{2-} + OH;\ SF_6;\ H_2O_2 \rightarrow SO_4^{2-} \ . \qquad (9)$$

The Photochemical Effect of Infrared Radiation

Basov et al. [218], who studied the effect of infrared radiation from a $CO_2$ laser ($\lambda = 10.6\ \mu m$) on reactive gaseous systems, established that at certain intensities the vibrationally excited molecules react chemically. Thus irradiation of the $N_2F_4$–NO–$C_2F_4(C_2F_6)$ system results in a bright greenish-yellow flash, accompanying the process, and the starting materials react completely. It is noteworthy that, on normal heating of the system, the process is possible only at temperatures above 1500 K.

Irradiation of the $SF_6$–NO mixture also leads to an instantaneous reaction accompanied by a flash. $SOF_2$ is formed as one of the products. According to the authors, the mixture temperature does not then exceed 700°C, while the thermally activated mixture remains unreactive up to 1000°C. However, one should note that the conversion of $SF_6$ and NO is not complete. Pankratov [219] noted that this is due to the fact that the appearance of chemical reactivity may be caused by the excitation of stretching vibrations alone, while the radiation generated by the laser corresponds to the range of $SF_6$ deformation vibrations.

The results demonstrate the possibility of specific reactions, since the reaction of mixtures of starting materials under the influence of infrared radiation can be different from that at elevated temperatures when heated in the usual way. This factor is extremely important, since it leads to a method of synthesising new compounds involving extensive application of lasers in chemistry.

The Reaction on Heating

It is noteworthy that the simple and generally adopted method of accelerating reactions such as ordinary heating has for a long time been ignored by investigators, evidently in view of the negative results of the early studies mentioned above.

Despite Moissan's view that sodium is not acted upon by sulphur hexafluoride up to the boiling point of the metal (880°C), it was established in 1953 [220] that the reaction occurs even at 247°C ($K = 2.23 \times 10^{13}$ cm$^3$ mole$^{-1}$ s$^{-1}$). At 500°C the reaction is accompanied by chemiluminescence, the most likely explanation of which is that one of the five stages is exothermic with liberation of sufficient energy to excite the sodium D line:

$$SF_6 + n\,Na \rightarrow SF_{6-n} + n\,NaF \quad .$$

At relatively low temperatures (180–200°C) sulphur hexafluoride fluorinates aluminium trichloride with an $AlF_3$ yield of the order of 15% and at 250°C it reacts with $SO_3$, forming sulphuryl fluoride in approximately 20% yield [221]:

$$2SO_3 + SF_6 = 3SO_2F_2 \quad .$$

Technological reports dealing with the regeneration of waste from nuclear fuel by its fluorination with sulphur hexafluoride were published recently [52,53]. For example, the fluorination of $UO_2$ in corundum reactors at 750 to 900°C with an $SF_6 : O_2 = 1 : 1$ mixture is accompanied by the formation of $UF_6$. The authors believe that the process proceeds in accordance with the following general reaction mechanism [52]:

$$UO_2 + SF_6 = UF_6 + SO_2 \quad .$$

The use of high temperatures (1000°C) made it possible to obtain under laboratory conditions comparatively pure protactinium pentafluoride by fluorinating protactinium pentoxide with sulphur hexafluoride [53]:

$$3Pa_2O_5 + 5SF_6 = 6PaF_5 + 5SO_2 + 2.5O_2 \quad .$$

Moreover, the same authors' thermodynamic calculation has shown that the high-temperature fluorination of $PuO_2$ can yield $PuF_4$ via the reaction

$$PuO_2 + SF_6 = PuF_4 + SO_2F_2$$

or

$$^3/_2PuO_2 + SF_6 = ^3/_2PuF_4 + SO_2 + ^1/_2O_2 \quad .$$

However, these calculations have not so far been confirmed experimentally.

Naturally the problem of the reactivity or inertness of sulphur hexafluoride can be solved in the light of the above facts only by a comprehensive investigation of its reactivity in relation to a number of elements and their compounds. Such a study was undertaken by the authors of the present review [60–67] and showed that the widely held view that $SF_6$ is chemically inert is extremely arbitrary and that the example quoted constitute exceptions rather than the rule.

It was established by differential thermal analysis (DTA) that the vast majority of the metals investigated (Table 6) react at a high rate in the range 500–600°C. [61]

The reactions with titanium and the lanthanides proceed particularly vigorously with inflamation. The rate of reaction with boron and silicon is not so high as with titanium or lanthanum, apparently because of the kinetic characteristics of the process, since, on raising the $SF_6$ flow rate, the reaction is so vigorous in this case too that the mixture becomes incandescent. In many instances the occurrence of the reaction can be detected from the change in the weight of the reaction product relative to that of the starting material.

Our thermodynamic assessment of the most probable processes occurring in the $SF_6$–M systems led to the following findings:

$$(1/n)M(solid) + \tfrac{1}{2}SF_6(gas) = (1/n)MF_n(solid) + \tfrac{1}{2}SF_4(gas), \qquad (I)$$

$$\Delta G_I^\circ = \Delta H^\circ_{MF_n} - T(S^\circ_{MF_n} - S^\circ_M) + 52250 \text{ cal equiv.}^{-1};$$

$$\tfrac{4}{3}nM(solid) + \tfrac{1}{6}SF_6(gas) = (1/n)MF_n(solid) + \tfrac{1}{6}nM_2S_n(gas), \qquad (II)$$

$$\Delta G_{II}^\circ = \Delta H^\circ_{MF_n} + \tfrac{1}{3}\Delta H^\circ_{M_2S_n} + \tfrac{1}{3}(4S^\circ_M - 3S^\circ_{MF_n} - S^\circ_{M_2S_n} + 34.9) + 48100 \text{ cal equiv.}^{-1};$$

$$(1/n)M(solid) + \tfrac{1}{6}SF_6(gas) = (1/n)MF_n(solid) + \tfrac{1}{12}S_2(gas), \qquad (III)$$

where $\Delta H^\circ_{MF_n}$ and $\Delta H^\circ_{M_2Sn}$ are the standard enthalpies of formation of the fluoride and sulphide respectively (in cal equiv.$^{-1}$), $S^\circ_{MF_n}$ and $S^\circ_{M_2S_n}$ are the standard entropies of formation of the fluoride and sulphide respectively (in cal equiv.$^{-1}$ deg$^{-1}$), and $S^\circ_M$ is the standard entropy of the metal (in cal equiv.$^{-1}$ deg$^{-1}$).

**Table 6.** Conditions in the reaction of sulphur hexafluoride with metals and oxides.

| Metal or oxide | $T$, °C | $\Delta P$, % | Metal or oxide | $T$, °C | $\Delta P$, % | Metal or oxide | $T$, °C | $\Delta P$, % |
|---|---|---|---|---|---|---|---|---|
| K | 400 | — | Sb | none | — | $Tb_4O_7$ | 637 | — |
| Cu | none | +30 | W | 648 | −88 | $Dy_2O_3$ | 645 | 14.5 |
| Mg | none | +9.5 | Re | none | — | $Ho_2O_3$ | 642 | 14.6 |
| Ca | 470 | — | MgO | 795 | +61 | $Er_2O_3$ | 597 | +11.7 |
| Zn | 613 | +33 | CaO | 727 | +23.1 | $Tm_2O_3$ | 670 | +12.5 |
| Cd | 530 | — | SrO | 628 | +12.7 | $Yb_2O_3$ | 700 | +14 |
| B | 680 | — | BaO | 480 | +13.4 | $Lu_2O_3$ | 590 | +12 |
| Al | 560 | — | $B_2O_3$ | none | — | $TiO_2$ | none | +13.5 |
| Ga | 690 | — | $Al_2O_3$ | 530 | +24.5 | $Cr_2O_3$ | none | +14.5 |
| In | 480 | — | $Ga_2O_3$ | none | +12.3 | $WO_3$ | none | — |
| La | 450 | — | $In_2O_3$ | none | +20.6 | MnO | none | — |
| Pr | 460 | — | $Sc_2O_3$ | none | +28.7 | CuO+KF | 526 | +19 |
| [illegible] | 550 | — | $Y_2O_3$ | 657 | +36.4 | MgO+KF | 474 | +7.9 |
| Tm | 550 | — | $La_2O_3$ | 714 | +5 | CaO+CsF | 563 | +7.8 |
| Yb | 500 | — | $Ge_2O_3$ | 450 | — | SrO+RbF | none | +16 |
| C | none | −8.4 | $Pr_6O_{11}$ | 584 | +13.2 | ZnO+KF | none | +6 |
| Si | 662 | −5 | $Nd_2O_3$ | 647 | +15.4 | SnO+KF | 332 | +20 |
| Sn | none | — | $Sm_2O_3$ | 670 | +8 | $TiO_2$+NaF | none | −48 |
| Ti | 494 | −84.6 | $Eu_2O_3$ | 560 | +18.7 | $VO_2$+KF | 429 | — |
| Zr | 560 | — | $Gd_2O_3$ | 594 | +12.6 | $Ni_2O_3$+KF | none | +23 |

Note. 1) "none" implies that a thermal effect was not recorded on the thermograms; 2) $\Delta P$ is the relative change in weight (wt.%); 3) implies that an increase in weight was not determined.

It can be easily shown that under standard conditions $\Delta G^\circ_{II} < \Delta G^\circ_I < \Delta G^\circ_{III}$, but at high temperatures this relation can change. By solving the inequality $\Delta G^\circ_I - \Delta G^\circ_{II} < 0$ for $T$, we find that $\Delta G^\circ_I < \Delta G^\circ_{II} < \Delta G^\circ_{III}$ when $T \geq (12450 - \Delta H_{M_2S_n})/S^\circ_M - S^\circ_{M_2S_n} + 34.9)$, i.e. reaction (II), accompanied by the formation of the metal sulphide and fluoride, is thermodynamically most favoured when $T' < T$ and reaction (I), involving the formation of the metal fluoride only, is most likely at $T'' > T$.

A test of the thermodynamic calculations for the metal–$SF_6$ systems led to their confirmation in a detailed experimental study of the conditions and the nature of the interaction of sulphur hexafluoride with zinc and cadmium [62].

Both metals react with $SF_6$ after their fusion. X-Ray diffraction established that the reactions of zinc and cadmium with $SF_6$ involve the formation of the metal fluorides and sulphides.

The products of the reaction between cadmium and $SF_6$ were separated in water using the different solubilities of CdS and $CdF_2$. Chemical analysis established that the solute is $CdF_2$ and that the solid in equilibrium with the solution is CdS. The molar ratio of the two phases is close to $CdF_2 : CdS = 3 : 1$, which makes it possible to formulate the process as follows:

$$4Cd + SF_6 = 3CdF_2 + CdS \quad .$$

As for cadmium, the reaction between zinc and $SF_6$ is also accompanied by the formation of zinc fluoride and sulphide in the molar proportions $ZnF_2 : ZnS = 3 : 1$. As mentioned above, when the temperature is raised, reaction (I) with the metal becomes thermodynamically favoured. Using inequality (10), it can be shown that the required temperature is above 650°C for cadmium and above 750°C for zinc. Indeed the fluorination of cadmium at this temperature leads to the formation of $CdF_2$ alone; the reaction with zinc is also accompanied by an increase in the mole fraction of the fluoride up to the formation of pure $ZnF_2$.

Thus our experimental data in no way confirm a marked chemical inertness of sulphur hexafluoride, showing in fact that, even on moderate heating, $SF_6$ becomes an active fluorinating agent capable of "supplying" its fluorine to reactions involving the fluorination of both elements and compounds. However, the reaction with oxides takes place at higher temperatures (Table 6). The only solid product is the difluoride of the corresponding metal.

Thermodynamic analysis (under standard conditions) of the reactions between sulphur hexafluoride and metals of one of the types

$$^1/_2n\,M_2O_n + {}^1/_4SF_6 = 1/n\,MF_n + {}^1/_4SO_2F_2 \quad , \qquad (10)$$

$$^1/_2n\,M_2O_n + {}^1/_6SF_6 = 1/n\,MF_n + {}^1/_6SO_3 \quad , \qquad (11)$$

$$^1/_2n\,M_2O_n + {}^1/_4SF_6 = 1/n\,MF_n + {}^1/_4SOF_2 + {}^1/_8O_2 \quad , \qquad (12)$$

$$^1/_2n\,M_2O_n + {}^1/_6SF_6 = 1/n\,MF_n + {}^1/_6SO_2 + {}^1/_{12}O_2 \quad , \qquad (13)$$

$$^1/_2n\,M_2O_n + {}^1/_2SF_6 = 1/n\,MF_n + {}^1/_2SOF_4 \quad . \qquad (14)$$

shows that at 550°C all the reactions [except reaction (14)] are already thermodynamically feasible. A mass-spectrometric study of the composition of the gas phase showed[63] that the reaction products are sulphur dioxide and sulphuryl fluoride. The absence of sulphur trioxide can be readily accounted for, on the one hand, by its dissociation at the given temperatures and, on the other, by the possibility of its interaction with $SF_6$. Nor can one rule out the possibility that the sulphur oxide fluorides formed can themselves behave as fluorinating agents. The latter is of fundamental importance from the standpoint of the maximum utilisation of the fluorine contained in the initial sulphur hexafluoride. One may also note that the thermodynamic calculations are fully consistent with the experimental data, which showed the absence of sulphur oxide tetrafluoride from the gaseous reaction products, since $\Delta G^\circ_{290}$ for reaction (14) is positive over the entire temperature range.

A number of investigators[222-225] have recently attempted to establish a quantitative relation between thermodynamic and kinetic process characteristics for reactions of the same type. Thus a study of reactions between the oxide of a Group IVA element and chlorine demonstrated the existence of an approximately linear relation between the free energy of reaction $\Delta G^\circ$ and the temperature of the onset of reaction $T_i$, determined by the DTA method. If it is assumed that such correlations for reactions of the same type [reactions (10)–(13)] do occur, then $T_i$ for any of the above reactions will be determined mainly by the difference $\Delta H^\circ_{MF_n} - \Delta H^\circ_{M_2O_n}$ kcal equiv.$^{-1}$, decreasing as the difference diminishes. It is noteworthy that $T_i$ for reactions of the same type, whose rates do not differ appreciably, can serve as a qualitative measure of the reactivity of a particular component.

On the basis of the above hypothesis, $T_i$ presumably decreases (and the reactivity of $SF_6$ increases) in the vertical series of the oxides of Group IA elements: $Li_2O > Na_2O > Cs_2O > K_2O = Rb_2O$, since $\Delta H^\circ_{MF_n} - \Delta H^\circ_{M_2O_n}$ varies in the sequence $Rb_2O = K_2O > Cs_2O > Na_2O > Li_2O$; for the oxides of Group IIA elements, we have $BeO > MgO > CaO > SrO > BaO$, since $\Delta H^\circ_{MF_n} - \Delta H^\circ_{M_2O_n}$ varies in the sequence $BaO > SrO > CaO > MgO > BeO$; finally for the oxides of Group IIIA elements we have $Al_2O_3 > In_2O_3 > Ga_2O_3 > Tl_2O_3$, since $\Delta H^\circ_{MF_n} - \Delta H^\circ_{M_2O_n}$ varies in the sequence $Tl_2O_3 > Ga_2O_3 > In_2O_3 > Al_2O_3$.

Table 6 shows that a similar correspondence is in fact observed for the oxides of Group IIA elements (MgO, CaO, SrO, and BaO) and Group IIIA elements ($Al_2O_3$, $Ga_2O_3$, and $In_2O_3$), despite the fact that $T_i$ for $In_2O_3$ (610°C) and $Ga_2O_3$ (680°C) were determined by differential thermogravimetric analysis. All the lanthanide oxides react in the temperature range 450–700°C like the oxides of alkaline earth metals but even more vigorously (Table 6). Consideration of data for the oxides $La_2O_3$, $Nd_2O_3$, and $Pr_6O_{11}$ shows that, according to the results of chemical and X-ray diffraction analyses, they react with sulphur hexafluoride, forming the corresponding metal trifluorides.

It is noteworthy that $SF_6$ is an extremely vigorous fluorinating agent on heating in the synthesis of not only binary fluorides but also complex fluorides. We showed this in a study of the reaction of sulphur hexafluoride with alkaline earth metal oxides in the presence of an alkali metal fluoride[64]. Alkaline earth metal complexes of the type $M^IMF_3$ synthesised in the solid phase are formed only at fairly high temperatures above 1000°C,[226,227] which naturally gives rise to certain difficulties both in the synthesis and in the subsequent purification of the products. On the other hand, in the fluorination of a mixture of an alkaline earth metal oxide and an alkali metal fluoride in specific stoichiometric proportions the corresponding complexes are formed at lower temperatures. For example, $KMgF_3$ was obtained under these conditions at 660°C, while the solid-phase synthesis requires the use of temperatures above 1000°C. The syntheses of the corresponding fluoro-complexes of alkaline earth metals were achieved under similar conditions: $K_2MgF_4$, $CsMgF_3$, $CsGaF_3$, $CsSrF_3$, and $BaLiF_3$. It was established by the DTA method that the temperature of the onset of reaction between $SF_6$, MO, and MF does not exceed 500°C in all cases. Under these conditions and up to 900°C, the $MF_2$–MF mixture does not undergo any changes associated with the formation of complex fluorides. The latter can be obtained in the $MF_2$–MF system only at temperatures not less than 1100–1200°C.[226,227]

Thus the above results show that sulphur hexafluoride is an extremely active fluorinating agent and can be used successfully in the synthesis of anhydrous binary and complex fluorides.

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Presumably further advances in the application of sulphur hexafluoride (one of the most widely used hexafluorides) will be achieved primarily in connection with studies on its chemical properties, since the level of present research on the physical and physicochemical properties meets practical requirements adequately.

In this respect the most interesting and in practise most important results may be expected in studies on reactions where $SF_6$ behaves as a fluorinating agent. The practical interest in reactions of this kind is due to the high fluorine content in sulphur hexafluoride (78%), its inertness and non-toxicity under the usual conditions, and also the possibility of its activation by various procedures, ranging from the effect of electromagnetic radiation to ordinary heating. The data obtained by the present authors for the synthesis of both simple and complex inorganic fluorides involving sulphur hexafluoride suggest that $SF_6$ can be regarded as a new and very promising fluorinating agent, the possibilities of which have been by no means fully explored. It is quite evident that the requirements of both scientific research and industry involve extensive employment of increasing numbers of new fluorinating agents. Traditional fluorine, fluorine halides, and hydrogen fluorides can be in many cases replaced successfully by noble gas fluorides[228,229], alkali metal fluoride halides[230] and hydrogen fluorides[230-233], nitrogen[234] and phosphorus[235] fluorides, and the highest fluorides of certain metals[236]. There is no doubt that one is fully justified in including sulphur hexafluoride in the above by no means exhaustive list of the possible and promising fluorinating agents, this being confirmed by the advances in the chemistry of this compound.

The reactions of $SF_6$ with various gaseous compounds initiated by laser radiation are extremely interesting from the standpoint of the synthesis of new fluorine-containing compounds.

The study of the solubility of sulphur hexafluoride in water and other solvents is extremely fruitful in relation to further investigations of the nature of non-electrolytes and is of interest in connection with the possible synthesis of various derivatives of sulphur hexafluoride in non-aqueous media.

It is noteworthy that, although the method of synthesis of sulphur hexafluoride from the elements is fairly simple, it requires the use of expensive fluorine and of expensive apparatus in view of the corrosive nature of fluorine. The advances in recent years nevertheless give rise to the hope that it will be possible to introduce methods for the synthesis of sulphur hexafluoride without the direct use of fluorine, for example by the electrolysis of sulphur-containing compounds in liquid hydrogen fluoride.

The development of studies on the chemistry of this compound will undoubtedly entail the necessity for the development of the analytical chemistry of $SF_6$ and it appears likely that gas or gas–liquid chromatography will prove to be most useful in this field too.

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