

INTERACTION OF SULPHUR HEXAFLUORIDE WITH METALS AND OXIDES

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SUMMARY

The interaction of SF₆ with metals and oxides has been studied by thermal analysis techniques. It has been shown that sulphur hexafluoride is an active fluorinating agent. It reacts both with oxides at temperatures about 600–700° and with metals at about 500–600°, to produce fluorides with the former and fluorides as well as sulphides with the latter. Higher temperatures bring about transformation of metals and their sulphides into pure fluorides.

Thermodynamic evaluation of possible processes taking place in the fluorination of metals and oxides has been carried out.

X-Ray diffraction and chemical analyses were used to identify final products for such metals and oxides as Zn, Cd, La₂O₃, Nd₂O₃ and Pr₆O₁₁.

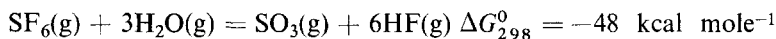
INTRODUCTION

Sulphur hexafluoride has customarily been considered to be chemically inert. This lack of reactivity, and its non-toxicity and high dielectric strength have led to the use of SF₆ as an insulating atmosphere in high-voltage electrical equipment. Its availability has stimulated research dealing mainly with the study of its physical properties. There is also much theoretical interest in its structure and in the nature of the chemical bond involved. The chemistry of sulphur fluorides, and the hexafluoride in particular, is not at all well developed. Data on the properties of SF₆ have been restricted to information about its interaction with metals under conditions similar to those in its application as a dielectric, where the possible chemical activity of the compound is a rather undesirable factor restricting the application of sulphur hexafluoride under certain conditions. For these reasons, modern concepts of the reactivity of SF₆ have not changed essentially since 1900, when the material was first produced by Moissan¹.

A number of papers dealing with inorganic sulphur fluorides²⁻⁶ have noted the high chemical inertness of SF₆ with respect to some substances and have given examples supporting this fact. Even at red heat it does not attack glass, nor decompose, nor react with some elements (Mg, Ca, B, C, Ag, P and halogens) and compounds (CuO, PbCrO₄). It does not react with H₂O up to 500° nor with oxygen even in an electric discharge. This is virtually a complete summary of all the information concerning the reactivity of sulphur hexafluoride.

The extreme chemical stability of SF₆, particularly toward hydrolysis, is presumably due to a combination of factors, including the high S-F bond strength and the fact that sulphur is both coordinately saturated and sterically hindered, particularly in the case of sulphur hexafluoride, due to the lack of polarity of the molecule.

The low reactivity is also due to kinetic factors and not to thermodynamic stability, since the reaction



is decidedly favourable. It should be noted that the average bond energy of SF₆ (76 kcal mole⁻¹) is slightly lower than that of SF₄ (78-79 kcal mole⁻¹), a compound which is extremely reactive being instantly hydrolyzed by water.

We have already mentioned the fact that there have been, in general, few investigations on the chemistry of sulphur hexafluoride, in particular as far as its interactions with elements and compounds are concerned. In recent work various activation methods have been applied⁸⁻¹³ but even such a simple and widely accepted method of accelerating the reaction as ordinary heating has not attracted much attention, probably because of the negative results of earlier workers²⁻⁷.

However, as noted by Simons¹⁴, it was already obvious that sulphur hexafluoride as well as selenium and tellurium hexafluorides "... are potentially very strong oxidants or fluorinating agents...". SF₆ is of interest as a potential fluorinating agent due to its high fluorine content; its application may also lead to new methods of synthesis of already known inorganic fluorides and possibly hitherto unknown compounds. It is evident that a detailed investigation of the reactivity of sulphur hexafluoride on heating with a number of substances such as metals, oxides, sulfides and halides could help to establish whether the current opinions regarding its chemical inertness are correct or if the earlier examples given above prove to be an exception rather than the rule. The present paper deals with the nature and conditions of interaction of metals and oxides with sulphur hexafluoride.

EXPERIMENTAL

Differential thermal analysis (DTA) has been applied to a study of the interaction of SF₆ with metals and oxides. A linear rate of heating of 10° min⁻¹

was used throughout and thermograms were recorded on an EPP-09M3 potentiometric recorder. Temperature measurements were made with Pt/Pt–Rh thermocouples, the samples being contained in conical platinum crucibles. The sample (0.05–0.15 g) and inert reference material (Al₂O₃) were contained in 10 mm diameter quartz ampoules and the experiments were conducted in an atmosphere of SF₆, using a flow rate of 200–300 cm³ min⁻¹.

The fluorinating process was studied using a horizontal nickel reactor, in which a nickel or platinum boat containing the sample (0.4–0.7 g) was placed. After the SF₆ flow had started (0.2–0.3 l h⁻¹), the reactor was heated up to the reaction temperature which had been first established thermographically. Fluorination was continued until the weight of the reaction product became practically constant, *i.e.* until the change in weight of the sample was not more than 0.3–0.5% per hour. Usually two or three such heatings (of 50–60 min duration) were sufficient, the product being thoroughly ground in a jasper mortar after each heating process.

Chemical analysis of the reaction products was carried out as follows: metals were determined by compleximetric titration^{15,16}, fluoride ion was estimated acidimetrically or thoriometrically¹⁷ and sulphur was estimated as barium sulphate.

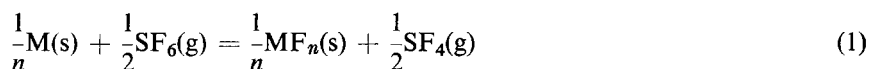
X-Ray analyses of all residues were carried out using the standard Debye–Scherrer method with Fe radiation. Sodium chloride or crystalline silicon served as standards.

RESULTS AND DISCUSSION

Interaction of sulphur hexafluoride with metals

Most metals investigated (Table 1) were found to react with SF₆ over the temperature range 500–600°, the DTA thermograms obtained being shown in Figure 1. Reactions with titanium and rare earth metals (La, Pr, Tb) resulted in spontaneous ignition. The rate of the reaction of B and Si with SF₆ is however not so high as that of titanium or lanthanum. This may possibly be explained by kinetic factors, as increasing the flow of fluorinating agent made the reaction so vigorous that the mixture became red hot. Some of the DTA curves do not exhibit exothermal or endothermal peaks, but despite this fact the reactions concerned occur as a change is observed in the weight of the starting materials (Table 1).

Thermodynamic evaluations of the proposed reactions taking place in M + SF₆ systems (where M = metal) are given below:

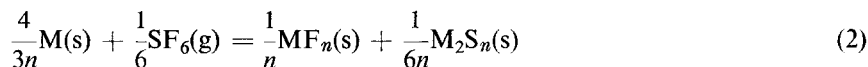


$$\Delta H^0 = \Delta H_{\text{MF}_n}^0 - T(S_{\text{MF}_n}^0 - S_{\text{M}}^0) + 52\,250 \text{ cal (g equiv)}^{-1}$$

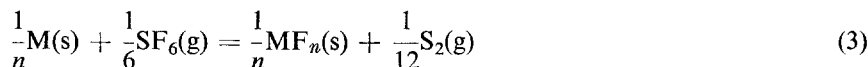
TABLE 1

EXPERIMENTAL CONDITIONS FOR THE REACTION OF SULPHUR HEXAFLUORIDE WITH METALS AND OXIDES

Substance	T(°C)	ΔP ^b (%)	Substance	T(°C)	ΔP(%)	Substance	T(°C)	ΔP(%)
K	400	—	Sb	none	—	Tb ₄ O ₇	637	—
Cu	none ^a	30	W	648	—88	Dy ₂ O ₃	645	14.5
Mg	none	9.5	Re	none	—	Ho ₂ O ₃	642	14.6
Ca	470	—	MgO	795	61	Er ₂ O ₃	597	11.7
Zn	613	33	CaO	727	23.1	Tm ₂ O ₃	670	12.7
Cd	530	—	SrO	628	12.7	Yb ₂ O ₃	700	14
B	680	—	BaO	480	13.4	Lu ₂ O ₃	590	12.1
Al	560	—	B ₂ O ₃	none	—	TiO ₂	none	13.5
Ga	690	—	Al ₂ O ₃	530	24.5	Cr ₂ O ₃	none	14.5
In	480	—	Ga ₂ O ₃	none	12.3	WO ₃	none	—
La	450	—	In ₂ O ₃	none	20.6	MnO	none	—
Pr	400	—	Sc ₂ O ₃	none	28.7	CuO + KF	526	19
Tb	550	—	Y ₂ O ₃	657	36.4	MgO + KF	474	7.9
Tm	550	—	La ₂ O ₃	714	5	CaO + CaF	563	7.8
Yb	500	—	Ce ₂ O ₃	450	—	SrO + RbF	none	16.7
C	none	—8.4	Pr ₆ O ₁₁	584	13.2	ZnO + KF	none	6
Si	662	—5	Nd ₂ O ₃	647	15.4	SnO + KF	332	20
Sn	none	—	Sm ₂ O ₃	670	8	TiO ₂ + NaF	none	—48
Ti	494	—84.6	Eu ₂ O ₃	560	18.7	VO ₂ + KF	429	—
Zr	560	—	Gd ₂ O ₃	594	12.6	Ni ₂ O ₃ + KF	none	23

^a “none” is a thermal effect not registered in DTA.^b ΔP is the weight change relative to the starting weight.

$$\Delta G_2^0 = \Delta H_{MF_n}^0 + \frac{1}{3}\Delta H_{M_2S_n}^0 - \frac{T}{3}(4S_M^0 - 3S_{MF_n}^0 - S_{M_2S_n}^0 + 34.9) + 48\,100 \text{ cal (g equiv)}^{-1}$$



where $\Delta H_{MF_n}^0$ and $\Delta H_{M_2S_n}^0$ are the standard enthalpies of fluoride and sulfide, respectively, in cal (g equiv)⁻¹, $S_{MF_n}^0$ and $S_{M_2S_n}^0$ are the standard entropies of fluoride and sulfide, respectively, in cal deg⁻¹ (g equiv)⁻¹ and S_M^0 is the standard entropy of the metal, in cal deg⁻¹ (g equiv)⁻¹.

It can be easily seen that under normal conditions $\Delta G_2^0 < \Delta G_1^0 < \Delta G_3^0$ (when algebraic values are taken). However, at higher temperatures this ratio can change. Thus, solving the inequality $\Delta G_1^0 - \Delta G_2^0 < 0$ with respect to T , with

$$T \geq \frac{12\,450 - \Delta H_{M_2S_n}^0}{S_M^0 - S_{M_2S_n}^0 + 34.9} \quad (4)$$

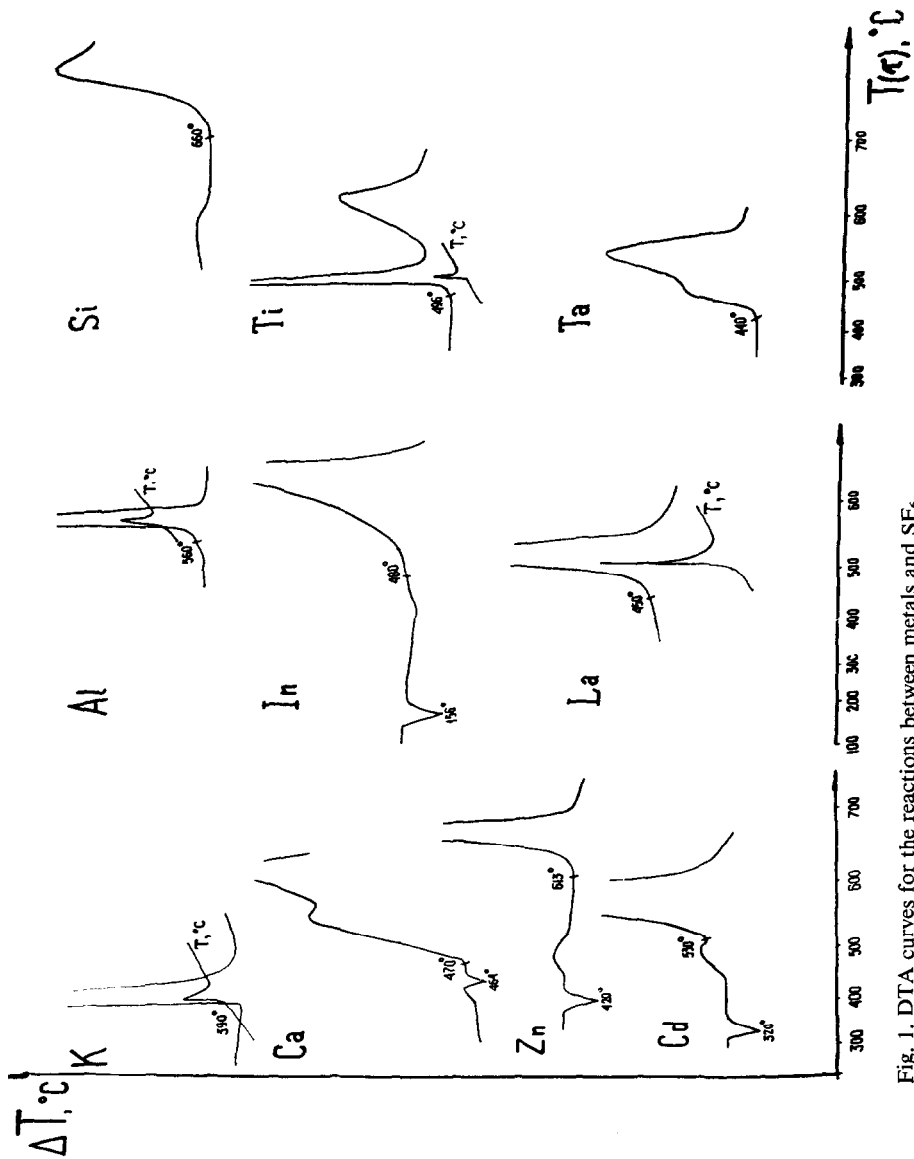


Fig. 1. DTA curves for the reactions between metals and SF₆.

we get $\Delta G_1^0 < \Delta G_2^0 < \Delta G_3^0$, i.e. with $T_1 < T$, reaction (2) yielding sulphide and fluoride is the most suitable thermodynamically, while in reaction (1) with $T_2 > T$ only the fluoride of the metal is formed.

A more detailed analysis of the conditions and character of the interaction of SF_6 with metals is given below, where Zn and Cd are considered.

DTA curves for $\text{SF}_6 + \text{Zn}$ (Cd) (Fig. 1) indicate the existence of an intensely exothermal reaction which occurs after melting of the metal¹⁹. X-Ray phase analysis established the presence of fluorides and sulphides of these metals. Separation of the Cd + SF_6 products was carried out in water, as cadmium fluoride is readily soluble in water²⁰ (43.5 g l^{-1} at 25°), the solubility of CdS being extremely low²¹ ($K_{\text{so}} = 7.9 \times 10^{-27}$).

Chemical analysis established that the water-soluble phase from the Cd + SF_6 reaction is CdF_2 and the insoluble phase is CdS (Table 2). The molar ratio of the phases $\text{CdF}_2:\text{CdS}$ is close to 3:1. The stoichiometry of the reaction may be represented by the equation



The increase in weight of the system resulting from reaction (5) in relation to the initial weight of cadmium is somewhat smaller (28–30%) than that calculated (32.48%). This may be explained by the partial fusion of the unreacted metal. In a similar manner to the reaction with cadmium, the Zn + SF_6 reaction yields zinc fluoride and sulphide (Table 2), the excess weight being 49–52%, although when calculated by an equation similar to (5) it should be 55.85%. The molar ratio of the phases $\text{ZnF}_2:\text{ZnS}$ is close to 3:1.

As mentioned above, reaction (1) becomes thermodynamically more favourable for metals at higher temperature. Using inequality (4)*, it is possible to show that this temperature is above 650° for cadmium, whereas for zinc it is above 750° . Fluorination of cadmium leads to the formation of pure CdF_2 whereas with zinc the reaction is accompanied by an increase of the molar proportion of fluoride up to the formation of practically pure ZnF_2 (Table 2). The calculated crystallographic unit cell parameters for the products of reaction Cd + SF_6 are in good agreement with literature data²² while for ZnF_2 the parameter a is somewhat greater than that quoted (Table 2).

Reaction of sulphur hexafluoride with oxides

Differential thermal analysis has established that, as with metals, most of the oxides investigated react with sulphur hexafluoride (Table 1) but at somewhat higher temperatures. This temperature can be lowered significantly if fluorination is carried out in the presence of a fluoride of an alkaline metal (Fig. 2). In some cases when the rate of the reaction is close to the threshold sensitivity of the

* Thermodynamic constants relate to standard conditions.

TABLE 2
CHEMICAL AND X-RAY ANALYSES OF THE INTERACTION PRODUCTS OF SOME METALS AND OXIDES WITH SULPHUR HEXAFLUORIDE

Substance	Temperature (°C)	Quantitative composition (%)			Mass (%)	Ratio	Formula	Symmetry	Cell parameters (Å)		
		M*	S	F					a	b	c
Cd	520-540	74.7	-	25.8	100.5	Cd:F = 1:2.05	CdF ₂ (aqueous phase)	-	-	-	-
		77.7	22.2	-	99.9	Cd:S = 1:1	CdS (low temp. phase)	hexag.	4.137 ± 0.002	-	6.714 ± 0.001
Cd	650-670	75.4	-	25.1	100.5	Cd:F = 1:1.97	CdF ₂	cubic	5.388 ± 0.001	-	-
		63.6	7.6	18.8	100	Zn:S:F = 4.1:1:6.4	ZnS + 3ZnF ₂	-	-	-	-
Zn	750-770	63.5	-	36.5	100	ZnF ₂ :ZnS = 15:1	ZnF ₂ (96%)	tetrag.	4.703 ± 0.001	-	3.133 ± 0.001
		71.0	-	28.9	99.9	La:F = 1:3.03	LaF ₃	hexag.	7.182 ± 0.003	-	7.350 ± 0.005
Pr ₆ O ₁₁	590-610	71.0	-	28.7	99.7	Pr:F = 1:3.00	PrF ₃	hexag.	7.072	-	7.234
		71.4	-	28.0	99.4	Nd:F = 1:2.98	NdF ₃	hexag.	7.032	-	7.200

* M = metal.

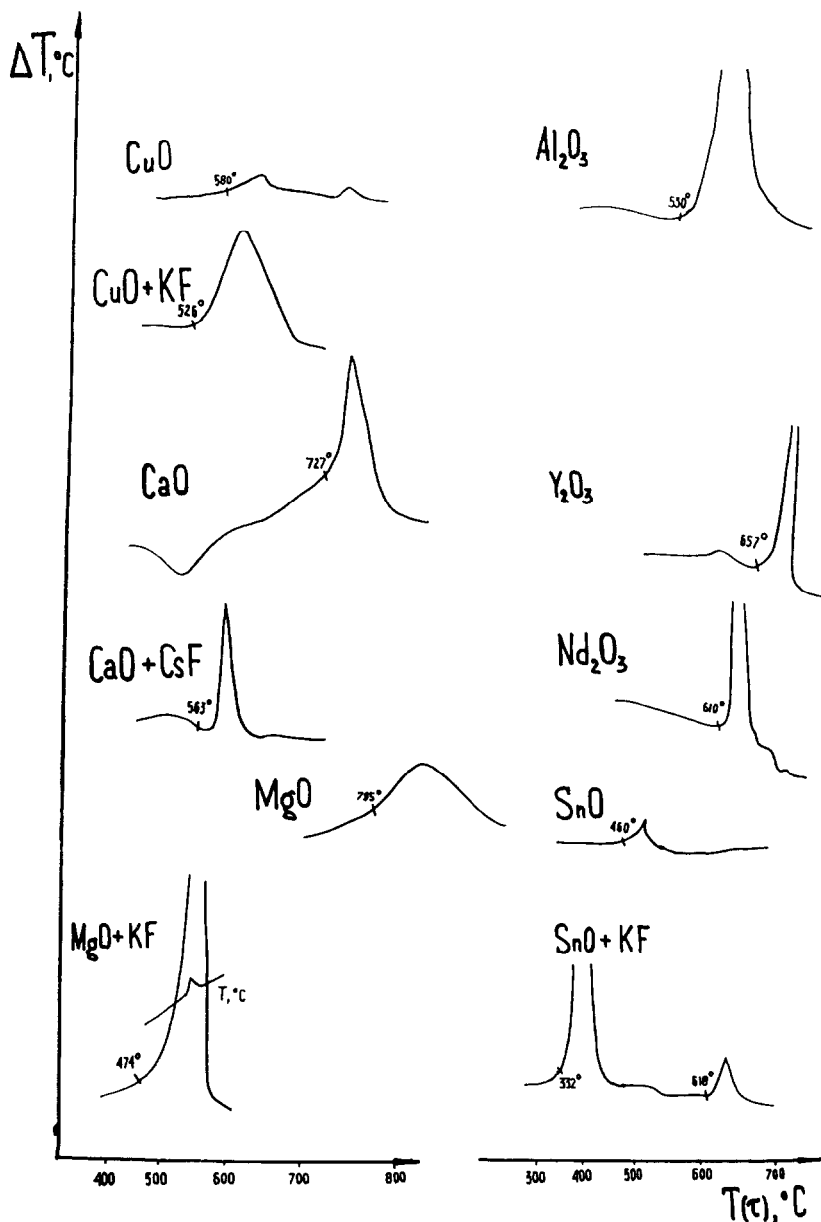
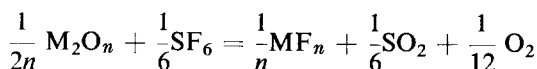
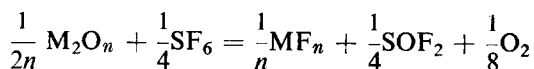
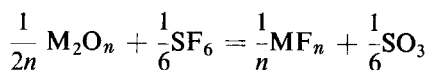
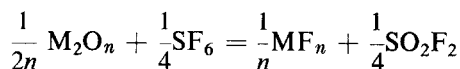


Fig. 2. DTA curves for the reactions $\text{M}_m\text{O}_n + \text{SF}_6$ and $\text{M}_m\text{O}_n + \text{MF} + \text{SF}_6$, where M = metal.

thermographic method, thermal effects are not clearly distinguishable but despite this the increase in weight of the system shows that interaction has occurred (Table 1, Ga_2O_3 , In_2O_3 , Cr_2O_3).

Some authors²³⁻²⁶ have tried to establish a quantitative relationship between

the thermodynamic and kinetic characteristics of the process in the case of a number of reactions. Thus in studying the reaction "Group IVA oxide + chlorine", the authors²⁶ noted the existence of an approximately linear dependence between the free energy change of the reaction (ΔG_{298}^0) and the starting temperature (T_s). If we assume that such relationships exist in the reactions listed below



then T_s for any reaction will be defined in general by the difference $\Delta H_{MF_n}^0 - \Delta H_{M_2O_n}^0$. It should be noted that for those reactions whose rates do not differ much, T_s may serve for the qualitative estimation of the reactivity.

From the above it is not unreasonable to expect that T_s will decrease as we descend Group I of the Periodic Table, *i.e.* as we go from Li₂O to Cs₂O, in the same sequence as the difference $\Delta H_{MF_n}^0 - \Delta H_{M_2O_n}^0$ (expressed in kcal (g equiv⁻¹)) decreases, namely Li₂O > Na₂O > K₂O = Rb₂O < Cs₂O. Similarly, for Group IIA metal oxides we find that BeO > MgO > CaO > SrO > BaO.

With Group IIIA metals, T_s for In₂O₃ must be smaller than that for Ga₂O₃ as the value of $\Delta H_{MF_n}^0 - \Delta H_{M_2O_n}^0$ decreases in this Group in the series Tl₂O₃ > Ga₂O₃ > In₂O₃ > Al₂O₃.

The latter assumption is supported by thermal analysis results of the systems $M_nO_n + SF_6$ for Group IIA oxides (MgO, CaO, SrO, BaO) and Group IIIA oxides (Al₂O₃, Ga₂O₃, In₂O₃). Thus Figure 3 and Table 1 show that there is a correlation between T_s and $\Delta H_{MF_n}^0 - \Delta H_{M_nO_n}^0$ for the oxides of these Groups of the Periodic Table. It should be noted that Group IIA oxides react with SF₆ more vigorously than those of Group IIIA. For example, values of T_s could not be obtained for indium and gallium oxides by the DTA method and this quantity had to be determined by another method.

All oxides of rare earth metals react with SF₆ in a similar manner to the oxides of the alkaline earth metals but with greater vigour over the temperature range 450–700° (Table 1). With La₂O₃, Pr₆O₁₁ and Nd₂O₃, it should be noted that the results of chemical and X-ray analyses (Table 2) indicate that these oxides react with SF₆ to yield the trifluorides of the respective metals. This process could thus be employed for the synthesis of these particular fluorides of the rare earth metals in an anhydrous state.

CONCLUSION

The thermal analysis studies of the reaction of sulphur hexafluoride with metals and oxides reported in this paper, when taken in conjunction with thermodynamic, chemical and X-ray analyses of the various systems, have shown that SF_6 is capable of functioning as an active fluorinating agent, reacting with both metals and oxides over the respective temperature ranges $500\text{--}600^\circ$ and $600\text{--}700^\circ$.

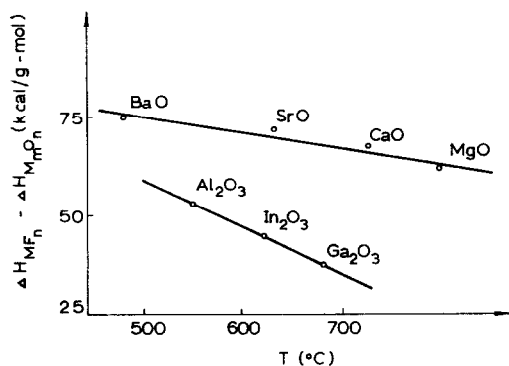


Fig. 3. The interrelationship between $\Delta H_{MF_n}^0 - \Delta H_{M_nO_n}^0$ and T_s for reactions involving the oxides of Groups IIA and IIIA of the Periodic Table and SF_6 .

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