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Reactivity and Thermal Stability of Hexafluorides

N.P.Galkin and Yu.N.Tumanov

The review deals with the possibility of using various physicochemical characteristics of the hexafluorides of *p*, *d*, and *f* elements for a comparative estimation of their thermal stability and reactivity. The force constants of EF_6 molecules, the average bond energy and length, and also the thermodynamic stability constants of the octahedral EF_6 molecules have been used as characteristic properties.
It has been shown that the force constants of the E-F bond are not effective characteristics of the thermal stability and reactivity of all hexafluorides in reactions where more than one E-F bond is dissociated.
Only the thermodynamic stability constants can serve as an objective criterion for the assessment when account is taken of definite dissociation mechanisms of EF_6 molecules (complete or incomplete dissociation).
Within the limits of individual groups of 4*d*, 5*d*, and 5*f* elements and also sulphur, selenium, and tellurium, the variation of the force constants and thermodynamic stability in relation to the incomplete dissociation of the hexafluorides corresponds to the experimental sequences of their thermal stabilities.
The bibliography includes 85 references.

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I. INTRODUCTION

Hexafluorides are a class of fluoride compounds formed by certain elements having not less than six *p*, *d*, or *f* valence electrons. Up to the present time, the hexafluorides of 18 elements have been identified: sulphur, chromium, selenium, molybdenum, technetium, ruthenium, rhodium, tellurium, xenon, tungsten, rhenium, osmium, iridium, platinum, polonium, uranium, neptunium, and plutonium. In addition one may expect, by analogy, the formation of the hexafluorides of palladium, iodine, astatine, radon, and americium.

The common properties of hexafluorides are low melting and boiling points and comparatively high volatility under ordinary conditions (Table 1). With the exception of XeF_6, the molecules of hexafluorides EF_6 have the configuration of a regular octahedron belonging to the O_h point group with the element E in the centre. The reactivities of hexafluorides are not the same. Some hexafluorides, for example CrF_6, are so unstable that they can be synthesised and investigated only at very low temperatures, while others (for example sulphur hexafluoride) resemble the noble gases in their chemical inertness.

Hexafluorides have attracted much interest, since those of many elements are obtained and used in individual stages of the technology of the manufacture of nuclear fuel[1-3]. In particular, this accounts for the publication of a large number of studies on the physicochemical properties of both individual hexafluorides and individual groups. Reviews have also appeared on hexafluorides, among which mention should be made in the first place of those by Weinstock[2-4] and O'Donnel and coworkers[5-8].

In Weinstock's work attention was concentrated on the molecular constants of hexafluorides. However, there are certain data on their thermal stabilities[3,4]. O'Donnel and coworkers attempted to make a systematic arrangement of the hexafluorides of certain elements in terms of their reactivities. In particular, they showed that the reactivities of hexafluorides fall on moving down the Groups of the Periodic System, while the thermal stabilities increase on going from elements with 3*d* electrons to elements with 5*d* electrons[5-7].

Table 1. Physicochemical properties of hexafluorides[3,4,8].

Hexafluoride	Type of characteristic electrons of element E	No. of free electrons	Symmetry of ground state of EF_6	M.p., °C	B.p. (sublimation temp.) at p = 1 atm., °C	Critical temp., °C	Vapour pressure at 15°C, mmHg
SF_6	3 *p*	0	A_{1g}	−50.4*	−63.7	45.5	—
SeF_6	4 *p*	—	A_{1g}	−34.7*	−45.9	72.35	—
TeF_6	5 *p*	—	A_{1g}	−37.0*	−38.9	83.25	—
PoF_6	6 *p*	—	A_{1g}	—	—	—	—
CrF_6	3 *d*	0	—	—	—	—	—
MoF_6		0	A_{1g}	17.4	35	—	361
TcF_6	4 *d*	1	$G_{3/2g}$	37.4	55.3	—	135
RuF_6		2	F_{2g}	50.4	45.9	—	58
RhF_6		3	$G_{3/2g}$	70	—	—	38
WF_6		0	A_{1g}	2.0	17.5	—	698
ReF_6	5 *d*	1	$G_{3/2g}$	18.5	33.7	—	358
OsF_6		2	E_g, F_{2g}	32.1	45.9	—	312
IrF_6		3	$G_{3/2g}$	43.8	53.6	177	227
PtF_6		4	A_g	61.3	69.14	—	66
UF_6		0	A_{1g}	64.1**	56.5	245	56
NpF_6	5 *f*	1	$E_{5/2}$ *u*	55.1**	55.2	—	64
PuF_6		2	A_{1g}	51.6**	62.2	—	53
XeF_6		2	—	26	—	—	12

* Under the pressure of its own vapour.
** Triple point.

In the solution of certain practical problems associated with the presence in a chemical system of the hexafluorides of several elements or their lower fluorides, it is necessary to employ some qualitative criterion in order to predict the changes in the system which are potentially possible. Thermodynamic analysis is in many cases impossible, since the thermochemical and thermodynamic constants of many fluorides are unknown. On the other hand, an empirical systematic arrangement may prove to be unreliable, since the rate of a chemical reaction depends on the experimental conditions. For example, in the system "uranium hexafluoride–hydrogen" the products may be uranium pentafluoride, tetrafluoride, trifluoride, or the so called "intermediate" fluorides U_2F_9, U_4F_{17}, etc., depending on the temperature, the reactant ratio, and the effect of light. Until recently it was also believed that molybdenum and tungsten hexafluorides are vigorous fluorinating agents[9,10], but later studies[5,11] showed that these two hexafluorides are inert.

In the present review the possibility of using various physicochemical characteristics of hexafluorides for a comparative estimation of their reactivities and thermal stabilities is discussed. Such characteristics may be the force constants of the EF_6 molecules, the E – F bond energies and lengths, and the equilibrium dissociation constants of hexafluorides. An attempt has been made to discover regularities in thermal stability both for the entire class of hexafluorides and for individual series.

II. PRINCIPAL GROUPS OF HEXAFLUORIDES

Depending on the nature of the valence shell of the element forming the hexafluoride or the type of its valence electrons, all hexafluorides can be arranged systematically in groups according to the position of the elements in the Periodic System. The positions of the hexafluorides of various elements in these groups are consistent with the positions of the elements themselves, either in the Periods (horizontal series) or in the Group (vertical series) of the Periodic System. The horizontal series of hexafluorides comprise the groups of hexafluorides of 3*d* (CrF_6), 4*d* (MoF_6, TcF_6, RuF_6, RhF_6), 5*d* (WF_6, ReF_6, OsF_6, IrF_6, PtF_6), and 5*f* elements (UF_6, NpF_6, PuF_6). The vertical series of hexafluorides comprise (1) the hexafluorides of the non-metals in Group VI of the Periodic System (SF_6, SeF_6, TeF_6, PoF_6), (2) the hexafluorides of the transition elements of Group VI (CrF_6, MoF_6, WF_6, UF_6), (3) the hexafluorides of elements with one unshared electron (TcF_6, ReF_6, NpF_6), (4) the hexafluorides of elements with two unshared electrons (RuF_6, OsF_6, PuF_6), (5) the hexafluorides of elements with three unshared electrons (RhF_6, IrF_6), and (6) platinum hexafluoride (PtF_6). The platinum atom in this molecule has four unshared electrons which, judging from the type of the ground state of the PtF_6 molecule (Table 1), are paired. Xenon hexafluoride, the molecule of which does not belong to the symmetry point group O_h, occupies a special place.

The electronic ground states of eleven hexafluorides of sulphur, selenium, tellurium, molybdenum, tungsten, uranium, neptunium, plutonium, rhodium, iridium, and platinum are either non-degenerate or the degeneracy is predominantly of the spin type. The normal vibrational spectra of these molecules correspond to O_h symmetry. The vibrational spectra of the hexafluorides of technetium, ruthenium, rhenium, and osmium have appreciable anomalies (compared with the preceding hexafluorides), which are attributed to the dynamic Jahn–Teller effect[4,12-15]. According to the Jahn–Teller theorem[16], the orbital degeneracy of the electronic ground state of octahedral molecules is reduced by distortion of their configuration, i.e. by a decrease of molecular symmetry. This is the so called static Jahn–Teller effect. However, in the present case the static Jahn–Teller effect is not observed, but there is an anomaly in the infrared absorption spectra owing to a vibronic interaction.

Table 2. Width of the half-absorption bands of certain hexafluorides (cm^{-1}) [4].

Molecule	$\nu_{1/2}$		$\Delta\nu_{1/2}$	Molecule	$\nu_{1/2}$		$\Delta\nu_{1/2}$
	$\nu_1+\nu_3$	$\nu_2+\nu_3$			$\nu_1+\nu_3$	$\nu_2+\nu_3$	
MoF_6	20	31	0	WF_6	17	24	0
TcF_6	23	113	84	ReF_6	36	68	43
RuF_6	21	—	—	OsF_6	23	84	59
RhF_6	19	27	0	IrF_6	18	26	0
				PtF_6	20	26	0
Mean*	21	29		Mean*	20	25	

* The band widths for "anomalous" hexafluorides were disregarded in the averages.

The infrared spectra of the "normal" hexafluorides usually have two characteristic bands corresponding to the compound frequencies $\nu_1 + \nu_3$ and $\nu_2 + \nu_3$ in the region of 1140–1710 cm^{-1} and having almost identical intensities and outlines (Table 2). For each hexafluoride, the long wavelength band corresponds to the compound frequency $\nu_2 + \nu_3$ and the short wavelength band to the frequency $\nu_1 + \nu_3$. However, whereas the outlines of the $\nu_1 + \nu_3$ bands are virtually identical for both "normal" and "anomalous" hexafluorides, those of the $\nu_2 + \nu_3$ bands for different types of hexafluorides are not the same, which is a qualitative criterion of the "anomaly" of the hexafluorides.

The relations between the observed frequencies and the number of unshared valence electrons in the molecules of the "normal" hexafluorides, derived by Weinstock and Goodman[3,4], make it possible to estimate the vibration frequencies ν_2 and ν_5 which the molecules of the hexafluorides of technetium, ruthenium, rhenium, and osmium would have in the absence of the dynamic Jahn–Teller effect. The points corresponding to the ν_2 and ν_5 frequencies of the "anomalous" hexafluorides deviate from the graphical relations. It is interesting to note that the anomalies in the vibrational spectra of the hexafluorides of 4*d* and 5*d* elements are not repeated in the series of the hexafluorides of 5*f* elements.

III. RELATION BETWEEN THE VARIATION OF THE FORCE CONSTANTS OF HEXAFLUORIDES AND THEIR THERMAL STABILITIES AND REACTIVITIES

In certain reviews (for example those of O'Donnel and Stewart[5,6]) attempts are made to relate the regularities in the variation of the reactivities of hexafluorides in the first vertical series (CrF_6, MoF_6, WF_6, UF_6) to the valence force constants (f_d in Wilson's terminology[17]) and average energies of the E – F bonds. Several comments of

a general nature must be made concerning the estimation of the reactivities of hexafluorides with the aid of the force constants. The force constant† $f_d = (\partial^2 V/\partial q^2)_{q \to 0}$, where V is the potential energy of the molecule and q the vibrational coordinate, characterises the resistance of the molecule to the deformation of the equilibrium configuration. However, even for diatomic molecules there is no unambiguous relation between the force constant and the dissociation energy[18]. The quantity $(\partial^2 V/\partial q^2)_{q \to 0}$ characterises merely the curvature of the potential well in the vicinity of the equilibrium position but does not necessarily indicate its depth[19].

The multiplicity of models proposed for the description of the force field of a polyatomic molecule is due to the existence of a set of elastic structural elements the number of which is greater than the number of chemical bonds and independent nuclear coordinates. However, regardless of the choice of model, none of the different types of coefficients can provide a simple individual characteristic of a bond in a polyatomic molecule[20]. The extension of one bond involves a whole group of structural elements, since the valence force constant f_d depends not only on the interaction between two atoms but also on their interaction with other structural elements of the molecule. Only a set of force constants characterises an individual bond in a polyatomic molecule[21].

We shall consider to what extent various force constants of hexafluoride molecules can characterise their thermal stability and reactivity. In the present paper we shall employ the terminology adopted by Claassen[22]:

(1) f_d—valence force constant;
(2) f_α—deformation force constant for the bond angle;

Interaction Constants

(3) f_{dd}—for the interaction of bonds at right angles to one another;
(4) $f_{\alpha\alpha}$—for the interaction of adjacent angles in the same plane;
(5) $f_{d\alpha}$—for the interaction of an angle with the bonds forming its sides;
(6) δ—for the interaction of two opposite bonds;
(7) γ—for the interaction of an angle with a bond perpendicular to its plane;
(8) k—for the interaction between two angles in perpendicular planes having a bond in common;
(9) ϵ—for the interaction between two angles in perpendicular planes without a bond in common.

Seven independent force constants may be isolated for hexafluoride molecules[4]:

(1) $A = f_d$;
(2) $B = \delta$;
(3) $C = 2f_{dd}$;
(4) $D = 2(f_{d\alpha} - \delta)$;
(5) $E = f_\alpha - \gamma$;
(6) $F = 2(f_{\alpha\alpha} - \gamma)$;
(7) $G = 2(k - \epsilon)$.

Many investigators[4,22-36] analysed the normal vibrations of octahedral hexafluoride molecules and calculated the force constants. The force constants depend on the choice of model for the force field. In the present study only the force constants quoted in the review of Weinstock and Goodman[4] are considered. They are listed in Table 3.

† For diatomic molecules.

Figs. 1 and 2 present a graphical interpretation of the relation between the force constants of EF_6 molecules and the charge number of the element E (see p. 157).

Analysis of these relations permits the following conclusions: (1) the valence force constant exceeds approximately by two powers of ten all the remaining force constants; this is a general rule[37]; (2) the independent force constants A, B, E, and partly G of hexafluoride molecules increase on going from 4*d* to 5*d* elements and sharply decrease on going to 5*f* elements; (3) the force constants C and F also increase on going from 4*d* to 5*d* elements; on going to 5*f* elements, the constant C increases and the constant F changes in different ways for each of the vertical series; (4) the constant D decreases on moving downwards along the vertical series; (5) the constants A, B, C, and partly G decrease sharply on moving along the series of 4*d*, 5*d*, and 5*f* elements from left to right, which is consistent with the variation of the thermal stabilities of the hexafluorides; (6) the constants D, E, and F increase along the series of 4*d*, 5*d*, and 5*f* elements (from left to right).

Table 3. Force constants of octahedral hexafluoride molecules[4] [$cm^{-1}/(0.01\ Å)^2$].

Force constant	SF_6	SeF_6	MoF_6	TeF_6	RuF_6	RhF_6	TeF_6	WF_6
A	28.163	25.663	24.673	24.483	23.304	21.770	26.032	26.480
B	−1.125	0.666	1.673	0.860	0.331	−0.654	0.773	2.246
C	3.580	1.232	2.597	1.888	1.268	0.986	0.711	0.709
D	5.634	2.160	0.713	0.720	0.767	0.806	0.499	0.488
E	4.346	2.648	0.843	1.083	1.199	1.260	1.090	0.970
F	0.443	0.316	−0.555	−0.183	0.050	0.221	−0.317	−0.455
G	0.848	0.676	−0.415	0.214	0.205	0.234	−0.002	0.454

	ReF_6	OsF_6	IrF_6	PtF_6	UF_6	NpF_6	PuF_6
A	26.353	26.185	25.181	23.033	19.412	19.029	18.451
B	1.802	1.190	0.209	−1.033	0.066	−0.314	−0.425
C	2.293	1.744	1.418	1.322	3.038	2.702	2.314
D	0.480	0.531	0.543	0.526	0.210	0.244	0.255
E	1.243	1.400	1.432	1.446	0.663	0.832	0.899
F	−0.006	0.307	0.476	0.605	0.083	0.229	0.255
G	0.173	0.194	0.213	0.168	0.100	0.050	0.035

One may conclude that the variation of the majority of force constants along the horizontal and vertical series of hexafluorides is of the same type as that of the valence force constant f_d (A). The force constants for sulphur, selenium, and tellurium hexafluorides are quoted only for comparison.

Analysis of the feasible configurations of the xenon hexafluoride molecule[38] showed that it cannot have the structure of a regular octahedron. A model close to the structure of iodine heptafluoride, in which the missing bond is replaced by the electron pair of xenon, is more likely. This is confirmed both by the analysis of the infrared spectrum of xenon hexafluoride[39] and by the study of its structure by electron diffraction[40,41]. Therefore the force constants of XeF_6 cannot be compared with those of other hexafluorides.

On the hypothesis of a relation between the force constants, thermal stabilities, and reactivities of EF_6 molecules, the latter can be arranged in the following series in terms of their thermal stability:

Vertical series:

$$SF_6 > TeF_6 > SeF_6;$$
$$WF_6 > MoF_6 > UF_6;$$
$$ReF_6 > TcF_6 > NpF_6;$$
$$OsF_6 > RuF_6 > PuF_6;$$
$$IrF_6 > RhF_6.$$

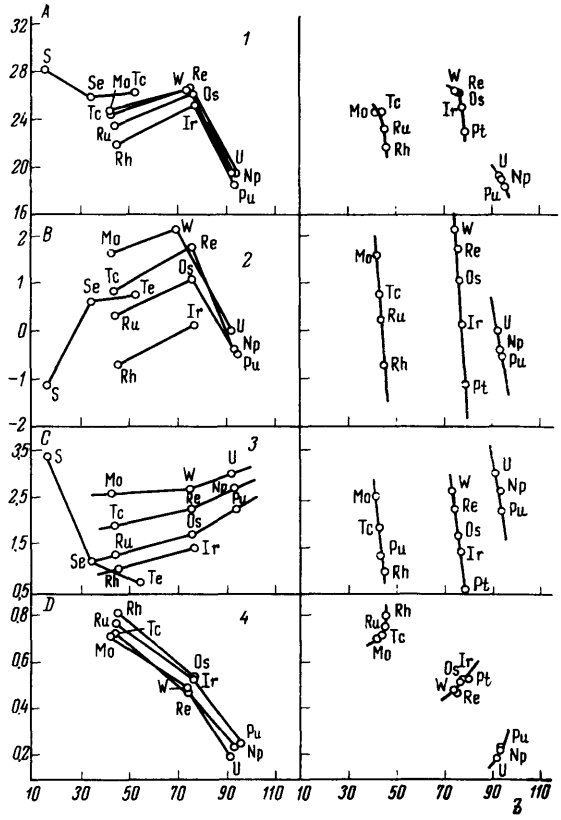


Figure 1. Variation of the force constants A, B, C, and D of EF_6 molecules with the charge number of the central atom of the element E in the vertical and horizontal series of hexafluorides.

Horizontal series:

$$MoF > TcF_6 > RuF_6 > RhF_6;$$
$$WF_6 > ReF_6 > OsF_6 > IrF_6 > PtF_6;$$
$$UF_6 > NpF_6 > PuF_6.$$

When all the elements are arranged in a single series, the following sequence is obtained:

$$SF_6 > WF_6 > ReF_6 > OsF_6 > TeF_6 > SeF_6 > IrF_6 > MoF_6 > TcF_6 > RuF_6 > PtF_6 > RhF_6 > UF_6 > NpF_6 > PuF_6.$$

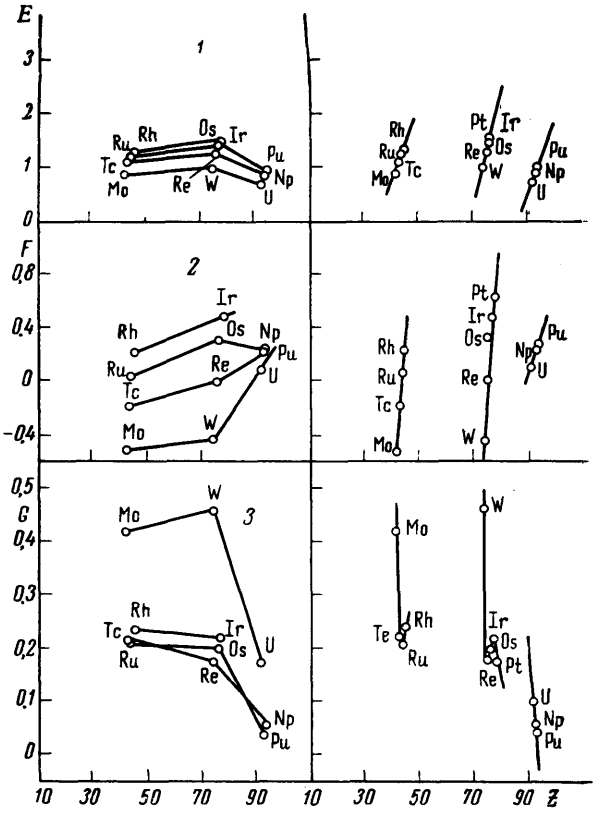


Figure 2. Variation of the force constants E, F, and G of EF_6 molecules with the charge number of the element E in the vertical and horizontal series of hexafluorides.

The last series probably does not fully reflect the actual relation between the thermal stabilities and reactivities of the hexafluorides. Therefore, before dealing with a comparative analysis of the experimental data, it is necessary to analyse the above relations by other methods.

IV. VARIATION OF THE AVERAGE BOND ENERGIES OF HEXAFLUORIDES IN HORIZONTAL AND VERTICAL SERIES

The average bond energy E_0 of the EF_n molecule is defined by the formula

$$E_0 = \frac{D_0^0}{n}, \qquad (1)$$

where D_0^0 is the heat of atomisation of the molecule and n is the number of bonds. The values of D_0^0 are not known for all hexafluorides and the accuracy of the calculation or estimation of some of them is low. For example, one may mention the discrepancy between the data of different workers for the heat of formation of gaseous plutonium hexafluoride: −460 kcal mole^{-1},[42] −473 kcal mole^{-1},[43] −411.2 kcal mole^{-1},[44] and −418 ± 8 kcal mole^{-1} [45]. The last value was recommended by Rand[45] as the most accurate.

The bond energies and heats of atomisation of certain hexafluorides are listed in Table 4. For the majority of the known hexafluorides, the heats of formation are known only under standard conditions, i.e. only the values of $\Delta H^{\circ}_{f,298}$ are available, and in order to find D^0_0 ($-\Delta H^0_0$) a correction must be calculated from the equation

$$\left[\frac{\partial(\Delta H^{\circ}_T)}{\partial T}\right]_p = \Delta C_p, \qquad (2)$$

where ΔC_p is the heat capacity change from 0° to 298°K.

Table 4. Heats of formation, heats of atomisation, and bond lengths and energies in hexafluoride molecules.

Hexafluoride	Heat of formation of hexafluoride from elements under standard conditions $\Delta H^{\circ}_{f,298}$, kcal mole^{-1}	References	Heat of atomisation of hexafluoride under standard conditions $-D^{\circ}_{298}$, kcal mole^{-1}	References	Heat of atomisation of hexafluoride at absolute zero D^0_0, kcal mole^{-1}*	References	Bond dissociation energy E^0_0, kcal	References	E–F bond length, Å	References
SF_6	−291.7	46	478.93	51	474.6	55	79.0		1.564±0.01	57
SeF_6	−266.9	46	439.2	51	434.9	56	72.5		1.688±0.010	57
TeF_6	−327.2	46	487.7	51	483.2		80.6		1.84±0.03	58
MoF_6	−382	47	653.5	51.52	649.2	55	108.2		1.83	60
TcF_6	−300	42	569	51.52	565		94.2		1.8512	56
RuF_6	—	—	—	—	—		—		1.8775	60
RhF_6	—	—	—	—	—		—		1.8738	60
WF_6	−411.5	48	729	51.53	725	55	120.9		1.833	59
ReF_6	−278	42	577	49.51	573		~95.5		—	
OsF_6	−225	42	526	51.52	522		~86.9		1.83	22
IrF_6	−130	42	403.8	51.52	399.5	55	66.55		1.833	22
PtF_6	—	—			—		—			
UF_6	−510.5	49	740.5	54	735.96	55	122.64		1.994	22
NpF_6	−461	42	680	51.52	675.6	55	112.8		1.980	22
PuF_6	−418	45	624	51.52	619.5	55	103.21		1.972	22
XeF_6	−82.9 kcal at 393° K	50					32.3	50	1.90	38

* Estimated from Eqn. (2).

The accuracy of the determination of ΔH°_{298} is usually not sufficiently high to make this correction, but nevertheless in the present study the correction was introduced.

Analysis of the results in Table 4 shows that the bond energies decrease in the horizontal series from left to right like the valence force constants (A) and the constant B, C, and partly G (see curves *1–3* in Fig. 1 and curve *3* in Fig. 2). In the vertical series the bond energy increases in the series of hexafluorides of 4*d*, 5*d*, and 5*f* elements. In the series of hexafluorides of sulphur, selenium, and tellurium, the E – F bond energy is 79.0, 72.5, and 80.6 kcal mole^{-1} respectively. The Xe–F bond has the lowest dissociation energy (only 32.3 kcal mole^{-1}).

Thus if it is supposed that the average bond energy characterises the thermal stability and reactivity of hexafluoride molecules (as was done by O'Donnel and Stewart[5]), then hexafluorides can be arranged in the following series in terms of decreasing thermal stability:

$$UF_6 > WF_6 > NpF_6 > MoF_6 > PuF_6 > ReF_6 > TcF_6 > OsF_6 > TeF_6 > SF_6 > SeF_6 > IrF_6 > XeF_6 .$$

The discrepancy between this series and the experimental stabilities and activities of hexafluorides will be discussed below.

V. INTERATOMIC DISTANCES AND BOND STRENGTH

The use of interatomic E–F distances to characterise the chemical properties of hexafluorides (Table 4) appears to be of doubtful value. In the series of hexafluorides of uranium, neptunium, and plutonium, the interatomic E–F distances decrease but in the series of hexafluorides of 4*d* and 5*d* elements it is difficult to establish a similar sequence. Probably Badger's equation[61], whereby the E–F bond lengths were found (see, for example, Ref. 56 and 60), does not ensure the necessary accuracy owing to the dependence of the calculated force constants on the force field model.

VI. ANALYSIS OF THE THERMODYNAMIC STABILITIES OF HEXAFLUORIDES

A rigorous characteristic of the dissociation of any chemical compound is its thermodynamic stability in this reaction. The thermodynamic stability is characterised by the reciprocal of the equilibrium constants K_e for the corresponding dissociation process:

$$\alpha = \frac{1}{K_e} = \exp\left(\frac{\Delta H^0_0}{RT} - \frac{\Delta \Phi^*_T}{R}\right), \qquad (3)$$

where $\Delta\Phi^*_T$ is the reduced free energy of the dissociation reaction, R the gas constant, and T the absolute temperature. The values of $K_e(\alpha)$ may be related to the corresponding yields of the dissociation products of hexafluorides. For example, for the reaction

$$(EF_6)_{gas} \rightarrow (E)_{gas} + 6(F)_{gas}, \qquad (4)$$

$$\alpha = \frac{(1-x)(1+6x)}{4.6656 \cdot 10^4 x^7 p^6}, \qquad (5)$$

where p is the pressure and x the number of moles of hexafluoride which have reacted.

The values of α depend both on the enthalpy change (ΔH^0_0) and on the change in the reduced free energy ($\Delta\Phi^*_T$), which are calculated from energy and geometrical molecular constants.

The thermodynamic functions for gases consisting of polyatomic molecules (including EF_6 molecules) are calculated in many cases in terms of the rigid rotator—harmonic oscillator approximation. The components of the thermodynamic functions due to translational, rotational, and vibrational motion are calculated. This is because the electronic ground states of polyatomic molecules are as a rule of the singlet type and therefore the partition function with respect to the intramolecular motion of the polyatomic molecule is equal to the sum of the vibrational and rotational partition functions of the electronic ground state[17]. The thermodynamic functions obtained are called virtual, since they do not include the components due to nuclear spins and the mixing of isotopes.

The multiplicity of the electronic ground state is taken into account by introducing into the thermodynamic functions the term $R \ln p_M$, where p_M is the statistical weight of this state.

It is assumed[17] that the electronic ground state of polyatomic molecules with an even number of electrons is of the singlet type (the statistical weight of the state is unity); electronic states with one free electron have a statistical weight of two. Some workers have calculated the thermodynamic properties of many hexafluorides in

terms of the approximation of the rigid rotator–harmonic oscillator model. The entropies, reduced free energies, heat capacities, and enthalpy changes have been calculated in the range 50–1600°K at $p = 1$ atm. for the hexafluorides of uranium[55], plutonium[55,62], molybdenum, tungsten, iridium, and neptunium[55] and in the range 50–2000°K for the hexafluorides of ruthenium, rhodium[60], and technetium[56]. It should be noted that some of the molecular constants employed by Nagarajan to calculate the thermodynamic functions of the above hexafluorides were subsequently revised by Weinstock and Goodman[4] (Table 5).

Table 5. Fundamental vibration frequencies of hexafluoride molecules.

Molecule*	ν_1 (1)	ν_2 (2)	ν_3 (3)	ν_4 (3)	ν_5 (3)	ν_6 (3)
SF_6	770	640	639	614	522	349
SeF_6	708	(661)	780	437	(403)	(262)
TeF_6	701	674	752	325	313	(195)
PoF_6	[700]	[682]	[741]	[253]	[243]	[144]
MoF_6	741	643	741	262	(312)	(122)
TcF_6	(712)	(639)**	748	265	(257)**	[174]
RuF_6	(675)	(624)**	735	275	(283)**	[186]
RhF_6	(634)	(592)	724	283	269	(189)
PdF_6	[590]	[525]	[711]	[280]	[258]	[191]
WF_6	(771)	(673)	711	258	(315)	(134)
ReF_6	755	(671)**	715	257	(295)**	(193)
OsF_6	(733)	(668)**	720	272	(276)**	[205]
IrF_6	(701)	(646)**	719	276	(258)	(206)
PtF_6	655	(600)	705	273	(242)	[211]
UF_6	667	535	624	(184)	(201)	(140)
NpF_6	(648)	(528)	624	(198)	(205)	(165)
PuF_6	(628)	(523)	616	(203)	(211)	(173)
AmF_6	[609]	[500]	[603]	[205]	[216]	[178]
CrF_6	(720)	(650)	790	[266]	[309]	[110]

*The degree of degeneracy of the given vibration is indicated in brackets after ν_1, ν_2, etc.

** The estimate was made from the variation of the vibration frequencies with the number of free electrons in the hexafluoride molecules[4]; these are postulated frequencies in the absence of vibronic interaction. The frequencies obtained from the above relation and virtually identical with the experimental values are indicated in round brackets; the frequencies calculated from the Raman frequencies are indicated in square brackets.

The ν_6 frequencies for molybdenum and tungsten hexafluorides, the ν_2 frequency for technetium hexafluoride, etc. have been revised. The Mo–F bond length in the MoF_6 molecule, assumed by Nagarajan to be 1.56 Å,[63] is inconsistent with a later value of 1.83 Å.[59] Moreover, the statistical weight of the electronic ground state in the case of its degeneracy was not taken into account in any of the calculations. This applies to the hexafluorides of technetium, ruthenium, rhodium, rhenium, osmium, iridium, and neptunium.

According to Moffit et al.[64] the lower electronic states of the hexafluorides of rhenium and osmium are orbitally degenerate and the Jahn–Teller theorem predicts instability of the octahedral configuration. As already mentioned above, such instability does not lead to a static distortion of the symmetrical configuration in the gas phase. This is shown by the similarity of the electronic spectra of the hexafluorides of rhenium and osmium on the one hand and those of iridium and platinum on the other. For the last two hexafluorides, the Jahn–Teller theorem does not predict instability of the octahedral configuration. The number of electronic bands in the spectra of all four hexafluorides corresponds to the number predicted by the ligand field theory for the configuration with the O_h symmetry; the absence of the static distortion of the EF_6 molecules was demonstrated by electron diffraction[4] and by the analysis of the infrared spectra of the "anomalous" hexafluorides. In the case of static distortion, one might expect that the force constants for the longer bonds (or larger angles) would differ from the force constants for the shorter bonds (or smaller angles); moreover, one might observe splitting of the infrared absorption bands. The analogies in the vibrational spectra have been interpreted on the basis of a vibronic interaction[12,65]. Quantitatively this interaction was investigated by Weinstock and coworkers[4,14,15,66].

Table 6. Effect of vibronic interaction on the thermodynamic properties of hexafluorides[4].

Hexafluoride	T, °K	$\Delta\Phi^*_T$, cal mole^{-1} deg^{-1}	$\Delta(H^0_T - H^0_0)$, cal mole^{-1}	ΔS^0_T, cal mole^{-1} deg^{-1}
ReF_6	200	0.103	18.5	0.196
	298.15	0.136	20.2	0.203
	900	0.175	12.4	0.189
TcF_6	200	0.087	17.1	0.172
	298.15	0.117	19.1	0.181
	900	0.154	11.1	0.166

The empirical relations between the ground vibration frequencies and the number of unbound electrons[4] enabled Weinstock and Goodman to estimate the frequencies of the hitherto not investigated (CrF_6, PoF_6) and not even synthesised (AmF_6) hexafluorides. The effect of the vibronic interaction on the thermodynamic properties was also estimated by Weinstock and Goodman[4] (Table 6). The corrections obtained ($\Delta\Phi^*_T$ and ΔS^0_T) are virtually negligible for TcF_6 and ReF_6 in the range 200–900°K. Such an error in the calculations of the thermodynamic functions is possible as a result of an error of 1–2 cm^{-1} in the estimation of the vibration frequencies.

For the hexafluorides of osmium and ruthenium, the corrections are of the same order of magnitude as those for ReF_6 and TcF_6, which are listed in Table 6. This implies that the ν_2 and ν_5 frequencies (Table 5) may be employed without additional correction to calculate the thermodynamic properties of rhenium, technetium, ruthenium, and osmium hexafluorides.

Table 7 lists the reduced free energies of certain hexafluorides required for the calculation of their thermodynamic stabilities. They were calculated in terms of the rigid rotator–harmonic oscillator approximation taking into account the corrections for frequencies in the review of Weinstock and Goodman[4] and for the degeneracy of the electronic ground state.

The reduced free energies of the elements forming hexafluorides were taken from Kulikov's monograph[52] and the paper of Gurvitsh and Jungman[67]. The thermodynamic stability constants of the hexafluorides of certain elements were calculated by Eqn. (3) (Table 8).

Fig. 3 presents the logarithms of the thermodynamic stability constants of the hexafluorides in the vertical series at 298°, 1200°, and 2400°K. Analysis of these relations permits the following conclusions:

1. The thermodynamic stabilities of hexafluorides in relation to atomisation reactions decrease along the horizontal series (4*d*, 5*d*, and 5*f* elements).

Table 7. Reduced free energies of certain hexafluorides (cal mole^{-1} deg^{-1}) at p = 1 atm. in the ideal gas state.

T, °K	SF_6	SeF_6	TeF_6	MoF_6	TcF_6	WF_6	ReF_6	OsF_6	IrF_6	UF_6	NpF_6	PuF_6
298	56.64	59.06	62.42	64.46	65.90	65.11	66.63	66.93	66.68	68.74	69.48	67.36
400	62.01	64.21	68.13	70.52	71.83	71.16	72.56	72.84	72.65	75.44	76.08	73.93
800	74.88	80.07	85.06	88.10	89.30	88.67	89.89	90.13	90.06	94.26	94.73	92.54
1200	85.21	91.46	96.88	100.17	101.82	100.71	101.87	102.10	102.08	106.85	107.26	105.06
1600	93.38	100.27	105.91	109.32	110.47	109.86	110.99	111.22	111.23	116.30	116.67	114.48
2000	100.11	107.43	113.22	116.72	117.84	117.23	118.34	118.57	118.60	123.86	124.22	122.02
2400	105.84	113.46	119.34	122.85	124.01	123.40	124.50	124.73	124.77	130.15	130.50	128.30
2800	110.82	118.67	124.61	128.19	129.32	128.71	129.80	130.03	130.07	135.55	135.89	133.69
3200	115.21	123.24	129.24	132.84	133.37	133.36	134.45	134.67	134.73	140.28	140.61	138.41
3600	119.16	127.33	133.36	136.99	138.10	137.51	138.15	138.75	138.85	144.37	144.82	142.62
4000	122.72	131.01	137.08	140.73	141.85	141.25	141.90	142.43	142.60	148.15	148.58	146.38

Table 8. Thermodynamic stability constants of hexafluorides

T°, K	SF_6	SeF_6	TeF_6	MoF_6	TcF_6	WF_6	ReF_6	OsF_6	IrF_6	UF_6	NpF_6	PuF_6
1200	$2.24\cdot10^{41}$	$1.12\cdot10^{42}$	10^{46}	$3.17\cdot10^{27}$	$1.45\cdot10^{60}$	$4\cdot10^{91}$	$5.62\cdot10^{51}$	$5.62\cdot10^{51}$	$1.91\cdot10^{30}$	$4.47\cdot10^{93}$	$1.59\cdot10^{63}$	$1.7\cdot10^{73}$
1600	$6.32\cdot10^{19}$	$4.47\cdot10^{34}$	$5.61\cdot10^{38}$	$5.38\cdot10^{47}$	$5\cdot10^{34}$	$1.78\cdot10^{55}$	$7.93\cdot10^{35}$	$1.26\cdot10^{28}$	$1.59\cdot10^{12}$	$6.31\cdot10^{59}$	$2\cdot10^{52}$	$7.94\cdot10^{42}$
2000	$8.69\cdot10^{6}$	$5.13\cdot10^{3}$	$4.17\cdot10^{10}$	$7.88\cdot10^{29}$	$3.17\cdot10^{19}$	$2\cdot10^{38}$	$1.26\cdot10^{20}$	$1.15\cdot10^{14}$	$1.74\cdot10^{1}$	$7.95\cdot10^{39}$	$7.93\cdot10^{33}$	$7.94\cdot10^{27}$
2400	$1.8\cdot10^{-2}$	$6.45\cdot10^{-5}$	$6.38\ 10^{1}$	$9.13\cdot10^{17}$	$1.66\cdot10^{9}$	$1.6\cdot10^{27}$	10^{10}	$4.17\cdot10^{4}$	$1.23\cdot10^{-6}$	$1.59\cdot10^{26}$	$2.3\cdot10^{21}$	$1.5\cdot10^{15}$
2800	$1.48\cdot10^{-8}$	$1.48\cdot10^{-10}$	$3.72\ 10^{-5}$	$4.21\cdot10^{9}$	$9.6\cdot10^{1}$	$1.74\cdot10^{17}$	$3.39\cdot10^{2}$	$8.84\cdot10^{-3}$	$1.2\cdot10^{-12}$	$2.82\cdot10^{14}$	$3.8\cdot10^{12}$	$9.5\cdot10^{8}$
3200	$3.02\cdot10^{-13}$	$4.67\cdot10^{-15}$	$6.03\cdot10^{-10}$	$1.63\cdot10^{3}$	$2.35\cdot10^{-4}$	$1.34\cdot10^{8}$	$1.13\cdot10^{-3}$	$6.17\cdot10^{-8}$	$1.82\cdot10^{-15}$	$2.37\cdot10^{9}$	$5.94\cdot10^{5}$	$9\cdot10^{1}$
3600	$7.07\cdot10^{-17}$	$5.49\cdot10^{-18}$	$1.42\cdot10^{-13}$	$1.91\cdot10^{-2}$	$1.48\cdot10^{-8}$	$4.46\cdot10^{2}$	$4.22\cdot10^{-8}$	$8.5\cdot10^{-11}$	$3.98\cdot10^{-19}$	$6.02\cdot10^{3}$	2.82	$1.55\cdot10^{-3}$
4000	$1.2\cdot10^{-19}$	$1.55\cdot10^{-20}$	$2.83\cdot10^{-17}$	$2.69\cdot10^{-1}$	$7.1\cdot10^{-13}$	$1.94\cdot10^{-2}$	$1.29\cdot10^{-11}$	$7.24\cdot10^{-15}$	$8.9\cdot10^{-21}$	$2.56\cdot10^{-1}$	$1.44\cdot10^{-5}$	$6.68\cdot10^{-8}$

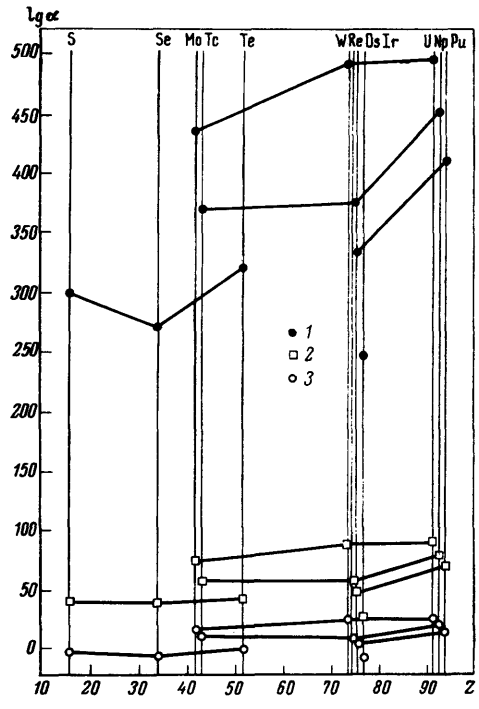


Figure 3. Variation of the logarithms of the thermal stability constants of hexafluorides with the charge number of the central atom; temperature (°K): 1) 298; 2) 1200; 3) 2400.

2. The sequence of hexafluorides in terms of decreasing thermodynamic stability depends little on temperature. In the vertical series the hexafluorides of the actinide elements are the most stable:

$$UF_6 > WF_6 > MoF_6;\ NpF_6 > ReF_6 > TcF_6;\ PuF_6 > OsF_6.$$

However, the difference between the values of $\lg\alpha$ diminishes as the temperature is raised, owing to an increase of the contribution by the entropy factor to the equation $\Delta G = \Delta H - T\Delta S$ compared with the heat of reaction.

3. In the series of non-metal hexafluorides the stability falls from sulphur hexafluoride to selenium hexafluoride, but increases sharply on going to tellurium hexafluoride, so that $TeF_6 > SF_6 > SeF_6$.

4. The sequence of hexafluorides in terms of decreasing thermodynamic stability in relation to the atomisation reaction is as follows:

$$UF_6 > WF_6 > NpF_6 > MoF_6 > PuF_6 > TcF_6 > ReF_6 > OsF_6 > TeF_6 > SF_6 > SeF_6 > IrF_6.$$

The positions of the hexafluorides in this series depend to a considerable degree on the accuracy of the determination of ΔH_0^0 (Table 9). Xenon hexafluoride should occupy the last place in this series.

We shall examine the changes in the thermodynamic stability of hexafluorides in partial dissociation reactions in the first vertical and third horizontal series. The decomposition to the tetrafluoride may be employed as a reaction of this kind:

$$(EF_6)_{gas} \rightarrow (EF_4)_{gas} + 2(F)_{gas}. \qquad (6)$$

The reduced free energies of the tetrafluorides required for the calculation of the stability constants were evaluated

in terms of the rigid rotator–harmonic oscillator model using an empirical method for the estimation of the equivalent geometrical and energy constants[68]. The results of the calculation are presented in Table 10. The calculation was made for only six hexafluorides, since only in these cases was it possible to calculate the heats of reaction at the standard temperature (298.16°K) and the absolute zero (Table 9).

Table 9. Enthalpies of dissociation of hexafluorides by reaction (6) under standard conditions (298.16°K) and at the absolute zero (kcal mole^{-1}).

Hexafluoride	ΔH°_{298}	ΔH°	References to literature employed in calculations	Hexafluoride	ΔH°_{298}	ΔH°	References to literature employed in calculations
UF_6	184.4	181.4	49,69,70	WF_6	234	232	42.48
NpF_6	131	129	42,71	MoF_6	194	191	42.47
PuF_6	102.5	101.3	45	SF_6	—	152,261	17

Table 10. Thermodynamic stability constants of hexafluorides in reaction (6).

T°, K	UF_6	NpF_6	PuF_6	WF_6	MoF_6	SF_6
800	10^{93}	$1.32\cdot10^{21}$	$2.24\cdot10^{13}$	$1.78\cdot10^{48}$	$7.93\cdot10^{37}$	$4.36\cdot10^{28}$
1200	$1.12\cdot10^{17}$	$1.12\cdot10^{9}$	$4.8\cdot10^{3}$	$5.38\cdot10^{23}$	$1.13\cdot10^{20}$	$2.1\cdot10^{14}$
1600	$1.2\cdot10^{9}$	$1.23\cdot10^{3}$	$1.04\cdot10^{-1}$	$1.27\cdot10^{16}$	$1.76\cdot10^{11}$	$1.48\cdot10^{4}$
2000	$2.76\cdot10^{4}$	$1.34\cdot10^{-1}$	$1.78\cdot10^{-4}$	$5.49\cdot10^{9}$	$7.24\cdot10^{5}$	$8.9\cdot10^{-1}$
2400	$1.66\cdot10^{1}$	$1.37\cdot10^{-3}$	$2.29\cdot10^{-6}$	$3.03\cdot10^{5}$	$2.21\cdot10^{2}$	$1.23\cdot10^{-3}$
2800	$8.92\cdot10^{-1}$	$2.81\cdot10^{-5}$	$1.1\cdot10^{-7}$	$2.95\cdot10^{2}$	$6.88\cdot10^{0}$	$2.2\cdot10^{-5}$
3200	$1.74\cdot10^{-3}$	$1.62\cdot10^{-6}$	$1.15\cdot10^{-8}$	$1.61\cdot10^{0}$	9.10^{-3}	$3.81\cdot10^{-7}$

The logarithms of the thermodynamic stability constants of the hexafluorides decrease from left to right along the series of 5*f* elements. When the hexafluorides are arranged in a common series in terms of decreasing thermal stability with respect to reaction (6), the following sequence is observed up to 2300°K: $WF_6 > MoF_6 > UF_6 > SF_6 > NpF_6 > PuF_6$. Above 2300°K, SF_6 and NpF_6 change places.

VII. ANALYSIS OF EXPERIMENTAL DATA FOR THE THERMAL STABILITIES AND REACTIVITIES OF HEXAFLUORIDES

The chemical reactivities‡ of non-metal hexafluorides differ markedly from those of metal hexafluorides. With the exception of polonium hexafluoride, non-metal hexafluorides exhibit unusual chemical inertness. In the reviews by Weinstock already mentioned[2,3], it is reported that the thermal stabilities in this series decrease and the chemical reactivities increase from sulphur hexafluoride to tellurium hexafluoride, the hydrolysis of tellurium hexafluoride, which is the most reactive of the three hexafluorides, requiring not less than 24 h for its completion at room temperature[3]. The information available at present about the thermal stability of sulphur hexafluoride is fairly adequate. The compound is stable in an electric arc[72], which can be accounted for[3] by its high thermal stability. At 2300–2500°K sulphur hexafluoride molecules dissociate into atoms[46]. A wide variety of fragments of SF_6 molecules, obtained in an electric arc, have been isolated[73,74]. The reason for the pronounced insulating properties of sulphur hexafluoride is probably the high electron affinity not only of fluorine atoms and molecules, but also of SF_6 molecules and their fragments[75].

We shall consider the experimental regularities in the variation of the thermal stability and reactivity in the vertical and horizontal series of metal hexafluorides. The first vertical series includes the hexafluorides of chromium (3*d*), molybdenum (4*d*), tungsten (5*d*), and uranium (5*f*). The molecules of all these hexafluorides do not have free electrons. Their chemical reactivity may be characterised by the reactions involving the fluorination of the lower fluorides of various elements (including the lower fluorides of the elements forming the hexafluorides), the sensitivity to hydrolysis, substitution and addition reactions, etc.

The feasibility of reaction (3) is a direct indication that tungsten hexafluoride is chemically less reactive than molybdenum hexafluoride:

$$(WF_4)_{solid} + 2(MoF_6)_{gas} \rightarrow 2(MoF_5)_{solid} + (WF_6)_{gas}. \quad (7)$$

Chromium hexafluoride is thermally unstable at −100°C.[76] Even chromium pentafluoride is more reactive than the hexafluorides of molybdenum, tungsten[11], and uranium[6]. This was demonstrated by studies of the reactions of the above fluorides with the trifluorides of phosphorus, arsenic, bismuth, etc. The reaction with carbon disulphide is particularly instructive:

$$CS_2 + 8CrF_5 \rightarrow 8CrF_3 + CF_4 + 2SF_6, \quad (8)$$

$$2CS_2 + 6MoF_6 \rightarrow (CF_3)_2S_2 + 2S + 6MoF_5. \quad (9)$$

Reaction (8) takes place explosively[11], reaction (9) is also vigorous[11], but tungsten hexafluoride does not react with carbon disulphide[11]. Uranium hexafluoride fluorinates carbon disulphide, various fluorination products being obtained, depending on temperature.[6,77]

On the basis of studies of the behaviour of these four hexafluorides, O'Donnel[6,7,11] believes that the reactivity of the hexafluorides in the first vertical series diminishes in the following sequence: $CrF_6 > UF_6 > MoF_6 > WF_6$. Thus the hexafluoride of uranium (a 5*f* element) is more reactive than the hexafluorides of molybdenum (4*d*) and tungsten (5*d*).

In the series of hexafluorides of 5*f* elements (uranium, neptunium, and plutonium), the reactivity increases from UF_6 to PuF_6.[2-4,6,71]. Uranium hexafluoride may be obtained by the fluorination of the tetrafluoride with plutonium hexafluoride[88]. Neptunium and plutonium hexafluorides are readily decomposed photochemically, so that it is impossible to record their Raman spectra. Americium hexafluoride, the existence of which may be postulated by analogy with platinum hexafluoride, is probably even more unstable[79].

The transition elements of the second intercalary decade (4*d* elements) form four hexafluorides: MoF_6, TcF_6, RuF_6, and RhF_6. Ruthenium and rhodium hexafluorides oxidise xenon even at room temperature, like platinum and plutonium hexafluoride[50], in contrast to UF_6, NpF_6, IrF_6, and OsF_6. Technetium hexafluoride is reduced more readily than rhenium hexafluoride[80]. The hexafluorides of technetium and ruthenium are thermally

‡ As in the work of Canterford and O'Donnel[7], it is assumed that the increase of the thermal stability of the molecule is accompanied by a decrease of its chemical reactivity.

and photochemically unstable, so that it is impossible to obtain their Raman spectra. Molybdenum hexafluoride is the most stable in this series, the other hexafluorides being probably thermally unstable. The experimental evidence for the increase of the reactivity of the hexafluorides from left to right in this series is inadequate, but it is postulated that rhodium hexafluoride is thermally less stable than ruthenium hexafluoride[81].

The series of hexafluorides of 5*d* elements contains WF_6, ReF_6, OsF_6, IrF_6, and PtF_6. Platinum hexafluoride fluorinates the fluorides of neptunium and plutonium to the corresponding hexafluorides[72]. Selenium tetrafluoride reduces platinum hexafluoride to the tetrafluoride, but the hexafluorides of osmium and iridium pass to the pentavalent state under the same conditions[82]. Tungsten hexafluoride does not react with nitric oxide[83], osmium hexafluoride forms $NO^+OsF_6^-$,[83] and iridium and platinum form $(NO)_2IrF_6$ [85] and $(NO)_2PtF_6$ [84] respectively. Canterford and O'Donnel arranged the hexafluorides of 5*d* elements in the following sequence in terms of decreasing thermal stability: $WF_6 > OsF_6 > IrF_6 > PtF_6$. In addition[7], $OsF_6 > RuF_6$, $IrF_6 > RhF_6$.

Among the least thermally stable metal hexafluorides of various series, plutonium hexafluoride has a higher thermal stability than platinum hexafluoride; neptunium and uranium hexafluorides are more stable than ruthenium, rhodium, and platinum hexafluorides. The least stable hexafluoride is probably that of chromium§. There is evidence that the thermal stability of rhodium hexafluoride is lower than that of platinum hexafluoride[85]. From this standpoint, the least stable metal hexafluorides can probably be arranged in the following series in terms of decreasing thermal stability: $PuF_6 > PtF_6 > RhF_6 > CrF_6$.

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Analysis of the results presented in this review leads to the conclusion that the thermal stability of a particular hexafluoride, as a characteristic of its reactivity, depends on the type of the dissociation reaction considered. Depending on whether the hexafluoride dissociates completely into atoms or only partially to the penta- or tetrafluoride, a particular sequence of hexafluorides in the vertical and horizontal series in terms of varying thermal stability is obtained.

The experimental thermal stability and reactivity series characterising the incomplete conversion of metal hexafluorides, mainly to the penta- or tetra-fluorides within the limits of individual groups, correspond to changes in the majority of the force constants.

However, if all the hexafluorides are arranged in a single sequence in terms of decreasing valence force constants, the latter is not consistent with the experimental thermal stability series.

The experimental data for non-metal hexafluorides do not agree fully with the variation of the force constants. Probably a higher force constant for the bond is a necessary but not sufficient condition for a higher thermal stability of the hexafluoride. The shifts occurring in the dissociation of the E – F bond are so large, even on partial dissociation, that they no longer depend on the force constants. Moreover, if stepwise dissociation of the E – F bond is postulated, then for reactions (6) one must consider not only the *fd* constant of the EF_6 molecule, but also the *fd* constant of the EF_5 molecule, since on transition from the hexafluoride to the pentafluoride both the geometrical configuration and the average bond energy of the molecule change. For example, the average energy of the U – F bond in the uranium hexafluoride molecule is 122.24 kcal and in the pentafluoride 137 kcal $mole^{-1}$.

The equilibrium constants for the dissociation of hexafluorides to the corresponding tetrafluorides [reaction (6)] probably constitute a more objective criterion of the stability of the hexafluoride in relation to incomplete dissociation (Table 10). In this case the thermal stability of the hexafluoride decreases in the following sequence:

$$WF_6 > MoF_6 > UF_6 > SF_6 > NpF_6 > PuF_6 > PtF_6 > RhF_6 > CrF_6 .$$

From this point of view, the great inertness of sulphur hexafluoride is to be accounted for not by thermodynamics but by kinetic characteristics. The reasons for the position of the hexafluorides SeF_6, TeF_6, TcF_6, OsF_6, IrF_6, and RuF_6 in this series are still not quite clear.

Probably the most objective characteristic of the stability of hexafluorides in relation to total dissociation (atomisation) is provided by the thermodynamic stability constants. The estimates of thermal stability from the average energies of the E – F bonds in hexafluoride molecules agree fully, except for rhenium hexafluoride, with the thermodynamic estimates. The valence force constants are altogether unsuitable to characterise the stability of hexafluorides in relation to the atomisation reaction. The discrepancy between the thermal stability and force constant series constitutes indirect evidence that the decomposition of hexafluorides to atoms takes place via stepwise abstraction of fluorine atoms and, instead of a single force constant of the bond, one must take into account all the force constants of the E – F bonds in the molecules of the hexa-, penta-, tetra-, tri-, di-, and mono-fluorides of the elements.

§ Only the hexafluorides having the octahedral configuration with the O_h symmetry are considered.

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