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Endohedral metal derivatives and exohedral fluorine derivatives of fullerenes

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Abstract. The thermodynamic studies of fullerenes and their stable derivatives, namely, endohedral metallofullerenes and exohedral fullerene fluorides, are generalised. The methods of synthesis and purification of fullerene fluorides are considered and the structures of these compounds are characterised. The thermodynamic properties of fullerenes and fullerene fluorides are discussed. The bibliography includes 150 references.

I. Introduction

In 1985, it was established experimentally that carbon, one of the most abundant elements in the Earth, can form stable cage structures consisting of 60 or more atoms.[1] This new allotropic form of carbon was termed 'fullerene.' The discovery of fullerenes was recognised as a remarkable and one of the most important events in science of the XX Century. In 1990, methods for the preparation of macroscopic quantities of fullerenes were developed[2] and methods for their isolation and purification were found.[3] In addition, important structural and physicochemical characteristics of C_{60} fullerene, which is the most frequently encountered representative of this class of compound, were determined. Currently, the total number of publications dealing with fullerenes exceeds 10 000, and the 'fullerene rush' has embraced fields of knowledge that seem to be far from one another such as astronomy and organic chemistry, solid-state physics and medical biology, inorganic chemistry and geology. Fullerenes can be classified as both inorganic materials (a new allotropic modification of carbon) and organic compounds because they exhibit many properties of unsaturated hydrocarbons in chemical transformations. More recently, unique possibilities of chemical modification of fullerenes have been found, including the addition of various functional groups at the double bonds to give exo derivatives, in particular, complexes with transition metals; insertion of atoms and whole clusters inside the carbon sphere (endo derivatives) and replacement of some carbon atoms by heteroatoms (heterofullerenes).

It is impossible to cover all the results obtained during the last 10 years within the framework of one review. The purpose of this review is to shed light on some lines of research that have developed successfully in the chemistry of fullerenes and their endo metal and fluoro derivatives. The structure of this review corresponds to the chronological sequence of investigations. For example, in the early stages, especially in the experiments leading to the discovery of fullerenes, the crucial role was played by mass spectrometry. Therefore, the review begins with a description of mass-spectrometric studies dealing with determination of the fundamental characteristics of higher fullerenes and endohedral metal fullerenes such as ionisation energy and electron affinity.

The next important stage — fullerene functionalisation — is reflected by a series of works dealing with the synthesis of fluorinated derivatives. Primary attention is devoted to selective synthesis of individual compounds, which has required modification of traditional or development of new methods. The use of HPLC for separation and purification of fullerenes is described. Chromatographic studies in which the authors succeeded in isolating geometric isomers of individual fluorofullerenes are specially noted.

Systematic research into the physicochemical properties of fullerenes and their derivatives became possible only after thorough development of methods for the synthesis and purification of macroscopic quantities of these compounds. Study of fluorofullerenes by NMR spectroscopy and X-ray diffraction analysis revealed that the addition of fluorine atoms to the fullerene carbon atoms with formation of strong valence bonds results in a pronounced deformation of the carbon cage. This is illustrated taking the structures of flattened, squashed and indented fluorofullerenes as examples. The thermodynamic properties of fullerenes and their fluoro derivatives are discussed and the possible applications of fluorofullerenes are considered.

II. Ions and molecules of fullerenes and their derivatives in the gas phase

Electron affinity (*EA*) and ionisation energy (*IE*) are fundamental characteristics of molecules. For C_{60} ([60]fullerene), the *EA* and *IE* values are equal to 2.667 ± 0.001 eV (see Ref. 4) and 7.57 ± 0.01 eV (see Ref. 5), respectively. This *EA* value is substantially higher than these values for most aromatic compounds, indicating a fairly high electron-withdrawing capacity of fullerene molecules.

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The combination of rather high electron affinity with low ionisation energy (for comparison, for the benzene molecule, *IE* is 9.24 eV and *EA* is negative), which is seldom encountered in chemistry, indicates that fullerene molecules can act as both electron donors and electron acceptors in chemical processes. The data concerning other representatives of this class of compound, so-called higher fullerenes, C_{2n} ($n > 30$), some of which can also be prepared in macroquantities, showed that they differ substantially in their properties from [60]fullerene. These differences are manifested, first of all, in fundamental characteristics such as ionisation energy and electron affinity.

Experimental research of negative ions in the gas phase has been actively carried out since the 1970s. One experimental method used successfully to determine ions of non-volatile inorganic compounds was called 'the method of ion-molecular equibria' (IME).[6] This method is based on either the classical effusion technique with mass-spectroscopic detection of vaporisation products or high-temperature mass-spectrometry (Knudsen Cell Mass Spectrometry, KCMS), which is used to assess the contents of neutral species. The improved KCMS – IME procedure allows one to detect charged species present in the saturated vapour of inorganic compounds. To obtain measurable concentrations of ions in the vapours of inorganic compounds, salts such as $KAlF_4$ characterised by a low energy of heterolytic dissociation into ions, are added. Even at 1000 K, the vapours of these salts contain such high amounts of cations and anions that the Debye shielding radius becomes smaller than the effusion cell dimensions and, consequently, electron-free plasma is formed. The pressure of neutral species remains 5 to 7 orders of magnitude higher than the ion pressure.[6] The addition of these salts to other inorganic compounds whose vapours do not contain measurable concentrations of ions results in systems with large amounts of ion – molecular associates. In particular, the addition of KF to the $Pt - MnF_3$ system gave rise to a set of negative ions including PtF_4^- and PtF_6^- and enabled the first direct experimental measurements of the *EA* values of platinum tetra- and hexafluorides.[7] Subsequently, a series of studies dealing with the determination of the electron affinities of transition metal oxides and fluorides have been carried out.[8] For several years, the authors of the review[8] attempted to extend this method to organic compounds (in particular, compounds containing electronegative substituents and having high thermal stability, for example, perfluorinated derivatives) but were unable even to detect thermal anions (*i.e.*, those resulting from thermal ionisation). Therefore, when publications appeared pointing to unique properties of fullerenes[9] and data on their thermal stability were obtained,[10, 11] it became clear that the use of the IME method to study compounds of this class may prove successful. The first publication opening a series of IME experiments aimed at determining the electron affinity and ionisation energy of fullerenes appeared in 1993.[12] The description of the IME method as applied to fullerenes has been reported in detail.[12] Here, we shall only consider several key procedural points and the most important results.

1. Procedure for the measurement of equilibrium constants of ion – molecule reactions and the proof of thermodynamic equilibration

The first task to be accomplished by experimentalists was to generate thermal negative ions in the fullerene vapour under equilibrium conditions and within temperature limits where fullerenes are still thermally stable. Of numerous experimental parameters, the electron work function of the metal surface is the most significant, because the efficiency of thermal ionisation resulting in the generation of ions largely depends on the properties of the surface where thermal ionisation takes place. In the IME method, this is the internal surface of the Knudsen effusion cell the work function for which can vary over a broad range. For example, the addition of alkali metals and their compounds to the cell decreases, while fluorination of the walls increases the electron work function for the internal surface of the effusion cell. Practically, it was possible to control the work function in the 4 – 6.5 eV range.[13, 14] The *EA* and *IE* values of fullerenes were found to be at the boundaries of this range. This opened up broad and unique opportunities for the generation of both positive and negative thermal ions of fullerenes and initiated an extensive series of studies involving fullerene gas-phase ions.

In the KCMS – IME analysis of charged species, the technique of relative measurements is widely used; this implies measurement of the equilibrium constants of isomolecular reactions with participation of a reference species (B), whose thermochemical characteristics have been reliably established

$$A^- + B = A + B^-; \quad \Delta H_0^\circ = EA(A) - EA(B), \tag{1}$$

$$AF^- + B = A + BF^-; \quad \Delta H_0^\circ = FA(A) - FA(B), \tag{2}$$

where ΔH_0° is the standard enthalpy of the reaction at 0 K, and *EA* and *FA* are the electron and fluoride-ion affinities, respectively.

The reference should have a volatility close to that of the specimen under study, and the absolute magnitude of the enthalpy of reactions (1) and (2) should not exceed 100 kJ mol^{-1}. Thus, the thermochemical characteristics of the reference should be similar to those of compound A under study determined in the reaction. When investigating the negative ions of fullerenes, the addition of alkali metal compounds was used to lower the work function. When working with cations, iron trifluoride was added to increase the electron work function of the internal surface of the nickel effusion cell.[14]

Yet another difficulty arising in the production of measurable concentrations of ions in fullerene vapours lies in the fact that the temperature of thermal ionisation of fullerenes does not coincide with their sublimation point. To attain the required degree of ionisation, the vapour should, most often, be superheated. It was proposed to use double effusion cells of 'Russian matreshka' type (Fig. 1). The more volatile substance (fullerene) was placed in the smaller cell and an inorganic fluoride was put in the larger one. By controlling the relative sizes of the effusion orifices in the internal and external cells, it was possible to desaturate the vapour of the volatile component by a factor of 7 – 10, so it became possible to raise the temperature without violating the conditions of molecular effusion from the orifice of the external cell.[13] The experimental setup permitted the ratios of the partial pressures of both neutral and charged components of the vapour to be measured consecutively within one experiment. The neutral species were measured by recording the ion currents resulting from the electron impact on the molecular beam coming from the effusion cell. Then the ratio of partial pressures (p) was calculated using the equation relating the ion currents to the partial pressures of neutral species

$$\frac{p_A}{p_B} = \frac{I_A}{I_B}\frac{\sigma_B}{\sigma_A},$$

where I is the ion current intensity; σ the full ionisation section of the molecule.

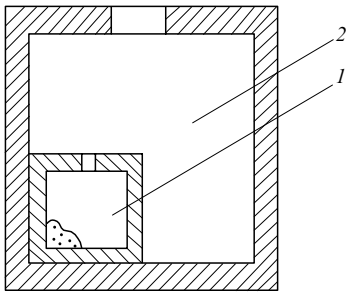


Figure 1. Effusion cell of the 'Russian matreshka' type:
(*1*) internal cell with the fullerene; (*2*) external cell with the metal fluoride.[13]

The partial pressures of charged species were measured by recording the ion currents generated upon direct drawing of thermal ions out of the effusion cell by an electric field. The ratios of the pressures of thermal anions were calculated from the equation

$$\frac{p_{A^-}}{p_{B^-}} = \frac{I_{A^-}}{I_{B^-}} \frac{\sqrt{M_{A^-}}}{\sqrt{M_{B^-}}},$$

where M is the molecular mass. This gave the equilibrium constants of the ion–molecule reactions.

Particular attention was devoted to verification of the thermodynamic equilibration. For this purpose, the composition of the gas phase was varied over a broad range and the equilibrium constants were measured. At equilibrium, the constants determined for the same temperature should remain invariable, no matter how the partial pressures of the reactants (or products) may change.

The experimental data [12, 15] obtained for the reaction

$$C_{60} + C_{70}^- = C_{60}^- + C_{70}, \quad (3)$$

indicate that even upon a change in the $C_{60}:C_{70}$ ratio by two orders of magnitude, the equilibrium constant remains invariant to within the experimental error (Table 1). Similar verifications of the thermodynamic equilibration by varying the composition of the reaction mixtures have also been carried out for other reactions, in particular, for electron exchange in the vapours of higher fullerenes and for fluorine exchange. Conversely, it was found that in ionic and molecular reactions involving rearrangement of the fullerene carbon skeleton

$$C_{70}^- + C_{84}^- = C_{76}^- + C_{78}^-,$$

$$C_{70} + C_{84} = C_{76} + C_{78},$$

no equilibrium is established, and the number of components in a mixture of higher fullerenes is determined as the number of substances.

Table 1. Experimental values of the ion current intensity (I), the equilibrium constant (K_p) and the Gibbs energy ($\Delta_r G_T^\circ$) for reaction (3).[15]

System [a]	T/K	N [b]	$I(C_{70}^+):I(C_{60}^+)$	$I(C_{60}^-):I(C_{70}^-)$	K_p	$\Delta_r G_T^\circ$ (see [c])
1	810	1	1.52	0.33	0.36	6.83
1 + 2	936	4	0.50	0.90	0.33	8.81
	957	4	0.42	1.12	0.35	8.46
	966	2	0.67	0.76	0.37	7.90
	1019	3	0.60	0.87	0.38	8.13
2	820	2	0.267	1.768	0.35	7.16
	846	3	0.280	1.478	0.30	8.37
	865	2	0.310	1.222	0.27	9.22
	877	3	0.125	4.456	0.41	6.52
	887	2	0.195	1.844	0.32	8.48
3	815	4	71.62	0.0073	0.38	6.49
	826	5	60.56	0.0095	0.42	5.92
	836	4	80.26	0.0076	0.45	5.55
	854	3	56.58	0.0094	0.39	6.69
	872	3	13.02	0.0500	0.48	5.35

[a] Composition of specimens: **1**, 50% C_{60}, 50% C_{70}; **2**, 75% C_{60}, 24% C_{70}, 1% C_n ($n > 70$); **3**, 1.5% C_{60}, 98.5% C_{70}. [b] The number of measurements. [c] The $\Delta_r G_T^\circ$ value is expressed in kJ mol^{-1}; the average $\Delta_r G_T^\circ$ is 7.77 ± 1.43 kJ mol^{-1}.

2. Electron affinity, ionisation energy and electronegativity of higher fullerenes

Owing to the use of the KCMS–IME procedure, in addition to the frequently encountered C_{70}, C_{76}, C_{78} and C_{84} fullerenes, it was also possible to study other fullerenes [15] present in the specimens in minor amounts (the dynamic range of measurable concentrations reaches eight orders of magnitude), up to C_{106} fullerene, which have not been isolated in a pure state. Due to the high sensitivity together with the capacity of mass-spectrometric analysis of the components, the KCMS–IME procedure is superior over traditional spectroscopic methods used to determine the *EA* and *IE* values, although the latter are, in principle, more accurate. An *EA* value for C_{60} fullerene found by the photodetachment method has been reported.[9] The first experimental *EA* value for C_{70} fullerene was reported by Boltalina *et al.*;[12] later, this value was estimated from the photodetachment threshold of an electron from the C_{70}^- anions, which were preliminarily cooled upon collisions with helium atoms in an ASTRID storage ring.[4] The resulting vertical electron affinity of C_{70} fullerene (2.68 eV) proved to be somewhat lower than the value (2.73 eV) determined from the KCMS–IME measurement of the electron exchange enthalpy, which is the adiabatic *EA* value.[15] Note that the last-mentioned result is in good agreement with the results of measurements of the relative ion mobility of C_{60}^- and C_{70}^- in non-polar solvents [16] and also with the *EA* estimates from the reduction electrochemical potentials of C_{60} and C_{70}, which also refer to the adiabatic electron affinity.[17] Experimental data on the *EA* of higher fullerenes have been obtained only using the KCMS–IME procedure.[15] Theoretical calculations [18, 19] have been carried out only for C_{74}–C_{84} molecules.

Particular attention should be paid to studies devoted to determination of isomer compositions of mixtures of higher fullerenes and to assignment of the experimental ionisaton characteristics to the molecules of particular geometric isomers. According to published data, only for several fullerenes (C_{78}–C_{92}), was the isomer composition determined sufficiently reliably by analysing the structures of individual compounds obtained by chromatographic separation and by using NMR spectroscopy. Thus it was found that C_{76} fullerene forms only one isomer, C_{78} has two major isomers, and for C_{84}, seven geometric isomers have been found, the isomers with D_{2d} and D_2 symmetry being the most widespread;[20] the calculated *EA* values for these two isomers virtually coincide.

Curious observations have been made for C_{72} and C_{74} fullerenes, which fall out of the general series of C_{2n} fullerene homologues, first of all, due to the fact that they have not yet been isolated as individual compounds from typical fullerene extracts. It can be seen from the dependence of the *EA* on the fullerene size (Fig. 2, curve *2*) that the values for the C_{72} and C_{74} molecules are abnormally high, which violates the monotonic pattern of *EA* variation. The diagram of the energy levels of molecular orbitals (MO) of C_{74} fullerene (Fig. 3) [21] indicates that the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which allows one to judge the relative kinetic stability of a molecule, is very small and equals only 0.05 eV, whereas for C_{60}, this difference is 1.6 eV. This finding is in line with the fact that C_{74} fullerene, which is present in perceptible amounts in soot, is lost almost entirely during subsequent extraction with organic solvents (apparently, due to degradation or polymerisation and transition into an insoluble form). Only recently, two research groups in the USA [21] and China [22] proposed procedures for the synthesis and isolation of C_{74} fullerene; however, this compound has not yet been isolated in a pure state or characterised by spectroscopic methods.

Comparison of the experimental *EA* values for C_{72} fullerene with the theoretical values for the single isomer that obeys the rule of isolated pentagons and for isomers in which this rule is violated

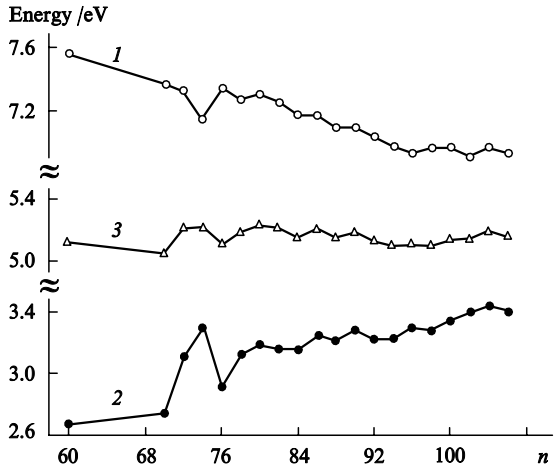


Figure 2. Ionisation energy (*1*), electron affinity (*2*) and their half-sum (Mulliken electronegativity) (*3*) *vs.* the number of carbon atoms (*n*) in the fullerene molecule.[14]

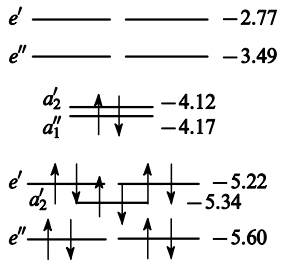


Figure 3. Diagram of the MO energy levels for the C_{74} molecule (the D_{3h} group of symmetry) calculated by the BLYP/6-31G*//3-21G* procedure. The numerals at the energy levels are energies (in eV).[21]

showed that the best agreement between the experimental and theoretical results is attained for the molecule with C_{2v} symmetry, which contains both isolated and conjugated five-membered rings.[23]

Later, thermal cations in the vapours of higher fullerenes have been studied,[14] and for a series of C_{2n} molecules, the equilibrium constants for the reaction

$$C_{60}^{+} + C_{2n} = C_{2n}^{+} + C_{60},$$

where $n = 35-53$, were measured. The resulting *EA* and *IE* values for the higher fullerenes and the corresponding electronegativity values are shown in Fig. 2.

The simple physical model in which fullerene is considered as a rigid conducting sphere [14] makes it possible to derive an equation that relates the electron affinity and the ionisation energy to the radius of a sphere (R_N)

$$EA = \varphi_\infty - 0.5R_N^{-1},$$

$$IE = \varphi_\infty + 0.5R_N^{-1},$$

where φ_∞ is the electron work function of a graphite monolayer, which is the limiting value for both the *EA* and the *IE* as the size of the fullerene molecule tends to infinity; a theoretical estimate of this value gives 5.37 eV. The effective sphere radius R_N is proportional to the square root of its mass, because the surface area of the molecule is proportional to the number of carbon atoms located on it. The appropriate proportionality coefficients can be found using the known geometric parameters and the known *EA* and *IE* values for [60]fullerene. However, in reality, the shapes of many fullerene molecules deviate from a sphere, which may result in deviations of experimental data from theoretical predictions concerning the pattern of the dependence of the *EA* on the fullerene size. Nevertheless, this simple model generally provides a satisfactory description of experimental data — both the monotonic increase in the electron affinity and the decrease in the ionisation energy following an increase in the size of the molecule. The rate of variation of both parameters markedly decreases on passing to heavy fullerenes with about 100 carbon atoms in the molecule. Noteworthy are clearly mirror patterns of variation of the *EA* and *IE* curves, which shows itself as a rather narrow energy range fitting the electronegativity values $(EA + IE)/2$ for the whole series of fullerenes studied, 5.2 ± 0.2 eV (see Fig. 2); the above-mentioned theoretical estimate of the electron work function for a graphite monolayer also falls in this range.

3. Ion-molecular equilibria in the vapours of fullerene derivatives

Fullerene derivatives can be classified into two main groups, namely, exo- and endohedral fullerenes. Exohedral fullerenes are those compounds in which functional groups add on the outside of the fullerene cage; as a rule, the species add in pairs with rupture of the double bonds. The term 'endohedral' means 'enclosed inside'. These derivatives have been obtained by admixing oxides of some metals (mainly, lanthanides) to the graphite rods used in fullerene synthesis in the discharge arc. The space inside the fullerene cage suffices to accommodate one, two and, according to the latest data, even three or four metal atoms, some of these compounds being characterised by high thermal stability. Endohedral compounds of noble gases are also known.

In studies of ion–molecule equilibria involving fullerene derivatives, the researchers meant to find out how these two types of functionalisation influence the electron-withdrawing properties of fullerenes. Whereas in the case of fluorofullerenes, one could expect an increase in the *EA* compared to that for the initial C_{60} due to the high electronegativity of fluorine, it was difficult to predict the effect of the intra-sphere metal on the electron-withdrawing properties of fullerene. This problem could not be solved until experimental results were obtained.

a. Endohedral metallofullerenes

The equilibrium constants for the ion–molecule reactions of the type

$$Gd@C_{2n}^{-} + C_{74} = Gd@C_{2n} + C_{74}^{-},$$

where $n = 37-41$, were measured using specimens manufactured by the 'TDA Research' company by evaporation of graphite rods in the discharge arc, followed by sublimation of fullerenes and metallofullerenes from the soot accumulated on the cold walls of the reactor. These specimens were free from soot; hence, there was no need to carry out extraction in a Sohxlet apparatus, which may be accompanied by solvent-induced destruction of metallofullerenes. Although the content of endohedral compounds in the mixtures did not exceed several percent, $Gd@C_{2n}$ ions were detected in the mass spectra recorded at 900–960 K. The ratio of the partial pressures of endohedral and empty fullerenes proved to be higher for negative ions than for neutral molecules, which points to more pronounced electron-withdrawing properties of endohedral fullerenes compared to the analogues containing no metal atoms. The calculations of the *EA* values for $Gd@C_{2n}$ showed that all values are fitted into a narrow range (3.2–3.3 eV, Table 2) and, on average, they are higher than the *EA* of the corresponding hollow fullerenes. Thus, it was found that accommodation of a rare earth metal (gadolinium) inside the fullerene cage results in an increase, although slight, in the *EA* with respect to that of the hollow fullerene molecule; the only exception is $Gd@C_{74}$, which shows an opposite effect. In addition, it was found that for fullerenes containing the same metal atom inside the cage, an increase in the size of the C_{2n} molecule in the series $C_{74}-C_{84}$ has no substantial influence on the electron affinity. This result differs from the pattern of *EA* variation established for

Table 2. Electron affinity of endohedral fullerene compounds.

Compound	*EA* /eV	Ref.
$La@C_{74}$	> 2.9	24
$La@C_{80}$	3.32	see [a]
$Gd@C_{60}$	2.85	24
$Gd@C_{74}$	3.2 ± 0.1	24
$Gd@C_{76}$	3.22 ± 0.02	24
$Gd@C_{78}$	3.41 ± 0.09	24
$Gd@C_{80}$	3.37 ± 0.05	24
$Gd@C_{82}$	3.38 ± 0.06	24
$Sc_2@C_{80}$	3.20 ± 0.04	25
$Sc_2@C_{82}$	3.21 ± 0.04	25
$Sc_2@C_{84}$	3.10 ± 0.04	25
$Sc_3N@C_{80}$	2.81 ± 0.05	25

[a] Author's unpublished results.

hollow fullerenes, where C_{74} fullerene exhibits an abnormally high *EA* value. These data suggest that in the case of endohedral compounds, the electron-withdrawing properties of the molecule are dictated by the charge on the intra-sphere metal atom. This hypothesis is supported by theoretical calculations. We were also able to determine the *EA* for some endohedral metallofullerenes with two scandium atoms inside the sphere and for a new type of endo compound with a trimetallic nitride cluster, $Sc_3N@C_{80}$ (Fig. 4, see Table 2).

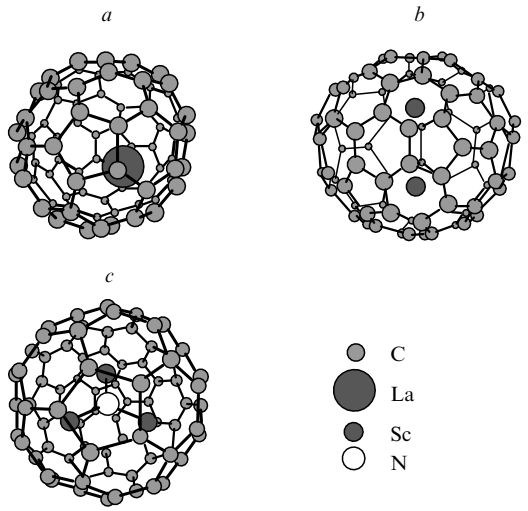


Figure 4. Structures of the compounds $La@C_{82}$ (*a*), $Sc_2@C_{82}$ (*b*) and $Sc_3N@C_{80}$ (*c*). [The structure of $Sc_3N@C_{80}$ is published by authority of the journal Nature (www.nature.com)].

Endohedral metallofullerenes had attracted the attention of theoretical chemists even before they were prepared in macroquantities. The first quantum-chemical study of the model $La@C_{60}$ molecule with the lanthanum atom located at the centre of gravity was reported by Rosen and Wastberg.[26] The calculations showed strong interaction between the 5*d* orbitals of the lanthanum atom and the π-system of the carbon cage, which results, in particular, in an increase in the electron affinity of the endohedral molecule relative to that of the hollow C_{60} molecule by several tenths of electron-volt. Subsequently, the theoretical studies devoted to the structure of endohedral metallofullerenes have also been ahead of experiments and usually gave correct predictions.

In a series of quantum-chemical works performed by Japanese researchers [27–29] and devoted to endohedral metallofullerenes containing Group III metal atoms (Sc, Y) and lanthanide atoms, it was shown, first, that the metal atom is markedly shifted out of the centre of the molecule, and, second, that substantial charge transfer from the metal atom to the carbon cage takes place; as a consequence, the former acquires a charge of 2+ to 3+ (this is true for both mono- and di- or trimetallofullerenes). The ionisation potential of the endohedral metallofullerene is markedly lower, while the electron affinity is somewhat higher, despite the negative charge on the carbon cage, compared to that of the corresponding metal-free fullerene.[27–29]

Evidence supporting these theoretical conclusions was first obtained in electrochemical investigations of endohedral metallofullerenes.[30] The oxidation and reduction potentials of these compounds demonstrated that they give off or accept an electron more easily than fullerenes themselves. This was also confirmed by the results of mass-spectrometric studies (see above). The presence of a charge on metal atoms was confirmed indirectly by EPR data,[31] according to which the putative terms of electron states corresponded to metal ions rather than to atoms. Later, it was found by photoelectron spectroscopy [32, 33] that the HOMO in the molecules of endohedral metallofullerenes have higher energies than similar orbitals of hollow fullerenes.

With progress in developing methods of isolation and purification of endohedral molecules, direct evidence confirming the theoretical predictions also appeared. An important role was played by powder X-ray diffraction studies of the polycrystalline specimens of endohedral metallofullerenes, $Y@C_{82}$, $Sc_2@C_{84}$, $Sc@C_{82}$ and $Sc_3@C_{82}$ with utilisation of the Rietveld method and the maximum entropy method.[34–37] The maps of electron density distribution in these molecules constructed on the basis of these results clearly demonstrated the displacement of metal atoms from the centre of the molecule and the presence of a charge of ~2+ on these atoms. The cross-sections of the electron density maps for scandium endohedral fullerenes are shown in Fig. 5. Similar data on the distances between the metal atom and the nearest carbon atoms in an endohedral fullerene have been obtained for some molecules by EXAFS.[38]

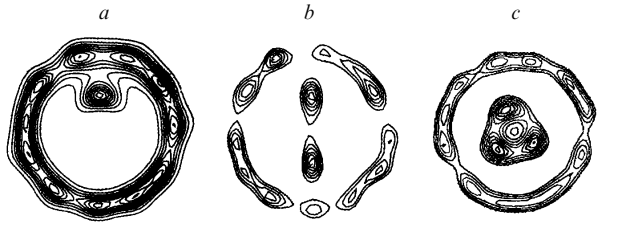


Figure 5. Cross-sections of the electron density maps for the molecules of $Sc@C_{82}$ (*a*), $Sc_2@C_{84}$ (*b*) and $Sc_3@C_{82}$ (*c*).[34–37]
Level lines for bulk charge density from 0.3 (1.0 for $Sc_2@C_{84}$) to 6.0 e $Å^{-3}$ with a step of 0.3 e $Å^{-3}$ are shown. (Published by authority of the American Physical Society and Elsevier publishing house).

Since the distribution of the products of synthesis of endohedral fullerenes over the number of carbon atoms in the molecule differed appreciably from that for hollow fullerenes, the question arose as to whether the carbon cage topology is the same for the major isomers of hollow and endohedral fullerenes for a given number of carbon atoms. An answer to this question was provided, first of all, by X-ray diffraction results. It was found that the symmetry of the carbon cage in $Sc@C_{82}$ differs from that in C_{82} fullerene, while the $Sc_2@C_{84}$ molecule has the same carbon cage as one of the major isomers of C_{84}. It is noteworthy that these results were also first predicted by a group of Japanese theoretical chemists,[27–29] who thus demonstrated high efficiency of quantum-chemical techniques for the study of fullerenes and their derivatives.

b. Fluorofullerenes

The electron affinity of fullerene difluorides was determined using the reactions

$$C_{60}F_2 + C_{60}^- = C_{60}F_2^- + C_{60},$$

$$C_{70}F_2 + C_{60}^- = C_{70}F_2^- + C_{60}.$$

The *EA* values of $C_{60}F_2$ and $C_{70}F_2$ fluorofullerenes found in this way are equal to 2.73 and 2.82 eV, respectively.[39] These data indicate that upon the addition of two fluorine atoms to C_{60} and C_{70} fullerenes, the *EA* increases, although insignificantly. Naturally, a higher electron affinity is expected of a molecule with a higher content of fluorine atoms. Evidence supporting this assumption was gained from measurements of the reduction electrochemical potentials of $C_{60}F_{36}$ fluorofullerene and by comparison of the results with the data for C_{60}. On the basis of a known correlation between the electrochemical potential and the electron affinity, the *EA* for $C_{60}F_{36}$ was estimated to be 3.48 eV.[40] In a study by the 'brackets' method in terms of the ion cyclotron resonance mass spectrometry of the electron exchange between $C_{60}F_{44}-C_{60}F_{48}$ fluorofullerenes and various standards, a substantial increase in the *EA* (4.05 ± 0.5 eV)[41] with an increase in the number of fluorine atoms added was found.

Experiments on the determination of the dissociation energy of the C–F bond in fluorofullerene molecules and anions were carried out using the same equipment as was used for *EA* measurements; however, this time fluorine exchange between fullerenes and fullerene anions was the object of investigation. The compounds FeF_3, UF_4, UO_2F_2 and $C_{60}F_{48}$ were used as mild fluorinating agents. In these systems, fullerene mono- and difluoride anions were detected at 800–1000 K (Fig. 6).[42,43] This allowed the researchers to calculate the absolute magnitudes of the C–F bond energy for $C_{60}F_n$ fluorofullerenes from the reaction

$$FeF_4^- + C_{60}F_n = FeF_3^- + C_{60}F_{n+1}$$

or

$$2\,FeF_4^- + C_{60}F_n = 2\,FeF_3^- + C_{60}F_{n+2}.$$

It was found that the C–F bond energy in the fullerene difluorides under study and their anions is 370–400 kJ mol^{-1}, *i.e.*, this bond is much stronger than was predicted by theoretical calculations (Tables 3, 4). A similar value was found, for example, for the C–F bond energy in the difluoroethane molecule. It is of interest to compare these results with the data on the thermodynamic stability of highly fluorinated fullerenes. The measurements of the combustion energies for C_{60},[46] $C_{60}F_{36}$[47] and $C_{60}F_{48}$[48] and the enthalpies of sublimation of these compounds gave average values for the C–F bond energy in $C_{60}F_{36}$ and $C_{60}F_{48}$ fluorofullerenes equal to 295.0 ± 5.6 and 287.5 ± 3.5 kJ mol^{-1}, respectively. These data also made it possible to estimate the enthalpy of the reaction

$$C_{60}F_{36} + 12\,F = C_{60}F_{48}$$

per fluorine atom; the result was 265 kJ mol^{-1}.[47] This value can be regarded as being approximately equal to the average C–F bond energy for the formation of $C_{60}F_{48}$ from $C_{60}F_{36}$. It follows from these results that the bond energy decreases, although slightly, with an increase in the number of fluorine atoms attached. This is apparently due to the enhancement of the steric strain in the molecules of highly fluorinated fullerenes. Presumably, the decrease in the bond energy would not be monotonic: the most pronounced changes in the D(C–F) value would be expected for the formation of energetically and kinetically favourable compounds, namely, $C_{60}F_{18}$, $C_{60}F_{36}$ and $C_{60}F_{48}$. Although no quantitative data confirming this hypothesis have been obtained yet, the assumption is supported by the highly selective formation of compounds of exactly this composition observed experimentally.

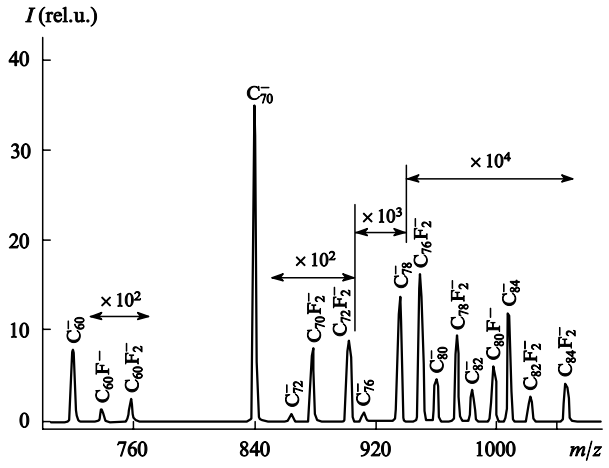


Figure 6. Electron impact (EI) mass spectrum of thermal anions in the vapour of the $C_{60}-C_{60}F_{46}$ system.[42,43]
I is relative intensity.

Table 3. Energies of C–F bond rupture [D(C–F)] in mono- and difluorides of C_{60} and C_{70} fullerenes and their anions.

Compound	D(C–F) /kJ mol^{-1}	Ref.
$C_{60}F$	$\geqslant 362$	42, 43
	403	44
$C_{60}F^-$	388	42, 43
$C_{60}F_2$	369	42, 43
	365	44
	306	45
$C_{60}F_2^-$	372	42, 43
$C_{70}F_2$	366	42, 43
$C_{70}F_2^-$	370	42, 43

Table 4. Thermodynamic parameters (ΔH_0° and ΔG_T°) and energies of C–F bond rupture for higher fullerenes.[39,42,43]

Reaction	ΔG_T° kJ mol^{-1}	ΔH_0° kJ mol^{-1}	D(C–F) kJ mol^{-1}
$C_{60}^- + 2\,F = C_{60}F_2^-$	−496	−744	372
$C_{70}^- + 2\,F = C_{70}F_2^-$	−492	−740	370
$C_{72}^- + 2\,F = C_{72}F_2^-$	−527	−774	387
$C_{74}^- + 2\,F = C_{74}F_2^-$	−548	−796	398
$C_{76}^- + 2\,F = C_{76}F_2^-$	−519	−767	384
$C_{78}^- + 2\,F = C_{78}F_2^-$	−523	−770	385
$C_{80}^- + 2\,F = C_{80}F_2^-$	−546	−793	397
$C_{82}^- + 2\,F = C_{82}F_2^-$	−541	−788	394
$C_{84}^- + 2\,F = C_{84}F_2^-$	−535	−782	391
$C_{60}^- + F = C_{60}F^-$	−267	−388	388
$C_{70}^- + F = C_{70}F^-$	−274	−395	395
$C_{60}F^- + F = C_{60}F_2^-$	−237	−361	361
$C_{60}F_2^- + 2\,F = C_{60}F_4^-$	−412	−665	332
$C_{60} + F = C_{60}F$	$\geqslant -242$	$\geqslant -363$	$\leqslant 363$
$C_{70} + F = C_{70}F$	$\geqslant -253$	$\geqslant -374$	$\leqslant 374$

III. Synthesis of fluorofullerenes

1. Mass-spectrometric studies of reactions of fullerenes with transition metal fluorides

The idea of using a mass-spectrometric setup as a chemical reactor is not new; it is widely employed in investigations of the reactivity of gaseous species (neutral molecules and ions). An attractive feature of these investigations is that they provide information about the reaction 'just as it is', *i.e.*, not complicated by processes

of solvation (if the reaction takes place in solution) or by the state of reactants in heterogeneous processes. A typical scheme of these experiments is as follows. Gaseous species of a reactant are generated by vaporisation of appropriate chemical compounds and are let into a cell in which they are mixed with the other reactant. By recording the mass spectrum of the gas phase formed in the cell, one can gain information about the reactivity of the species and about the reaction products. More complex cases include the study of reactions as functions of temperature, reactant pressure or the charge of the reacting species.

The use of a mass-spectrometric setup as the main tool in the investigation of fullerene fluorination was started, as a matter of fact, due to a fortuitous discovery. As noted in the previous Section, the preparation of $C_{60}F_n$ in the gas phase and the determination of the energies of addition of fluorine atoms and fluoride ions to fullerene molecules was associated with the use of transition metal fluorides. The ion–molecule equilibria in the vapours of these compounds have been studied in detail previously and, what is especially important, the energies of addition of F atoms and F^- ions to transition metal difluorides and trifluorides have been determined.[49] Therefore, these compounds served not only as good fluorinating agents in the synthesis of fluorofullerenes but also as standards in the calculation of thermochemical characteristics from the equilibrium constants of fluorine exchange.

In one experiment, manganese trifluoride was used to generate fluorinated species in the gas phase.[50] When this compound was heated as a mixture with fullerene, it was noted that in a narrow temperature range, the vapour consisted mainly of $C_{60}F_{36}$ molecules. The condensate formed on the cold parts of the ion source was subjected to mass-spectrometric analysis, which confirmed that the fullerene reaction with manganese trifluoride occurs selectively, *i.e.*, $C_{60}F_{36}$ is formed as the predominant product.[50] This finding, fortuitous in a certain sense, gave impetus to the development of a new method of solid-phase selective synthesis of fluorofullerenes accompanied by evaporation of volatile products. The last-mentioned circumstance, *i.e.*, the removal of the target products from the reaction area, is a crucial factor, because the attempts to perform a similar synthesis in a closed reactor failed. They resulted in fullerene destruction to give thermodynamically the most stable compound — tetrafluoromethane.

The subsequent studies included the search for new fluorinating agents having different fluorinating capacities, which would enable the preparation of products with fluorine contents varying over a broad range. In the study,[51] researchers' attention was focused on the fluorides of transition and rare earth metals in higher oxidation states.

All fluorination experiments were carried out in two stages. The first stage included *in situ* experiments in a mass spectrometer with continuous monitoring of gaseous reaction products. The reaction mixture consisting of thoroughly blended fullerene and fluorinating agent taken in definite mass ratios was charged to the effusion cell of the high-temperature evaporating chamber of the ion source of a mass spectrometer and heated under a high vacuum over a broad temperature range. The gaseous products of fluorination were detected as positive (electron impact) or negative (thermal ionisation) ions by the output recording unit of the mass spectrometer.

The use of this approach, which included a preliminary stage of synthesis inside the mass spectrometer, provided obvious advantages over the traditional one-step synthesis [50] carried out in a chemical reactor. First, it was possible to gain information on the product distribution as a function of time and temperature directly during the reaction. Second, the number of experiments needed to select the optimal conditions for the preparation of compounds of particular stoichiometric composition markedly diminished.

Thus it was found that fluorination of [60]fullerene by MnF_3 at 615 K gives virtually a single compound, $C_{60}F_{36}$, whereas the reaction of C_{60} with K_2PtF_6 at 730 K gives mainly $C_{60}F_{18}$.[52] In addition, experiments in the Knudsen cell require much less reactants and minimise the loss of products, which is especially important for expensive fullerenes C_n ($n > 70$) or derivatives such as bisazafullerene $(C_{59}N)_2$ (see Ref. 53).

The second stage included preparation of macroquantities of compounds in a setup representing a vacuum reactor with a cooling area for collection of volatile products. A detailed description of these experiments has been published.[54] This procedure was used to prepare gramme amounts of $C_{60}F_{36}$ and $C_{60}F_{18}$ fluorofullerenes, which were used for physicochemical investigations, in particular, for determination of the enthalpies of their formation by combustion (bomb) calorimetry.

2. Solid-phase topochemical reactions with evaporation of the volatile products $C_{60}F_{18}$ and $C_{60}F_{36}$

Heterogeneous solid-phase fluorination reactions proceed in mechanical mixtures of fullerenes with higher metal fluorides, which can give off fluorine on heating, thus being converted into fluorides with a lower oxidation state of the metal. The temperatures at which fluorofullerenes are formed (350–400 °C) are sufficiently high for these products to be removed from the reaction mixture *via* the gas phase and to condense on cooler surfaces of the reactor. Meanwhile, the temperatures are insufficient for evaporation of the reactants and decomposition products formed from metal fluorides; this allows one to avoid contamination of the resulting fluorofullerenes by the initial compounds or side products. By selecting an appropriate solid fluorinating agent (SFA) and reaction conditions, the researchers accomplished a selective process and prepared for the first time virtually pure $C_{60}F_{18}$ (see Ref. 51) and $C_{60}F_{36}$ (see Ref. 50).

It should be noted that selective solid-phase synthesis of fluorofullerenes normally gives, along with the major $C_{60}F_{2m}$ product, side products with similar chemical compositions. Thus in the case of a C_{60}–MF_n reaction mixture (M = Mn, Co) in a dynamic vacuum at temperatures of 330–380 °C, apart from $C_{60}F_{36}$ fluorofullerene formed predominantly, its close analogues $C_{60}F_{34}$ and $C_{60}F_{38}$ also pass to the gas phase.[50, 51] The contents of the side products, as shown by experiments, depend somewhat on both the degree of dispersion of the initial materials and the procedure used for mixing them, in particular, on how thorough the mixture components have been blended or on the degree of pressing. The latter circumstance is illustrated in Table 5 in relation to the reaction of C_{60} with CeF_4. The compaction of the

Table 5. Effect of the method of preparation of specimens on the product yield in the reaction of C_{60} with CeF_4 (data of mass spectrometry).[54]

Reactants	C_{60} : CeF_4 (mol : mol)	T /K	Relative intensities of ion signals		
			$C_{60}F_{34}^+$	$C_{60}F_{36}^+$	$C_{60}F_{38}^+$
CeF_4(cryst.) +	1 : 15	515	25.0	100	–
+ C_{60}(cryst.)		549	8.9	100	–
		553	18.6	100	–
		640	35.7	100	–
CeF_4(cryst.) +	1 : 36	500	7.4	100	–
+ C_{60}(cryst.)		560	7.6	100	–
		640	8.4	100	–
CeF_4(cryst.) +	1 : 18	535	26.1	100	1.3
+ C_{60}(ground)		683	32.1	100	0.7
		701	39.4	100	0.9
CeF_4(cryst.) +	1 : 18	563	8.5	100	–
+ C_{60}(ground),		613	6.5	100	–
compression,		641	12.4	100	–
100 atm		673	1.3	100	–
		708	0.1	100	–
		793	0.2	100	–

mixture under pressure decreases the content of $C_{60}F_{34}$ in the reaction products and, at a definite temperature, this allows one to attain an almost 100% yield of the major product, $C_{60}F_{36}$. The influence of the reactant ratio on the product yield is shown in Table 6, which presents the data for reactions of C_{60} with MnF_3 carried out over a broad range of initial concentrations. It can be seen from Table 5 that the dependence of the product composition on the procedure of sample preparation is rather weak and has no substantial influence on the qualitative pattern of fluorination. It is also noteworthy that the reaction rate (monitored based on the intensity of product vaporisation) remains nearly constant throughout almost the whole process (except for the initial section where the temperature approaches the specified one and for the final stage), although the composition of the reaction mixture constantly changes during fluorination because of gradual accumulation of the decomposition products of the SFA, which are lower metal fluorides (see Table 6).

Table 6. Mass spectrum of volatile products formed in the $C_{60}-MnF_3$ system at different component ratios.[55]

$C_{60}:MnF_3$ (mol : mol)	T/K	Relative intensities of ion signals		
		$C_{60}F_{34}^+$	$C_{60}F_{36}^+$	$C_{60}F_{38}^+$
1 : 1	603	11.5	100	–
	644	18.1	100	–
	664	18.9	100	–
1 : 18	572	6.6	100	8.1
	631	7.5	100	–
	648	7.3	100	–
	675	18.4	100	–
	704	37.7	100	–
1 : 36	592	1.3	100	2.9
	648	3.2	100	–
	729	13.1	100	–

Thus, the qualitative outcome of reactions, including the selectivity with respect to a particular compound or the absence of selectivity, is determined by the nature of the SFA used. It was found that the reactions of C_{60} with MnF_3, CoF_3 or CeF_4 give $C_{60}F_{36}$ as the major product.[50, 51, 54, 56] Potassium hexafluoroplatinate ensures the selective synthesis of $C_{60}F_{18}$.[52] Iron trifluoride does not react with C_{60} to give highly fluorinated derivatives, whereas TbF_4 (the strongest SFA) yields a rather broad spectrum of $C_{60}F_{2m}$ fluorofullerenes including those with the number of fluorine atoms $m > 24$ and even slight amounts of hyperfluorinated molecules ($m > 30$).[56]

In view of the constant accumulation of the SFA decomposition products, *i.e.*, lower metal fluorides, it would be reasonable to expect that the reaction rate would decrease with time; however, this is at variance with experimental results. Evidently, heterogeneous solid-phase reactions take place only in limited areas where the solid reactants are in direct contact with each other. In particular, it can be assumed that the MnF_2 formed in the area where C_{60} reacts with MnF_3 would hamper the contact between grains of the reactants. Thus, there must exist an effective mechanism to compensate for the deficiency of fluorine and to maintain a steady-state reaction course. It is rather unlikely that the gas phase plays any significant role in the transfer of fluorine from SFA to C_{60}, as the equilibrium partial pressures of both molecular and atomic fluorine above the metal fluorides used are too low at given temperatures to ensure the observed concentrations of the fluorination products, which correspond to pressures of about 0.1 Pa. Perhaps, atomic fluorine, which is rather mobile, enters the reaction area through surface diffusion. Note that the high mobility of F atoms in systems based on inorganic metal fluorides has been confirmed experimentally.[57] Finally, it was found [55] that evaporation of fluorofullerenes is not only a convenient way to accumulate the products of synthesis as a condensate but it is also a necessary condition for fluorination to take place. The attempts to obtain a fluorofullerene in the reaction between C_{60} and MnF_3 in a sealed tube kept in a furnace at 330 °C for several hours have not met with success. Mass-spectrometric analysis did not reveal any traces of fluorinated fullerene. Evidently, the presence of even microscopic amounts of these compounds between the surfaces of the reactant grains results in the cessation of fluorination.

3. Selectivity of fluorination

The question naturally arises of why the solid-phase reactions of C_{60} with SFA, unlike those with molecular fluorine, can proceed as selective fluorination to give $C_{60}F_{18}$ and $C_{60}F_{36}$ fluorofullerenes. To answer this question, a number of experiments have been conducted on fluorination of [60]fullerene by molecular fluorine with evaporation of volatile reaction products and continuous monitoring by mass spectrometry (see Fig. 7).[58] To this end, a mass-spectroscopic setup equipped by a Knudsen effusion cell and a system for the inlet of molecular fluorine was used. A [60]full-

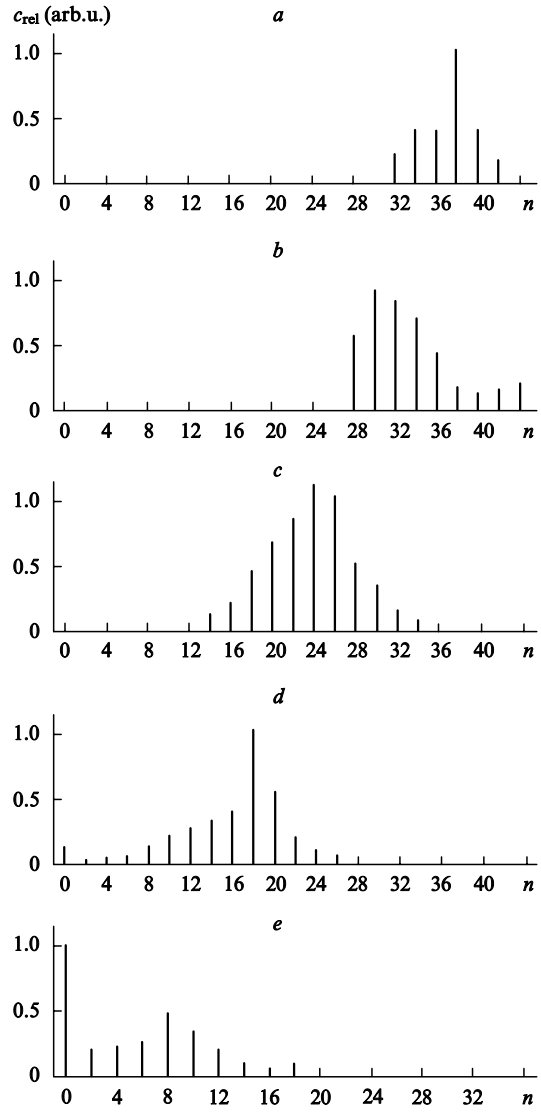


Figure 7. Composition of the gas phase *vs.* temperature for similar fluorination times and a constant fluorine flow rate in the C_{60}(solid) – F_2 system.[58]
T = 510 (*a*), 615 (*b*), 670 (*c*), 720 (*d*) and 760 K (*e*).
Here and in Figs 9 and 10, the following designations are used: c_{rel} is the relative concentration of $C_{60}F_n$, n is the number of fluorine atoms.

erene powder was placed in the cell. Fluorination was studied in the temperature range of 500–800 K with fluorine delivered to the reaction area at two flow rates which differed by an order of magnitude and created fluorine pressures of 10^{-4} and 10^{-5} atm, respectively, in an empty reactor. The volatile products of the reaction, fluorofullerenes, came out of the reactor through the effusion orifice and entered the ionisation area where they were subjected to the impact of the electron beam with an energy of 60–100 eV. The positive ions thus formed were analysed on a mass spectrometer and the results of analysis were used to determine the molecular composition of the reaction products (Fig. 7). It can be seen from Fig. 7 that the gaseous products are characterised by a broad distribution over the number of fluorine atoms: they contain almost all $C_{60}F_n$ molecules with even n values up to 44. This distribution depends on the temperature, fluorination time and the flow rate of fluorine entering the reaction area. For constant flow rates and fluorination times, raising the reaction temperature results in displacement of the distribution maximum towards smaller n values, which is illustrated in Fig. 7.

No signs of selectivity are observed in the fluorination in this case. In particular, at 615 K (which is the optimal temperature for selective solid-phase fluorination of [60]fullerene by manganese trifluoride), the electron impact mass spectrum of the $C_{60}-F_2$ system exhibits a series of peaks for $C_{60}F_{28}^+-C_{60}F_{44}^+$ with a feebly defined maximum at about $n = 30$. Conversely, in the mass spectrum of the $C_{60}-MnF_3$ system, the signal for $C_{60}F_{36}^+$ clearly stands out against the background of the closest homologues; the reaction products do not contain measurable amounts of the $C_{60}F_{32}^+$ ion or ions with lower contents of fluorine (Fig. 8).

The partial pressures of the products of fullerene fluorination in the experiments described were 0.1–1.0 Pa. The distribution of the products of direct fluorination of [60]fullerene over the number of F atoms starts to change when manganese difluoride is added to the mixture. These changes become visible in the mass spectrum when the mole fraction of manganese difluoride is ~50%. If the fluorination system contains C_{60} and 97 mol.% of MnF_2, selective formation of $C_{60}F_{18}$ can be observed at 720 K, and $C_{60}F_{36}$ is formed selectively at 615 K. This is illustrated in Figs 9 and 10.[59]

Thus, it can be concluded that direct fluorination with molecular fluorine of a mechanical mixture $C_{60}-MnF_2$ (97 mol.%) provides the possibility of selective preparation of both $C_{60}F_{18}$ and $C_{60}F_{36}$ in the gas phase. If fluorination is carried out at 615 K, the major volatile reaction product is $C_{60}F_{36}$.[59] This result coincides with the results of experiments on solid-phase fluorination of C_{60} with manganese trifluoride, which also gives predominantly $C_{60}F_{36}$. If fluorination is carried out at 720 K, the major volatile product formed is $C_{60}F_{18}$,[59] which is in line with the results of experiments on solid-phase fluorination of [60]fullerene with potassium hexafluoroplatinate (K_2PtF_6).

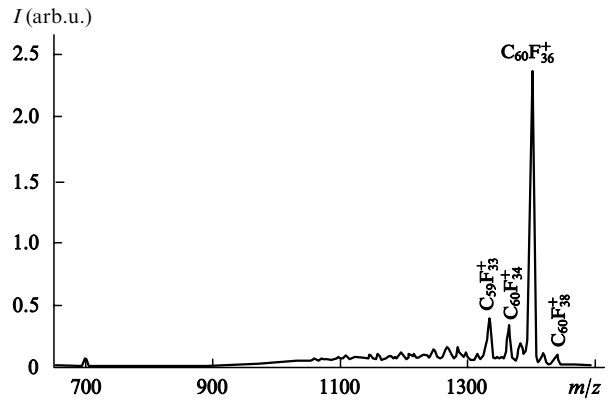


Figure 8. Electron impact mass spectrum of the volatile products of the solid-phase reaction between C_{60} fullerene and MnF_3.

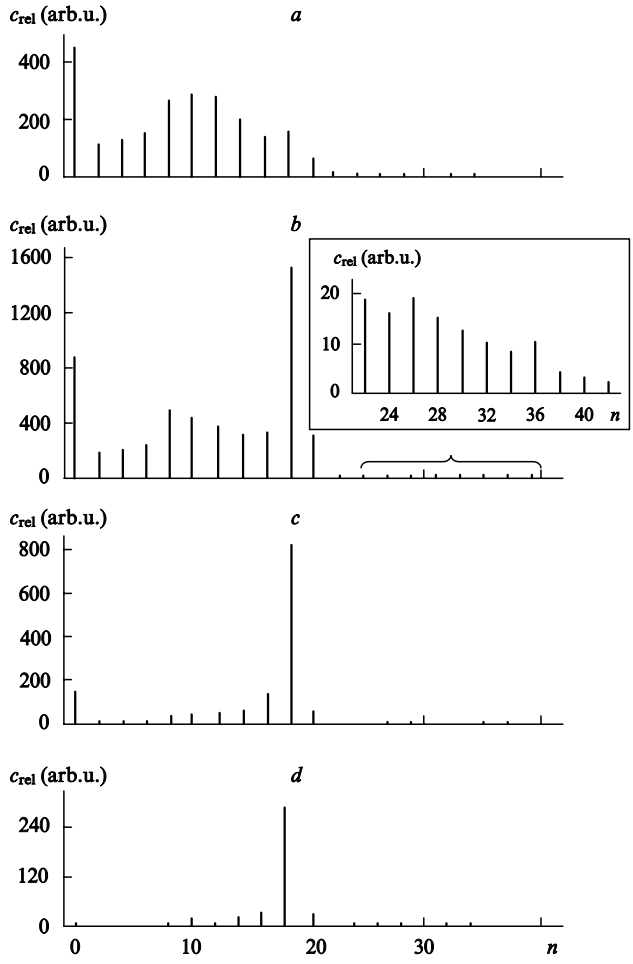


Figure 9. Composition of the gas phase after fluorination with molecular fluorine of a mixture of solid C_{60} with MnF_2 at approximately equal time intervals (2.5 h, initial stage) at $T = 720$ K.[59]
(*a*) pure C_{60}; (*b*) $C_{60}+MnF_2$ (50%); (*c*) $C_{60}+MnF_2$ (90%); (*d*) $C_{60}+MnF_2$ (97%).

At present, we have data at our disposal on the saturated vapour pressures of $C_{60}F_{18}$ and $C_{60}F_{36}$ fluorofullerenes (see Section VI), which can be used to explain the results obtained. At 720 K (see Fig. 9), the $C_{60}F_{18}$ fluoride is sublimed and fluorination stops at this stage. When the process is carried out

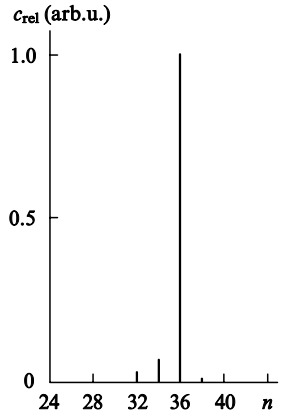


Figure 10. Composition of the volatile products of fluorination with molecular fluorine of a mixture of solid C_{60} and MnF_2 (97%) for 4.68 h at $T = 615$ K.[59]

at 615 K (see Fig. 10), the $C_{60}F_{18}$ fluoride remains in the reaction mixture and fluorination goes on up to the formation of $C_{60}F_{36}$, which is sublimed at this temperature. The formation of the same product, $C_{60}F_{36}$, in the direct fluorination of a $C_{60}-MnF_2$ mixture by molecular fluorine and in the solid-phase reaction of C_{60} with MnF_3 indicates that these two processes include a common step responsible for selectivity. Apparently, this is the transition of F atoms from the chemisorbed state to the chemically bound state in the fluorofullerene molecule. The fluorination process can be represented as a sequence of three steps: (1) surface diffusion of fluorine to the reaction area; (2) transition of the F atoms adsorbed on the surface of the lower metal fluoride to the chemically bound (C–F) state in the fluorofullerene molecule; (3) transfer of the resulting fluorinated molecules to the gas phase. In the case of heterogeneous fluorination, the first step is preceded by adsorption of molecular fluorine from the gas phase on the surface of metal fluoride.

The surface diffusion is involved both in the direct fluorination by molecular fluorine and in the solid-state synthesis. Indeed, in the former case, selectivity is attained only after fluorine has passed through the layer of manganese difluoride and occurs in the chemisorbed state. The same is true for the solid-state synthesis because MnF_3 and C_{60} are separated by a layer of manganese difluoride formed during the reaction. Note that in both cases, the deficiency of fluorine in the reaction area at the boundary between the reactants is made up by the 'flow' of fluorine over the manganese difluoride surface, and the reactions proceed at a constant rate.

In the final step, evaporation of the reaction products takes place, which prevents them from accumulating in the reaction mixture. Apparently, due to this fact and to the relatively high rate of fluorine diffusion over the difluoride surface, the observed pattern of time variation of the reaction rate is atypical of topochemical reactions, *i.e.*, the rate remains constant and shows no significant attenuation caused by accumulation of the reaction products.

The key step can be represented as the following equation:

$$C_{60}F_{2m}(\text{sol}) + 2\,F(\text{ads})\{MF_{n-1}(\text{s})\} = \quad (4)$$
$$= C_{60}F_{2m+2}(\text{sol}) + \{MF_{n-1}(\text{s})\}$$

or

$$C_{60}F_{2m}(\text{g}) + 2\,F(\text{ads})\{MF_{n-1}(\text{s})\} = \quad (5)$$
$$= C_{60}F_{2m+2}(\text{g}) + \{MF_{n-1}(\text{s})\},$$

where ads is adsorbate and s is solid, and the fullerene-containing components are either taken as solid solutions (sol) [reaction (4)] or (with allowance for the final step) occur as gases (g) [reaction (5)].

The question arises as to why this manner of fluorine transfer easily ensures predominant formation of a particular single product, whereas the use of F_2 or some other gaseous fluorinating agents affords, as a rule, mixtures of fluorofullerenes of different compositions.

A correlation is known to exist between the reaction rate and enthalpy. Highly exothermal reactions usually proceed faster. This implies that the activation energy of the reaction (E_a) decreases as the enthalpy (ΔH) becomes more negative. If a quantitative relationship between these values is established, thermodynamic characteristics of reactions, in particular, the enthalpy, can be used to estimate the relative reaction rates. Usually, a set of reactions is chosen for this purpose in which the reactants differ from one another only by the functional group involved in the reaction. (This is called a one-parameter sequence. An example is the empirical correlation established by Brønsted between the reaction rates and the strength of acids or bases that catalyse these reactions.)

The reactions (4) and (5) considered here are members of such a one-parameter sequence in which the parameter is represented by the number of fluorine atoms ($2m$) in the reacting fluorofullerene molecule. This gives grounds for using the correlation approach similar to the so-called Bell–Evans–Polanyi (BEP) model, well-known in organic chemistry.[60]

The BEP model is based on consideration of rather large numbers of reactions as processes of independent rupture and formation of chemical bonds in ensembles of isomeric molecular species which yield the same products. According to this model, the energy characteristics of reactions are described using two potential curves dependent on the same reaction coordinate. The first (descending) curve corresponds to the formation of a chemical bond between two species of the ensemble, while the second (ascending) curve describes the energy variation in the rupture of the same bond in one of the isomeric species. The point of intersection of these curves corresponds to the transition state; its y-coordinate determines the activation energy of the reaction (E_a).

The groups of reactions that obey the BEP principles are characterised by a nearly linear relationship between the activation energy and the reaction enthalpy; the latter should vary insignificantly within this group

$$E_{ai} = a + b\Delta H_i. \quad (6)$$

The proportionality factor b tends to decrease as $|\Delta H|$ increases, therefore, in comparison of two groups of reactions with markedly different enthalpies, the most pronounced dependence of E_{ai} on ΔH_i is expected for the group where the enthalpies are close to zero, because even a slight shift of ΔH_i would ensure a considerable change in the E_{ai} value. The described concept forms the basis of the Brown selectivity rule for aromatic substitution.

Figure 11 shows the possible pattern of the Evans–Polanyi curves for a pair of neighbouring homologues of fluorofullerenes ($\Delta m = 1$), each reacting with two SFA ($M^{I}F_n$ and $M^{II}F_l$) which differ appreciably in fluorinating capacity.[55] Due to this difference, if the ΔH_i^{I} values for the reactions of fluorofullerenes with the first SFA (group I) are small, their reactions with the second SFA (group II) are highly exothermal. Correspondingly, in the case of the 'weaker' $M^{I}F_n$ reagent, the a_1(I) and a_2(I) curves for the formation of bonds in fluorofullerene molecules intersect the b(I) curve for the abstraction of fluorine from SFA in the region where the slope of this curve is much greater than that in the case of the 'stronger' $M^{II}F_l$ reagent. As a consequence, the change in the activation energy for the first reaction (δE_a^{I}) is much greater than that for the second reaction (δE_a^{II}), although the enthalpy jumps ($\delta \Delta H_i^{j}$) are equal in both cases.

The relationship between the reaction rate constant and the activation energy is described by the equation

$$K = A\exp\left(\frac{E_a}{RT}\right).$$

By substituting into this expression [see Eqn (6)] the E_a values determined for two successive steps with the rate constants k and K and by taking their ratio, we obtain the key condition of selectivity

$$\frac{k}{K} = \exp\frac{b\delta\Delta H}{RT} \ll 1, \quad (7)$$

where k and K are the rate constants for the slow and fast steps, respectively, in the sequence of successive reactions. We neglected the difference between the pre-exponential factors, *i.e.*, we assumed that $A(k) = A(K)$.

Thus, if the BEP principles are applicable to solid-phase reactions of the given type, we can conclude that in the optimal case, the selective formation of a particular product requires transition from a slightly exothermal to slightly endothermal reaction to take place for the sequence member that corresponds to the fluorination of the given compound. However, this is not an obligatory condition. It is only necessary that the jump in enthalpy should ensure a sufficient change in the activation energy. Recall

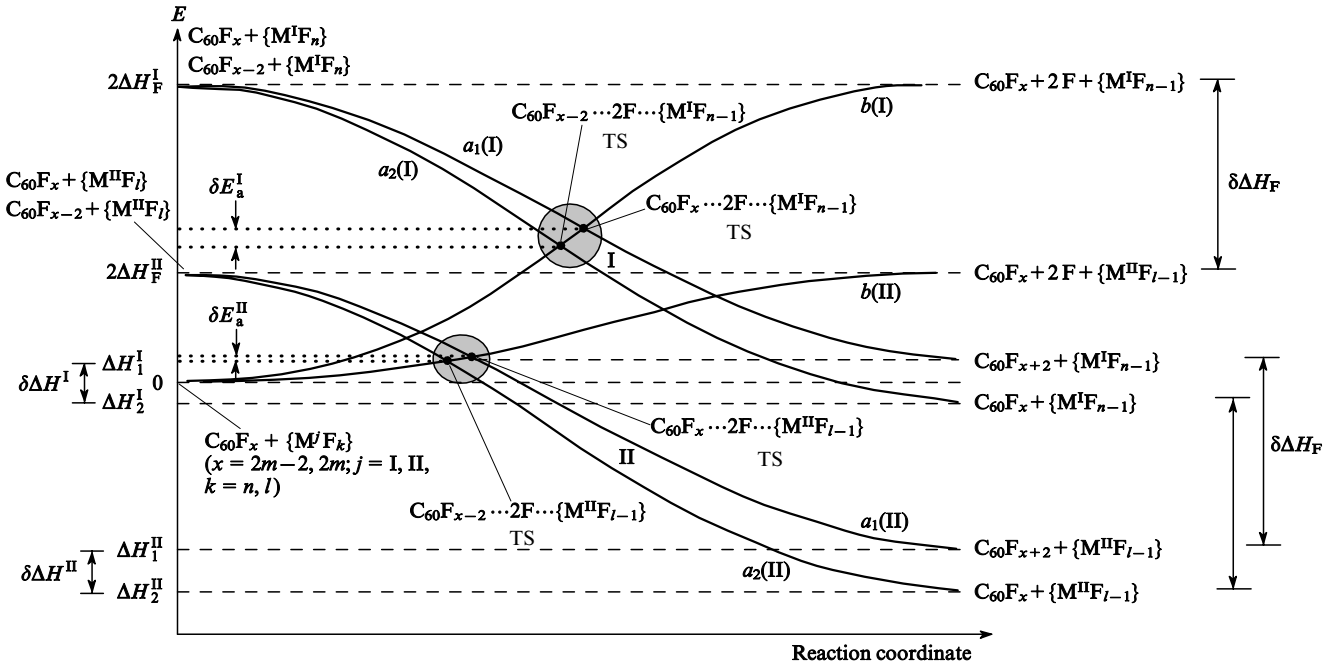


Figure 11. Evans–Polanyi curves for an elementary step of the solid-state reaction $C_{60}F_x + M^jF_k$ (TS is the transition state).[55] For explanations, see the text.

also that we are dealing with the enthalpies of reactions (4) determined by the difference between the C–F bond energies in fluorofullerene molecules and in the SFA.

A specific feature of fluorofullerenes hampering the selective synthesis of these compounds is, apparently, the fact that the reactivity with respect to fluorine changes only slightly over the $C_{60}F_{2m}$ series (m = 1–24). The difference between the energies of successive cleavage of the C–F bonds for this series is also relatively small. The success in the synthesis of individual $C_{60}F_{18}$ and $C_{60}F_{36}$ is attributable to the appearance of slow steps at m = 9 and 18 in the sequence of reactions of successive addition of fluorine atoms to [60]fullerene. These steps are due to the decrease in the exothermal effect of fluorination and the corresponding increase in the activation energies of each individual reaction.

It follows from the foregoing that, according to the approach proposed by Borcshchevsky *et al.*,[55] the energy characteristics of one elementary step of solid-phase fluorination, namely, the step of fluorine transfer from the SFA to fullerene, is the criterion for the selection of reagents for preparation of individual fluorofullerenes. As noted above, by selecting the SFA in such a way that ΔH of the step responsible for the selectivity of the whole process is close to zero, we ensure the jump in the activation energy for two consecutive reactions, needed for the selectivity, and thus trigger the whole set of transformations along the chosen pathway.

Analysis of the experimental results from the standpoint of this approach provides an explanation for the non-selective pattern of direct fluorination. The enthalpy of dissociation of the F_2 molecule is ~150 kJ mol^{-1}. The average C–F bond energies in the $C_{60}F_{48}$(g) and $C_{60}F_{36}$(g) molecules are 287.5 and 295 kJ mol^{-1}, respectively.[47,48] This allows one to calculate the average C–F bond energy for the addition of 12 fluorine atoms to the $C_{60}F_{36}$ molecule, which equals 265 kJ mol^{-1} (see Section VI.3.b). On the basis of these data, the jump in the C–F bond energy on passing from n < 36 to n > 36 in the series of $C_{60}F_n$ is estimated as 30 kJ mol^{-1}. These values imply that the direct fluorination by molecular fluorine is a highly exothermal reaction. As compared with the enthalpy of this reaction, the difference between the enthalpies of two successive steps involving $C_{60}F_{34}$ and $C_{60}F_{36}$ (30 kJ mol^{-1}) is too small, and, hence, the change in the sign of ΔH is by no means expected. However, when MnF_2 is added, the crystals of [60]fullerene become mainly isolated from direct contact with gaseous fluorine. As a consequence, the vast majority of fluorine atoms get into the reaction area (near the contact between C_{60} and MnF_2 grains) through surface diffusion over the crystals of manganese difluoride on which they are adsorbed. This reproduces the conditions inherent in the solid-phase fluorination by manganese trifluoride, and, hence, the selectivity is ensured. If the enthalpy of fluorine desorption is taken to be equal to the enthalpy of the reaction $MnF_3(s) = MnF_2(s) + F(g)$ (244 kJ mol^{-1}),[61] the exothermal effect of the reaction of [60]fullerene with the fluorine attached to the surface of manganese difluoride sharply decreases, giving rise to conditions under which the difference between the properties of individual representatives of the $C_{60}F_{2m}$ series becomes observable. In particular, slow steps appear and the key condition of selectivity holds [see Eqn (7)].

Yet another important feature of solid-phase fluorination with evaporation of volatile products is that the reaction takes place in the fullerene–SFA contact area without accumulation of products in the solid phase. In this case, in the sequence of fluorination processes, sublimation proceeds as a side reaction having a lower order and independent of the fluorine concentration. As a result, fulfillment of the key condition of selectivity [see Eqn (7)] does not suffice for the preparation of the target product, and additional conditions taking into account the ratios between the rates of fluorination and the rates of sublimation of fluorination products need to be satisfied. This has been reported in more detail.[55]

4. Preparation of the $C_{60}F_{48}$ fluorofullerene

The reaction of [60]fullerene with molecular fluorine proceeds even at room temperature; the products are normally mixtures of highly fluorinated $C_{60}F_n$ compounds (n = 36–48). Gakh *et al.*[62] passed a stream of molecular fluorine above a mixture of C_{60} fullerene with NaF at 250 °C and, after 20 h, they obtained a product, which was extracted with $CFCl_3$, dried, and treated again with an F_2 stream for 30 h at 275 °C with the addition of a fresh portion of NaF. After extraction and drying, the sample composition was estimated by mass-spectrometric analysis. The content of $C_{60}F_{48}$ was ~70%. The NMR spectrum of this compound was recorded, which exhibited eight equal-intensity lines.

Table 7. Experimental data on fluorination of [60]fullerene with molecular fluorine.[63]

Regime	T /°C	t /h	Element composition (C : F)	I_{rel} (%) (see [a])		
				$C_{60}F_{44}^+$	$C_{60}F_{46}^+$	$C_{60}F_{48}^+$
Static	315	2.3	$60:(44\pm1)$[b]	41	100	22
	315	10		19	91	100
Quasi-	313	2.5		82	100	63
static	315	5.5	$60:(48\pm1)$[b]	13	33	100
	315	10.5	$60:(48\pm1)$[b]	–	5	100
			$60:(46\pm2)$[c]			
Dynamic	315	10.5	$60:(49\pm1)$[b]	5	51	100
(flow)	350	2	$60:(48.0\pm0.5)$[b]	–	16	100
	345	3		–	5	100

[a] The relative intensity of the ion signal in the mass spectrum. [b] Elemental analysis data. [c] ESCA data.

Somewhat later, one-step synthesis of $C_{60}F_{48}$ was performed.[63] In order to find the optimal conditions for fluorination, a number of experiments have been carried out with variation of the conditions, duration and temperature of the reaction of C_{60} fullerene with molecular fluorine. Series of specimens were synthesised in three regimes, namely, static, quasi-static and dynamic ones (Table 7). In the static regime, C_{60} fullerene powder was kept at a temperature of 315 °C and at a fluorine pressure of 50–300 Torr in a closed cell for 2.3 and 10 h. Under these conditions, the highest degree of fluorination, estimated conventionally as the ratio of the intensity of the signal of the $C_{60}F_{48}^+$ ion to the total intensity of ion signals in the mass spectrum, was 63%. The quasi-static reaction conditions, embodied as the periodical renewal of fluorine portions in the reactor at 315 °C, resulted in a higher degree of fluorination of fullerene (68%). In the dynamic regime of fluorination where a fluorine flow (1 atm) was passed at 315 °C over powdered C_{60} fullerene at a constant rate, the proportion of $C_{60}F_{48}$ in the resulting mixture of fluorofullerenes increased with an increase in the reaction time. As a result, fluorination for 10.5 h at 315 °C yielded a sample, whose elemental analysis corresponded to the ratio C : F ≈ 60 : 48 (see Table 7). The mass spectrum of this product contains only $C_{60}F_{48}^+$ and $C_{60}F_{46}^+$ molecular ions, the other peaks correspond to fragment ions (Fig. 12).

Meanwhile, at these high temperatures, the loss of fluorofullerenes due to destruction induced by fluorine becomes noticeable. This is indicated by analysis of a sample of the gas phase taken directly from the reaction area. According to mass-spectrometry data, CF_4 and C_nF_{2n+2} perfluorocarbons ($n = 2-4$) were the major combustion products.

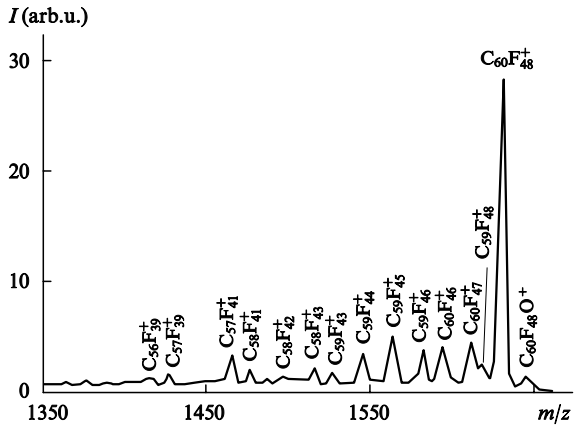


Figure 12. Electron impact mass spectrum (70 eV) of $C_{60}F_{48}$ vapour (I is the ion current intensity).[63]

5. 'Hyperfluorination' of C_{60} fullerene

The interest in $C_{60}F_{60}$ perfluorofullerene, in which the double bonds have been fully utilised for the addition of fluorine was triggered by the publication in 1991 of a study by Kroto and coworkers,[64] who suggested that the perfluorinated fullerene can prove to be an analogue of Teflon and possess unique properties (for example, it could be suitable as a lubricant). Theoretical calculations[45] showed that this molecule can, in principle, exist; however, its structure should be distorted due to steric crowding. Moreover, the formation of structures with cleavage of several C–C bonds and arrangement of fluorine atoms inside the fullerene carbon cage has been suggested.

The phenomenon of fullerene 'hyperfluorination' was discovered in a study of the fluorination products obtained under more rigorous conditions such as UV irradiation of a mixture of C_{60} with molecular fluorine,[65] or the use of powerful fluorinating oxidants (KrF_2).[66] These experiments were aimed at the attainment of the highest degree of fluorination and, finally, preparation of the perfluorinated fullerene ($C_{60}F_{60}$).

Later, the formation of [60]fullerene hyperfluorides was observed in the reaction of C_{60} with terbium tetrafluoride.[56] In the reaction of [60]fullerene with terbium tetrafluoride, when a temperature of 350 °C has been attained, an explosion-like blow-out of the reaction mixture from the hot zone of the reactor takes place, and the fluorination products are found to contain $C_{60}F_n$ ($n > 60$) fluorides. This reaction carried out below 350 °C also gives fluorofullerenes but no hyperfluorinated species are detected in the mass spectrum of the products. Apparently, in the explosion mode, the C–C bonds of the fullerene carbon skeleton are partially cleaved and excess fluorine atoms are added. Although this has not been confirmed by structural experiments due to the too small content of these species in the synthesised samples. Neverheless, as noted above, species corresponding to $C_{60}F_n$ hyperfluorides ($n > 60$) were still detected in the mass-spectrometric investigation of the products obtained in the reaction of C_{60} with KrF_2[66] or TbF_4[56] (Fig. 13).

It is notable that these structures are not destroyed under the action of high temperatures (300 °C) or electron impact ionisation (70 eV), although the content of these species is relatively low and equals 0.01%–0.10% relative to the content of major components, $C_{60}F_{42}$–$C_{60}F_{46}$. Analysis of the mass spectra shows that hyperfluoride molecules undergo more extensive fragmentation than $C_{60}F_n$ molecules with lower contents of fluorine ($n < 48$); the intensity of signals corresponding to fragment ions formed upon abstraction of the CF_3 group reaches 50%–60%, whereas for species containing less than 48 fluorine atoms fragmentation is insignificant under the same ionisation conditions and equals 5%–10%. This suggests that further progress in the study of fullerene hyperfluorides would depend on the choice of investigation techniques. In particular, 'mild' methods of ionisation such as electrospray and field desorption may prove rather promising. Note that the use of laser ionisation (which is a harsher method than electron impact), even in the matrix isolation variant, did not show the presence of any hyperfluorides in the mass spectra of the same specimens.

The phenomenon of hyperfluorination is still to be studied, in particular, in the context of possible applications of these compounds. Thus it is necessary to develop methods of analysis and techniques for the synthesis of macroquantities of fullerene hyperfluorides in the condensed phase. Nevertheless, even at the current stage, one can understand the fundamental significance of this type of transformation in which 'windows' with sizes exceeding those of five- or six-membered rings are formed with retention of the basic cage as a whole. Hypothetically, these 'windows' could be used to insert atoms and molecules into the fullerene cavity, which would result finally in the preparation of endohedral compounds of a new type.

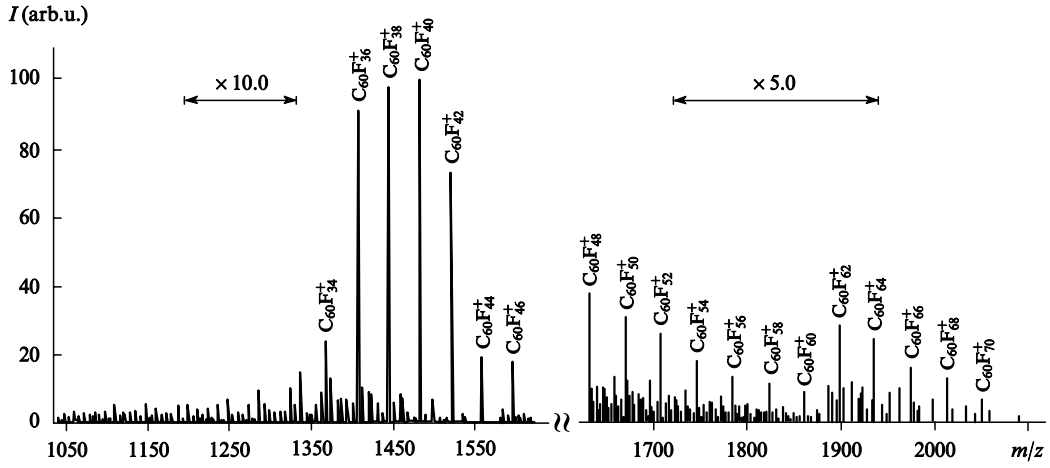


Figure 13. Electron impact mass spectrum of the products of fluorination of C_{60} fullerene with terbium tetrafluoride (T = 350 °C).[56] The left-hand and right-hand parts of the spectra are given with different magnifications.

6. Fluorination of C_{70} and higher fullerenes

Functionalisation of higher fullerenes has scarcely been studied. Only several works have been reported dealing with the preparation of hydrides of a number of higher fullerenes.[67] In experiments on hydrogenation of C_{76} and C_{84} fullerenes, it was found that 40–50 hydrogen atoms can add to the former molecule and 54 hydrogen atoms can be attached to the latter one.[68] Heating of these compounds in an effusion cell entails thermal degradation of hydrides of higher fullerenes. This is accompanied by not only partial loss of the hydrogen atoms but also destruction of the carbon cage itself to give C_{60} and C_{70} hydrides containing 36 and 38–40 hydrogen atoms, respectively.[69]

The theoretical studies dealing with functionalisation of higher fullerenes have not progressed significantly either. Higher fullerenes are characterised by a lower symmetry than C_{60}, and large numbers of isomers are possible for them, which greatly complicates the calculations.

Experiments on fluorination of higher fullerenes have been reported.[70] It was found that, as in the case of [60]fullerene, reactions with transition metal fluorides proceed selectively, the 'magic numbers' of the fluorine atoms added being different for different fullerenes. Fluorination of C_{84} on treatment with K_2PtF_6, which is a milder fluorinating agent, gives mainly $C_{84}F_{40}$, while C_{76} adds only 26 fluorine atoms. Surprisingly, the reaction of C_{70} fullerene with K_2PtF_6 does not yield fluorinated products at all, no matter how the experimental conditions (temperature, composition of the reaction mixture) are varied. The $C_{70}F_{36}$–$C_{70}F_{40}$ fluorofullerenes can be readily obtained by the reaction of C_{70} with MnF_3, while the fluorinating capacity of K_2PtF_6 does not suffice for the formation of these products. Apparently, due to specific features of the structure of the C_{70} molecule, the first step of fluorination gives $C_{70}F_{36}$–$C_{70}F_{40}$, while a stable intermediate structure similar to $C_{60}F_{18}$ simply does not exist.

In the case of higher fullerenes C_{76} and C_{84}, both reactions proceed to give similar degrees of fluorination, although the products prepared on treatment with MnF_3 contained slight amounts of more extensively fluorinated compounds, which, in principle, corresponds to the difference between the fluorinating capacities of these reagents.

Thus, the stability regions for functionalisation of higher fullerenes have been established:[70] for $C_{84}F_m$ and $C_{76}F_m$, the m values are 40 and 26, respectively. The results are presented in Table 8 and in Fig. 14. Detailed reviews of the studies on direct fluorination of fullerenes by molecular fluorine [71] and transition metal fluorides [54] have been published.

Table 8. Fluorination products of higher fullerenes.[70]

Fullerene	Fluorinating agent	T/K	m_{max} in $C_{2n}F_m$	Major products
C_{70}	K_2PtF_6	670	–	–
	MnF_3	660	40	$C_{70}F_{38}$
	F_2	590	56	$C_{70}F_{54}$
C_{76}	K_2PtF_6	711	30	$C_{76}F_{26}$
	MnF_3	660	30	$C_{76}F_{26}$
C_{78}	MnF_3	660	36	$C_{78}F_{32}$–$C_{78}F_{36}$
	F_2	590	54	$C_{78}F_{54}$
C_{84}	K_2PtF_6	711	40	$C_{84}F_{40}$
	MnF_3	660	44	$C_{84}F_{40}$
	F_2	590	62	$C_{84}F_{56}$, $C_{84}F_{58}$, $C_{84}F_{60}$

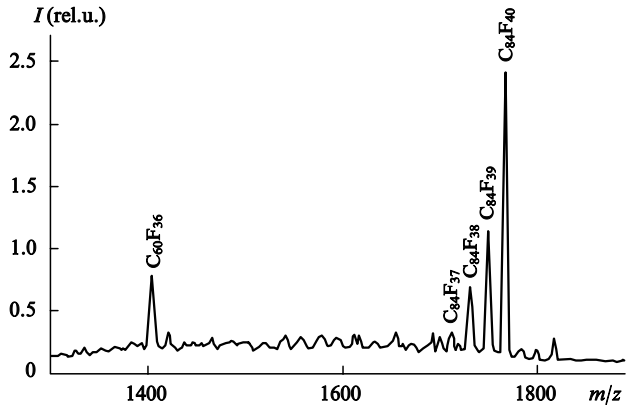


Figure 14. Electron impact mass spectrum of the product of fluorination of C_{84} fullerene.[70]

IV. The use of HPLC for the separation of fluorofullerenes

Chromatography is used successfully to separate the product mixtures resulting from the synthesis of fullerenes in a discharge arc followed by extraction with organic solvents from soot in the Sohxlet apparatus.[3] The use of chromatography for the separation of endohedral metallofullerenes [72] and numerous exohedral derivatives [73] is documented. Nevertheless, this method was considered to be inapplicable to mixtures of fluorinated fullerenes

because their properties are virtually identical. The attempts to separate mixtures of highly fluorinated fullerenes by fractional sublimation were unsuccessful.[74] Experiments on sublimation of fluorofullerene mixtures have shown that the sublimate becomes depleted in more extensively fluorinated components compared to the initial specimen, apparently, due to their predominant thermal degradation, but separation of the mixture into individual components does not take place.

The first publication on the use of HPLC for the separation of fluorofullerenes, devoted to the preparation of $C_{60}F_{18}$ in a pure state, appeared in 1996.[52] Since $C_{60}F_{18}$ is much more polar than the unreacted C_{60} or the side product impurities present in the specimen after the synthesis, the retention times of these compounds were found to be markedly different. This stipulated the successful use of chromatography for the isolation of the pure product. For key fluorofullerenes, a correlation has been established between the number of fluorine atoms in the molecule and the retention time: the higher the degree of fluorination, the shorter the retention time ($C_{60}F_{18} > C_{60}F_{36} > C_{60}F_{48}$). However, the compound $C_{60}F_2$ is eluted far ahead of the $C_{60}F_{18}$ fluoride, which is due to the high polarity of the latter.

Subsequently, it was shown [75] that HPLC is suitable for the separation of not only compounds with substantially different compositions and molecular structures but also fluorofullerenes with rather similar structures, for example, two $C_{60}F_{36}$ isomers. An even more vivid example should be mentioned, namely, the isolation and spectroscopic characterisation (IR spectroscopy, mass spectrometry and, in some cases, NMR spectroscopy) of 49 isomers of C_{70} fluorides.[76] In the two last-mentioned cases, the composition of the eluent had to be changed stepwise during the separation, ranging from pure toluene through toluene–hexane mixtures of various compositions to pure hexane. Thus, in the early stages, the most polar fractions with long retention times were separated and, after that, fractions with short retention times were subjected to separation in mixed eluents.

In addition to the $C_{60}F_{36}$ and $C_{70}F_{2m}$ isomers mentioned above, a series of low-fluorinated oxides of C_{60} fullerene were isolated from a sample synthesised by the reaction of C_{60} with potassium hexafluoroplatinate.[77] Note that according to mass-spectra, the fluorination products did not contain any noticeable amounts of fluorofullerene oxides, while the corresponding $C_{60}F_2$, $C_{60}F_4$, $C_{60}F_6$ and $C_{60}F_8$ fluorides were present in concentrations of the order of several percent of the concentration of the major component, $C_{60}F_{18}$. Nevertheless, the cycles of chromatographic purification and separation into fractions gave the $C_{60}F_4O$, $C_{60}F_6O$ and $C_{60}F_8O$ oxyfluorides in amounts sufficient for spectroscopic characterisation. Presumably, these oxyfluorides were not formed during the synthesis but appeared as a result of interaction of the corresponding fluorides with traces of water, present inevitably in the solvents used in chromatographic experiments. Thus, the above examples of using HPLC for the separation and purification of some fullerenes convincingly demonstrate that virtually any mixtures of fluorinated fullerenes can be separated by chromatography into individual compounds. However, when performing these works, special precautions are required because even traces of water present in the solvent can destroy fluorofullerenes.

V. Characterisation of the structure of fluorofullerenes by NMR spectroscopy and X-ray diffraction analysis

The most interesting feature of fullerenes is that they combine the properties of dienes and aromatic compounds. This can be clearly seen upon comparison of the C–C bond lengths in benzene (1.40 Å), butadiene (1.35 and 1.47 Å for the double and single bonds, respectively)[78] and [60]fullerene in which the distances between the carbon atoms at double and single bonds are 1.40 and 1.46 Å, respectively.[79] It is clear that the addition of functional groups to the fullerene double bonds giving rise to isolated aromatic rings, diene chains, or isolated double bonds on the carbon sphere changes the π-electron system of the molecule. These aspects were discussed back in 1991–1993,[80,81] when the first fullerene derivatives were prepared and characterised. Naturally, the mutual arrangement of functional groups on the carbon cage depends on their size. It is known that the addition of several bulky functional groups results in adducts with a uniform distribution of these groups over the carbon sphere. For example, in the hexaadduct of [60]fullerene with diethyl malonate, the functional groups are symmetrically distributed over the surface of the sphere.[82] This gives rise to eight aromatic rings, which contribute to the stabilisation of the molecular system formed. A large number of other cycloaddition products have been described. The most frequently encountered situation is the formation of a bridging bond with addends at the 6–6 bond between two neighbouring hexagonal rings. A large variety of products is observed in the synthesis of fullerene derivatives with small functional groups or halogen or hydrogen atoms. Oxygen derivatives of fullerene can contain not more than three O atoms; therefore, they are not of special interest.

Two fundamental problems are to be solved in considering polyaddition reactions to fullerene double bonds. The first one is to elucidate the pathway along which the carbon sphere is covered successively by X atoms added in pairs and to understand the factors that dictate this pathway. The other task concerns the determination of the most preferable geometric isomers of the many thousands of isomers theoretically possible. Below, we present the numbers of theoretically possible positional isomers for the addition of X atoms to [60]fullerene.[83]

n in $C_{60}X_n$	The number of isomers	n in $C_{60}X_n$	The number of isomers
2	23	10	628 330 629
4	4 190	12	11 661 527 055
6	418 470	20	34 932 048 763 560
8	21 330 558	30	985 538 239 868 528

It can be seen that even for $n = 8$, the number of possible $C_{60}X_8$ isomers is an astronomical value which is beyond the potential of theoretical calculations. Therefore, various approaches are used to restrict the number of probable structures. It is clear that much fewer isomers can really be synthesised. The researchers need to find out what factors favour stabilisation of particular structures and also to elucidate the cases where either kinetic or thermodynamic factors play crucial role.

It may seem that the C_{60}–hydrogen system is the most natural model system for these studies. Indeed, several hydrides of [60]fullerene have been described: $C_{60}H_2$, $C_{60}H_4$ and $C_{60}H_6$; the molecular structure of $C_{60}H_{18}$ has been determined; the compound $C_{60}H_{36}$ has been obtained in macroscopic quantities.[68] However, the structural characterisation of hydrides is far from being complete due to the low stability of these species in solutions. In particular, the isomeric composition of $C_{60}H_{36}$, which is prepared most easily, is still unknown. No successful X-ray diffraction studies have been carried out for this class of compound.

The number of fullerene halides characterised to date increases in the series: $C_{60}I_x$, $C_{60}Cl_x$, $C_{60}Br_x$, $C_{60}F_x$. Whereas for iodinated derivatives, only the formation of an unstable molecular complex $C_{60}\cdot I_2$ has been described,[84] the chloride $C_{60}Cl_6$ has been fully characterised,[85] and unconfirmed data on the existence of $C_{60}Cl_{24}$ and $C_{60}Cl_{40}$ have been reported.[86,87] Three bromofullerenes are known, $C_{60}Br_6$, $C_{60}Br_8$ and $C_{60}Br_{24}$; for each of them, X-ray diffraction data have been reported.[88,89] The C_{60}–fluorine system clearly stands out in this series of halogenated derivatives. First, the existence of the whole series of $C_{60}F_{2x}$ fluorofullerenes, from $C_{60}F_2$ to $C_{60}F_{60}$ has been proven experimentally.[53] Second, the three most stable compounds,

$C_{60}F_{18}$, $C_{60}F_{36}$ and $C_{60}F_{48}$, have been obtained in macroscopic amounts and their structures have been determined. Third, the chemical structures of a series of fluorofullerenes with low fluorine contents, including $C_{60}F_2$, have been determined. Thus fluorinated fullerenes can serve as a 'training ground' for working-out the main approaches to the preparation of fullerene derivatives with small functional groups. First of all, this is associated with the fact that, due to the exceptional strength of the C–F bond, fluorofullerenes are stable in air, rather thermally stable and can be subjected to virtually any type of physicochemical investigations. The good solubility of these compounds in many organic solvents has played an important role in the development of methods for chromatographic separation of fluorofullerenes according to the number of added groups or into individual geometric isomers. After the first successful experiments on chromatographic isolation of individual $C_{60}F_{18}$ fluoride and separation of the two major isomers of $C_{60}F_{36}$, it became clear that it is possible to prepare pure products of C_{60} fluorination over a broad range of fluorine contents. Although not all fluorinated fullerenes have been isolated and characterised, the spectroscopic and X-ray diffraction data concerning their structures make it possible to establish some important features of successive addition of fluorine atoms to the fullerene double bonds.

1. [60]Fullerene difluoride

The difluoride of [60]fullerene and difluorides of higher fullerenes have been detected [13, 39] during mass-spectrometric analysis of fluorofullerene vapours (the results of experiments on determination of the electron affinity and the C–F bond energies of these molecules are described in Section II). However, it was not until the year 2000 that [60]fullerene difluoride was prepared in macroscopic amounts.[90] The ^{19}F NMR spectrum of the $C_{60}F_2$ fluorofullerene exhibits a singlet at 148.3 ppm. The 1,2- and 1,4-isomers have been considered as possible alternatives, because, according to theoretical calculations, they are much more stable than the other formally conceivable isomers and also because of the fact that the first fluorine atom added polarises most of all the nearest region of the π-system of the molecule.[90] The 1,2-isomer of $C_{60}F_2$ is more stable than the 1,4-isomer, as the latter contains a double bond in a five-membered ring, which destabilises the compound. This compound is formed only with relatively large substituents. For example, methylation of [60]fullerene gives a mixture of 1,2- and 1,4-methyl derivatives, whereas benzylation results in the formation of the 1,4-benzyl derivative.[91] Since the fluorine atom is smaller than the carbon atom, there are no pre-requisites for the formation of the 1,4-derivative.

The position of the peak in the ^{19}F NMR spectrum of $C_{60}F_2$ fluorofullerene is more consistent with the 1,2-isomer rather than with the 1,4-isomer. In the latter compound, each sp^3-hybridised carbon atom bearing a fluorine atom is surrounded by three sp^2-hybridised carbon atoms, whereas in the 1,2-isomer, only by two sp^2 carbon atoms. Therefore, in the case of the 1,4-isomer, it would be reasonable to expect a peak in the region of 120–130 ppm.

Additional information on the structure of $C_{60}F_2$ was gained from its ^{13}C NMR spectrum. The 1,4-isomer of $C_{60}F_2$ (C_s symmetry) should account for $27 \times 2C + 4 \times 1C = 31$ lines in the spectral region corresponding to sp^2 atoms, while the 1,2-isomer (C_{2v} symmetry) should give rise to $3 \times 2C + 13 \times 4C = 16$ lines. The spectrum of the $C_{60}F_2$ fluorofullerene displays less than 28 peaks. This confirms once again that the 1,2-isomer of $C_{60}F_2$ was isolated.

2. Oxyfluoride $C_{60}F_4O$

The ^{19}F NMR spectrum of the $C_{60}F_4O$ oxyfluoride consists of two lines of equal intensity. The structure proposed for this compound [77] is presented in Fig. 15 *a*. As can be seen from the Figure, the fluorine atoms added occur in positions 1, 2, 3 and 4, and the oxygen atom is, apparently, attached to the carbon atoms of the 6–5 bond, *i.e.*, this compound is an intramolecular ether.

3. Oxyfluoride $C_{60}F_6O$

The ^{19}F NMR spectrum of $C_{60}F_6O$ reported by Boltalina *et al.*[77] consists of six lines of equal intensity. The positions of lines lead to the conclusion that the fluorine atoms in $C_{60}F_6O$ fall into two groups, one comprising two F atoms and one comprising four F atoms. The chemical shifts of the first-group fluorine atoms are much smaller. This suggests that they are attached to the same carbon atoms as oxygen. In addition, two fluorine atoms of the second group are characterised by similar chemical shifts, which may attest to their similar positions with respect to the oxygen bridge. On the basis of these data, a structure was proposed for this compound (Fig. 15 *b*).

4. Oxyfluoride $C_{60}F_8O$

The ^{19}F NMR spectrum of $C_{60}F_8O$ consists of four lines of equal intensity.[77] It was concluded that the $C_{60}F_8O$ molecule has, most probably, C_s symmetry. A structure consistent with these conditions was proposed (Fig. 15 *c*).

5. Fluorofullerene $C_{60}F_{16}$

The ^{19}F NMR spectrum of $C_{60}F_{16}$ fluorofullerene consists of eight lines of equal intensity.[92] The fluorine atoms attached to the carbon atoms that are surrounded by three sp^3-hybridised C atoms are responsible, in most cases, for a signal at about −150 to −160 ppm. The $C_{60}F_{16}$ molecule contains two fluorine atoms of this type (B). The signals of fluorine atoms attached to the carbon atoms whose environment comprises one sp^3 and two sp^2 carbon atoms are usually displayed in the region of −120 to −130 ppm. Two pairs of these fluorine atoms (A and H) are present in the $C_{60}F_{16}$ molecule. The positions of other fluorine atoms were established using 2D COSY ^{19}F NMR spectra. On the basis of the results obtained, a structure for $C_{60}F_{16}$ was proposed

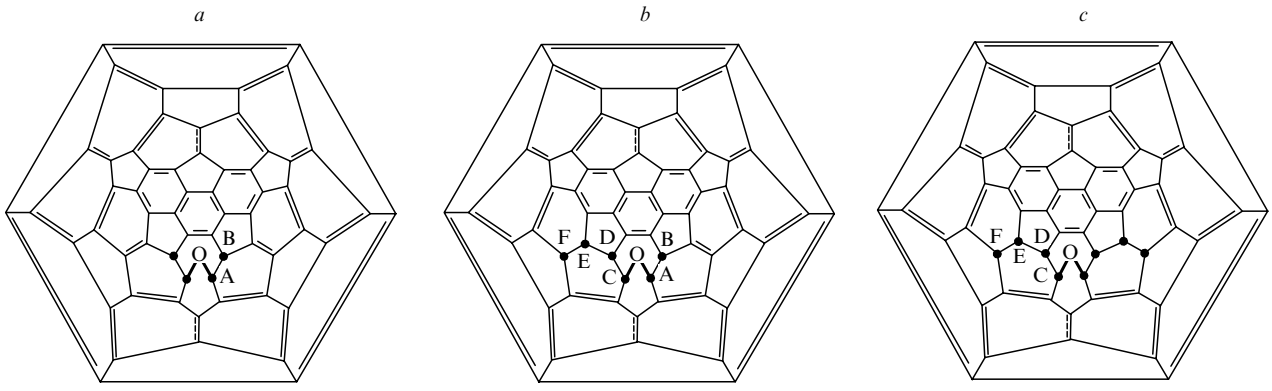


Figure 15. Schlegel diagrams of $C_{60}F_4O$ (*a*), $C_{60}F_6O$ (*b*) and $C_{60}F_8O$ (*c*).[77] The dark circles show the positions of fluorine atoms.

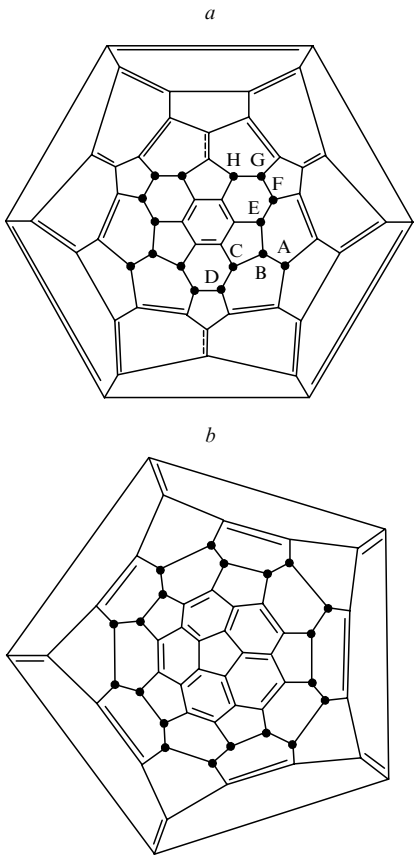


Figure 16. Schlegel diagrams of $C_{60}F_{16}$ (*a*)[92] and $C_{60}F_{20}$ (*b*)[93]. The dark circles show the positions of fluorine atoms.

(Fig. 16 *a*). Researchers were able to prove convincingly that this structure differs from the structure established for the $C_{60}F_{18}$ fluorofullerene (see below) only by the absence of the two fluorine atoms attached to the 6–6 bond.

6. Fluorofullerene $C_{60}F_{20}$

The ^{19}F NMR spectrum of $C_{60}F_{20}$ fluorofullerene contains only one line at −138.8 ppm (see Ref. 93). The structure proposed in the study cited is shown in Fig. 16 *b*. A specific feature of the structure is that all 20 fluorine atoms are arranged along the equator, while the poles are occupied by five-membered rings surrounded by five six-membered aromatic rings. This molecule, the carbon cage of which is 'squashed' along a fivefold axis and is surrounded by an annulus made of fluorine atoms along the equator, has been called 'saturnene.'

7. Compounds $C_{60}F_{18}$ and $C_{60}F_{18}O$

These two compounds are remarkable due to the fact that single crystals suitable for X-ray diffraction analysis were grown for them and the full set of interatomic distances was obtained. Therefore, we shall discuss these compounds in more detail.

The ^{19}F NMR spectrum of $C_{60}F_{18}$ fluorofullerene (376.14 MHz, $CDCl_3$) was first recorded in 1996.[52] The spectrum consists of four lines with $\delta = -131.6$ (d); −136.0 (dd); −143.4 (d) and −158.1 ppm (dt) with an intensity ratio of 1 : 2 : 2 : 1 (Fig. 17).

Of all kinds of structures, the isomer with C_{3v} symmetry complies best with this spectrum; the Schlegel diagram for this molecule is presented in Fig. 18. This structure was confirmed by ^{13}C NMR spectroscopy. As can be seen from Fig. 18, all the fluorine atoms are located in one hemisphere. The six-membered ring consisting of sp^2-hybridised carbon atoms is entirely surrounded by the sp^3-hybridised carbon atoms that bear fluorine atoms.

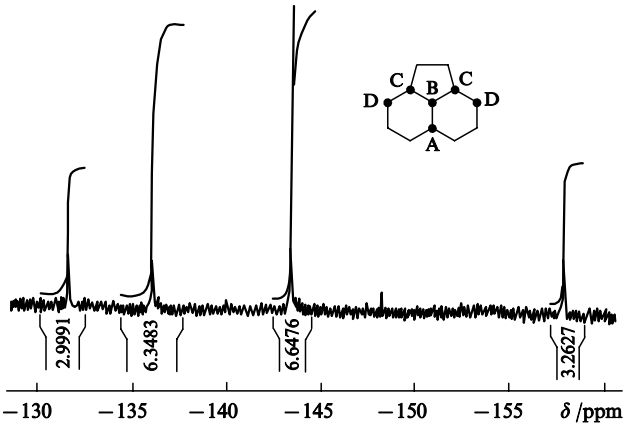


Figure 17. ^{19}F NMR spectrum of $C_{60}F_{18}$ fluorofullerene.[52]

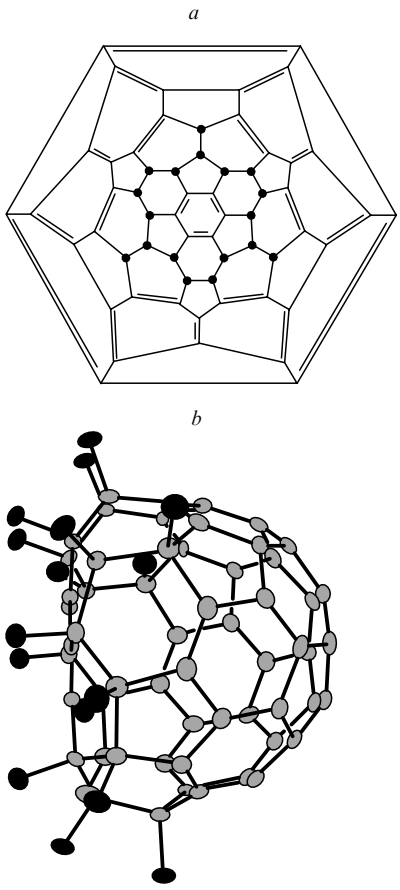


Figure 18. Schlegel diagram (*a*) and the structure (*b*) of the $C_{60}F_{18}$ molecule.[95] The dark circles show the positions of fluorine atoms.

The $C_{60}F_{18}O$ oxyfluoride was first isolated by HPLC in 1998 as a side product of the reaction between C_{60} fullerene and K_2PtF_6; the ^{19}F NMR spectrum of this compound was recorded.[94] The fluorine atoms are arranged in the same way as in the $C_{60}F_{18}$ molecule. Elucidation of the position of oxygen appears to be a key point because the character of the C–O bond in this compound is of prime importance for the understanding of the structure of other fullerene oxyfluorides. If oxygen is incorporated either along or across the plane of symmetry (three options), the ^{19}F NMR spectrum should consist of ten lines, $8 \times 2F$ and $2 \times 1F$. For other variants of oxygen addition, the number of lines

in the spectrum should increase to eighteen due to the loss of symmetry. Analysis of the ^{19}F NMR spectrum (10 lines) and 2D COSY ^{19}F NMR spectrum showed that this isomer has C_s symmetry. The positions of three peaks are characteristic, namely, at −94.60 (K), −161.27 (B) and −168.81 ppm (G). The peak of atoms K occurs in the spectral region typical of fluorine atoms located in the close vicinity of the oxygen atom. The positions of peaks of atoms B and G are similar to the peaks in the spectra of fullerene fluorides for the fluorine atoms attached to carbon atoms surrounded by three sp^3-hybridised C atoms.

The structure of $C_{60}F_{18}O$ will have C_s symmetry in the case where oxygen adds either at the cleaved 6−5 bond forming an ether bridge (to the fullerene cage) or at the 6−6 bond to give an epoxide. In one publication,[94] preference was given to the epoxide structure on the basis of NMR data. In 2000, we succeeded in growing single crystals and performing full X-ray diffraction analysis of the molecular complexes of $C_{60}F_{18}$ and $C_{60}F_{18}O$ with toluene and the complexes of $C_{60}F_{18}$ with *m*- and *p*-xylenes. These were the first crystallographic data for fluorinated fullerenes.[95–97] The resulting structures of the $C_{60}F_{18}$ and $C_{60}F_{18}O$ molecules are presented in Fig. 19. First of all, note that $C_{60}F_{18}O$ is an ether in which the ether bridge is located in place of the 6−5 bond (see Fig. 19 *a*). The oxygen atom is inserted into the weakest (longest) C−C bond to give the so-called intra-ether derivative. This is the first structure of this type among fullerene compounds. Relying on the results obtained for $C_{60}F_{18}O$,[95] structures with ether bridges were ascribed to all oxyfluorides considered. The X-ray diffraction analysis of molecular complexes formed by $C_{60}F_{18}$ confirmed the NMR data pointing to the location of the 18 fluorine atoms on one half of the carbon sphere. Moreover, it was shown that this accumulation of fluorine around one six-membered ring results in a substantial change in the C−C bond lengths, in particular, the bond lengths in this six-membered fragment become equal, and it becomes a fully aromatic (benzene-like) ring. Global changes in the fluorinated hemisphere itself have also been noted: in particular, the curvature radius of the benzene-like fragment substantially increases, the fragment is flattened, whereas the second half not occupied by fluorine largely retains its size and shape, as in the initial fullerene molecule.[95–97] The carbon cage of this molecule has been termed 'flattened'.

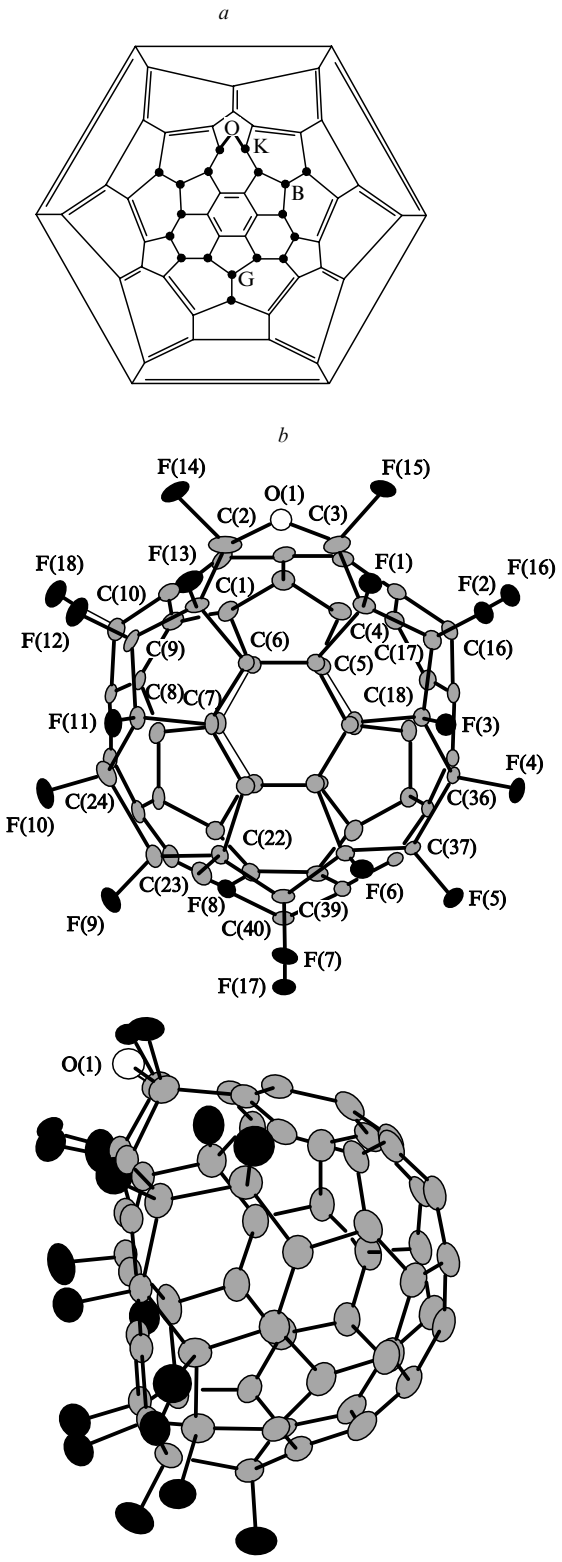


Figure 19. Schlegel diagram (*a*) and the structure (*b*, two projections are given) of the $C_{60}F_{18}O$ molecule.[95] The dark circles show the positions of fluorine atoms.

8. Fluorofullerene $C_{60}F_{36}$

The first fullerene derivative, obtained in 1991,[68] was the $C_{60}H_{36}$ hydride. Since then, attempts at determining the structure of this compound were repeatedly undertaken; however, no apparent progress was made. A large number of theoretical studies have been devoted to calculations of the molecular structure of $C_{60}X_{36}$ (X = H, F). The isomer with *T* symmetry containing four isolated benzene-like rings was found to be the most stable.[98]

It was natural to suggest that the products of hydrogenation and fluorination of [60]fullerene ($C_{60}H_x$ and $C_{60}F_x$) would be isostructural at identical *x*. An important factor is the similarity of steric effects; the fluorine and hydrogen atoms are smaller than the carbon atom, and similar radical mechanisms have been suggested for both reactions.

Initially, it was found that the first stages of both fluorination and hydrogenation give compounds with 18 addends, which are characterised by a highly symmetric structure (C_{3v} symmetry), and the X atoms are arranged on the carbon cage like a crown framing a six-membered ring.[52]

The second stage of both hydrogenation and fluorination is the formation of the $C_{60}X_{36}$ structure. In the fluorination of C_{60} on treatment with MnF_3, $C_{60}F_{36}$ is the major product.

Nevertheless, the ^{19}F NMR spectrum of the resulting material displayed up to 30 lines; this can indicate either low symmetry of the $C_{60}X_{36}$ molecule or the presence of a mixture of positional isomers.

After purification of the sample by sublimation, the number of lines decreased to 12, and analysis of the 2D COSY spectrum pointed to the presence of several positional isomers. It was assumed that one isomer responsible for only three lines with equal intensity had *T* symmetry. Chromatography gave two major fractions exhibiting virtually identical mass spectra. The ^{19}F NMR spectrum of the first fraction that had a shorter retention time contained 12 equally intense lines. Theoretical

analysis indicated that this spectrum could correspond to a structure with C_3 symmetry.

The ^{19}F NMR spectrum of the second fraction exhibited only three lines with an intensity ratio of 1 : 1 : 1, as was to be expected for a structure with T symmetry. However, three isomers with D_{3d} symmetry also comply theoretically with the observed spectrum. The final decision in favour of the T structure was based on the ^{13}C NMR spectrum of the second fraction, which contained two equally intense lines at 136.6 and 137.5 ppm (the region corresponding to sp^2-hybridised carbon atoms). Meanwhile, the D_{3d} isomers would require the presence of three lines with a 1 : 1 : 2 intensity ratio. The Schlegel diagram for the $C_{60}F_{36}$ fluorofullerene with T symmetry [75] is shown in Fig. 20 *a*.

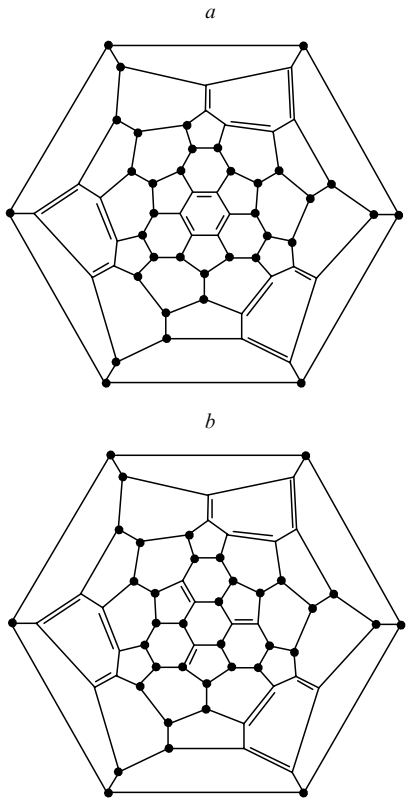


Figure 20. Schlegel diagrams of T (*a*)[75] and C_3 isomers (*b*)[100] of $C_{60}F_{36}$ fluorofullerene.
The dark circles show the positions of fluorine atoms.

The isomer with C_3 symmetry was suggested initially to contain three benzene-like rings of the four rings present in the T isomer and three isolated double bonds of the 6–6 type.[99] This conclusion was based on kinetic reasoning according to which pairs of fluorine atoms are added successively to 6–6 double bonds; therefore, the double bonds of the same type remaining in the molecule should not change positions. Boltalina *et al.*[99] have found evidence for this assumptions in a study of $C_{60}F_{36}$ by 2D COSY ^{19}F NMR spectroscopy. However, according to the data of quantum-chemical calculations, the proposed isomer was markedly less stable than the isomer with T symmetry. Conversely, a recent NMR study of the C_3 isomer of $C_{60}F_{36}$ attests in favour of a structure that also contains three benzene-like rings and three isolated double bonds but the latter occupy 6–5 positions.[100] The Schlegel diagram of this isomer is shown in Fig. 20 *b*. According to theoretical calculations, it is comparable in stability with the isomer having T symmetry, which suggests thermodynamic control in the formation of $C_{60}F_{36}$. This might imply the possibility of rearrangements of fluorine atoms on the carbon cage during fluorination.

9. Fluorofullerene $C_{60}F_{48}$

The first experimental data on the structure of $C_{60}F_{48}$ were obtained by Gakh *et al.*[62] Later, these data were confirmed using more pure specimens.[101] The ^{19}F NMR spectrum of the $C_{60}F_{48}$ fluorofullerene was found to display eight equally intense lines corresponding to eight nonequivalent fluorine atoms. According to theoretical data, this spectrum is consistent with nine possible structures, namely, five enantiomer pairs with D_3 symmetry and four S_6 isomers. The Schlegel diagrams for the $C_{60}F_{48}$ molecule with D_3 symmetry [62] and for the molecule with S_6 symmetry, which are the most stable according to calculations,[102] are shown in Fig. 21.

It should be noted that analysis of 2D COSY spectra recorded in the study cited [62] showed the presence of 1,2-interactions (A–E, A–G, B–F, B–G, C–H, D–F, D–H, E–F), which corresponded to the theoretical structure with D_3 symmetry; however, of the set of predicted 1,3-interactions (A–B, A–D, A–F, B–C, B–D, B–E, C–D, D–E, E–G, F–G, F–H), only the first, the second, the fourth and the seventh ones were detected. Later,[101] a 2D COSY spectrum was recorded pointing to the existence of the A–F, D–E, E–G and F–G interactions. This confirms the D_3 structure proposed by Gakh *et al.*,[62] but does not rule out the molecule with S_6 symmetry. The final decision concerning the structure of this fluorofullerene was based on the results of X-ray diffraction analysis of a $C_{60}F_{48}$ single crystal grown from a mesitylene solution,[103] which showed that the reaction of C_{60}

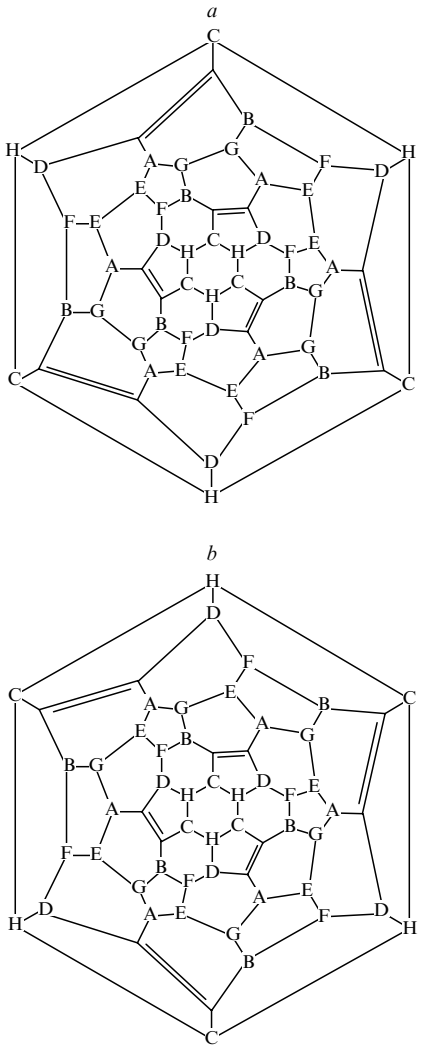


Figure 21. Schlegel diagrams of D_3 (*a*) and S_6 isomers (*b*) of $C_{60}F_{48}$ fluorofullerene.[62]

with gaseous fluorine gives comparable amounts of both isomers. Note that the carbon cage regions near the double bonds in these molecules are characterised by a slight negative curvature; therefore, they are called 'indented'. It is remarkable that of the many millions of $C_{60}F_{48}$ isomers possible theoretically, the reaction with gaseous fluorine gives only two isomers. According to the results of MNDO [104] and AM1 [105] semiempirical calculations, these molecules are thermodynamically much more stable than the other possible isomers with exohedral addition of fluorine atoms. Our calculations by the density functional method predict that the isomer with D_3 symmetry is 15 kJ mol^{-1} more stable than that with S_6 symmetry. Note that according to AM1 calculations,[105] an isomer in which six fluorine atoms are attached to the inside of the carbon cage is expected to be even more stable. However, the formation of such a compound should be kinetically hampered, and no experimental data confirming its existence have been obtained.

Thus, the amount of experimental data accumulated to date is sufficient for evaluating its correspondence to the theoretical descriptions of such systems. The good coincidence of the theoretical estimates for the thermodynamically stable $C_{60}F_{48}$ isomers with the experimental data on the enthalpies of formation and the molecular structures of the isomers having S_6 and D_3 symmetry can be taken as the starting point.

The NMR spectra of solid samples usually do not provide enough information to draw conclusions about the molecular structure of the compound, due to the strong interactions between the nuclei in the solid. The fine spectral structure is observed rather rarely in these cases. Nevertheless, having prepared reasonable (> 1 g) amounts of the $C_{60}F_{48}$ fluorofullerene, Boltalina *et al.*[101] attempted to study the crystalline specimen by ^{19}F NMR spectroscopy.

The high-resolution MAS ^{19}F NMR spectrum of crystalline $C_{60}F_{48}$ recorded at 340 K consists of eight principal lines with equal intensity (Fig. 22) corresponding to eight non-equivalent fluorine atoms attached to positions A – H in the $C_{60}F_{48}$ molecule (see Fig. 21). Note that the chemical shifts in the ^{19}F NMR spectrum recorded in solution virtually coincide with those for the solid specimen, indicating the absence of an appreciable influence of the solvent. Apart from the eight principal lines, the spectrum contains four groups of low-intensity lines (10% of the total intensity), which refer apparently to $C_{60}F_{2n}$ ($2n < 48$) impurities or to $C_{60}F_{48}$ with a different symmetry.

The data on the molecular structures of compounds $C_{60}F_4O$, $C_{60}F_6O$, $C_{60}F_8O$, $C_{60}F_{16}$, $C_{60}F_{18}$ and $C_{60}F_{20}$ derived from NMR spectra and presented as Schlegel diagrams (see Figs 15, 16, 18), allow one to consider the possible mechanism of successive addition of small functional groups to C_{60} fullerene. After addition of the first two fluorine atoms, the localised double bonds in the two conjugated six-membered rings that have lost the common double bond and contain two sp^3 carbon atoms become the reaction centres of choice. Further addition of atoms is directed at these particular bonds and partial or complete aromatisation of the six-membered rings which have retained three double bonds takes place at certain degrees of saturation. Yet another specific feature of the mechanism of fullerene fluorination is that fluorine atoms are able to migrate over the surface of the carbon cage. This results in the formation of thermodynamically the most stable isomers. As a consequence, each subsequent fluorofullerene in the series $C_{60}F_{18}$, $C_{60}F_{36}$, $C_{60}F_{48}$ does not contain the substructure of the preceding one, *i.e.*, it cannot be prepared from the preceding isomer by mere addition of more fluorine atoms. These aspects have been considered in detail.[106]

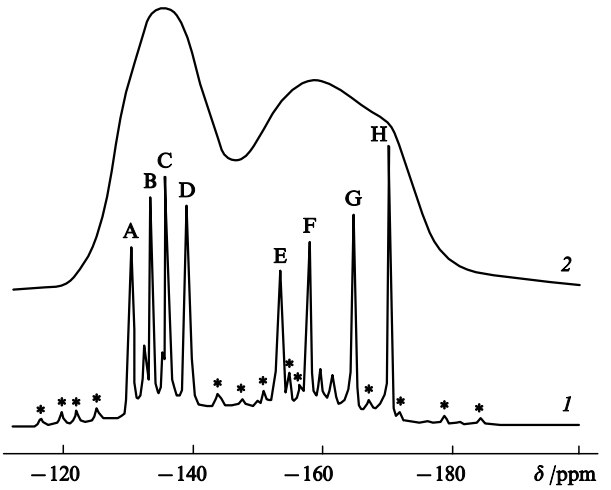


Figure 22. High-resolution MAS ^{19}F NMR spectrum of crystalline $C_{60}F_{48}$.[101]
(*1*) MAS/Ω = 4050 Hz; (*2*) Ω = 0 Hz.
The asterisks show the satellites caused by rotation.

To date, only three compounds of the $C_{60}F_{2n}$ series have been synthesised in macroscopic quantities and comprehensively characterised. These are $C_{60}F_{48}$, $C_{60}F_{36}$ (two isomers with T and C_3 symmetry) and $C_{60}F_{18}$. The stability of two isomers of $C_{60}F_{36}$ and $C_{60}F_{18}$ is due to delocalisation of π-electrons in six-membered rings, *i.e.*, to the formation of aromatic substructures. In addition, one hemisphere of the carbon cage of the $C_{60}F_{18}$ fluorofullerene inherits the π-system of [60]fullerene. However, the existence of the C_3 isomer of the $C_{60}F_{36}$ fluorofullerene indicates that in the presence of 36 attached fluorine atoms, steric factors, namely, deformation of the carbon cage upon transition of some carbon atoms to the sp^3 state and repulsion of substituents, already play an important role. The bond angles typical of both sp^3- and sp^2-hybridised carbon atoms cannot be attained simultaneously for all of the atoms due to geometric restrictions, which results in a rather strained structure. In addition, the proximity of the fluorine atoms (in fluorofullerene molecules, especially in $C_{60}F_{48}$, the distances between neighbouring fluorine atoms are often several tenths of an angstrom smaller than twice the van der Waals radius of fluorine [103]) leads to their repulsion and, as a consequence, weaken the σ-bonds in the carbon cage; in some cases, these bonds become 1.63 – 1.67 Å long. Stabilisation of the carbon cage could, apparently, be expected for a more uniform distribution of the carbon – carbon double bonds, although this results in separation of the bonds from one another and, hence, a decrease in the π – π conjugation. This might account for the formation of an isomer with C_3 symmetry with three isolated carbon – carbon double bonds, apart from the T isomer in which all double bonds are combined in benzene-like aromatic rings. In the case of $C_{60}F_{48}$ fluorofullerene, the steric factor predominates. Note that the remaining six double bonds are practically difficult to access and attempts at further fluorination under more drastic conditions lead to the partial destruction of the carbon cage. It is of interest that according to some theoretical calculations,[105] stabilisation of fullerene fluorides containing ~48 fluorine atoms could be attained by repudiating the convexity of the carbon cage, assuming that some fluorine atoms are attached on the inside. In this type of structure containing both *exo*- and *endo*-fluorine atoms, the bond angle could be more consistent with hybridisation states of the carbon atoms, *i.e.*, strain relaxation in the carbon cage could take place. At present, it is difficult to verify this hypothesis because the pathway to these isomers should face, in any case, substantial kinetic impediments.

Full sets of structural parameters have been obtained only for the $C_{60}F_{18}$, $C_{60}F_{48}$, $C_{60}F_{18}O$ and $C_{60}F_{17}CF_3$ fluorinated fullerenes, which crystallise as molecular complexes with various aromatic compounds. The study of $C_{60}F_{36}$ fluorofullerene is appreciably hampered by two factors. These are, first, rotation of molecules and, second, the presence of structural isomers. For other fluorofullerenes, the task is reduced to the preparation of compounds in macroscopic quantities sufficient for growing single crystals. Studies along this line are in progress.

VI. Thermodynamic properties

1. Heat capacity and orientational phase transitions

Low-temperature heat capacities of $C_{60}F_{48}$ and $C_{60}F_{36}$ were determined in 1999 [107] (no other data have appeared thereafter). The heat capacity was measured in a fully automated vacuum adiabatic calorimeter described in the literature.[108, 109]

The temperature dependence of the heat capacity of $C_{60}F_{48}$ (Fig. 23) exhibits a thermal anomaly represented by a reversible order–disorder phase transition in the temperature range of 315–345 K. To establish the nature of the anomaly, the substance was studied by NMR spectroscopy and powder X-ray diffraction analysis.[107] According to calorimetric measurements,[107] NMR spectroscopy and X-ray diffraction data, the $C_{60}F_{48}$ fluorofullerene undergoes a reversible non-isothermal phase transition 'ordered crystal II → plastic crystal I' accompanied by rearrangement of the body-centered tetragonal (BCT) crystal structure into a face-centred cubic (FCC) structure.[110] The phase transition temperature in $C_{60}F_{48}$ was taken to be 329.6 ± 0.4 K. At this temperature, the apparent heat capacity is a maximum. The thermodynamic parameters of the 'order–disorder' transitions for $C_{60}F_{48}$ fluorofullerene and C_{60} fullerene [111] are listed in Table 9. The enthalpies of the transitions ($\Delta_{trs}H^\circ$) were determined by calorimetry [108] on the basis of the total amount of energy required for the phase transition. The $\Delta_{trs}H^\circ$ value is lower for $C_{60}F_{48}$ fluorofullerene than for C_{60} fullerene. The resulting temperature dependences of the heat capacities, enthalpy, and entropy of phase transitions were used to calculate the thermodynamic functions at 298.15 K [112] (see Table 9).

It can be seen from Fig. 24 that the temperature dependence of the heat capacity of $C_{60}F_{36}$ plotted using the data of adiabatic calorimetry displays no anomalies in the range of 8–356 K. A phase transition was discovered by differential scanning calorimetry (DSC) at a higher temperature, namely, at 370 K.[113] The high-temperature phase of $C_{60}F_{36}$ existing at $T > 370$ K has a FCC lattice, which passes to a simple cubic (SC) lattice as the temperature decreases.[114] According to NMR and powder X-ray diffraction data, this is also an orientational transition. The orientational transitions discovered in fluorofullerenes are similar to the well-known phase transition in [60]fullerene. The molecules of C_{60} are known to form a FCC lattice at temperatures $T > 260$ K and an SC lattice at $T < 260$ K.[115] It was found that at 260 K, a first-order phase transition takes place caused by transformation of a high-temperature orientationally ordered phase into a low-temperature orientationally ordered one. As this takes place, the centres of gravity of the molecules virtually do not shift, and the C_{60} molecules assume a quite definite orientation, thus changing the translational symmetry of the crystal. A specific feature of the orientational phase transition is that the C_{60} molecules execute re-orientations, fast on the ^{13}C NMR time scale ($\nu \approx 10^{-13}$ s^{-1}). At high temperatures ($T > 260$ K), these are chaotic isotropic re-orientations, while at $T < 260$ K, correlated group re-orientations take place.[115]

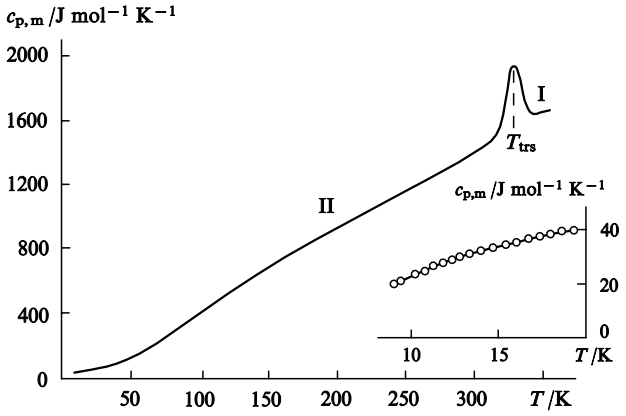


Figure 23. Temperature dependence of the heat capacity of $C_{60}F_{48}$ fluorofullerene.
Here and in the inset in Fig. 24, the initial pattern of the dependence is shown.

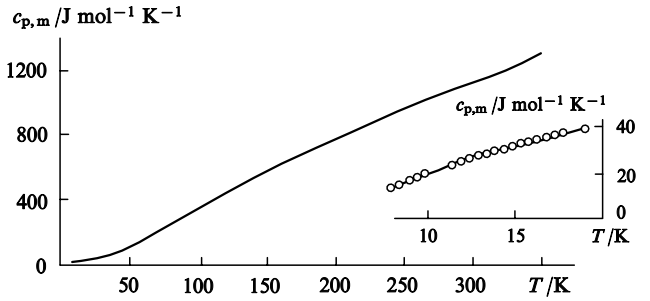


Figure 24. Temperature dependence of the heat capacity of $C_{60}F_{36}$ fluorofullerene.

Table 9. Thermodynamic parameters of 'order–disorder' phase transitions for $C_{60}F_{36}$, $C_{60}F_{48}$ and C_{60} and absolute entropies and entropies of formation of these fluorofullerenes at 298.15 K.

Parameter	Compound		
	C_{60}	$C_{60}F_{48}$	$C_{60}F_{36}$
$\Delta_{trs}T$ /K	185–275	315–345	
T_{trs} /K	260.7	329.6 ± 0.4	370
$\Delta_{trs}H^\circ$ /kJ mol^{-1}	7.46 ± 0.15	7.0 ± 0.7	
$\Delta_{trs}H^\circ$ /J g^{-1}	10.4 ± 0.2	4.8 ± 0.4	
$\Delta_{trs}S^\circ$ /J mol^{-1} K^{-1}	28.6 ± 0.6	21.2 ± 2.4	
S°_m /J mol^{-1} K^{-1}	426.5	1137.2 ± 6	1014.5 ± 5
$\Delta_f S^\circ_m$ /J mol^{-1} K^{-1}	84.5	-4071.6 ± 6	-2978.2 ± 5

Note. ΔT_{trs}, T_{trs}, $\Delta_{trs}H^\circ$ and $\Delta_{trs}S^\circ$ are the temperature range, the temperature, and the enthalpy and entropy of the phase transition, respectively; S°_m and $\Delta_f S^\circ_m$ are the absolute entropy and the entropy of formation of fluorofullerene, respectively.

During calorimetric measurements of the characteristics of the orientational phase transition (enthalpy and temperature) in a C_{60} fullerene crystal, an interesting feature was discovered: after mechanical grinding in a mortar, the temperature and the enthalpy of phase transition of the C_{60} specimen decreased down to the complete disappearance of the maximum in the temperature dependence of heat capacity, the fullerene crystallinity being retained.[116–119] Meanwhile, the NMR study of the temperature dependence of the spin–lattice relaxation time of ^{13}C nuclei showed that at 260 K, this value changes jumpwise for both the initial and ground C_{60} specimens, although the jump is less pronounced in the latter case.[119, 120] These results were interpreted [121] in the following way. The spatial defects that originated upon the mechanical treatment of a [60]fullerene specimen break the crystalline phase of C_{60} into a great number of regions in which the orientational ordering of the C_{60} molecules occurs independently. In other words, local transitions take place instead of a collective effect throughout the whole phase (specimen). Finally, the orientational phase transition in a calorimetric experiment becomes smeared, but the low-temperature phase is still formed (as indicated by the step in the temperature dependence of the spin–lattice relaxation time of ^{13}C nuclei). It should also be noted that the presence of impurities (solvent molecules) barely influences the parameters of the orientational phase transition,[118] but it

does influence the ^{13}C spin – lattice relaxation time, although only in the high-temperature phase,[120] in which the C_{60} molecules execute orientationally disordered motion.

The influence of an increase in the rate of crystallisation (from solutions) or vacuum sublimation is similar to mechanical grinding: both processes increase the degree of defectiveness of crystals, which results in smearing of the orientational phase transition. Unfortunately, no theoretical description of these phenomena is available to date. The works that can be regarded as the latest achievements along this line include the development of theoretical approaches to the description of the orientational phase transition in the C_{60} crystal, namely, the model of thermal behaviour of a thermoelastic medium with internal orientation based on the Landau theory and the model of anisotropic reorientations of the C_{60} molecules for the description of the spin – lattice relaxation time.[122, 123]

The characteristic features of phase transformations in $C_{60}F_{36}$ or $C_{60}F_{48}$ fluorofullerenes, which are molecular crystals, are probably similar to those in crystalline C_{60} fullerene. In any case, mechanical grinding of both C_{60} and $C_{60}F_{36}$ and $C_{60}F_{48}$ specimens brings about the same effect, namely, disappearance of the phase transitions from the temperature dependences of heat capacity.[113] No data on the heat capacity of $C_{60}F_{18}$ fluorofullerene have been obtained yet, although works along this line are in progress. Apparently, the presence of a dipole moment in $C_{60}F_{18}$ would also influence the heat capacity curves and would stipulate substantial differences between the behaviours of $C_{60}F_{18}$, on the one hand, and $C_{60}F_{36}$ or $C_{60}F_{48}$, on the other hand, during heating. The heat capacities of higher and endohedral fullerenes have not yet been determined.

2. Enthalpy of sublimation

a. Fullerenes C_{60}, C_{70}, C_{78} and C_{84}

After crystalline [60]fullerene had been obtained in macroscopic quantities at the end of 1990,[2] vigorous studies into the physicochemical properties of this compound were started. Later, studies of higher fullerenes also began (as these compounds have been isolated in a pure state). As soon as 1991, it was found [124] that C_{60} fullerene is sublimed *in vacuo* (1 Pa) without decomposition even at temperatures of about $\sim$1000 K. This result is a sort of sensation if one recalls that graphite is sublimed at this pressure at temperatures of about 3000 K. Thus, there appeared the possibility of producing pure carbon in the gas phase at temperatures of $\sim$1000 K. Later, this property of fullerene has been used in diamond synthesis from the gas phase.[125]

The high thermal stability of fullerenes and the possibility of transferring them to the gas phase allowed determination of the characteristics of their free molecules. The electron affinity and ionisation energy of C_{60}, the electron capture and light absorption energies, and cross-sections of various chemical reactions of fullerenes have been determined. For these measurements and for film deposition experiments or growth of single crystals from the vapour phase, data on the saturated vapour pressure of fullerene are needed. The saturated vapour pressure and the enthalpy of sublimation have been measured repeatedly (see, for example, the review [126]). Virtually all measurements were carried out by the Knudsen effusion method implemented either in the classical version or with mass-spectrometric analysis of the vaporisation products. Since the experiments were carried out by research groups from different countries (Germany, India, Italy, Russia, Slovenia, and the USA), naturally, some scatter of the results can be noted.

Analysis of the data on the saturated vapour pressure of fullerene shows that the scatter in the obtained values goes far beyond the inaccuracy inherent in the effusion method. At present, the reasons for the substantial discrepancies are more or less clear. First, this is the quality of specimens. Preparation of sufficiently pure and thoroughly characterised specimens is a fairly difficult task. The second, more specific reason for the discrepancies is related to the fact that fullerene represents a metastable phase and transition to more stable phases (amorphous carbon) might take place, and this transition can often be catalysed by an impurity or the surface of the container. Finally, the most significant point responsible for the differences between the data on the saturated vapour pressure is the fact that experiments were carried out in different temperature regimes. Elevated temperatures required for the generation of measurable saturated vapour pressures accelerate the thermal degradation of fullerenes, giving rise to noticeable amounts of the amorphous carbon phase. The accumulation of this non-volatile form results in underestimated saturated vapour pressures. This destruction of fullerene is markedly facilitated by an organic solvent contained in fullerene specimens. However, it has been reported [127] that fullerene specimens containing no solvent also undergo this transformation but to a substantially lesser extent. It was shown that the time of storage has a more pronounced influence on the degree of conversion than temperature.[127] This, apparently, accounts for the fact that the non-fullerene carbon forms are sometimes present even in the initial specimens not subjected to high temperatures.[128]

The effusion experiments on fullerene sublimation were normally carried out after prolonged many-hour storage of specimens at 400 – 500 K in a dynamic vacuum. Under these conditions, the solvent should have been completely removed. However, it is still retained in the samples in concentrations of 0.01% – 1.0% and occurs in the adsorbed state in closed space dislocations.[121] These minor amounts of the solvent barely influence the weight loss of the specimen but they accelerate the transformation of fullerene into non-fullerene carbon. As a consequence, the saturated vapour pressure decreases in the course of measurements, giving rise to substantial scatter of the thermodynamic data obtained. As noted above, the destruction rate depends on many factors but the presence of solvents is normally the most significant among them. The saturated vapour pressures for the number of fullerenes recommended in a study by Markov *et al.*[126] are shown in the logarithmic form in Fig. 25, and the parameters of the corresponding equations are given in Table 10. It can be seen that the enthalpy of sublimation increases rather smoothly with an increase in the size of the fullerene molecule, *i.e.*, heavier fullerenes are less volatile. Apparently, this trend should be retained throughout the whole series of higher fullerenes. At present, more precise determination of the saturated vapour pressures of C_{76} (see Refs 129, 130) and C_{84} (see Ref. 128, 131) using repeatedly sublimed samples and the study of the sublimation of other higher fullerenes as they are prepared in macroscopic quantities remain topical tasks. Indirect experimental data attest that endohedral metallofullerenes exhibit lower volatilities than the corresponding hollow fullerenes. However, no quantitative data have been obtained so far.

In conclusion, we would like to mention the problem of interpretation of thermodynamic data obtained for higher full-

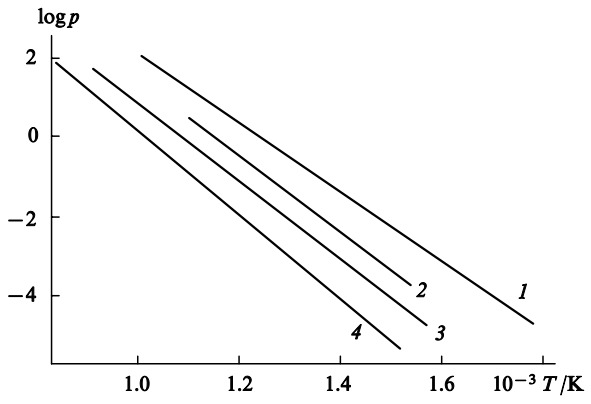


Figure 25. Logarithmic dependence of the saturated vapour pressure of fullerenes C_{60} (*1*), C_{70} (*2*), C_{76} (*3*) and C_{84} (*4*) on temperature.[126]

Table 10. Equations for the temperature dependence of the saturated vapour pressure and recommended values for the sublimation enthalpy.[126]

Fullerene	Temperature range	$\log p = -BT^{-1} + A$ [a]		T/K (see [b])	$\Delta_{sub}H^{\circ}_{T}$ /kJ mol^{-1}
		B/K	A		
C_{60}	560 – 990	8738 ± 472	10.85 ± 0.76	750	167 ± 9
C_{70}	650 – 904	9768 ± 774	11.23 ± 1.49	773	187 ± 15
C_{76}	637 – 1069	10027 ± 253	10.94 ± 0.33	831	192 ± 6
C_{84}	658 – 1190	10760 ± 267	10.92 ± 0.29	899	206 ± 5

[a] The pressure in this equation (p) is expressed in Pascals. [b] The temperature to which the $\Delta_{sub}H^{\circ}_{T}$ value should be referred.

erenes, which is related to the existence of various geometric isomers. For fullerenes containing 78 or more carbon atoms, two or more isomers which obey the rules of isolated pentagons have been obtained;[132] however, thermodynamic measurements were carried out only for isomer mixtures. Quantum-mechanical estimates show that the difference between the energies of stable isomers, for example of C_{84} fullerene, can reach 100 – 120 kJ mol^{-1} (see Ref. 133). Hence, the enthalpies of sublimation of these isomers may also be appreciably different. It is clear that the data advised in a study by Markov *et al.*[126] for C_{84} refer to a mixture of isomers (according to an original publication,[134] a C_{84} specimen isolated by chromatography consists of at least seven isomers). The success of further work on the determination of the saturated vapour pressures of higher fullerenes will be directly related to the progress in the elaboration of effective and economical techniques both for isolation and collection of individual fullerenes and for separation of them into pure isomers.

b. Fluorofullerenes $C_{60}F_{18}$, $C_{60}F_{36}$, $C_{60}F_{48}$

Two experimental methods were used for the measurements, namely, the classical Knudsen effusion method (KEM) combined with the mass analyser (KCMS)[135, 136] or with effusion-torsional (ET) technique.[137]

Fluorofullerene $C_{60}F_{36}$. The recommended [137] value for the enthalpy of sublimation $\Delta_{sub}H^{\circ}_{T}(C_{60}F_{36})$ was calculated by least-squares processing of experimental data obtained by both the KEM and KCMS methods. The values obtained by different methods were averaged with weight factors inversely proportional to their variances; and the resulting recommended value is $\Delta_{sub}H^{\circ}_{466}(C_{60}F_{36}) = 135 \pm 8$ kJ mol^{-1}.

Combination of the above value of the sublimation enthalpy and the absolute pressure measured by the Knudsen effusion method gave the following equation for the temperature dependence of the saturated vapour pressure of $C_{60}F_{36}$ in the temperature range of 408 – 539 K:[137]

$$\ln p(C_{60}F_{36}) = (-16292 \pm 939)T^{-1} + (30.90 \pm 1.97).$$

Here and in the subsequent equations, pressure is expressed in Pascals and the temperature is in Kelvins

Fluorofullerene $C_{60}F_{48}$. The saturated vapour pressure above $C_{60}F_{48}$ in the temperature range of 473 – 527 K was determined by the Knudsen effusion method (KEM) and, in parallel, by the effusion-torsional measurements.[137] On the basis of these measurements, the average molecular masses at temperatures of 499, 508 and 530 K were calculated; the resulting values were 1616, 1660 and 1620 amu, respectively. The average value, 1633 amu, is in good agreement with the molecular mass of $C_{60}F_{48}$ (1632 amu). This proves convincingly that $C_{60}F_{48}$ is sublimed without decomposition. This result is confirmed by mass spectra, in which $C_{60}F_{48}^{+}$ was identified as the predominant fullerene-containing ion. The overall pressures measured by the effusion-torsional method at the temperatures mentioned above were 0.10, 0.13 and 0.56 Pa, respectively, which is in good agreement with the KEM results.[137]

The enthalpy of sublimation of $C_{60}F_{48}$ is 108 ± 7 (KEM) or 111 ± 7 kJ mol^{-1} (KCMS). In order to compare the partial pressures of $C_{60}F_{36}$ and $C_{60}F_{48}$, an additional KCMS experiment was carried out.[137] Fluorofullerene specimens were placed in two separate compartments of a double Knudsen cell. On the basis of direct measurements of the $C_{60}F_{48}^{+} : C_{60}F_{36}^{+}$ ratio of ion currents, the ratio of partial pressures was calculated. The ratio of ionisation cross-sections $\sigma(C_{60}F_{36}) : \sigma(C_{60}F_{48}) = 0.93$ found using the additivity rule, was utilised in the calculations.[138] The ratios of the partial pressures of $C_{60}F_{36}$ and $C_{60}F_{48}$ at 481 and 528 K were 0.37 and 0.54, respectively.

The recommended [137] enthalpy of sublimation is $\Delta_{sub}H^{\circ}_{476}(C_{60}F_{48}) = 109 \pm 7$ kJ mol^{-1}. The temperature dependence of the saturated vapour pressure in the temperature range of 395 – 528 K is described by the following equation:[137]

$$\ln p(C_{60}F_{48}) = (-13146 \pm 827)T^{-1} + (24.34 \pm 1.71).$$

Fluorofullerene $C_{60}F_{18}$. The saturated vapour pressure was measured by the effusion method.[139] The recommended [139] equation for the temperature dependence of the saturated vapour pressure in the temperature range of 591 – 671 K has the form

$$\ln p(C_{60}F_{18}) = (-23739 \pm 1234)T^{-1} + (33.23 \pm 1.97).$$

The enthalpy of sublimation $\Delta_{sub}H^{\circ}_{627}(C_{60}F_{18})$ determined by the classical effusion method equals 197 ± 10 kJ mol^{-1}. According to KCMS data, $\Delta_{sub}H^{\circ}_{585}(C_{60}F_{18}) = 186 \pm 9$ kJ mol^{-1}.

Comparison of the data on the vapour pressure of $C_{60}F_{18}$, $C_{60}F_{36}$ and $C_{60}F_{48}$. In the temperature range studied by Boltalina *et al.*,[137] the saturated vapour pressures of $C_{60}F_{36}$ and $C_{60}F_{48}$ are rather similar to each other. This can be easily explained in terms of the structures of these molecules. Both molecules can be represented as spheres whose radius is equal to the sum of the radius of the fullerene cage (3.5 Å) and the C – F bond length (1.29 Å). The enthalpy of sublimation of $C_{60}F_{36}$ (135 ± 8 kJ mol^{-1}) is markedly higher than that for $C_{60}F_{48}$ (109 ± 7 kJ mol^{-1}). This difference indicates that the enthalpy of sublimation of fluorinated fullerenes tends to decrease with an increase in the total number of fluorine atoms on the carbon cage. {For comparison, the enthalpy of sublimation of [60]fullerene [126] is $\Delta_{sub}H^{\circ}_{298}(C_{60}) = 172 \pm 11$ kJ mol^{-1}.} The entropies of sublimation of $C_{60}F_{36}$ and $C_{60}F_{48}$ (see Ref. 137) are also substantially different

$$\Delta_{sub}S^{\circ}_{466}(C_{60}F_{36}) = 161 \pm 16 \text{ J mol}^{-1} \text{ K}^{-1},$$

$$\Delta_{sub}S^{\circ}_{476}(C_{60}F_{48}) = 107 \pm 14 \text{ J mol}^{-1} \text{ K}^{-1}.$$

The value for the enthalpy of sublimation obtained for $C_{60}F_{18}$ was much higher than those for $C_{60}F_{36}$ and $C_{60}F_{48}$. Even pure C_{60} fullerene has a lower enthalpy of sublimation. Thus, $C_{60}F_{18}$ clearly does not comply with the general trend of the enthalpy to decrease in the series C_{60}, $C_{60}F_{36}$, $C_{60}F_{48}$. This anomaly in the thermal properties of $C_{60}F_{18}$ can be easily explained by specific features of its molecular structure. All the 18 fluorine atoms are located in one hemisphere of the carbon cage, and the $C_{60}F_{18}$ molecule (C_{3v} symmetry) has a dipole moment of 6.3 or 6.9 D according to MNDO or density functional theory (DFT) calculations. The C_{60} and $C_{60}F_{48}$ molecules have no dipole moment and in the case of $C_{60}F_{36}$, the dipole moment is also absent for the T isomer. The dipole moment of the C_3 isomer of $C_{60}F_{36}$ (2.3 D, according to our estimates done by MNDO) is much lower than that of $C_{60}F_{18}$ (7 – 9 D).[139] The presence of a dipole moment results in a stronger interaction between the $C_{60}F_{18}$ molecules in the crystal compared to the dispersion interactions in the crystals of C_{60}, $C_{60}F_{36}$ or $C_{60}F_{48}$. As a consequence, more energy is required to transfer $C_{60}F_{18}$ molecules from the solid sate to the vapour. The relatively long retention time of the $C_{60}F_{18}$ fluorofullerene in the HPLC separation (~40 min *vs.* 2.9 min for $C_{60}F_{36}$)[139] also points to the polar structure of this molecule.

3. The enthalpies of formation

a. Fullerenes C_{60} and C_{70}

The thermal properties of [60]- and [70]fullerenes are surveyed in detail in a review by Dikii and Kabo.[140] Here we shall consider only the most recent studies devoted to this topic.[46, 141]

Fullerene C_{60}. An *et al.*[141] measured the energy of combustion of [60]fullerene using a liquid calorimeter with an isothermal shell. The average energy of combustion of C_{60} fullerene found from five experiments was -36036.06 ± 6.04 J g^{-1}, and the enthalpy of formation of solid C_{60} was 2359.47 ± 9.72 kJ mol^{-1}. A significant difference between the study cited [141] and the preceding works is that the authors [141] had a substantial amount of [60]fullerene at their disposal. In combustion experiments, 0.5 g weighed portions of fullerene were used, and the energy of combustion of C_{60} accounted for up to 70% of the total energy evolved in the experiment. This increases the reliability of the values presented above compared to other data on the energy of combustion. In 1997, An *et al.*[142] determined once again the enthalpies of combustion and formation of C_{60} fullerene using a microcalorimeter. The researchers did not analyse the gaseous products of combustion for carbon dioxide. The energy of combustion of [60]fullerene they found (-36004.6 ± 11.8 J g^{-1}) was close to the value determined previously.[141]

Kolesov *et al.*[46] were the first to pay attention to the dependence of the enthalpies of combustion and formation of [60]fullerene on the crystal size. They studied two specimens of C_{60}. One specimen prepared by a standard procedure (fast crystallisation of fullerene from a solution and removal of the solvent *in vacuo*) was a brown-coloured finely crystalline powder. The other specimen was prepared using a special procedure: small crystals (0.1–0.2 mm) were grown by slow crystallisation of C_{60} from a solution in toluene. This material was coloured black and had a characteristic metallic lustre. HPLC analysis showed that the former specimen contained 0.4 mol.% of C_{70}, and the second one was found to contain neither C_{70}, nor $C_{60}O$.

To determine the energy of combustion of C_{60} fullerene, Kolesov *et al.*[46] used a liquid calorimeter with an isothermal shell and a stationary bomb. The energy of combustion of the first specimen found in a series of three experiments was -35896 J g^{-1}, and that for the second specimen found in eight experiments was -36030 ± 16 J g^{-1}.

In the study in question,[46] the gaseous products of combustion were analysed for carbon dioxide. For the first material, the amount of CO_2 found experimentally was markedly lower than the value calculated theoretically, the average content of CO_2 being 99.80%. In the second specimen, the content of CO_2 in the combustion products virtually coincided with the calculated value (99.99 ± 0.02%). These results of the analysis for the second C_{60} specimen point to complete burning of the substance and confirm additionally the material purity.

Proceeding from this fact, the researchers [46] chose as reliable the standard energy of combustion determined for the second C_{60} specimen with a well-developed crystal structure. The standard enthalpy of formation of crystalline C_{60} fullerene is equal to 2355 ± 15 kJ mol^{-1} (see Ref. 46); this is the most reliable value. The results of An's and Kolesov's studies described above are in good agreement with each other.

Fullerene C_{70}. In 1997, An *et al.*[142] also determined the energy of combustion of [70]fullerene. The energy of combustion of C_{70} calculated based on the sample weight was -35629.4 ± 10.6 J g^{-1} and the enthalpy of formation was 2410.4 ± 8.9 kJ mol^{-1}, which did not coincide with earlier data (see the review [140]).

The same year Kolesov *et al.*[143] determined the energy of combustion of C_{70} fullerene using a liquid calorimeter with an isothermal shell. According to HPLC, the C_{70} specimen contained an impurity of C_{60} fullerene (2.0 mass %). Five experiments were carried out, each being accompanied by analysis of the gaseous products of C_{70} combustion for carbon dioxide; the average result was $99.81\% \pm 0.02\%$. The energy of combustion of C_{70} fullerene (specimen 1) calculated from the sample weight with correction for the energy of combustion of the C_{60} impurity amounts to -35664 ± 44 J g^{-1}. The same procedure was also used to burn the coarsely crystalline C_{70} fullerene (specimen 2), which contained 0.23 mass % of C_{60} and 0.40 mass % of C_{84}. Nine experiments were carried out for specimen 2; in all experiments, the gaseous products did not contain carbon monoxide. In seven experiments, the gaseous products were analysed for carbon dioxide. The amount of CO_2 determined experimentally (on average, $99.95\% \pm 0.05\%$) coincided, to within the accuracy of analysis, with the theoretical value. The average energy of combustion of C_{70} for specimen 2 amounted to -35679 ± 38 J g^{-1} (see Ref. 144), which is very close to the value obtained previously for specimen 1. The enthalpies of formation of crystalline C_{70} reported in two publications [143, 144] are 2439 ± 38 and 2452 ± 33 kJ mol^{-1}, respectively. As in the case of [60]fullerene, the data of the two last-mentioned works coincide within experimental error with the results obtained by An *et al.*[142]

b. Fluorofullerenes $C_{60}F_{48}$ and $C_{60}F_{36}$

The enthalpies of formation of $C_{60}F_{48}$ (see Ref. 48) and $C_{60}F_{36}$ (see Ref. 47) fluorofullerenes were first determined experimentally at the laboratory of thermochemistry of the Moscow State University.

The energies of combustion of fluorofullerenes were found using a calorimeter with an isothermal shell and with a rotating bomb platinum-lined from the inside. The rise of temperature was recorded by a copper resistance thermometer included in a bridge circuit. The sensitivity of the temperature measurement was 5×10^{-5} K.

Each of the two fluorofullerenes was pressed to form a pellet, which was then crushed into pieces. Several pieces with a total weight of 60–70 mg were placed into a terylene-film bag (produced and weighed beforehand), the bag was hermetically sealed, weighed, and heated in a platinum crucible together with a weighed pellet of benzoic acid. Benzoic acid served as the auxiliary material that ensured virtually complete combustion of fluorofullerenes to give only a small amount of soot in the crucible. The correction for this non-burnt residue was only 0.6–2.3 J, while the total amount of heat evolved in the experiment was $\sim 13\,000$ J. The heat of combustion of the auxiliary substances, benzoic acid and the terylene film, accounted for 92%–93% of the whole measured heat in the case of $C_{60}F_{48}$ and 90%–92% for $C_{60}F_{36}$. After the calorimetric experiments, the combustion products were analysed for the contents of CO_2, HF and HNO_3. The results of the analysis were used to calculate the amount of tetrafluoromethane formed upon combustion, and appropriate corrections were applied (2–10 and 0–4 J for $C_{60}F_{48}$ and $C_{60}F_{36}$, respectively).

After all the corrections were applied (including those for impurities contained in the specimens and those for adjustment to the standard conditions), the standard energies of combustion were found in relation to the reactions

$$C_{60}F_{48}(\text{cryst.}) + 48\,O_2(g) + 24\,H_2O(\text{liq}) = \\ = 60\,CO_2(g) + 48\,HF[HF(\text{liq}) \cdot 20\,H_2O],$$

$$C_{60}F_{36}(\text{cryst.}) + 51\,O_2(g) + 18\,H_2O(\text{liq}) = \\ = 60\,CO_2(g) + 36\,HF[HF(\text{liq}) \cdot 20\,H_2O].$$

Five experiments were carried out for each substance. The average standard energies of combustion thus obtained and the standard enthalpies of combustion and formation calculated from these values are presented in Table 11. The errors were determined for a 95% significance level. The same Table presents the enthalpies of sublimation of fluorofullerenes [137] and the standard entropies measured by Druzhinina *et al.*[107] Proceeding from these values, the standard enthalpies of formation of fluorofullerenes in the gaseous state and the Gibbs energies of formation of these compounds in the crystalline state were calculated.

Table 11. Thermodynamic characteristics of $C_{60}F_{48}$ and $C_{60}F_{36}$ fluorofullerenes at 298.15 K.[47, 48, 107, 137]

Parameter	$C_{60}F_{48}$	$C_{60}F_{36}$
$-\Delta_c U^\circ_m$(cr) /kJ mol^{-1}	24668 ± 163	24714 ± 199
$-\Delta_c H^\circ_m$(cr) /kJ mol^{-1}	24638 ± 163	24692 ± 199
$-\Delta_f H^\circ_m$(cr) /kJ mol^{-1}	7563 ± 166	5362 ± 201
$\Delta_{sub} H^\circ_m$ /kJ mol^{-1}	109 ± 7	139 ± 8
$-\Delta_f H^\circ_m$(g) /kJ mol^{-1}	7454 ± 166	5223 ± 201
S° /J mol^{-1} K^{-1}	1137.2 ± 5.7	1014.5 ± 5.1
$-\Delta_f G^\circ_m$(cr) /kJ mol^{-1}	6349 ± 166	4474 ± 201

Note. $\Delta_c U^\circ_m$ is the standard combustion energy, $\Delta_c H^\circ_m$, $\Delta_f H^\circ_m$ and $\Delta_{sub} H^\circ_m$ are the standard enthalpies of combustion, formation and sublimation, respectively, S° is the standard entropy, and $\Delta_f G^\circ_m$ is the Gibbs energy of formation of fluorofullerenes.

The resulting $\Delta_f H^\circ_m$(g) values for $C_{60}F_{48}$ and $C_{60}F_{36}$, the enthalpy of formation of crystalline C_{60} recommended above (2355 ± 15 kJ mol^{-1}), the enthalpy of sublimation of C_{60} (181 ± 2 kJ mol^{-1})[145] and the enthalpy of formation of gaseous molecular fluorine (79.38 ± 0.30 kJ mol^{-1})[112] were used to calculate the enthalpies of gas-phase decomposition of the fluorofullerenes into fullerene and gaseous fluorine

$$C_{60}F_{48}(g) = C_{60}(g) + 48\,F(g), \quad (8)$$

$$C_{60}F_{36}(g) = C_{60}(g) + 36\,F(g). \quad (9)$$

This gave $\Delta_r H(8) = 13800 \pm 167$ kJ mol^{-1} (or 287.5 ± 3.5 kJ per C–F bond) and $\Delta_r H(9) = 10617 \pm 202$ kJ mol^{-1} (or 294.9 ± 5.6 kJ per C–F bond).

For the reaction

$$C_{60}F_{48}(g) = C_{60}F_{36}(g) + 12\,F(g), \quad (10)$$

the calculations gave $\Delta_r H(10) = 3184 \pm 261$ kJ mol^{-1} (or 265 ± 22 kJ for each of the twelve C–F bonds that are cleaved on passing from $C_{60}F_{48}$ to $C_{60}F_{36}$). Thus, the first experimental data on the energy characteristics of the C–F bonds in fluorofullerenes with high fluorine contents were obtained.

VII. Conclusion

We shall consider some promising lines of research related to fullerenes and their derivatives. A necessary condition for further advancement of thermochemical studies, *i.e.*, accumulation of fundamental thermochemical characteristics of individual fullerene compounds, is the preparation of these compounds in macroscopic amounts (about hundreds of milligrammes) and with satisfactory purity. One may expect that the progress along this line would depend, among other factors, on the practical interest in useful properties of fullerene derivatives. From a fundamental standpoint, it would be of interest to obtain data on the enthalpies of formation and heat capacities of a number of simple fullerene halides (for example, $C_{60}Br_{24}$, $C_{60}Cl_6$), the synthesis of which is documented. In combination with the currently available data on C_{60}, C_{70} and [60]fullerene fluorides and hydrides ($C_{60}X_{36}$), this would provide a more comprehensive picture of the energy characteristics of the fullerene–hydrogen and fullerene–halogen systems. In turn, creation of even a small thermodynamic database based on experimental results would facilitate development of new theoretical approaches to the description of these systems. For example, this would increase the accuracy of calculations of the relative stability of various fullerene derivatives. It appears rather unlikely that the thermochemical characteristics of endohedral or organic derivatives of fullerenes will be determined in the near future, because in the vast majority of cases, preparation of pure compounds of this class (free from side products and having a homogeneous isomer composition) is associated with a tedious and expensive HPLC procedure.

Studies of fullerene derivatives in the gas phase will undoubtedly be continued in the near future, because insufficient amounts and purity of substances will not hold up mass-spectrometric measurements. For example, previously, ion–molecule equilibria have been studied successfully even with 3–5 mg samples of mixtures of endohedral metallofullerenes.

The number of objects with interesting ionisation characteristics is constantly extending. For example, mention should be made of a new class of endofullerenes with inner-sphere nitrogen clusters of lanthanides and recently discovered small fullerenes C_{20}[146] and C_{36}.[147]

The synthetic works of fluorination of fullerenes would be carried out in the following directions. First, the search for pathways to the fully saturated compound $C_{60}F_{60}$ and fullerene hyperfluorides, the possibility of whose existence has been shown experimentally,[65, 66] still is of interest. The use of superoxidants, fluorides of metals in higher oxidation states, can lead to new compounds with unique properties. Naturally, it is necessary to continue the attempts to perform the targeted synthesis of compounds with low content of fluorine. These compounds could serve as convenient objects for investigating addition reactions and replacement of fluorine atoms by functional groups. A reaction of this type was first reported in 1997, when the compound $C_{60}F_{15}Ph_3$ (the product of the replacement of the three sterically most accessible fluorine atoms by three phenyl groups) was synthesised and its structure was characterised.[148]

The development of reliable and effective procedures for the preparation of individual fluorofullerene derivatives accomplished in the last two or three years, the presence of data on their structure and purity, and determination of the key physical properties (thermal stability, solubility, air stability, volatility) make it possible to thoroughly and systematically research the chemical and physical properties of these compounds. The few publications on electrochemical properties of fluorofullerenes[149] indicate that fluorofullerenes can prove to be valuable materials for cathodic coatings in electrochemical cells. By varying the fluorine content in fluorofullerene molecules, it should be possible to design materials with desired electrochemical redox potentials; the reductive potential was found to increase by 0.5 V on passing from $C_{60}F_{36}$ to $C_{60}F_{48}$.[40]

We have mentioned above that $C_{60}F_x$ fluorofullerenes can be used as fluorinating agents or oxidants; however, this point has not been studied in detail. An interesting applied aspect is the use of $C_{60}F_{18}$ as a component in the construction of nanostructural charge transfer complexes. Quite recent works on the synthesis of such complexes with C_{60} resulted in the design of solar batteries based on these compounds.[150] The replacement of [60]fullerene by $C_{60}F_{18}$ fluorofullerene, which is a more polar molecule with higher electron affinity, can markedly improve characteristics of light-sensitive devices. The exceptionally high polarity of the $C_{60}F_{18}$ molecule makes this fluorofullerene rather attractive for new fields of electronics; in particular, it could be of interest in the development of molecular transistors.

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