Russian Chemical Reviews **71** (5) 401 – 415 (2002) © 2002 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2002v071n05ABEH000712

Thermodynamic properties of halide compounds of tetravalent transactinides in solutions and in the gaseous and crystalline states †

G V Ionova

Contents

I.	Introduction	401
II.	Structural properties: covalent and ionic radii and interatomic distances	403
III.	Standard formation enthalpies of gaseous and crystalline tetrahalides	404
IV.	Volatility of transactinide compounds as a function of their structure in the crystalline and gaseous states	407
V.	Standard formation enthalpies of gaseous MCl_6^{2-} anions and affinity of tetrachlorides towards chloride ions	410
VI.	Solution behaviour of transactinides	410
VII.	Standard formation enthalpies, $\Delta_f H^\circ(A_2MCl_6)$, of crystalline compounds	412
VIII.	Conclusion	413

Abstract. Experimental and theoretical data on the structure and properties of compounds of tetravalent transactinides (TAn^{IV}) Rf ($Z = 104$), Db ($Z = 105$), Sg ($Z = 106$), Bh ($Z = 107$), Hs ($Z = 108$), Mt ($Z = 109$) and ^{110}TAn ($Z = 110$) are described systematically. The problem of disposition of the transactinide elements in the Periodic system is discussed and the properties of the 6*d*-, 5*d*-, 4*d*-, 3*d*- and 5*f*-elements are compared. Regularities of changes in the thermodynamic characteristics of TAn^{IV} compounds *versus* the atomic number, *Z*(TAn), are elucidated. Peculiarities of changes in thermodynamic properties upon the formation of nitrate, fluoride and chloride TAn^{IV} complexes in solution are discussed. The bibliography includes 140 references.

I. Introduction

Theoretical investigations into the chemical properties of the heavy elements, *viz*., actinides (An) and transactinides (TAn)[1–10] involve assessment of the influence of relativistic effects (RE) on these properties. One of the major propositions of the relativity theory is that the velocity of a particle cannot exceed the velocity of light, as follows from the relativistic mass equation:

$$m = \frac{m_0}{\sqrt{1 - (v/c)^2}},$$

where m is the mass of the moving particle, m_0 is the mass of the particle at rest, v is the velocity of the particle and c is the velocity of light.

Since the mass appears in the denominator of the expression for the Bohr radius (a_0), the relativistic mean radius is smaller than the nonrelativistic radius:

$$a_0 = \frac{h^2}{\pi m Z^2 e^2},$$

where h is the Planck constant, Z is the charge of the atom and e is the charge of the electron.

There are three types of possible influence of RE on the electron shells of atoms.

1. Contraction and, hence, stabilisation of the *s*-, $p_{1/2}$- and $p_{3/2}$-shells. The *s*- and $p_{1/2}$-shells are contracted to nearly the same extent while the $p_{3/2}$-shells are much less contracted.

2. Expansion of the *f*- and *d*-shells. The *s*- and $p_{1/2}$-electrons screen nuclear attraction more effectively than the *f*- and *d*-electrons which experience weaker nuclear attraction and the corresponding orbitals become more diffuse and energetically destabilised.

3. Spin – orbit splitting, which increases as Z increases.

In addition to RE, the *s*-, *p*-, *d*- and *f*-electrons are also affected by nonrelativistic shell effects. It is appropriate to consider three types of the influence of RE on the physicochemical properties of heavy elements.

1. Relativistic effects completely determine a particular property and regular trends of its changes along the period and down the group of the Periodic system.

2. Relativistic effects make a particular property more pronounced, but the regularities of its changes are controlled by nonrelativistic shell effects.

3. Relativistic and nonrelativistic shell effects act in opposite directions.

On going from the 3*d*-elements to the 4*d*-, 5*d*- and 6*d*-elements the atomic radii increase and the *d*- and *s*-orbitals become more diffuse due to nonrelativistic shell effects. Relativistic effects cause destabilisation of the *d*-orbitals and stabilisation of the *s*-orbitals. Thus, the RE and the shell effects exhibit a synergistic effect in the case of *d*-orbitals and an antagonistic effect in the case of *s*-AOs (4*s*, 5*s*, 6*s*, 7*s*).

On going from the 3*d*-elements to the 4*d*-elements relativistic effects cause greater stabilisation of the 5*s*-electrons compared to the 4*s*-electrons. However, if we go from the 4*d*-elements to the 5*d*-elements, the effect of lanthanide contraction, which additionally stabilises the 6*s*-electrons, is superimposed on relativistic stabilisation of the 5*s*- and 6*s*-electrons. Assuming that relativistic stabilisation of the valence *s*-electrons dominates over the destabilising shell effects, one should expect a regular increase in the ionisation potentials (IPs) down the groups Ti – Zr – Hf,

G V Ionova Institute of Physical Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax (7-095) 335 17 78. Tel. (7-095) 429 94 66.
E-mail: ionova@ipc.rssi.ru

Received 12 February 2002
Uspekhi Khimii **71** (5) 461 – 476 (2002); translated by A M Raevsky

† Dedicated to V I Spitsyn on occasion of his 100th birthday.

Cu – Ag – Au, *etc*. However, the IP values change irregularly, which reflects a complex scheme of compensation effects.

For instance, on going from the 3*d*-elements to the 4*d*-elements stronger relativistic stabilisation of the 5*s*-electrons compared to 4*s*-electrons causes a decrease rather than the expected increase in the IPs of all elements except Zr and Mo. It is impossible to differentiate the influence of the shell and relativistic effects, lanthanide contraction, *etc*., even in the simplest case when analysing the properties of free atoms. Moreover, the contributions of these effects to the chemical properties of compounds cannot also be differentiated. This can be done only theoretically by performing calculations without and with inclusion of RE. However, calculations without inclusion of RE correspond to hypothetical systems rather than real atoms and molecules; therefore, only the experimental data can serve as a criterion for the significance of the influence of RE on the properties of heavy elements.

The actinides ($Z = 89 – 103$) precede the transactinide elements ($Z \geqslant 104$). The influence of RE on the properties of actinides, lanthanides (Ln) and transactinides has been analysed.[1–6] Important manifestations of RE in actinides include high oxidation states of U, Np, Pu and Am and the valence of 4 or 5 in the metallic state of early actinides, which is atypical of lanthanides.

Mention was also made [1] that, despite the great importance of the contribution of RE to the properties of heavy elements, it should not be overestimated. There are numerous examples of situations where, contrary to expectations, relativistic effects do not manifest themselves in the properties of An. Of particular importance is the analysis of the influence of RE on the properties of heavy An ($Z = 98 – 103$) which precede the transactinides ($Z \geqslant 104$).

For instance, relativistic destabilisation of the 5*f*-electrons increases with Z(An). At first glance, this should lead to stabilisation of high oxidation states of not only the early, but also late actinides. However, the opposite effect, that is, stabilisation of the divalent state of late actinides was established experimentally. Therefore, the effect of actinide contraction appears to be much stronger than relativistic destabilisation of the 5*f*-electrons for An with $Z > 96$.

Yet another example, which has been analysed in detail [4] using the published data, is provided by the correlations between changes in the sublimation enthalpies, $\Delta_s H^\circ$, of lanthanides and actinides and their valences V in the metallic state. Would RE affect the sublimation enthalpy, one should expect $V_{An} > V_{Ln}$ throughout the An and Ln series. However, experiments with the late An and Ln revealed another regularity, namely, $V_{Ln} > V_{An}$, which contradicts the assumption that RE have a crucial effect on the properties of the late An from Cf ($Z = 98$) to No ($Z = 102$).

Desclaux and Fricke hypothesised [7] that strong RE will violate the logic of the Periodic system. According to calculations,[7] the Lr atom has the $5f^{14}\ 7s^2\ 7p_{1/2}$ ($^2P^0_{1/2}$) ground-state electron configuration due to relativistic stabilisation of the $7p_{1/2}$-electron, which means that Lr should be considered as an analogue of the Ga rather than Lu subgroup elements. Probably, calculations [7] overestimated the influence of RE since this idea was not supported experimentally. It should be noted that the idea of relativistic stabilisation of the $7p_{1/2}$-electron seems to be rejected. In the studies cited in review [4] Lr was considered as an analogue of Lu and characterised by a $\Delta_s H^\circ$(Lr) value of ≈ 4 eV, which is close to the $\Delta_s H^\circ$ for Sc, Y, La, Gd, Lu, Ac and Cm, rather than ~ 2 eV for In, Ga and Tl. All estimates of the thermodynamic properties made for Lr^{III} aqua ions and for solid halides, oxides and sulfides reported in the chemical literature are close to corresponding values for Cm compounds.

According to Pyykkö's hypothesis,[8] the most important chemical anomalies in the second half of the Periodic system are due to RE. This has been repeatedly exemplified using the difference between the chemical properties of Ag and Au, which is due to the so-called 'relativistic maximum for gold'. However, this interpretation does not take into account specific features of the electronic structure of Ag atom (see Refs 9 and 10). Among the 3*d*-, 4*d*- and 5*d*-elements (a total of 27 elements from Sc to Au), the Ag atom has the most stable *d*-electrons: the excitation energy of the 4*d*-electron from the Ag($4d^{10}5s$) electron configuration is higher than for any other *d*-elements. It is the local nonrelativistic shell effect for Ag that is to a great extent responsible for distinctions between the chemical properties of Ag and Au.

Experimental data [11–20] on the chemistry of rutherfordium (Rf), dubnium (Db), seaborgium (Sg), bohrium (Bh) and hassium (Hs) allow some generalisations and predictions. However, no measurements of the properties of TAn, which could be unambiguously interpreted as a manifestation of RE, have been reported so far.[9] It was mentioned [8, 9, 21] that interpretation of the properties of TAn required a weighed analysis of the role played by relativistic and nonrelativistic effects.

Manifestation of the spin – orbit RE can be experimentally confirmed in studies of the spectral and magnetic properties, which depend on the spin – orbit splitting energy and on the fine structure of energy levels. However, these investigations are still a long way in the future. Currently, the main avenues of research into the properties of TAn involve studies of the gas-state behaviour of TAn (first of all, volatility measurements of halides and oxides [11, 14, 17]) and of the complexation of TAn in solutions.[12, 15, 16, 18, 19]

Flerov and Zvara (Joint Institute of Nuclear Research, Dubna, Russian Federation) laid the foundation for a general strategy of studying the properties of TAn, which involves comparison of the properties of the elements in higher oxidation states in the groups Rf – Hf – Zr, Db – Ta – Nb, Sg – W – Mo, Bh – Re – Tc and Hs – Os – Ru. Currently, there are three points of view on the disposition of TAn in the Periodic table and on their relation to the 4*d*-, 5*d*- and 5*f*-elements.

1. Relativistic effects cause an inversion of the trends of changes in the properties [14, 15, 19] on going from the 5*d*-elements to the 6*d*-elements, so that the properties are changed in the order 4*d* – 6*d* – 5*d*. Therefore the chemical properties of TAn cannot be extrapolated within particular groups. For Group IV elements, this conclusion was based on the results of quantum-chemical calculations of the effective charges q on the M atoms in gaseous molecules MCl_4, which were found to be $+1.18$, $+1.04$ and $+1.07$ for Zr, Hf and Rf, respectively. Nonmonotonic change in the charges q(Zr) > q(Rf) > q(Hf) was used to explain the processes occurring in solutions (complexation,[15, 16] hydrolysis [19]) and in the crystalline state (sublimation enthalpy [14]).

2. Regularities typical of the *d*-elements are logically extended to the transactinides, *i.e*., the passage 4*d* – 5*d* – 6*d* occurs without inversion of properties.[17]

3. The chemical properties of TAn are similar to those of the preceding actinide elements (Rf – Th).[12]

In this review, we analysed the thermodynamic properties of the TAn^{IV} compounds in the gas phase, aqueous solutions and in the crystalline state and compared them with the properties of compounds of the 3*d*-, 4*d*-, 5*d*- and 5*f*-elements. The subject of our study were the chlorides and bromides which are known to exist for all the TAn^{IV}, An^{IV} and *d*-transition elements M^{IV}.

When comparing the properties of TAn with those of (i) their *d*-analogues within the groups of the Periodic table and (ii) the corresponding An (Rf – Zr – Hf – Th; Db – Nb – Ta – Pa, *etc*.), researchers have to return to studying the properties of analogous compounds, since only the results obtained under the same conditions should be compared. Sometimes, the results of recent experiments with the 4*d*-, 5*d*- and 5*f*-elements are inconsistent with earlier results even at qualitative level. To appreciate the reasons for this inconsistency, in this review we considered the results of both recent (1990 – 2002) and earlier (1960 – 1975) experimental studies.

II. Structural properties: covalent and ionic radii and interatomic distances

Bokii [22] pointed out that in the molecules of the A_2MX_6 (A = K, Rb, Cs, X = Cl, Br) compounds, *e.g.*, K_2PtCl_6, the measured r_{Pt-Cl} distance (2.34 Å) differs from the sum of the ionic radii of Cl^- and Pt^{4+} (1.81 Å + 0.62 Å = 2.43 Å). This allowed him to suggest that the M−X bonds in these compounds are covalent rather than ionic and therefore the r_{M-X} distances cannot be calculated using the r_{ion} values. More recently,[23] the covalent radii, r_{cov}, along with the r_{ion} values were included in the set of commonly used structural parameters of the 4*d*- and 5*d*-elements.

It was found that the measured r_{M-X} distances in compounds of the 4*d*- and 5*d*-elements are linearly related to the maximum electron density radii, $r_{max}(nd)$, of the 4*d*- and 5*d*-AOs in the ground-state electron configurations of gaseous atoms

$$r_{M-X} = ar_{max}(nd) + c, \quad (1)$$

where *a* and *c* are constants and *n* = 4, 5.

Thus, if we know the $r_{max}(nd)$ values for all the 4*d*-, 5*d*- and 6*d*-elements and the r_{M-X} distances in compounds of the 4*d*- and 5*d*-elements, it is possible to estimate the corresponding distances in compounds of the 6*d*-elements. The $r_{max}(nd)$ values for the atoms of the 4*d*-, 5*d*- and 6*d*-elements were calculated using the relativistic Dirac–Fock approach.[24] The r_{M-Cl} values in gaseous MCl_4 (M = Ti, V, Zr, Hf, Mo and W) molecules and in crystalline A_2MCl_6 (A = K, Rb and Cs; M = Ti, Zr, Mo, Tc, Pd, Hf, W, Re, Ir, Os and Pt) salts were measured.[25–38] The r_{M-X} distances in compounds of the 4*d*- and 5*d*-elements were measured [25–38] while the $r_{max}(nd)$ distances in the atoms of the 4*d*-, 5*d*-, 6*d*-elements, averaged over the degree of degeneracy of quantum numbers $j = l \pm 0.5$, were calculated.[24] Formula (1) was used to estimate the structural parameters of TAn^{IV} compounds (see Refs 4 and 21), such as r_{M-X} and $r_{cov} = r_{M-X} - r_X$ (X = Cl, r_{Cl} = 0.99 Å; X = Br, r_{Br} = 1.14 Å).

The structural data for the TAn^{IV} compounds listed in Table 1 are the r_{cov} (CN = 4) and r_{cov} (CN = 6) values, the r_{M-Cl} and r_{M-Br} values for gaseous and crystalline tetrahalides, the r_{M-Cl} values for gaseous MCl_6^{2-} anions and the lattice constants *a* for A_2TAnCl_6 (A = K, Rb, Cs) compounds.

Though the use of the r_{ion} parameters for evaluation of the Pt−Cl distance in the $PtCl_6^{2-}$ anion overestimates this value by 0.09 Å (see Ref. 22), the ionic radii of the 3*d*-, 4*d*- and 5*d*-elements are listed in all crystallochemical tables, since for a particular oxidation state and CN value they determine both the horizontal and vertical trends of changes in the structural properties. The ionic radius of Rf^{IV} was first calculated three decades ago;[39] more recently, this value was refined.[40,41] For CN = 6, the estimates of $r_{ion}(Rf^{IV})$ are 0.74 (see Ref. 41), 0.75 (see Ref. 39) and 0.79 Å (see Ref. 40).

The $r_{ion}(TAn^{IV})$ values can also be estimated by extrapolating the ionic radii of the early analogues of the 4*d*-, 5*d*- and 5*f*-elements. On the one hand, the $r(M^{IV})$ values for transactinides were evaluated[21] using the $r_{ion}(M^{IV})$ [42] parameters of the 4*d*- and 5*d*-elements and the calculated r_{cov} values of the 4*d*-, 5*d*- and 6*d*-elements. The estimate of $r_{ion}(Rf^{IV})$ was found to be 0.78 Å (see Table 1). On the other hand, the $r(TAn^{IV})$ parameters were evaluated using the results obtained for An. Tetravalent transactinide compounds (Z = 104–110) extend the series of An^{IV} compounds, which were synthesised for all actinides from Th (Z = 90) to Es (Z = 99). The ionic radii, $r_{ion}(An^{IV})$, for CN = 6 and 8 were also reported (see Ref. 43). For CN = 6, they decrease on going from Th^{IV} (r_{ion} = 0.932 Å) to Es^{IV} (r_{ion} = 0.812 Å) following a power dependence on Z. This allowed one to estimate the $r_{ion}(Rf^{IV})$ parameter, which was found to be 0.75 Å. Thus, the former value (0.78 Å) reflects the covalent character of bonding, typical of compounds of the *d*-elements, while the latter value (0.75 Å) reflects more ionic character of bonding, characteristic of actinides. This points to dual properties of TAn that are similar to both the 4*d*- and 5*d*-elements and the actinides. For CN = 8, the calculated $r_{ion}(Rf^{IV})$ value is 0.836 Å.[21]

Not all crystal MX_4 compounds of the 4*d*- and 5*d*-elements are isostructural,[25–38] but for all of them the CN equals 6 rather than 4. As a rule, typical of these compounds is a distorted octahedral coordination of the M atom and the presence of both bridging and terminal X atoms. For $ZrCl_4$, the r_{Zr-Cl} distances vary between 2.307 and 2.655 Å (see Ref. 44). It is believed [4,21] that in the crystalline tetrahalides of the 6*d*-elements the CN also equals 6. The averaged r_{M-X} distances in the crystalline (c) MX_4 (M = Zr, Hf, Nb, Ta, Mo, W, Tc, Re and Os) compounds are linearly related to the $r_{max}(nd)$ values. This allowed estimation of the r_{M-X} distances in halide compounds of TAn based on the known [24] $r_{max}(6d)$ values (see Table 1). For both the MCl_6^{2-} anions in the gas (g) phase and MCl_4(c) chlorides the CN is 6; however, unlike the crystalline chlorides, the anions contain only terminal bonds, which could be the reason for the small difference between the r_{M-Cl} distances.

Table 1. Maximum electron density radii $r_{max}(6d)$, covalent (r_{cov}) and ionic (r_{ion}) radii of TAn^{IV} for CN = 4 and CN = 6 and distances r_{M-X} in gaseous MX_4 molecules and MX_6^{2-} anions and in crystalline MCl_4 compounds (see Ref. 4). Lattice constants *a* of compounds A_2MCl_6 (A = K, Rb, Cs). All values are given in Å.

Structural parameters	Transactinides (M)						
	Rf	Db	Sg	Bh	Hs	Mt	^{110}TAn
$r_{max}(6d)$ (see [a])	1.0417	0.976	0.924	0.881	0.846	0.814	0.786
r_{cov} (CN = 4)	1.427	1.389	1.359	1.334	1.314	1.296	1.279
r_{cov} (CN = 6)	1.551	1.514	1.486	1.462	1.442	1.424	1.409
r_{ion} (CN = 6)	0.78 (see [b])	0.76	0.73	0.72	0.70	0.69	0.68
	0.74 (see [c])	–	–	–	–	–	–
	0.75 (see [d])	–	–	–	–	–	–
	0.79 (see [e])	–	–	–	–	–	–
r_{M-Cl}, (MCl_4, g)	2.417	2.379	2.349	2.324	2.304	2.286	2.269
r_{M-Cl}, (MCl_6^{2-}, g)	2.541	2.504	2.476	2.452	2.432	2.414	2.399
r_{M-Cl}, (MCl_4, c)	2.556	2.532	2.507	2.465	2.439	2.414	2.372
r_{M-Br}, (MBr_4, g)	2.567	2.529	2.499	2.474	2.454	2.436	2.419
r_{M-Br}, (MBr_6^{2-}, g)	2.691	2.654	2.626	2.602	2.582	2.564	2.549
$a(K_2MCl_6)$ [f]	10.09	9.99	9.92	9.86	9.82	9.80	9.79
$a(Rb_2MCl_6)$ [f]	10.19	10.11	10.05	10.04	9.99	9.99	9.99
$a(Cs_2MCl_6)$ [f]	10.40	10.35	10.31	10.30	10.26	10.26	10.26

[a] Data taken from Ref. 24. [b] Data taken from Refs 4 and 21. [c] Data taken from Ref. 41. [d] Data taken from Ref. 39 and calculated by the author of this review. [e] Data taken from Ref. 40. [f] Calculated by the author of this review.

III. Standard formation enthalpies of gaseous and crystalline tetrahalides

Using the published thermodynamic [45–66] and structural data [25–38, 67–76] for tetrahalides of the 3*d*-, 4*d*-, 5*d*- and 5*f*-elements in the gas phase and in the crystalline state, we found some common parameters that were used for calculations of the standard formation enthalpies, $\Delta_f H^\circ(MX_4, g)$, of the MX_4 compounds of all elements including TAn (see Ref. 67) and for prediction of the $\Delta_f H^\circ(MX_4, g)$ values from the following equation

$$\Delta_f H^\circ(MX_4, g) = \Delta_s H^\circ(M) + 4\Delta_f H^\circ(X, g) - \left[a - \frac{b}{r(M-X)}\right], \quad (2)$$

where $\Delta_s H^\circ(M)$ is the standard sublimation enthalpy of M, $\Delta_f H^\circ(X, g)$ is the standard formation enthalpy of gaseous atoms X, $a - b/r(M-X)$ is the energy of all bonds, $D(MX_4, g)$, in gaseous MX_4 molecule and a and b are constants. This approximation was used for calculating the thermodynamic properties of the An and Ln compounds (including aqua ions) and their redox potentials.[45–48, 53, 59, 60, 67] Using the measured $\Delta_f H^\circ(MCl_4, g)$ values (M = Ti, V, Cr, Zr, Nb, Mo, Ru, Hf, Ta, W and Os),[30, 49–55] the a and b coefficients were determined and the $D(MX_4, g)$ and $\Delta_f H^\circ(MCl_4, g)$ parameters were calculated for all TAn and for Rh, Ir, Pd and Pt. The $\Delta_f H^\circ(AnCl_4, g)$ values for An = Th, U and Pu were measured [58, 61, 63, 64] while those for Am, Cm, Bk, Cf, Es were estimated.[48] The $\Delta_f H^\circ(MCl_4, g)$ parameters for TAn, calculated by the author of this review, are listed in Table 2. In Fig. 1 we compare the standard formation enthalpies of gaseous tetrachlorides of the 4*d*-, 5*d*-, 6*d*- and 5*f*-elements in graphical form.

As can be seen in Fig. 1, tetrachlorides of transactinide elements lose their thermodynamic stability as the number of antibonding electrons increases from $RfCl_4$ to the ^{110}TAn tetrachloride. The same trend is also observed for tetrachlorides of the 4*d*- and 5*d*-elements, namely, $RuCl_4$ and $OsCl_4$ have the highest (largest positive) formation enthalpies. A decrease in the thermodynamic stability along the TAn series was also predicted for gaseous tetrabromides. Gaseous tetrahalides of Group IV – VIII elements become thermodynamically more stable on going from the light to heavy elements; the stability sequence is $4d < 5d < 6d$, $4d \approx 5d < 6d$ and $4d > 6d > 5d$.

Theoretical aspects of comparison of the 5*f*- and 6*d*-elements have been studied for long. Zachariasen [57] proposed a thoride theory which treated the actinides as typical 6*d*-metals. This theory was repeatedly criticised; however, it contains a grain of truth, namely, the proposition that particular chemical properties of compounds of the 5*f*-elements are similar to those of the 6*d*-elements. This also still holds.[12, 18] In Fig. 2, we compare the bond energies, $D(MCl_4, g)$, of gaseous tetrachlorides of the 4*d*-, 5*d*- and 6*d*-elements and of the actinides. Again, the $D(MCl_4, g)$ values for gaseous MCl_4 (M = Zr, Nb, Mo, Ru, Hf, Ta, W, Os) molecules and the $D(AnCl_4, g)$ parameters for An = Th, U and Pu were calculated using Eqn (2) in which all the values, except D, *viz.*, $\Delta_f H^\circ(MX_4, g)$, $\Delta_s H^\circ(M)$ and $4\Delta_f H^\circ(X, g)$ were obtained experimentally. Therefore, the D values for these compounds can be considered experimental. The bond energies of compounds for which no experimental data are available (TAn; Rh, Ir; Pd, Pt and An = Pa, Np, Am, Cm) were calculated by the author of this review. Comparison of the data presented in Figs 1 and 2 shows that the bond energies, $D(AnCl_4, g)$ for the early actinides (Th – Cm) and $D(MCl_4, g)$ for TAn, differ insignificantly, whereas the

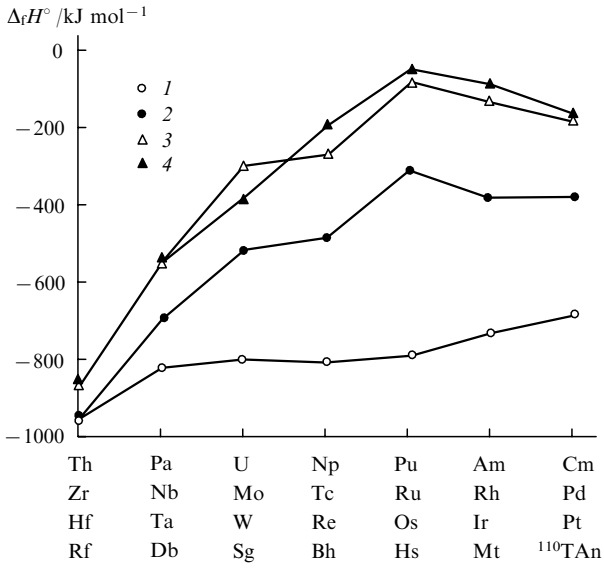


Figure 1. Comparison of $\Delta_f H^\circ(MCl_4, g)$ values for actinides (*1*) and for the 6*d*- (*2*), 5*d*- (*3*) and 4*d*-elements (*4*).

Table 2. Thermodynamic parameters of transactinide compounds (in kJ mol^{-1}).

Thermodynamic parameters	Transactinides (M)						
	Rf	Db	Sg	Bh	Hs	Mt	^{110}TAn
$\Delta_s H^\circ$	634	769	836	732	791	661	527
$\Delta_f H^\circ(MCl_4, g)$	−971	−707	−522	−489	−313	−381	−384
$\Delta_f H^\circ(MCl_4, c)$	−1077	−848	−680	−620	−460	−493	−461
$\Delta_s H^\circ(MCl_4)$	106	141	158	131	147	112	77
$\Delta_f H^\circ(MCl_4, aq)$	−1303	−1010	−808	−726	−568	−644	−662
$\Delta_f H^\circ(MCl_6^{2-}, g)$	−1724	−1420	−1209	−1127	−955	−1025	−1038
$A(Cl^-, g)$	−286	−246	−220	−171	−175	−177	−187
$A(Cl^-, c)$	−180	−105	−62	−40	−28	−65	−110
$\Delta_h H^\circ(MCl_6^{2-}, g)$ (see [a])	−784	−795	−804	−812	−818	−824	−829
$\Delta_f H^\circ(MCl_6^{2-}, aq)$	−1637	−1344	−1142	−1060	−902	−978	−996
$\Delta_f H^\circ(MBr_4, g)$	−759	−548	−401	−359	−234	−289	−291
$\Delta_f H^\circ(MBr_4, c)$	−879	−685	−544	−493	−358	−386	−359
$\Delta_s H^\circ(MBr_4)$	120	137	143	134	124	97	68
$A(Br^-, g)$	235	126	59	27	−31	23	26
$\Delta_f H^\circ(K_2MCl_6)$	−2036	−1767	−1580	−1507	−1354	−1417	−1428
$\Delta_f H^\circ(Rb_2MCl_6)$	−2065	−1792	−1603	−1528	−1373	−1437	−1448
$\Delta_f H^\circ(Cs_2MCl_6)$	−2085	−1820	−1636	−1565	−1414	−1476	−1487

[a] $\Delta_h H^\circ(MCl_6^{2-}, g)$ is the hydration enthalpy of gaseous MCl_6^{2-} anions.

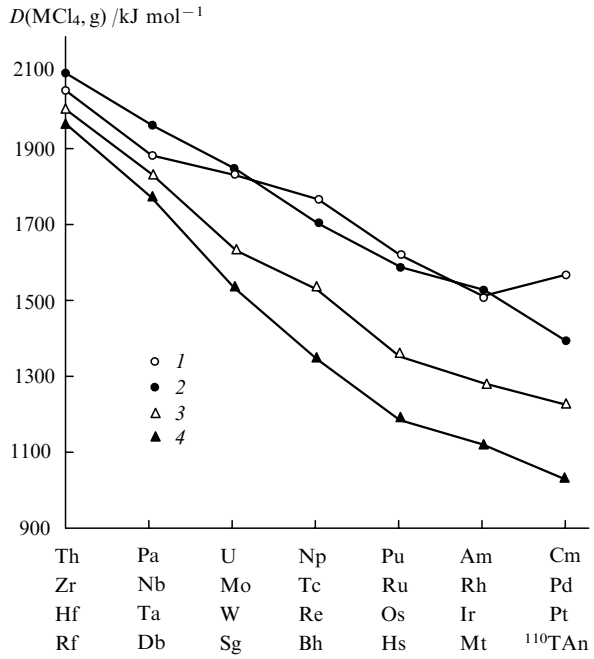


Figure 2. Bond energies $D(MCl_4, g)$ of actinides (*1*) and of the 6*d*- (*2*), 5*d*- (*3*) and 4*d*-elements (*4*).

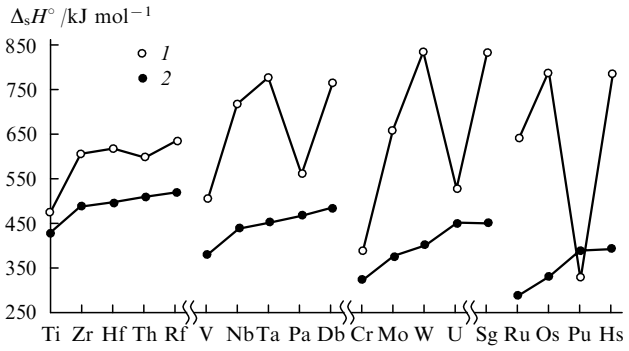


Figure 4. Changes in the $\Delta_sH^\circ(M)$ (*1*) and $D(M-Cl)$ (*2*) values for tetrachlorides of Group IV, V, VI and VIII elements and for the corresponding actinide pseudohomologues.

formation enthalpies for the following pairs of elements: Pa – Db, U – Sg, Np – Bh, Pu – Hs and Am – Mt (except for the pair Rf – Th) differ substantially, that is, smaller $\Delta_sH^\circ(An)$ values [compared to $\Delta_sH^\circ(M)$] lead to the higher thermodynamic stability of $AnCl_4$ compared to MCl_4.

Problems concerning monotonic (passage $4d \rightarrow 5d \rightarrow 6d$) or nonmonotonic (passage $4d \rightarrow 6d \rightarrow 5d$) changes in the properties within the groups of the Periodic table and analogies between the properties of the 5*f*- and 6*d*-elements have been the subject of a considerable literature. Nonmonotonic changes in properties are associated with RE. We believe that the chemical properties (in particular, thermodynamic properties) reflect the totality of many properties of free atoms and interactions between them. An increase or a decrease in certain parameters can lead to nonmonotonic changes in the thermodynamic properties within the groups of the Periodic table. From this standpoint, let us compare the properties of compounds $MCl_4(g)$ and $AnCl_4(g)$ within particular groups. According to Eqn (2), the main properties determining the changes in the thermodynamic stability of tetrachlorides within the groups are $\Delta_sH^\circ(M)$, r_{M-Cl} and $D(MCl_4, g)$. The bond energies $D(M-Cl)$ in tetrachlorides of the *d*-elements of Groups IV, V, VI and VIII including the actinide pseudohomologues are plotted in Fig. 3 as functions of the r^{-1}_{M-Cl} parameter. Figure 4 presents the dependence of $\Delta_sH^\circ(M)$ and $D(M-Cl)$ on Z in these groups.

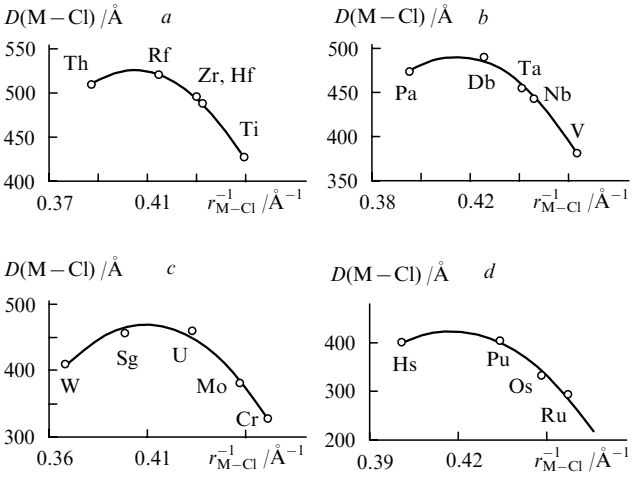


Figure 3. Bond energies $D(M-Cl)$ in tetrachlorides of the *d*-elements as functions of r^{-1}_{M-Cl} (g).
Group IV elements (*a*), Group V elements (*b*), Group VI elements (*c*) and Group VIII elements (*d*).

1. $TiCl_4$, $ZrCl_4$, $HfCl_4$, $ThCl_4$ and $RfCl_4$

For all gaseous tetrachlorides of Group IV elements (except $RfCl_4$), the interatomic distances were measured to an accuracy of ±0.02 Å and the $\Delta_fH^\circ(MCl_4, g)$ were determined. The interatomic distances are $r_{Ti-Cl} = 2.23$ Å; $r_{Zr-Cl} = 2.32$ Å, $r_{Hf-Cl} = 2.33$ Å (see Ref. 25) and $r_{Th-Cl} = 2.58$ Å (see Ref. 65).

Using the values $\Delta_fH^\circ(ThCl_4, g) = -964$ kJ mol^{-1} and $\Delta_sH^\circ(Th) = 597.1$ kJ mol^{-1} taken from Refs 61 and 66, one can obtain the $D(ThCl_4, g)$ value equal to 2047 kJ mol^{-1}. Therefore, the bond energies, $D(MCl_4, g)$, of tetrachlorides MCl_4 (M = Ti, Zr, Hf, Th and Rf) are equal to 1720, 1965, 1997, 2047 and 2090 kJ mol^{-1}, respectively. A sharp, experimentally observed increase in r_{Th-Cl} compared to r_{Hf-Cl} can be considered as manifestation of RE which destabilise the 6*d*-AO of thorium. Compared to $D(Hf-Cl)$, the $D(Th-Cl)$ value increases rather than decreases (see Fig. 3). Based on the $\Delta_fH^\circ(MCl_4, g)$ values for M = Zr, Hf, Th and Rf (−870, −889, −964 and −971 kJ mol^{-1}, respectively), Group IV elements can be divided into pairs Zr – Hf and Th – Rf with close values of the enthalpies $\Delta_fH^\circ(MCl_4, g)$. From the standpoint of thermodynamic properties, $ThCl_4$ belongs to the group of chlorides of the *d*-elements, which emphasises a specific feature of the early TAn, namely, similarity of their properties to those of An and of the *d*-homologues. All trends of changes in the chemical properties of compounds of Group IV elements and the similarity of Rf to Zr (see Refs 15 and 19) and to Th (see Ref. 18) are considered as manifestations of RE. Stability of the compounds under consideration, *i.e.*, the $\Delta_fH^\circ(MCl_4, g)$ value, depend on $\Delta_sH^\circ(M)$, r_{M-Cl} and $D(M-Cl)$. Each of these quantities changes within the group in its own manner. For instance, the $\Delta_sH^\circ(M)$ values increase from Th to Zr, Hf and Rf (597, 608, 622 and 634 kJ mol^{-1}, respectively).

$$\Delta_sH^\circ(Th) < \Delta_sH^\circ(Zr) < \Delta_sH^\circ(Hf) < \Delta_sH^\circ(Rf) \quad (3)$$

Thus, according to Eqn (2), the order of change in the sublimation enthalpies, $5f < 4d < 5d < 6d$, must correspond to the highest thermodynamic stability of $ThCl_4$.

However, the r_{M-Cl} values change in another manner, $4d \leqslant 5d < 6d < 5f$

$$r_{Zr-Cl} \leqslant r_{Hf-Cl} < r_{Rf-Cl} < r_{Th-Cl}, \quad (4)$$

which corresponds to the lowest thermodynamic stability of $ThCl_4$. This order is due to the geometry of the molecules in question. In the gas phase, $ZrCl_4$ and $HfCl_4$ are characterised by tetrahedral coordination. This type of coordination is also assumed for $RfCl_4$; however, an electron diffraction study [65] of $ThCl_4$ and UCl_4 revealed a distorted C_{2v} symmetry. As a result of superimposition of the effects denoted by sequences (3) and (4), we get

$$D(Zr-Cl) < D(Hf-Cl) < D(Th-Cl) < D(Rf-Cl)$$

$$\Delta_f H^\circ(ZrCl_4, g) \geqslant \Delta_f H^\circ(HfCl_4, g) > \Delta_f H^\circ(ThCl_4, g) \geqslant \geqslant \Delta_f H^\circ(RfCl_4, g).$$

Thus, two pairs of elements, *viz*., Zr–Hf and Th–Rf have similar thermodynamic properties.

Thorium is the second element of the An series. The atomic properties of Th are still not affected by the actinide contraction. Rutherfordium is the first element in the TAn series, whose properties are affected by both the actinide contraction and RE. Relativistic effects become stronger as Z increases:[8,24] in Rf(Z = 104), the 6*d*-AO should experience greater relativistic destabilisation than in Th(Z = 90). This means that the r_{Rf-Cl} distance in the $RfCl_4$ molecule must be at least comparable or longer than the r_{Th-Cl} distance in the $ThCl_4$ molecule. The measured r_{Th-Cl} distance (2.58 Å, see Ref. 65) and the calculated r_{Rf-Cl} distance (2.417 Å, see Ref. 4) undoubtedly indicate that the effect of actinide contraction appears to be stronger than both relativistic and nonrelativistic structural-shell destabilisation of the 6*d*-AO for Rf.

2. V, Nb, Ta, Pa and Db

For compounds of Group V elements, the $\Delta_f H^\circ(MCl_4, g)$ values (determined with an accuracy of ±15) decrease on going from the light to heavy elements.[4,68–69]

MCl_4	VCl_4	$NbCl_4$	$TaCl_4$	$DbCl_4$	$PaCl_4$
$\Delta_f H^\circ(MCl_4, g)$ /kJ mol^{-1}	−535	−567	−561	−707	−809

However, if the thermodynamic stability of $RfCl_4$ is close to that of $ThCl_4$, $DbCl_4$ appears to be less stable than $PaCl_4$ despite the fact that $r_{Pa-Cl} > r_{Db-Cl}$ (2.543 *vs*. 2.379 Å, respectively). On the other hand, the bond energy, $D(M-Cl)$, in gaseous MCl_4 increases from V to Db as Z increases. This trend of changes in the main parameters is due to the large difference (~200 kJ mol^{-1}) between the sublimation enthalpies, $\Delta_s H^\circ(M)$, of Pa and Db.

Element	V	Pa	Nb	Db	Ta
$\Delta_s H^\circ(M)$ /kJ mol^{-1}	513	570	722	769	782

It should be noted that for Th and Rf this difference is ~40 kJ mol^{-1}.

Figure 4 clearly displays a nonmonotonic trend in the changes in the parameters $\Delta_s H^\circ(M)$ and $\Delta_s H^\circ(An)$ with an increase in Z and a nearly monotonic trend of changes in $D(M-Cl)$.

We also analysed the changes in the properties determining the thermodynamics of gaseous tetrachlorides of Group V–VIII elements in order to show the disposition of the TAn and An elements relative to the 3*d*-, 4*d*- and 5*d*-elements (Table 3).

Trends in the changes of the chemical properties of *d*-elements down the groups of the Periodic table and their comparison with the properties of An have been the subject of a considerable amount of literature.[9,12–19] Particular emphasis is placed on how these properties change with Z, monotonically ($4d \rightarrow 5d \rightarrow 6d$) or nonmonotonically ($4d \rightarrow 6d \rightarrow 5d$). Nonmonotonic changes in particular properties are explained by nonmonotonic changes in the effective charges of gaseous molecules, which, in turn, are interpreted as the influence of RE.[14,15,19]

However, it was recently shown [9] that the effective charges cannot serve as quantitative criteria for the manifestation of RE. The data presented in Figs 3 and 4 and the above-mentioned $\Delta_f H^\circ(MCl_4, g)$ and $\Delta_s H^\circ(M)$ values taken from Refs 9, 10, 21, 48, 59, and 67 or calculated by the author of this review suggest that the thermodynamic properties represent a complex combination of different properties. For instance, compensation effects in the parameters $\Delta_s H^\circ(M)$ and $D(M-Cl)$ can cause both monotonic and nonmonotonic dependences of the $\Delta_f H^\circ(MCl_4, g)$ values within the groups. The absolute values of the parameters $\Delta_f H^\circ(MCl_4, g)$ are closest for Zr, Hf, Th and Rf. For heavier analogues, that is, Nb, Ta, Db, Pa; Mo, W, Sg, U; Tc, Re, Bh and Np the difference between TAn and An increases as the number of localised *f*-electrons in An increases; therefore, it is beyond reason to compare the TAn and An elements. The main regularities revealed for tetrachlorides also manifest themselves to a certain extent for tetrabromides.

A method for calculating the formation enthalpies of crystalline compounds (LnX_3, AnX_3 and AnX_4; X = F, Cl, Br, I) was proposed.[48,59] It is based on consideration of the formation of crystalline compounds from ions. This approach was used to calculate the formation enthalpies of crystalline compounds from gaseous atoms.[4,21,67] The formation enthalpies of crystalline compounds were calculated by the following equation

$$\Delta_f H^\circ(MX_4, c) = \Delta_s H^\circ(M) + 4\Delta_f H^\circ(X, g) - U(MX_4, c), \quad (5)$$

where $U(MX_4, c)$ is the crystal lattice energy.

The lattice energies can be estimated using the lattice parameters [30,45–48] or the r_{M-X} distances. For instance, calculations with known r_{M-X} and $U(MX_4, c)$ values or with r_{An-X} and $U(AnX_4, c)$ values determined from the experimental $\Delta_f H^\circ(MX_4, c)$ (M = Zr, Hf, Ta, Nb, Mo, W, Tc, Re, Ru, Os, Pt, Th, Pa, U, Np, Pu) parameters [45–76] revealed correlations between r_{M-X} and $U(MX_4, c)$ or between r_{An-X} and $U(AnX_4, c)$, which allowed one to calculate the $\Delta_f H^\circ(MX_4, c)$ values for all the crystalline tetrahalides of the *d*-elements of Rows 4–6 and for the actinides. The lattice energies of Pd, Rh, Ir and TAn were calculated [4,21] and those of Am, Cm, Bk, Cf and Es determined.[48] The $\Delta_f H^\circ(MX_4, c)$ values for TAn are listed in Table 2.

Table 3. Sequence of changes in the properties of Group V–VIII elements and their compounds.

Parameters	Sequence of changes in properties			
	Group V elements and Pa: V(3*d*), Nb(4*d*), Ta(5*d*), Db(6*d*), Pa(5*f*)	Group VI elements and U: Cr(3*d*), Mo(4*d*), W(5*d*), Sg(6*d*), U(5*f*)	Group VII elements and Np: Mn(3*d*),Tc(4*d*), Re(5*d*), Bh(6*d*), Np(5*f*)	Group VIII elements and Pu: Fe(3*d*), Ru(4*d*), Os(5*d*), Hs(6*d*), Pu(5*f*)
$\Delta_s H^\circ(M)$	$3d < 5f < 4d < 6d < 5d$	$3d < 5f < 4d < 6d \leqslant 5d$	$3d < 5f < 4d < 6d < 5d$	$5f < 3d < 4d < 5d \approx 6d$
$r(M-Cl)$	$3d < 4d < 5d < 6d < 5f$	$3d < 4d < 5d < 6d < 5f$	$3d < 4d < 5d < 6d < 5f$	$4d < 5d < 6d < 5f$
$D(M-Cl)$	$3d < 4d < 5d < 5f < 6d$	$3d < 4d < 5d < 5f \leqslant 6d$	$4d < 5d < 6d < 5f$	$4d < 5d < 6d < 5f$
$\Delta_f H^\circ(MCl_4, g)$	$3d > 5d \approx 4d > 6d > 5f$	$5d > 4d > 3d > 6d > 5f$	$4d > 5d > 6d > 5f$	$4d > 5d > 6d > 5f$

IV. Volatility of transactinide compounds as a function of their structure in the crystalline and gaseous states

1. Comparison of earlier and recently obtained results

One of the main experimental methods used for determining the sublimation enthalpies of TAn is the volatility measurements of their halides and oxyhalides.[11, 13, 14, 17, 77–85] Volatile compounds of metals are compounds that can undergo sublimation and condensation at moderate ($< 700-800$ K) temperatures. However, both the experimental data and their theoretical interpretation are contradictory. It was not an occasion that the authors of monograph [77] wrote that 'volatility belongs to such properties of chemical compounds that are hard to predict even qualitatively'. They also mentioned that, despite the existence of two experimental methods for studying the volatility properties (measurements of sublimation enthalpies and determination of the temperature dependence of the vapour pressure, $P = f(T)$, only the second approach allows one to obtain complete and reliable information on the volatility properties. For instance, the sublimation enthalpies of $ZrCl_4$ and $HfCl_4$ were reported to be equal, *viz.*, $\Delta_s H^\circ(ZrCl_4) = \Delta_s H^\circ(HfCl_4) = 100$ kJ mol^{-1};[26, 86] however, measurements of the $P = f(T)$ dependence over a wide temperature range pointed to the higher volatility of $HfCl_4$ compared to $ZrCl_4$. Theoretical predictions of volatility properties are also complicated by the need to take into account the molecular structure in the crystalline and gaseous states.

Chemical experiments with TAn are carried out using single atoms (the so-called 'one atom-at-a-time' technique). Since in these experiments we deal with single molecules, neither $P = f(T)$ nor $\Delta_s H^\circ$ can be measured. Therefore, TAn are studied by isothermal gas chromatography and thermochromatography. The parameter measured in gas chromatography studies [20] is the enthalpy of adsorption, $\Delta_a H^\circ_T$, on a chromatographic surface (usually, quartz). The sublimation enthalpies of chlorides and oxychlorides, $\Delta_s H^\circ_{298}$, are calculated from a linear correlation between these values, $\Delta_s H^\circ_{298}$ and $\Delta_a H^\circ_T$. However, the results obtained using this procedure are less reliable than those of the direct measurements of $\Delta_s H^\circ_{298}$. From the viewpoint of the reliability of the results obtained and based on conclusions drawn in monograph,[77] the experimental methods used in volatility studies can be listed in the following order

$$P = f(T) > \text{direct measurements of } \Delta_s H^\circ > \text{correlation of } \Delta_s H^\circ \text{ and } \Delta_a H^\circ_T.$$

In addition, a drawback of the experiments with TAn 'is that the chemical composition of compounds under study cannot be identified and that possible chemical formulae are postulated based on the results of experiments with early homologues'.[14] These experiments are carried out assuming a complete analogy between the chemical properties of the 4*d*-, 5*d*- and 6*d*-elements within the groups of the Periodic table and the same type of compounds of the same chemical composition, though it is not universally true. For instance, in Groups VI and VII almost all halide compounds of rhenium are volatile at room or higher temperatures.[70] ReO_3Cl and $ReOCl_4$ that are hard to separate are formed under the same conditions.[70] Even more complicated is the situation observed in the case of the identification of volatile compounds of Group VI elements.[70] For instance, pairs of compounds MoO_2Cl_2 and $MoOCl_4$ or WO_2Cl_2 and $WOCl_4$ are formed under the same conditions; MoO_2Cl_2 and $MoOCl_4$ can be chemically separated only by *in vacuo* sublimation at $70-80$ °C; WO_2Cl_2 undergoes disproportionation resulting in $WOCl_4$, which in dioxygen atmosphere adds a O_2 molecule and releases Cl_2, thus again forming WO_2Cl_2. Recently,[87] thermodynamic analysis was performed on all possible Mo and W compounds that can be formed in the gas phase.

Further, assuming a complete analogy between the chemical properties of the 4*d*-, 5*d*- and 6*d*-elements within the corresponding groups, the same adsorption mechanism is postulated for all homologues. Clearly, adsorption depends on the character of bonding between individual molecules or their ensembles and the surface. Surface reactions are neither microscopic nor macroscopic; they belong to a broad class of 'intermediate' reactions which comprises both microscopic and macroscopic reactions.[88]

The surface of quartz is an arena in which different chemical processes occur. Quartz possesses no strong basic or acid properties. Depending on temperature, its surface can adsorb protons, hydroxy groups, polarised siloxane groups, chlorine and dioxygen molecules, *etc.*[88] The minimum energy of the van der Waals interaction necessary for physisorption to occur is ≈ 20 kJ mol^{-1}. The $-\Delta_a H^\circ_T$ values measured in the experiments with TAn and their homologues lie between 50 and 250 kJ mol^{-1}. These magnitudes of the heats of adsorption suggest different adsorption mechanisms including the formation of chemical bonds M–Cl, M–Si, M–OH, *etc.*, between the adsorbed molecules and quartz surface irrespective of one molecule or ensemble of gaseous molecules is adsorbed on the surface. Yet another problem is the heterogeneity of the real quartz surface and possible modification of this surface by some components of the carrier gas. Therefore, taking into account the conclusions drawn in monograph [77] and the postulates proposed by the authors of other studies,[14, 17] the results obtained from the correlation of $\Delta_s H^\circ$ with $\Delta_a H^\circ_T$ seem to be even less reliable.

Theoretical chemistry uses four approaches to volatility studies.

The first approach is based on calculations of (i) bond covalencies and effective charges in gaseous molecules or (ii) dipole moments of these molecules using the same charges. Changes in the effective charges are interpreted as a manifestation of RE. This approach ignores the mechanism of adsorption and, hence, the structure of solids. The high covalency of the M–Cl bonds in gaseous molecules is assumed to correspond to high volatility of respective crystalline compounds. This model was used to rationalise the trend in the changes in the volatility of chlorides MCl_4 (M = Rf, Hf, Zr).[14] However, experimental data showed that the covalency of the M–X bonds in gaseous MX_4 molecules cannot serve as criterion for volatility. Undoubtedly, TiF_4 is a more ionic compound than TiI_4; nevertheless, both of them are characterised by the same volatility.[70] The volatility of the covalent compound UCl_6 is much lower than that of ionic compound UF_6; the ionic compounds UF_6, NpF_6 and PuF_6 exhibit the highest volatilities among all the simple and complex An compounds.[61] The results of calculations of gaseous Group VI dioxyhalides MO_2Cl_2 (M = Mo, W, Sg), carried out in the framework of a relativistic discrete variation approach have been reported.[15] According to calculations,[15] SgO_2Cl_2 is characterised by the largest contribution of covalent bonding and should be the most volatile compound within the group. However, experiments showed the opposite: SgO_2Cl_2 possesses the lowest volatility within the group of the Periodic table.[14] It was then assumed [15] that volatility is determined by the dipole moments of gaseous molecules, $\mu(MO_2Cl_2)$; however, experimental data revealed that neither bond covalency in nor dipole moments of gaseous molecules can serve as criterion for volatility. For instance, gaseous molecules AnF_6 (An = U, Np, Pu) have equal dipole moments, $\mu(AnF_6)$; however, NpF_6 in the crystalline state has abnormally high vapour pressure.[61] Experimental data showed that the approach based on calculations of bond covalencies and effective charges [14] and dipole moments [15] of gaseous molecules is incorrect and inapplicable in the case of the prediction of volatility.

The second approach was proposed by Zhuikov *et al.*[78] who assessed the volatility of the tetrachlorides $RfCl_4$, $HfCl_4$ and $ZrCl_4$ from the parameters of thermodynamic cycle including the cohesive energy of the metal. In contrast to the preceding case, this model, though indirectly, takes into account two states of matter.

Eichler [79] hypothesised that the formation enthalpy of gaseous metal atoms can serve as a measure of sublimation enthalpies of

chemical compounds and suggested a correlation between these parameters (third approach).

An experimental indication of the volatility of metal compounds is the possibility of sublimation of the substance under study.[77] Therefore, in early studies[21,67] researchers used the difference between the standard formation enthalpies of a compound in the crystalline and gaseous states as a possible characteristic of volatility (fourth approach).

The need to take into account the distinctions between the structure of two phase states (probably, in terms of adsorption mechanism) when calculating the sublimation enthalpies of chemical compounds has been proposed[11,13,67,77,78,79] and can be exemplified as follows.

Group IV. Titanium tetrachloride in the gaseous and crystalline states has a monomeric structure (CN = 4), which is responsible for the small $\Delta_s H^\circ(TiCl_4)$ value (52 kJ mol^{-1}).[26]

Similarly to $TiCl_4$, tetrachlorides of zirconium and hafnium in the gas phase have a tetrahedral structure (CN = 4). However, in the crystalline state these compounds are polymers with octahedral coordination (CN = 6). For the sublimation enthalpies of these compounds, we get $\Delta_s H^\circ(ZrCl_4) \approx \Delta_s H^\circ(HfCl_4) \approx$ 100 kJ mol^{-1}.[26] An increase of 2 in the CN for the crystalline state compared to the gaseous state causes a nearly twofold increase in the parameters $\Delta_s H^\circ(ZrCl_4)$ and $\Delta_s H^\circ(HfCl_4)$ compared to $\Delta_s H^\circ(TiCl_4)$.

For thorium tetrachloride, the CN is 4 in the gaseous state and 8 in the crystalline state.[61,65] An increase of 4 in the CN for the crystalline state compared to the gaseous state caused a nearly fourfold increase in the parameter $\Delta_s H^\circ(ThCl_4)$ (249 ± 20 kJ mol^{-1}) compared to $\Delta_s H^\circ(TiCl_4)$. Therefore, the CN in gaseous molecules remains unchanged (CN = 4) on going from $TiCl_4$ to $ThCl_4$; however, the structure of crystalline compounds becomes more complex, which results in an increase in $\Delta_s H^\circ(MCl_4)$. If all crystal compounds were built of monomeric molecules similar to $TiCl_4$, they would be characterised by a small sublimation enthalpy ($\sim$50 kJ mol^{-1}). Probably, the properties of adsorbed molecules are similar to those of the molecules in the crystalline rather than the gaseous state.

The sublimation enthalpies, $\Delta_s H^\circ(MCl_4)$, correlate with the $r(M^{IV})$ of Ti, Zr, Hf and Th in the crystalline state.

M^{IV}	CN	Ionic radius $r(M^{IV})$ /Å	$\Delta_s H^\circ(MCl_4)$ /kJ mol^{-1}
Ti	4	0.60	52
Zr	6	0.72	100
Hf	6	0.73	100
Th	8	1.048	249

The formula is as follows

$$\Delta_s H^\circ(MCl_4) \approx 442\, r(M^{IV}) - 215 \text{ kJ mol}^{-1}.$$

Substituting the value $r(Rf^{IV})(CN = 6) = 0.75-0.78$ Å, we get $\Delta_s H^\circ(RfCl_4) = 117-130$ kJ mol^{-1}, which is close to the experimental value $\Delta_s H^\circ(RfCl_4) = 109 \pm 10$ kJ mol^{-1}.[14] It seems logical to assume that adsorption of $RfCl_4$ causes expansion of its coordination sphere and an increase in CN to 6 (similarly to $ZrCl_4$ and $HfCl_4$) rather than 8 as in the case of $ThCl_4$.

Other values of the parameter $\Delta_s H^\circ(RfCl_4)$ reported in the literature are 90 ± 15 (see Ref. 80) and 122–138 kJ mol^{-1} (see Ref. 83). They lie within the interval 110 ± 30 kJ mol^{-1}, which is consistent with the value reported by Türler.[14]

Thus, the results of volatility studies can provide the possibility of modelling the structure of crystalline TAn compounds. The volatility of compounds of Group VI–VII elements can be analysed analogously.

Group VI. Nearly two decades ago Academician V I Spitsyn brought the attention of the author of this review to the problem[1] of analysing the chemical properties of Mo and W compounds in order to find optimum conditions for their separation. The main conclusion drawn after solving this problem was that separation of Mo and W requires the use of their compounds in their lower oxidation states. It was found that the higher the oxidation state the less significant the distinctions between the chemical behaviour of Mo and W and that maximum similarity of the Mo and W compounds is observed for the oxidation state VI. Currently, some effort has been made to reveal distinctions between the chemical behaviour of compounds of Mo^{VI}, W^{VI} and Sg^{VI} in the gaseous state and in solution. The main problem of volatility studies of Group VI compounds is to identify the substances formed in the gas phase.[70,87]

The thermodynamic stability of the W and Mo compounds was also used as a criterion for identification.[87] It was concluded[87] that MoO_2Cl_2, WO_2Cl_2 and SgO_2Cl_2 have similar thermodynamic properties (their boiling points are close). The stability of MO_2Cl_2 and $MOCl_4$ towards thermal decomposition was determined using the energy of the charge-transfer transition, ΔE_{ct}, in the electronic spectra.[15] This method was also used for estimating the redox potentials of Pu(VII)/Pu(VI), Np(VII)/Np(VI), *etc.*[1–3,45–47] in solutions from the measured ΔE_{ct} values for their complexes. However, these spectral transitions are by no means related to the gas-phase stability of compounds which is determined by the standard formation enthalpy. Based on the results of determination of ΔE_{ct} values, MO_2Cl_2 was suggested to be more stable towards thermal dissociation than $MOCl_4$ (see Ref. 15). However, the standard formation enthalpies ($\Delta_f H^\circ$) of gaseous MO_2Cl_2 and $MOCl_4$ (M = Mo, W) molecules changes in the order $WO_2Cl_2 < MoO_2Cl_2 = WOCl_4 < MoOCl_4$ (see Ref. 87). This trend is quite remarkable since it contradicts the conclusions drawn by Kratz.[15] Taking into account the results of studies,[70,87] the theoretically predicted[15] trend in changes in the volatility of oxychlorides of Mo, W and Sg seems to be doubtful; in addition, there is no proof so far that the experimental[14] sublimation enthalpies [$\Delta_s H^\circ = 114 \pm 11$, 124 ± 10 and $127 \pm 10(21)$ kJ mol^{-1}] can be unambiguously attributed to the compounds MoO_2Cl_2, WO_2Cl_2 and SgO_2Cl_2, respectively. In the gas phase, MoO_2Cl_2, WO_2Cl_2, $WOCl_4$ and $MoOCl_4$ mainly have the monomeric structure; however, in the crystalline state the CN increases and these compounds have a polymeric structure. Compounds MO_2Cl_2 (M = Mo, W) readily add neutral oxygen-containing molecules to give complexes $MO_2Cl_2 \cdot 2L$ (L = $HCONMe_2$, Me_2SO, *etc.*). In the crystalline state, $MoO_2Cl_2 \cdot 2L$ has a monomeric structure while $WO_2Cl_2 \cdot 2L$ has a polymeric structure.[70] In this connection, a new problem arises since different adsorption mechanisms of Mo and W(Sg) compounds become possible. Probably, a more conservative interpretation of the chemical properties of Sg in the gas phase is required, which takes into account the accuracy of the experimental data. It cannot be ruled out that conclusions drawn by Kratz[15] about the chemical behaviour of Sg should be revised since there is no proof that only one type of compounds, *viz.*, MO_2Cl_2 (M = Mo, W, Sg) is formed in the gas phase.

Group VII. In the gaseous state, the CN of oxychlorides MnO_3Cl, TcO_3Cl and ReO_3Cl equals 4. Transition to the crystalline state leads to the formation of bridging bonds and the CN value increases. This should cause an increase in volatility in the order $MnO_3Cl < TcO_3Cl < ReO_3Cl < BhO_3Cl$. For TcO_3Cl, ReO_3Cl and BhO_3Cl this sequence was obtained experimentally,[17] which is consistent with recently reported results. For instance, MnO_3Cl undergoes sublimation at -68 °C (see Ref. 70) while the sublimation temperatures of TcO_3Cl, ReO_3Cl and BhO_3Cl are respectively $-20-40$, $20-80$ and $80-180$ °C (see Ref. 17).

Group VIII. It does not always happen that the structure of compounds changes upon transition from the gaseous to the crystalline state. Compounds HsO_4 and OsO_4 were predicted[67] to have a monomeric structure in the crystalline state.

In conclusion, let us compare the results concerning the trend in changes of the volatility of tetrahalides and its interpretations given by different authors.

Earlier results[26] obtained from measurements of the temperature dependence of the vapour pressure, $P = f(T)$, show that the

volatility changes in the order $HfCl_4 > HfBr_4 > ZrCl_4 > ZrBr_4$. According to Türler,[14] it changes in another manner, namely, $ZrBr_4 \geqslant ZrCl_4 > HfCl_4 > HfBr_4$. Some other examples of inconsistency between the results of earlier and recent studies can be given. For instance, it was established that $NbBr_5$ has higher volatility than $TaBr_5$.[84] These results were shown[85] to contradict those obtained earlier from the $P = f(T)$ measurements [according to monograph,[26] all tantalum halides (TaF_5, $TaCl_5$, $TaBr_5$) have higher volatilities than the corresponding niobium halides (NbF_5, $NbCl_5$, $NbBr_5$)].

Seemingly, one can conclude that the results of volatility measurements performed by classical methods [$P = f(T)$] using macroamounts of substances always differ from those obtained in experiments with microamounts. However, sometimes the results of both types of experiments coincide. For instance, TcO_3F was reported [89] to be more volatile than ReO_3F and a similar trend was revealed for TcO_3Cl and ReO_3Cl.[17] Lower volatility of $NbOCl_3$ compared to $NbCl_5$ was reported in both earlier [26, 86] and recent studies.[14]

Inconsistency of the results obtained seems to be due not only to the fact that the volatility is measured using macroamounts or microamounts of chemical compounds. The main reason is that the chemical composition of compounds studied in modern experiments can hardly be established, whereas in earlier studies the chemical composition of the gas phase was thoroughly investigated. Earlier, all the compounds formed as well as decomposition products were analysed when performing $P = f(T)$ measurements. For instance, studies of $NbOCl_3$ were carried out taking into account the presence of accompanying chloride $NbCl_5$ in the vapour (see Ref. 26).

It is hard to agree with the conclusion [14] that 'relativistic effects are most experimentally pronounced' in the volatilities of TAn halides and oxyhalides determined using correlation with adsorption enthalpies. This conclusion is based on the results of bond covalency calculations in gaseous molecules; however, this parameter is by no means related to volatility. Türler also stated [14] that 'recent experiments demonstrated that the chemical properties of heavy elements can no longer be predicted based on simple down-the-group extrapolations because of the influence of RE'. At the same time, he postulated the same chemical composition and adsorption mechanism for all compounds of the 4*d*-, 5*d*-, 6*d*-elements within corresponding groups. Thus, these conclusions contradict the initial postulates.

The authors of studies [14, 15] pose illusive problems that are insoluble due to large experimental errors and the above-mentioned postulates. They draw definite conclusions about the influence of RE on the adsorption enthalpy without knowledge of the molecules that are formed on the surface.

Gas-state chemistry of TAn compounds has been successfully progressing in spite of great experimental problems. Probably, one can assume that the 6*d*-elements and the early 4*d*- and 5*d*-homologues can form compounds of analogous chemical composition; however, unambiguous identification of these compounds is impossible.

2. Sublimation enthalpies of TAn tetrahalides

The sublimation enthalpies, $\Delta_s H^\circ(MX_4)$, of MX_4 (X = Cl, Br) compounds were calculated by the author of this review for tetrahalides of the 4*d*-, 5*d*- and 6*d*-elements and actinides as the differences between the standard formation enthalpies of the corresponding compounds in the gaseous and crystalline states. The sublimation enthalpies of TAn compounds are listed in Table 2. Calculations were carried out assuming that the CN for compounds of the 4*d*-, 5*d*- and 6*d*-elements equals 4 in the gaseous state and 6 in the crystalline state. The experimental CN values for $AnCl_4$ compounds were reported by Brown.[61] Comparison of the calculated and experimental $\Delta_s H^\circ(MX_4)$ values for compounds of the 4*d*- and 5*d*-elements allowed us to estimate the error (uncertainty) of calculations at ± 15 kJ mol^{-1}. The $\Delta_s H^\circ(MCl_4)$ values (in kJ mol^{-1}) obtained for tetrachlorides of Group V–VIII elements are listed below:

M (Group IV)	Zr	Hf	Rf
$\Delta_s H^\circ(MCl_4)$ /kJ mol^{-1}	112	102	106
M (Group V)	Nb	Ta	Db
$\Delta_s H^\circ(MCl_4)$ /kJ mol^{-1}	128	144	141
M (Group VI)	Mo	W	Sg
$\Delta_s H^\circ(MCl_4)$ /kJ mol^{-1}	113	160	158
M (Group VII)	Tc	Re	Bh
$\Delta_s H^\circ(MCl_4)$ /kJ mol^{-1}	112	141	131
M (Group VIII)	Ru	Os	Hs
$\Delta_s H^\circ(MCl_4)$ /kJ mol^{-1}	109	147	147
M (Group VIII)	Rh	Ir	Mt
$\Delta_s H^\circ(MCl_4)$ /kJ mol^{-1}	83	115	112

Vertical trends in the changes of the $\Delta_s H^\circ(MCl_4)$ values are different, namely, $5d \leqslant 6d < 4d$ for Group IV, $4d < 6d \leqslant 5d$ for Group V and $4d < 6d \leqslant 5d$ for Group VI.

As mentioned above, many of the thermodynamic properties of Group IV elements are similar. The sublimation enthalpies of the tetrachlorides of Group IV elements are also close. The calculated sublimation enthalpies of An tetrachlorides (in kJ mol^{-1}) are listed below:

Actinide	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf
$\Delta_s H^\circ(AnCl_4)$	249	220	213	168	172	110	128	131	62

The error (uncertainty) of calculations of the $\Delta_s H^\circ(AnCl_4)$ parameters was estimated at ± 20 kJ mol^{-1} based on their comparison with the corresponding experimental values for An = Th, U and Pu (see Refs 61 and 70).

Two different trends should be recognised when comparing the sublimation enthalpies of tetrachlorides of the *d*- and 5*f*-elements, namely, the volatility of early An compounds decreases while that of the *d*-element compounds increase as Z increases. Among the early An compounds, the volatility of tetrachlorides is much higher than that of tetrachlorides of the *d*-elements (the difference is ≈ 100 kJ mol^{-1}). This difference decreases near the middle of the actinide series and then the volatilities of the tetrachlorides differ insignificantly. The volatility of tetrachlorides of the heavy *d*- and *f*-elements decreases with an increase in Z.

The trend in the changes in the volatility of $AnCl_4$ compounds and tetrachlorides of *d*-elements (MCl_4) deserves attention. Eichler [79] suggested a correlation between the $\Delta_s H^\circ(M)$ and $\Delta_s H^\circ(MCl_4)$ values. We tested this idea using An and $AnCl_4$ compounds as an example. Comparison of the experimental and calculated $\Delta_s H^\circ(An)$ and $\Delta_s H^\circ(AnCl_4)$ values along the actinide series confirmed that changes in these parameters follow the same trend. Based on correlation between these values, one can even estimate the $\Delta_s H^\circ(AnCl_4)$ parameters to an accuracy of ± 40 kJ mol^{-1}. This is quite good accuracy for prediction of a trend that reflects a decrease in $\Delta_s H(AnCl_4)$ with a decrease in $\Delta_s H(An)$. In turn, a dramatic decrease in $\Delta_s H^\circ(An)$ on going from early to late An is due to the change in the valence V_{An} in the metallic state.

For the 4*d*-, 5*d*- and 6*d*-transition metals the dependence of $\Delta_s H^\circ(M)$ on $Z(M)$ is nearly parabolic: the $\Delta_s H^\circ(M)$ values increase on going from the early to the middle of the series and then decrease towards the end of the series. It cannot be ruled out that this type of correlation [79] can be used for the first (Rf–Bh) and second (Bh–^{112}TAn) half of the TAn series separately.

V. Standard formation enthalpies of gaseous MCl_6^{2-} anions and affinity of tetrachlorides towards chloride ions

Using the formation enthalpies of gaseous MCl_6^{2-} anions, $\Delta_f H^\circ(MCl_6^{2-}, g)$, one can estimate the affinity of gaseous and crystalline tetrachlorides towards chloride ions and thus compare the trends of changes in these important parameters within the groups of the 4*d*-, 5*d*- and 6*d*-elements. In addition, this allows comparison of the thermodynamic properties of hexachlorides in aqueous solutions:

$$\Delta_f H^\circ(MCl_6^{2-}, g) = \Delta_f H^\circ(MCl_6^{2-}, aq) - \Delta_h H^\circ(MCl_6^{2-}, g) + C, \quad (6)$$

where $\Delta_h H^\circ(MCl_6^{2-}, g)$ is the hydration enthalpy of the gaseous MCl_6^{2-} anion and C is a constant [$C = -2\Delta_f H^\circ(H^+, g) - 2\Delta_h H^\circ(H^+, g)$].

The formation enthalpy of gaseous anions, $\Delta_f H^\circ(MCl_6^{2-}, g)$, is the main parameter used for calculating the formation enthalpy of crystalline salts A_2MCl_6. For the reaction listed below

$$M(g) + 4\,Cl(g) + 2\,Cl^-(g) = MCl_6^{2-}(g)$$

the $\Delta_f H^\circ(MCl_6^{2-}, g)$ values can be predicted using the equation

$$\Delta_f H^\circ(MCl_6^{2-}, g) = \Delta_s H^\circ(M) + 4\Delta_f H^\circ(Cl, g) + 2\Delta_f H^\circ(Cl^-, g) - \left[c - \frac{d}{r(M-Cl)}\right], \quad (7)$$

where the last term,

$$c - \frac{d}{r(M-Cl)} = D(MCl_6^{2-}),$$

is the bond energy in the anion, the coefficients c and d are found from experimental $\Delta_f H^\circ(MCl_6^{2-}, g)$ values for the 4*d*- and 5*d*-elements; the $r(M-Cl)$ values for CN = 6 are listed in Table 1.

Using Eqn (7), one can calculate the $D(M-Cl)$ values for all the 4*d*-, 5*d*- and 6*d*-elements and the $\Delta_f H^\circ(MCl_6^{2-}, g)$ values for TAn. These calculations were performed by the author of this review for anions of the 4*d*- and 5*d*-elements with an accuracy (uncertainty) of ± 15 kJ mol^{-1}. The formation enthalpies $\Delta_f H^\circ(MCl_6^{2-}, g)$, $\Delta_f H^\circ(MCl_6^{2-}, aq)$ and $\Delta_h H^\circ(MCl_6^{2-}, g)$ are listed in Table 2.

It was found that the thermodynamic stability of gaseous MCl_6^{2-} anions and aqua ions (MCl_6^{2-}, aq) decreases with an increase in Z(TAn), whereas the order of changes in these values within particular groups is as follows: $4d < 5d < 6d$. The same trends for the TAn series are also observed for MBr_6^{2-} anions.

The affinity $A(Cl^-, g)$ of MCl_4 compounds in the crystalline and gaseous states towards two Cl^- ions can be calculated using the following equations

$$A(Cl^-, g) = \Delta_f H^\circ(MCl_6^{2-}, g) - \Delta_f H^\circ(MCl_4, g) - 2\Delta_f H^\circ(Cl^-, g)$$

and

$$A(Cl^-, c) = \Delta_f H^\circ(MCl_6^{2-}, g) - \Delta_f H^\circ(MCl_4, c) - 2\Delta_f H^\circ(Cl^-, g).$$

Both monotonic and nonmonotonic trends in changes in the affinity towards chloride ions within groups were found experimentally for tetrachlorides of *p*- and *d*-elements [90]

$GeCl_4 < SnCl_4 > PbCl_4$; $SnCl_4 > TeCl_4$; $HfCl_4 > ZrCl_4 > TiCl_4$;

$TaCl_4 > NbCl_4$; $WCl_4 < MoCl_4$.

In the text below we compare the $A(Cl^-, g)$ values for tetrachlorides of the 4*d*-, 5*d*- and 6*d*-elements [21] and actinides.[91] (The values for $TiCl_4$ and $ThCl_4$ were taken from Ref. 30).

1. Tetrachlorides of Group IV elements

MCl_4	$RfCl_4$	$ThCl_4$	$HfCl_4$	$ZrCl_4$	$TiCl_4$
$A(Cl^-, g)$ /kJ mol^{-1}	−286	−287	−284	−190	−76

Thus, the heavy Group IV elements are characterised by nearly equal affinity towards chloride ions, which decreases on going to the early elements of this Group.

2. Tetrachlorides of Group V elements

MCl_4	$TaCl_4$	$DbCl_4$	$NbCl_4$
$A(Cl^-, g)$ /kJ mol^{-1}	−266	−246	−169

3. Tetrachlorides of Group VI elements

Inversion of $A(Cl^-, g)$ values [30, 90] for $MoCl_4$ and WCl_4 is observed, so that the $A(Cl^-, g)$ value for UCl_4 (−270 kJ mol^{-1}) [30] 'completes' the picture:

MCl_4	UCl_4	$SgCl_4$	$MoCl_4$	WCl_4
$A(Cl^-, g)$ /kJ mol^{-1}	−270	−220	−219	−214

4. Tetrachlorides of Group VII elements

MCl_4	$ReCl_4$	$BhCl_4$	$TcCl_4$
$A(Cl^-, g)$ /kJ mol^{-1}	−181	−171	−168

5. Tetrachlorides of Group VIII elements

MCl_4	$RuCl_4$	$OsCl_4$	$HsCl_4$
$A(Cl^-, g)$ /kJ mol^{-1}	−223	−209	−175

For actinides $NpCl_4$ and $PuCl_4$, the $A(Cl^-, g)$ values ($\approx -270 \pm 20$ kJ mol^{-1}) are larger than those obtained for the *d*-elements of Groups VII and VIII.

Thus, $RfCl_4$, $ThCl_4$ and $HfCl_4$ are better acceptors of chloride ions than $ZrCl_4$ while $DbCl_4$ and $TaCl_4$ are better acceptors of chloride ions compared to $NbCl_4$. From this point of view, chlorides of Group IV elements ($RfCl_4$, $ThCl_4$, $HfCl_4$, $ZrCl_4$) are 'better' than the corresponding chlorides of Group V elements ($DbCl_4$, $PaCl_4$, $TaCl_4$, $NbCl_4$). However, UCl_4 is a better acceptor of chloride ions than $SgCl_4$, $MoCl_4$ and WCl_4, while $NpCl_4$ and $PuCl_4$ are better acceptors of chloride ions compared to $BhCl_4$ and $HsCl_4$.

Some experimental studies on the chemistry of Rf, Db and Sg revealed nonmonotonic changes in the properties in the order $4d > 6d > 5d$. 'Prediction of an inverse trend for the properties on going from the 5*d*-elements to the 6*d*-elements' was stated [15] to be a new effect in chemistry. Theoretically, inversion was rationalised by the influence of Re on TAn; however, trends observed experimentally in the chemistry of the 3*d*-, 4*d*-, 5*d*- and 5*f*-elements are not reduced only to inversion. For instance, studying the above-mentioned property, *viz*. the affinity of tetrahalides towards chloride ions, reveals different trends.

The affinities of crystalline TAn tetrachlorides toward chloride ions, $A(Cl^-, c)$, are listed in Table 2. They are less negative than the corresponding $A(Cl^-, g)$ values.

VI. Solution behaviour of transactinides

A series of earlier and more recent studies concerned with the investigation of the nitrate, fluoride and chloride complexes of the *d*-elements including An was reported.[12, 15, 16, 18, 92–140] Recently, TAn complexes have been studied along with complexes of the 4*d*-, 5*d*- and 5*f*-elements. The behaviour of the compounds of the 4*d*- and 5*d*-elements in aqueous solutions was previously investigated by extraction in a two-phase system; this method has been used so far in studies of the 4*d*-, 5*d*- and 6*d*-elements. For as long as four or five decades, Zr and Hf have been extracted from solutions of mineral acids (HCl, HNO_3, $HClO_4$) by tri-*n*-butyl phosphate (TBP), which is also used for extraction of Zr and Hf with Rf additives in order to compare the stability of neutral complexes $(RfCl_4)_{aq}$, $(HfCl_4)_{aq}$ and $(ZrCl_4)_{aq}$. Previously, the influence of hydrolysis on the complexation and extraction of Zr^{IV} and Hf^{IV} was studied; recently, Rf^{IV} has been the subject of intensive research.

However, the conclusions drawn from the results of complexation investigations in the earlier and recent studies do not always coincide. In modern literature, the results are rationalised by the influence of RE and by specific features of single-atom experiments. We believe that there are also some other reasons for inconsistency between the recent and previously obtained results. They are discussed below.

1. Anionic chloride complexes

Quaternary ammonium salts are known to be extractants of Zr^{IV} and Hf^{IV} in the form of anions. Early studies revealed inhibition of both hydrolysis and polymerisation in the aqueous phase in the acid medium at a low concentration of cations.[140] These conditions are similar to those of the experiments with TAn (studies of the behaviour of single atoms) and their homologues within groups of the Periodic system. Extraction studies in the two-phase system using quaternary ammonium salts as extractants demonstrated [92,93] that Rf, Hf and Zr form anionic MCl_6^{2-} complexes which are more stable than $AnCl_6^{2-}$ complexes. It was also revealed [94] that the $RfCl_6^{2-}$ anion is more stable than the $HfCl_6^{2-}$ and $ZrCl_6^{2-}$ anions. The stability of MCl_6^{2-}(aq) anions for Group IV elements was shown to increase on going from the light to heavy elements.[21] For instance, the $\Delta_f H^\circ(MCl_6^{2-}, aq)$ for Zr, Hf and Rf are -1473, -1577 and -1637 kJ mol^{-1}, respectively. Thus, the stability of the anions increases in the order $ZrCl_6^{2-} < HfCl_6^{2-} < RfCl_6^{2-}$, which is consistent with the results of earlier studies.[92–94] It was also found that, despite greater stability of the MCl_6^{2-}(aq) anions (M = TAn) compared to the corresponding anions containing the 4*d*- and 5*d*-elements, no monotonic increase in stability on going from the 4*d*-elements to the 6*d*-elements is observed for all groups of the Periodic table. In particular, a nonmonotonic change in the thermodynamic stability of MCl_6^{2-}(g) and MCl_6^{2-}(aq) anions in the order Sg > Mo > W is predicted for the Group VI elements.

2. Neutral chloride complexes

It was pointed out [15,19] that the results of experimental extraction studies of neutral chloride complexes of Rf from concentrated (8–12 M) HCl solutions in TBP, obtained by different authors [12,15,16,19,116,129–132] contradict one another. It was suggested [12] that the extraction behaviour of Rf is similar to that of Th and Pu rather than Zr and Hf. Recently reported [19,130] extractive power sequences corresponding to the changes in stability of neutral complexes are different, that is Zr > Rf > Hf (see Ref. 19) and Zr > Hf > Rf (see Ref. 130). From the standpoint of the ability of the Zr, Hf and Rf complexes to undergo hydrolysis, these elements can be ordered as follows: Hf > Rf > Zr (see Ref. 19). Competition between hydrolysis and formation of inner-sphere complexes during extraction was suggested [15,19]

$$M(OH)_xCl_{4-x} + x\,HCl \rightleftharpoons MCl_4 + x\,H_2O.$$

It is believed [15] that no extraction of the hydrolysed complexes occurs in the organic phase because of the formation of strong hydrogen bonds between OH^- and H_2O in the aqueous phase.

Generally, earlier experimental studies [117–120,133–136] revealed that under specific conditions hydrolysed complexes of both Zr^{IV} and Hf^{IV} are extracted along with non-hydrolysed complexes. It was also shown that hydrolysed compounds of Zr and Hf exist in weak acid solutions only at high concentrations of Zr^{IV} and Hf^{IV}.

It was postulated [15,19] that the trend in the changes of the effective charges $q(Zr) > q(Rf) > q(Hf)$ in gaseous MCl_4 molecules [$q(ZrCl_4) = 1.18$, $q(RfCl_4) = 1.07$ and $q(HfCl_4) = 1.04$] holds for all processes occurring in solution: the ability to undergo hydrolysis (Hf > Rf > Zr), the formation of complexes MCl_4(aq) (Zr > Rf > Hf) and extractive power (Zr > Rf > Hf). However, the accuracy of quantum-chemical calculations of the effective charges was shown [9] to be by a factor of 25 to 30 lower than the difference between the charges q on Rf and Hf (± 1 *vs.* 0.03, respectively) which was used for the interpretation [15,19] of processes occurring in solution. Therefore, the use of similar quantum-chemical approaches in this case is incorrect.

Previously,[70] it was found that HCl solutions contain mainly hydrolysed polymeric outer-sphere complexes $[M_4(OH)_8(H_2O)_{16}]Cl_8$ (M = Zr, Hf) stabilised due to the formation of M–M bonds and bridging M–OH–M bonds. These data contradict the hypothesis proposed by Kratz.[15] Structural studies showed that in solution the metal atoms form trimeric and tetrameric clusters that also stabilise the hydrolysed complexes. Hydrolysed monomeric inner-sphere complexes are thermodynamically unstable in the absence of these stabilising factors in concentrated HCl solutions.

Specific conditions of experiments with single TAn atoms exclude the possibility of formation of hydrolysed cluster-like structures $[TAn_4(OH)_8(H_2O)_{16}]Cl_8$. Hydrolysed monomeric outer-sphere complexes $[TAn(OH)_2(H_2O)_4]Cl_2$ are unstable in this case. It should be noted that hydrolysis does not determine the extraction sequence in studies with single TAn atoms in concentrated HCl solutions.

Earlier studies [133–136,140] on extraction of Zr^{IV} and Hf^{IV} from concentrated acid solutions modelled modern experimental conditions. Therefore, the results obtained in these works can be used to support the idea proposed in this review that in the TAn chemistry hydrolysis does not determine the extraction sequence. In the above-mentioned studies, microamounts of Zr^{IV} and Hf^{IV} were used to inhibit both hydrolysis and formation of polymeric structures. The formation of simple adducts (MCl_4, aq)·2 TBP in the organic phase under favourable conditions (concentrated acid solutions at low concentration of Zr^{IV} and Hf^{IV}) was revealed.[134,135] This suggests that inner-sphere complexes $RfCl_4(H_2O)_m$ are mainly formed in solution and that two H_2O molecules are replaced by two TBP molecules in extraction. Kacher *et al.*[130] studied extraction from 8 M HCl in TBP and experimentally established the extraction sequence Zr > Hf > Rf, which is due to the formation of more stable complexes $RfCl_4$(aq). Formation of hydrated complexes $Rf^{IV}(H_2O)_x$ was postulated by Bilewicz *et al.*[122]

One would suggest the existence of hydrated TAn^{IV}(aq) complexes [in particular, Rf^{IV}(aq)] in specific conditions of single-atom experiments and estimate the $\Delta_f H^\circ(TAn^{IV}, aq)$ and $\Delta_f H^\circ(MCl_4, aq)$ values for TAn (see Table 2). For Group IV elements, the stability of M^{IV}(aq) and MCl_4(aq) increases nearly monotonically from Zr to Th: $\Delta_f H^\circ(ZrCl_4, aq) = -1139$, $\Delta_f H^\circ(HfCl_4, aq) = -1243$, $\Delta_f H^\circ(RfCl_4, aq) = -1303$ and $-\Delta_f H^\circ(ThCl_4, aq) = -1486$ kJ mol^{-1}.

Estimation of the hydrolysis constant for weak acid solutions seems to be of considerable interest. Gregorich [12] showed that the ability of Rf ^{IV} to undergo hydrolysis is similar to that of An^{IV} rather than Hf^{IV} and Zr^{IV}. Using experimental data, it was found that the first hydrolysis constant, $\log K_H$, for the Rf^{IV} ion lies between the $\log K_H$ values of thorium and plutonium ions: $\log K_H(Pu^{IV}) > \log K_H(Rf^{IV}) > \log K_H(Th^{IV})$. A rough qualitative correlation between the ionic radii $r(M^{IV}$, CN = 6) and $\log K_H(M^{IV})$ values, namely, a decrease in $\log K_H(M^{IV})$ with an increase in $r(M^{IV})$ can be observed:

Ion				Pu^{IV}	Ce^{IV}	U^{IV}	Th^{IV}
$\log K_H(M^{IV})$				−0.5	−0.7	−1.5	−3.2
Ion	Zr^{IV}	Hf^{IV}	Rf^{IV}	Pu^{IV}	Ce^{IV}	U^{IV}	Th^{IV}
$r(M^{IV})$ /Å	0.72	0.73	0.78	0.86	0.87	0.89	0.93

The ionic radius of Rf lies between those of Zr–Hf and An. This reflects a qualitative similarity of Rf to An established in hydrolysis studies.[12]

3. Nitrate complexes

Recently,[95,96] the stability of nitrate complexes of trivalent lanthanides was studied in the framework of the structural-thermodynamic model. Application of this model to stability studies of nitrate complexes of Zr^{IV}, Hf^{IV}, Rf^{IV}, Ce^{IV} and Th^{IV}

in weak acid solutions revealed that the formation of nitrate aqua complexes $[M(NO_3)_x]^{(4-x)+}$ (M = Zr, Hf, Rf, Pu, Ce, Th; $x = 1-3$) causes a decrease in ΔG° on going from Zr to Th.

Complexes	$\Delta G^\circ[M(NO_3)_x]^{(4-x)+}$					
	Zr	Hf	Rf	Pu	Ce	Th
$[MNO_3]^{3+}$(aq)	1.4	+0.9	−1.4	−3.8	−4.5	−6.9
$[M(NO_3)_2]^{2+}$(aq)	+6.0	+5.5	+0.4	−5.6	−6.7	−8.7

These results are consistent with those of earlier experimental studies,[97–105] according to which Rf forms cationic outer-sphere complexes with NO_3^- anions in weak nitrate solutions more readily than Zr and Hf but with somewhat more difficulty than *f*-elements.

4. Fluoride complexes

In the framework of the same model the author of this review showed that the change in the free energy, ΔG°, in the formation of inner-sphere complexes $[MF]^{3+}$(aq) corresponds to an insignificant change in the ΔG° energy on going from Zr to Th. The $\Delta G^\circ\{[MF]^{3+}(aq)\}$ values for M = Zr, Hf, Rf and Th are −42.0, −40.0, −38.0 and −36.0 kJ mol^{-1}, respectively. Therefore, based on the results of calculations of the stability of cationic complexes $[RfF]^{3+}$(aq), Rf is similar to its analogues and should be placed between Zr–Hf and Th, though the ΔG° values differ insignificantly. These theoretical results correlate with the ΔG°_{HF} and $\Delta G^\circ_{F^-}$ values obtained in earlier experimental studies[106–112, 139] of the formation of (i) cationic fluoride complexes of Zr, Hf and Th, *e.g.*, $\{[MF]^{3+}[H^+](aq)\}$, by addition of HF molecule followed by elimination of a proton and (ii) complexes $[MF]^{3+}$(aq). In the case of formation of inner-sphere complexes $[MF]^{3+}$(aq), the fluoride ligand can be considered as an undissociated acid or an anion, which leads to different ΔG°_{HF} and $\Delta G^\circ_{F^-}$ values for the same M (the difference is 5 to 10 kJ mol^{-1}). According to Tananaev,[106] the free energy changes by −34 kJ mol^{-1} upon the formation of the $[ThF]^{3+}$(aq) complex, whereas Ahrland[139] reported a value of −44 kJ mol^{-1}. Based on these results, one can conclude that stabilities of the cationic complexes $[ThF]^{3+}$(aq), $[HfF]^{3+}$(aq) and $[ZrF]^{3+}$(aq) differ insignificantly. The experimental[113–115] and calculated[4,21] stabilities (β) of the actinide complexes $[AnF]^{3+}$(aq) or $[AnF_2]^{2+}$(aq) suggest greater similarity of Rf to its analogues within the group (Hf and Zr) rather than to actinides:

$$\log\beta_2\{[RfF_2]^{2+}(aq)\} = 7.7;\ \log\beta_2\{[HfF_2]^{2+}(aq)\} = 7.8;$$
$$\log\beta_2\{[PaF_2]^{2+}(aq)\} = 8.3;\ \log\beta_2\{[UF_2]^{2+}(aq)\} = 12.4,$$

where β_2 is the stability constant of the complex containing two ligands.

Another conclusion was drawn from the sorption studies of Rf, Hf, Zr and Th in mixed HNO_3–HF solutions on both cation and anion exchange columns.[16,18,116] In the formation of fluoride complexes, Rf behaves in a different manner compared to Hf and Zr and is more similar to Th in accord with the decreasing stability of the complexes, $Zr^{IV} \approx Hf^{IV} > Rf^{IV} > Th^{IV}$. The trend was theoretically explained by the fact that F^- is a hard anion and better (stronger) interacts with small cations (Zr^{IV} and Hf^{IV}), whereas the behaviour of Rf is a direct consequence of RE.[18]

We believe that discussion of manifestations of RE in complexes of unknown chemical composition and type (fluoride, nitrate or mixed fluoride nitrate, inner-sphere or outer-sphere, *etc.*) is inadmissible. These statements discredit the basic idea of manifestation of relativism in chemical properties.

Based on the results of earlier studies,[107,117–120,133–138] one can conclude that mixed rather than simple fluoride complexes are formed under experimental conditions reported by Shädel *et al.*[16,18,116] A salient feature of the chemistry of Hf^{IV} and Zr^{IV} is a synergistic effect in the extraction of these elements from solutions of two inorganic acids (HNO_3–HF, HNO_3–HCl, HNO_3–$HClO_4$), that is, obtaining high separation coefficients of Zr^{IV} and Hf^{IV} as a result of the formation of mixed complexes upon addition of the second acid and variation of its concentration.[99,117–120,133–139] The synergistic effect is due to the formation of the Zr^{IV} and Hf^{IV} complexes of different composition, on which lies the basis of the process of their separation by extraction from a mixture of two inorganic acids. Earlier studies of mixed complexes, *e.g.*, $MF_x(NO_3)_{4-x}$, revealed changes in the number x (*i.e.*, the F^-/NO_3^- ratio) depending on the metal (Zr^{IV}, Hf^{IV}, Th^{IV}). The existence of the complexes $ZrF(NO_3)_3$ (see Ref. 117), $HfF_2(ClO_4)_2$ (see Ref. 107), $ZrCl_{4-x}(NO_3)_x$ (see Ref. 118), $M(NO_3)_x(ClO_4)_{4-x}$ (M = Zr, Hf) (see Refs 119, 136–138), $HfCl_x(ClO_4)_{4-x}$ (see Refs 136–138), $ZrCl_5NO_3^{2-}$ (see Ref. 136), *etc.*, was established. Thus, comparison of earlier results on the complexation and extraction of Zr^{IV}, Hf^{IV} and Th^{IV} with recently obtained data for Rf^{IV}, Zr^{IV}, Hf^{IV} and Th^{IV} provides strong evidence that the authors of study[18] did not take into account the results of earlier studies and were based on the assumptions that (i) NO_3^- anions are not involved in complexation and (ii) Zr^{IV}, Hf^{IV}, Th^{IV} and Rf^{IV} form the same type of fluoride complexes for all cations, which seems to be doubtful.[133–139]

The results of study[18] were recently revised[116] and the authors agreed that the NO_3^- anion may be involved in complex formation. However, their major conclusion that Rh is similar to Th and different from Zr and Hf in the formation of fluoride complexes remained unchanged.

The structure of neutral crystalline complexes $MF_4(H_2O)_3$ (M = Hf, Zr) was studied by X-ray diffraction analysis.[120,121] Complex $ZrF_4(H_2O)_3$ has a dimeric structure while complex $HfF_4(H_2O)_3$ has a polymeric structure. For both complexes, the CN value equals 8 due to the formation of bridging bonds. The $ZrF_4(H_2O)_3$ molecule has three Zr–OH_2 bonds and five Zr–F bonds while the $HfF_4(H_2O)_3$ molecule containing one molecule of bound water has six Hf–F bonds and two Hf–OH_2 bonds. As can be seen, Hf exhibits higher affinity towards F^- than Zr. One can assume that this trend will be more pronounced on going to Rf. This is confirmed by the formation enthalpies, $\Delta_f H^\circ(MF_4, c)$, of crystalline compounds, which decrease on going to heavier elements.

MF_4(c)	ZrF_4	HfF_4	RfF_4
$\Delta_f H^\circ$ /kJ mol^{-1}	−1912	−1930	−1997

The reliably proven[123–127] existence of anionic form $[RfF_6]^{2-}$ is in good agreement with the chemical properties of the 4*d*- and 5*d*-elements. At the same time, it is known that, despite the predominance of the complexes $[HfF_6]^{2-}$ in acidic aqueous solutions with the HF : Hf ratio greater than 1, changes in this ratio can also result in other anionic forms. In this connection, it is pertinent to remember the study by Tananaev and Guzeeva[128] who showed that the thermal stability of alkali metal salts of Zr and Hf changes in the order $[MF_7]^{3-} > [MF_6]^{2-} > [MF_5]^-$. In addition, Varga and Hume[107] revealed instability of $[HfF_5]^{2-}$ in solution. Taken together, these facts do not exclude the possibility of formation of not only $[RfF_6]^{2-}$, but also $[RfF_7]^{3-}$ in solution; however, this is only a hypothesis proposed by the author of this review.

VII. Standard formation enthalpies, $\Delta_f H^\circ(A_2MCl_6)$, of crystalline compounds

Standard formation enthalpies of crystalline compounds A_2MCl_6 with K^+, Rb^+ and Cs^+ cations were obtained for many 4*d*- and 5*d*-elements.[22,26,29,30,31,49–55] For instance, the $\Delta_f H^\circ(K_2MCl_6, c)$ values for K_2MCl_6 salts are known for all 5*d*-metals from Hf to Pt and for almost all 4*d*-metals. For the 3*d*-, 4*d*- and 5*d*-elements, the standard formation enthalpies of gaseous MCl_6^{2-} ions and crystalline salts K_2MCl_6 are linearly related. Knowing the standard formation enthalpies of gaseous MCl_6^{2-} ions for the 4*d*-, 5*d*- and 6*d*-elements and the experimental $\Delta_f H^\circ(K_2MCl_6, c)$ values for the

4*d*- and 5*d*-elements, one can calculate the $\Delta_f H^\circ(K_2MCl_6, c)$ parameters for TAn with an accuracy of ± 15 kJ mol^{-1}. The experimental $\Delta_f H^\circ(K_2MCl_6, c)$, $\Delta_f H^\circ(Rb_2MCl_6, c)$ and $\Delta_f H^\circ(Cs_2MCl_6, c)$ values for compounds of the 3*d*-, 4*d*- and 5*d*-elements are related by simple relationships that can be used for calculating the $\Delta_f H^\circ$ values for compounds of the 6*d*-elements ($\Delta_f H^\circ$ are given in kJ mol^{-1})

$$\Delta_f H^\circ(Rb_2MCl_6, c) = 1.014\,\Delta_f H^\circ(K_2MCl_6, c),$$

$$\Delta_f H^\circ(Cs_2MCl_6, c) = 0.983\,\Delta_f H^\circ(K_2MCl_6, c) - 83.$$

The calculated formation enthalpies, $\Delta_f H^\circ(K_2MCl_6, c)$, $\Delta_f H^\circ(Rb_2MCl_6, c)$ and $\Delta_f H^\circ(Cs_2MCl_6, c)$ of transactinide salts are listed in Table 2. The crystal lattice energies, $U(A_2MCl_6, c)$, and the lattice constants, $a(A_2MCl_6, c)$, are known to be linearly related.[30] Therefore, knowledge of the $\Delta_f H^\circ(A_2MCl_6, c)$ values allows calculations of $U(A_2MCl_6, c)$ and lattice constants $a(A_2MCl_6, c)$ for transactinide salts with K^+, Rb^+ and Cs^+ cations (see Table 1).

VIII. Conclusion

In this review we have shown that TAn possess dual properties, which can be similar to those of both the 4*d*- and 5*d*-elements and (in some instances) the early actinides. However, this similarity becomes less pronounced with an increase in Z(An) or Z(TAn). The volatility of the tetrahalides of early actinides becomes lower as the atomic number of An increases; however, it increases for compounds of the 4*d*- and 5*d*-elements. The greatest similarity is observed for the thermodynamic properties of Group IV elements (Zr – Hf – Rf – Th). The thermodynamic stability of halide compounds of tetravalent transactinides in the gaseous and crystalline states and in aqueous solution decreases with an increase in Z(TAn); however, it increases within particular groups of the Periodic table on going from the light to heavy elements.

A possible reason for the inconsistency between the results of earlier (1960 – 1970) and more recent (1990 – 2000) studies of the volatility of halides and oxyhalides of the *d*-elements and of extraction, hydrolysis and complexation in solution is that in transactinide chemistry the experimental data are interpreted in the framework of the hypothesis that RE cause changes in the chemical properties down the groups of the Periodic system. However, the influence of RE on the chemical properties of transactinides is to a great extent compensated by actinide contraction. It should be emphasised that no experimental data on the properties of TAn, which could be unambiguously interpreted as a manifestation of relativistic effects, have been reported so far.

Yet another reason for the above-mentioned inconsistency is the lack of methods that allow identification of the chemical composition of transactinide compounds formed. Single-atom experiments are carried out assuming complete analogy between the chemical properties of the 4*d*-, 5*d*- and 6*d*-elements within the groups of the Periodic system, *i.e.*, the same type of compounds of the same composition (this is not always true). In the early studies the chemical composition of newly formed compounds of the 4*d*- and 5*d*-elements was thoroughly analysed and, as a rule, established.

References

1. V I Spitsyn, G V Ionova *Usp. Khim.* **53** 1249 (1984) [*Russ. Chem. Rev.* **53** 725 (1984)]
2. G V Ionova *Usp. Khim.* **59** 66 (1990) [*Russ. Chem. Rev.* **53** 39 (1990)]
3. G V Ionova, G A Gerasimova *Usp. Khim.* **61** 1656 (1992) [*Russ. Chem. Rev.* **61** 907 (1992)]
4. G V Ionova *Zh. Koord. Khim.* (4) (2002) [a]
5. G Ionova, S Ionov, C Rabbe, C Hill, C Madic, R Guillaumont, G Modolo, J C Krupa *New J. Chem.* **25** 491 (2001)
6. G Ionova, S Ionov, C Rabbe, C Hill, C Madic, R Guillaumont, G Modolo, J C Krupa *Solv. Extract. Exchang.* **19** 391 (2001)
7. J P Desclaux, B Fricke *J. Phys.* **41** 943 (1980)
8. P Pyykkö *Acc. Chem. Res.* **12** 276 (1979)
9. G V Ionova, in *Proceedings of the 5th International Conference on Nuclear and Radiochemistry, Pontresina, 2000* p. 213
10. G V Ionova, in *Proceedings of the 5th International Conference 'Université d'ete 1999', MéJannes-le-Clape, 1999* p. 100
11. I Zvara, in *Proceedings of the 5th International Conference on Nuclear and Radiochemistry, Pontresina, 2000* p. 180
12. K E Gregorich, in *Proceedings of the 1th International Conference on the Chemistry and Physics of the Transactinide Elements, Seeheim, 1999* p. 10
13. B Eichler, in *Proceedings of the 5th International Conference on Nuclear and Radiochemistry, Pontresina, 2000* p. 203
14. A Türler, in *Proceedings of the 5th International Conference on Nuclear and Radiochemistry, Pontresina, 2000* p. 229
15. J V Kratz, in *Heavy Elements and Related New Phenomena* (New York: World Scientific, 1999) p. 129
16. M Shädel, in *Proceedings of the 5th International Conference on Nuclear and Radiochemistry, Pontresina, 2000* p. 184
17. R Eichler, W Brüchle, R Dressler, R Dressler, Ch Düllmann, B Eichler, H W Gägeller, K E Gregorich, D C Hoffmann, S Hübener, D T Jost, U Kirbach, C A Laue, V M Lavanchy, H Nitsche, J Patin, D Piquet, M Shädel, D Strellis, S Taut, L Tobler, Y Tsyganov, A Türler, A Vahle, P Volk, A Yakushev, in *Proceedings of the 5th International Conference on Nuclear and Radiochemistry, Pontresina, 2000* p. 191
18. E Strub, W Brüchle, R Eichler, H W Gägeller, J P Glatz, A Grund, M Gärtner, E Jäger, D T Jost, U Kirbach, J V Kratz, A Kronenberg, Z Li, A Nähler, Y Nagame, M Shädel, B Shausten, E Scimpf, D Schumann, P Torle, K Tsukada, A Türler, S Zauner, in *Proceedings of the 1th International Conference on the Chemistry and Physics of the Transactinide Elements, Seeheim, 1999* p. O-11
19. W Brüchle, B Eichler, W Gägeller, R Günter, E Jäger, D T Jost, J V Kratz, Y Nagame, W Paulus, V Pershina, M Shädel, B Schausten, D Shumann, A Seibert, P Törlle, A Türler, K Tsukada, S Zauner, in *Proceedings of the 1th International Conference on the Chemistry and Physics of the Transactinide Elements, Seeheim, 1999* p. 15
20. I Zvara, B Eishler, V Z Belov, T S Zvarova, Yu S Korotkin, M R Shalaevskii, V A Shchegolev, M Khussonnois *Radiokhimiya* **16** 709 (1974) [b]
21. G V Ionova *Zh. Neorg. Khim.* **47** 610 (2002) [c]
22. G B Bokii *Kristallokhimiya* (Crystal Chemistry) (Moscow: Moscow State University, 1960)
23. R D Shannon, H Vincent *Structure and Bonding* Vol. 19 (Berlin: Springer, 1974)
24. J P Desclaux *At. Data Nucl. Data Tables* **12** 311 (1973)
25. K S Krasnov (Ed.) *Molekulyarnye Postoyannye Neorganicheskikh Soedinenii* (Molecular Constants of Inorganic Compounds) (Leningrad: Khimiya, 1979)
26. J H Canterford, R Cotton *Halides of the Second and Third Row Transition Metals* (London: Wiley, 1968)
27. G V Girichev, V M Petrov, N I Giricheva, A N Utkin, V N Petrova *Zh. Strukt. Khim.* **22** (5) 65 (1981) [d]
28. R W Wyckoff *Crystal Structures* (New York: Wiley-Interscience, 1965)
29. F Cotton, G Wilkinson *Advances Inorganic Chemistry* (New York: Wiley-Interscience, 1988)
30. H D B Jenkins, K R Pratt *Adv. Inorg. Chem. Radiochem.* **22** 1 (1979)
31. A F Wells *Structural Inorganic Chemistry* (Oxford: Clarendon Press, 1962)
32. S Maniv *J. Appl. Cryst.* **9** 245 (1976)
33. C D Kennedy, R D Peacok *J. Chem. Soc.* **1** 3392 (1963)
34. H J Berthold, G Jakobson *Angew. Chem.* **76** 497 (1964)
35. F A Cotton *Inorg. Chem.* **3** 780 (1964)
36. H D Grundy, R D Brown *Can. J. Chem.* **48** 1151 (1970)
37. J D Bell, D Hall, T N Waters *Acta Crystallogr.* **21** 440 (1966)
38. N Elder, J E Fergusson, C J Gainsford, J H Hickford, B R Penfold *J. Chem. Soc., A* 1423 (1967)
39. B Fricke, J T Waber *Actinides Rev.* **1** 433 (1971)
40. E Johnson, B Fricke, O L Keller Jr., C W Nestor Jr., T C Tucker *J. Chem. Phys.* **93** 8041 (1990)

41. A Bilewicz, in *Proceedings of the 1th International Conference on the Chemistry and Physics of the Transactinide Elements, Seeheim, 1999* p. 87
42. R D Shannon *Acta Crystallogr, Sect. A* **32** 751 (1976)
43. G Choppin, E Rizkalla *Handbook on the Physics and Chemistry of Rare Earths. Lanthanide and Actinide Chemistry* Vol. 18 (Amsterdam: Elsevier, 1994)
44. B Krebs *Angew. Chem., Int. Ed.* **8** 146 (1969)
45. G V Ionova, V G Vokhmin, V I Spitsyn *Zakonomernosti Izmeneniya Svoistv Lantanidov i Aktinidov* (Regularities of Variation of Properties of Lanthanides and Actinides) (Moscow: Nauka, 1990)
46. G V Ionova, V I Spitsyn *Effektivnye Zaryady v Soedineniyakh Aktinidov* (Effective Charges in Actinide Compounds) (Moscow: Nauka, 1989)
47. V I Spitsyn, V G Vokhmin, G V Ionova *Int. Rev. Phys. Chem.* **4** 57 (1985)
48. S G Bratsch, J J Lagowski *J. Phys. Chem.* **90** 307 (1986)
49. D D Wagmann, W H William, V B Parker, R H Schumm, I Halow, S M Bailey, K L Churney, R L Nuttall *J. Phys. Chem. Ref. Data* **11** (Suppl. 2) (2) (1982)
50. *CODATA, Thermodynamic Tables* (Berlin: Hemisphere; Springer, 1987)
51. M W Chase *J. Phys. Chem. Ref. Data* **14** (Suppl. 1) (1985)
52. O Knacke, O Kubaschewski, K Hesselmann (Eds) *Thermochemical Properties of Inorganic Substances* Vols 1, 2 (Berlin: Springer, 1991)
53. G Ionova, C Madic, R Guillaumont *Polyhedron* **17** 1991 (1998)
54. *CODATA, Key Values for Thermodynamics* (New York; London: Hemisphere, 1989)
55. A I Efimov, L P Belorukova, I V Vasil'kova, V P Chechev *Svoistva Neorganicheskikh Soedinenii* (Properties of Inorganic Compounds) (Leningrad: Khimiya, 1983)
56. G V Ionova *Radiokhimiya* **37** 282 (1995) [b]
57. W H Zachariasen *Acta Crystallogr.* **5** 19 (1952)
58. J Fuger, V B Parker, W N Hubbard, F L Oetting *The Chemical Thermodynamics of Actinide Elements and Compounds* (Vienna: International Atomic Energy Agency, 1983) Pt. 8
59. G Ionova, C Madic, R Guillaumont *Radiochim. Acta* **78** 83 (1997)
60. G V Ionova, in *Proceedings of the 5th International Conference on Nuclear and Radiochemistry, Pontresina, 2000* p. 104
61. D Brown *Halides of Lanthanides and Actinides*. Wiley London 1968
62. V P Glushko, L V Gurvich, G A Bergman, I V Veits, V A Medvedev, G A Khachkuruzav, V S Yungman (Eds) *Termodinamicheskie Svoistva Individual'nykh Veshchestv* (Thermochemical Properties of Individual Substances) (Moscow: Nauka, 1982) Vol IV
63. F L Oetting, M Y Rand, R G Accerman *The Chemical Thermodynamics of Actinide Elements and Compounds* (Vienna: International Atomic Energy Agency, 1976) Pt. 1
64. L Morss, iIn *The Chemistry of the Actinide Elements* Vol. 2 (Ed. G Seaborg) (London: Chapman and Hall, 1971)
65. Yu S Ezhov, P A Akishin, N G Rambidi *Zh. Strukt. Khim.* **10** 763 (1969) [d]
66. L Morss *Handbook on the Physics and Chemistry of Rare Earths* Vol. 18 (Eds K A Gschneidner Jr., L Eyring) (New York: Elsevier, 1994)
67. S P Ionov, N T Kuznetsov *Ross. Khim. Zh.* **54** 4 (2000) [e]
68. P Gross, C Hayman *Trans. Faraday Soc.* **60** (Pt. 1) 45 (1964)
69. S A Shchukarev, N Tolmacheva, V M Tsintsius *Zh. Neorg. Kkhim.* **7** 679 (1962) [c]
70. *Comprehensive Inorganic Chemistry* Vols 1 – 5 (Eds J C Bailar, H J Emeleus, R Nyholm, A F Trotman-Dickenson) (New York: Pergamon Press, 1973)
71. J Weidlein, U Müller, K Dehnicke *Spectrochim. Acta A* **24** 253 (1968)
72. H G Schnering, K Wöhrle *Angew. Chem.* **75** 684 (1963)
73. R E McCarley, B A Torp *Inorg. Chem.* **2** 540 (1963)
74. M Elder, B R Penfold *Inorg. Chem.* **5** 1197 (1966)
75. I R Anderson, J C Sheldon *Inorg. Chem.* **7** 2602 (1968)
76. M J Bennett, F A Cotton, B M Foxman, P F Stokely *J. Am. Chem. Soc.* **89** 2759 (1967)
77. D N Suglobov, G V Sidorenko, E G Levin *Letuchie Organicheskie i Kompleksnye Soedineniya f-Elementov* (Volatile Organic and Complex Compounds of *f*-Elements) (Moscow: Energoatomizdat, 1987)
78. B Zhuikov, V Glebov, V Nefedov, in *Proceedings of the 1th International Conference on the Chemistry and Physics of the Transactinide Elements, Seeheim, 1999* p. 56
79. B Eichler, H Rossbach *Radiochim. Acta* **33**121 (1983)
80. I Zvara, V Belov, L P Chelnokov, V P Domanov, M Hussonois, Yu S Korotkin, V A Shegolev, M R Shalaevsky *J. Inorg. Nucl. Chem. Lett.* **7** 1109 (1971)
81. I Zvara *Radiochim. Acta* **81** 179 (1998)
82. B Eichler *Radiochim. Acta* **72** 19 (1996)
83. B Eichler, W A Türler, H W Gäggeler *J. Phys. Chem. A* **103** 9296 (1999)
84. H W Gägeller, D T Jost, U Baltensperger, Ya Nai-Qi, K E Gregorich, C M Gannett, H L Hall, R A Henderson, D M Lee, J D Li, M J Nurmia, D C Hoffman, A Türler, Ch Lienert, M Shädel, W Brüchle, J V Kratz, H P Zimmermann *First Results from Gaschemistry Experiments with Hahnium (Report of Paul Scherrer Institute No 49), Villigen, 1989*
85. V Pershina, B Fricke, G V Ionova, M Shädel *Thermodynamic Volatility of Element 105 Halides (GSI Scientific Report, 1991), Darmstadt, 1992*
86. V I Lavrentiev, Ya I Gerassimov *At. Energy Rev., Spec. Issue* (2) 7 (1968)
87. I Zvara, F B Yakushev, V Ya Lebedev, S N Timokhin, in *Proceedings of the 1th International Conference on the Chemistry and Physics of the Transactinide Elements, Seeheim, 1999* p. O-15
88. S Roy Morrison *The Chemical Physics of Surfaces* (New York: Plenum, 1977)
89. H Selig, J G Malm *J. Inorg. Nucl. Chem.* **25** 349 (1963)
90. P Gelbman, A D Westland *J. Chem. Soc., Dalton Trans.* **6** 1598 (1974)
91. G Ionova, J C Krupa, I Gerard, R Guillaumont *New J. Chem.* **19** 677 (1995)
92. R J Silva, J Harris, M Nurmia, K Eskola, A Chiorso *Inorg. Nucl. Chem. Lett.* **6** 871 (1970)
93. E K Hulet, R W Lougheed, J F Wild, J H Landrum, J M Nitschke, A Ghiorso *J. Inorg. Nucl. Chem.* **42** 79 (1979)
94. D C Hoffman *Radiochim. Acta* **61** 123 (1993)
95. S P Ionov, N T Kuznetsov *Koord. Khim.* **24** 896 (1998)
96. S P Ionov, G V Ionova, C Madic, R Guillaumont, in *Proceedings of International Conference Future of Nuclear Systems, Yokohama, 1997* Vol. 2, p. 1424
97. A S Solovkin, Z N Tsvetkova, A I Ivantsov *Zh. Neorg. Khim.* **12** 626 (1967) [c]
98. A N Ermakov, I N Marov G A Evtikova *Zh. Neorg. Khim.* **12** 3372 (1967) [c]
99. P H Tedesco, V B de Rumi, J A Gonzalez Quintana *J. Inorg. Nucl. Chem.* **30** 987 (1968)
100. E V Ukraintsev *Radiokhimiya* **7** 641 (1965) [b]
101. K A Petrov, V B Shevchenko, V G Timoshev, F A Maklyaev, A V Fokin, A V Rodionov, V V Balandina, A V El'kina, Z I Nagnibeda, A A Volkova *Zh. Neorg. Khim.* **5** 498 (1960) [c]
102. V G Timoshev, K A Petrov, A V Rodionov, V V Balandina, A A Volkova, A V El'kina, Z I Nagnibeda *Radiokhimiya* **2** 419 (1960) [b]
103. A G Rykov, G N Yakovlev *Radiokhimiya* **8** 27 (1966) [b]
104. I V Shilin, V K Nazarov *Radiokhimiya* **8** 514 (1966) [b]
105. V S Smelov, Yu I Vereshchagin *Zh. Neorg. Khim.* **9** 2775 (1964) [c]
106. I V Tananaev *Acta Chim. Sin.* **25** 391 (1959)
107. L P Varga, D N Hume *Inorg. Chem.* **3** 77 (1964)
108. R G Deshpande, P K Khopkar, C L Rao, H D Sharma. *J. Inorg. Nucl. Chem.* **27** 2171 (1965)
109. Yu A Buslaev, M P Gustyakova *Zh. Neorg. Khim.* **10** 1524 (1965) [c]
110. B Noren *Acta Chem. Scand.* **21** 2435 (1967)
111. B Noren *Acta Chem. Scand.* **21** 2449 (1967)
112. B Noren *Acta Chem. Scand.* **23** 931 (1969)
113. R Guillaumont *C. R. Hebd. Seances Acad. Sci.* **260** 4739 (1965)
114. V M Vdovenko, G A Romanov, V A Shcherbakov *Radiokhimiya* **5** 581 (1963) [b]
115. A Ahrland, L Brandt *Acta Chem. Scand.* **20** 328 (1966)

116. E Strub, J V Kratz, A Kronenberg, A Nähler, U Rieth, P Torle, S Zauner, W Brüchle, E Jäger, M Shädel, B Shausten, E Schimpf, Z Li, U Kirbach, D Schumann, D T Jost, A Türler, M Asai, Y Nagame, M Sakama, K Tzukada, H W Gägeller, J P Glatz, in *Proceedings of the 5th International Conference on Nuclear and Radiochemistry, Pontresina, 2000* p. 225
117. S S Korovin, A M Reznik, I A Apraksin *Zh. Neorg. Khim.* **7** 1483 (1962) [c]
118. A M Reznik, A M Rozen, S S Korovin, I A Apraksin *Radiokhimiya* **5** 49 (1963) [b]
119. S S Korovin, K Dedich, E N Lebedeva, A M Reznik *Zh. Neorg. Khim.* **7** 2475 (1962) [c]
120. A S Solovkin, G A Yagodin *Khimiya Ekstraktsii Tsirkoniya i Gafniya* (The Chemistry of Zirconium and Hafnium Extraction) (Moscow: Izd. VINITI, 1969) p. 120
121. D Hall, C E F Rickard, T N Waters *Nature (London)* **207** 405 (1965)
122. A Bilewicz, S Siekierski, C D Kacher, K E Gregorich, D M Lee, N J Stoyer, B Kadkhodayan, S A Kreek, M R Lane, E R Sylwester, M P Neu, M F Mohar, D C Hoffman *Radiochim. Acta* **75** 121 (1996)
123. H Bruchertseifer, B Eichler, J Estevez I Zvara *Radiochim. Acta* **47** 41 (1989)
124. Z Szeglowski, H Bruchertseifer, V P Domanov, B Gleisberg, L I Guseva, M Hussonnois, G S Tikhomirova, I Zvara, Yu Ts Oganessian *Radiochim. Acta* **51** 71 (1990)
125. G Pfrepper, R Pfrepper, A B Yakushev, S N Timokhin, I Zvara *Radiochim. Acta* **77** 201 (1997)
126. G Pfrepper, R Pfrepper, D Krauss, A B Yakushev, S N Timokhin, I Zvara *Radiochim. Acta* **80** 7 (1998)
127. M Shädel, W Brüchle, E Jäger, E Schimpf, J V Kratz, U W Scherer, H P Zimmermann *Radiochim. Acta* **48** 171 (1989)
128. I V Tananaev, L S Guzeeva *Izv. Akad. Nauk SSSR, Neorg. Mater.* **4** 207 (1968) [f]
129. K R Czerwinski, C D Kacher, K E Gregorich, T M Hamilton, N J Hannink, B Kadkhodayan, S A Kreek, D M Lee, M J Nurmia, A Türler, G T Seaborg, D C Hoffman *Radiochim. Acta* **64** 29 (1994)
130. C D Kacher, K E Gregorich, D M Lee, Y Watanabe, B Kadkhodayan, B Wierczinski, M R Lane, E R Sylwester, D A Keeney, M Hendriks, N J Stoyer, Y Yang, M Hsu, D C Hoffman, A Bilewicz *Radiochim. Acta* **75** 127 (1996)
131. K R Czerwinski, K E Gregorich, N J Hannink, C D Kacher, B Kadkhodayan, S A Kreek, D M Lee, M J Nurmia, A Türler, G T Seaborg, D C Hoffman *Radiochim. Acta* **64** 23 (1994)
132. C D Kacher, K E Gregorich, D M Lee, Y Watanabe, B Kadkhodayan, B Wierczinski, M R Lane, E R Sylwester, D A Keeney, M Hendrics, D C Hoffman, A Bilewicz *Radiochim. Acta* **75** 135 (1996)
133. R W Cattrall, S J E Slater *Coord. Chem. Rev.* **11** 131 (1967)
134. L M Zaitsev, V M Klyuchnikov, G N Voronskaya, I A Apraksin *Zh. Neorg. Khim.* **17** 2511 (1972) [c]
135. V M Klyuchnikov, L M Zaitsev, S S Korovin, I A Apraksin *Zh. Neorg. Khim.* **17** 3030 (1972) [c]
136. Yu N Nikitin, Yu I Mironov, A M Rozen *Usp. Khim.* **45** 2233 (1976) [*Russ. Chem. Rev.* **45** 1155 (1976)]
137. O Navratil, J Smola, R Kolouch *Collect. Czech. Chem. Commun.* **44** 3656 (1979)
138. O Navratil, R Kolouch *Hydrometallurgy* **7** 289 (1981)
139. S Ahrland, in *The Chemistry of Actinide Elements* Vol. 2 (Eds J J Katz, G Seaborg, L Morss) (New York: Elsevier, 1986) p. 1480
140. D H Liem, O Sinegribova *Acta Chem. Scand.* **25** 301 (1971)

[a] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[b] — *Radiochemistry (Engl. Transl.)*
[c] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[d] — *Russ. J. Struct. Chem. (Engl. Transl.)*
[e] — *Mendeleev Chem. J. (Engl. Transl.)*
[f] — *Inorg. Mater. (Engl. Transl.)*