Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

SPECIFIC EFFECTS OF HEAVY NUCLEI IN CHEMICAL EQUILIBRIUM

Dmitri A. Knyazev[a]; Nikolai F. Myasoedov[b]
[a] Department of Inorganic and Analytical Chemistry, Timiryazev Moscow Agricultural Academy, Moscow, Russia [b] Russian Academy of Sciences, Institute of Molecular Genetics, Moscow, Russia

To cite this Article Knyazev, Dmitri A. and Myasoedov, Nikolai F.(2001) 'SPECIFIC EFFECTS OF HEAVY NUCLEI IN CHEMICAL EQUILIBRIUM', Separation Science and Technology, 36: 8, 1677 — 1696
To link to this Article: DOI: 10.1081/SS-100104758
URL: http://dx.doi.org/10.1081/SS-100104758

SEPARATION SCIENCE AND TECHNOLOGY, 36(8&9), 1677–1696 (2001)

SPECIFIC EFFECTS OF HEAVY NUCLEI IN CHEMICAL EQUILIBRIUM

Dmitri A. Knyazev[1,*] **and Nikolai F. Myasoedov**[2]

[1]Department of Inorganic and Analytical Chemistry,
Timiryazev Moscow Agricultural Academy,
Moscow, Russia
[2]Institute of Molecular Genetics, Russian Academy of
Sciences, Moscow, Russia

ABSTRACT

The article reports the results of numerical estimations of the nuclear size equilibrium isotope effects for some medium-weight and heavy elements obtained by using the following equation: $\ln \alpha_{fs}(i,j) = (kT)^{-1}\,\Delta\rho(0)z^{-1}f(z)\langle r^2\rangle_{ij}$, where $\alpha_{fs}(i,j)$ are the equilibrium isotope separation factors corresponding to the nuclear size contribution of the nucleus field-shift for a given pair of isotopes i and j; $\Delta\rho(0)$ is the difference of the nucleus electron density for a pair of compounds; $z^{-1}f(z)$ is the tabulated nuclear charge (z) function characterizing the nucleus of the element being the same for all isotopic nuclei; $\delta\langle r^2\rangle_{ij}$ is the isotopic shift of the nucleus effective charge radius in square for the isotopes i and j, and k is the Boltzmann constant. The values $\Delta\rho(0)$ were determined from either theoretical or experimentally determined isotope field shifts and from the data of Mossbauer spectroscopy. The $\langle r^2\rangle_{ij}$ values were taken from experimental measurements followed by their

---

[*]Corresponding author.

standardization. The values of $\alpha_{fs}(i,j)$ increase from Fe to U and achieve sufficiently high level for lanthanides. For heavier elements, these specific isotope effects begin to exceed the classical chemical equilibrium isotope separation factors.

INTRODUCTION

Recently it has become clear that the classical quantum-statistical theory of equilibrium chemical isotope effects needs to be complemented through accounting for contributions resulting from the uneven charge distributions in the isotopic nuclei. Being essentially unremarkable in isotope exchange equilibrium of light and medium-mass elements, these effects compete or are summarized with classical isotope effects and dominate in the case of uranium and probably of other heavy elements.

The precise measurements of equilibrium isotope separation factors for uranium isotopes of different masses obtained in development of Japanese ASAHI process (1) along with less complete and precise data of the French CHEMEX process (2) revealed three anomalies, which cannot be explained within the theoretical approach considering isotopic variations of statistical sums for vibrations, rotations, and translational motion.

1. Separation factors of uranium isotopes appeared to be unexpectedly high.
2. Heavy isotopes are preferentially accumulated in compounds characterized by the lower oxidation states.
3. The logarithmic dependency of separation factors ln α on the reciprocal isotope masses demonstrates distinct deviations from the linear pattern for odd masses. The abnormally high separation factor of lead isotopes in the system without alteration of oxidation state (3) can also be referred to the above anomalies.

A productive concept for interpretation of the isotope separation factor anomalies of the ASAHI process through accounting for the differences in nuclei dimensions of uranium isotopes manifested both in these effects and in the electron spectra field shifts of uranium atoms was proposed by Bigeleisen (4). Later it was suggested that the interaction of nuclear quadruple moments with the electric field tension gradients near the nucleus must be also taken into consideration (5).

At present, this theoretical field is too far from the predicting ability to forecast isotope separation factors for the concrete reaction or type of reactions. The objective of the present work is to show the specific nature of equilibrium isotope effect of heavy atoms and to trace the possible ways for their prognosis.The nuclear contributions to the chemical isotope effects can be arranged in the decreas-

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

ing order as follows:

1. The effect of volume and shape of isotopic nuclei, or nuclear field shifts, resulted from the differences in the interaction energy of isotopic nuclei charge distributions with electron density overlapping nuclei volumes.
2. Nuclear-quadruple effects generated due to interaction of nuclei quadruples with non-homogeneous electrostatic fields of inner electron shells of atoms.
3. Nuclear-spin effects emerging due to the action of inter-atomic magnetic fields on the magnetic moments of nuclei with non-zero spins.

The third effect is two orders of magnitude less than the first one (4), and it is approximately an order of magnitude less than the second (5). Therefore, it is disregarded here. All three effects are displayed in thin and extra-thin atomic electron spectra (4,6) and practically are not examined with respect to molecules.

The first two effects are additive (7), although both are the result of the isotopic discrepancies in the total energy of electrostatic interactions of nuclear charges with the surrounding electric charges, including both the electric charge of inner electron shells and electron condensity and non-homogeneity of the electron density emerging in bond formation. The effects of volume and shape are characteristics of each nucleus of natural isotopic mixture and can be displayed for each isotopic species, whereas nuclear-quadruple effects can be detected only in the case of nuclei with considerable quadruple moments.

FIELD SHIFT: EFFECT OF NUCLEAR VOLUME AND SHAPE

Positive charge of protons is unevenly distributed in the volumes of isotopic nuclei. The light isotopic nuclei have slightly larger charge densities and smaller effective charge radii compared with heavy ones. The isotope increments of the charge radii are determined from the isotope shifts in electron spectra of atoms and atomic ions (8). The deviations from spherical symmetry may arise along with radius changes resulting in the ellipticity of charge distribution in nucleus. Both factors are manifested in the isotopic shift (FS) of interaction energy of nuclei with the electron shell of the atom. The energy shift of the basic (or any excited) state is connected with the nucleus electron density of the state for a pair of isotopic nucleus, denoted as i and j, as follows:

$$\delta T_{fs}(i,j) = \pi\,|\Psi(0)|^2 a_0^3 z^{-1} f(z)\delta\langle r^2\rangle_{ij} = \rho(0)\, z^{-1} f(z)\delta\langle r^2\rangle_{ij} \qquad (1)$$

where $\pi\,|\Psi(0)|^2 a_0^3$ is the nucleus electron density; $z^{-1}f(z)$ is the function of charge z characterizing the nucleus of the element, which is the same for all isotopic nuclei; $\delta\langle r^2\rangle_{ij}$ is the isotopic shift of the square of nucleus effective charge radius for a given pair of isotopes i and j.

In two compounds participating in a random isotope exchange reaction the nuclei electron densities of the isotopically substituted element are different and therefore, the difference in the isotopic shifts of the basic state energies $\Delta E_{fs}(i,j)$ can be expressed through electron density difference of the compound as follows:

$$\Delta E_{fs}(i,j) = \Delta\rho(0)z^{-1}f(z)\delta\langle r^2\rangle_{ij} \tag{2}$$

By assuming the proportionality between isotopic shifts $\Delta h\nu$ (measured from the atomic electron spectrum of free uranium atoms) and the contributions of the isotopic shifts of the basic state energies $\Delta E_{fs}(i,j)$ to the equilibrium isotope separation factor of uranium isotopes in the ASAHI reaction, Bigeleisen (4) defined the field shift ingredient in the ln α value in the following form:

$$\ln K_{fs} = \ln \alpha_{fs} = (kT)^{-1}\Delta E_{fs} = \ln \alpha - \ln \alpha_0. \tag{3}$$

Here α_{fs} is isotope field shift separation factor, α is effective (experimental) separation factor, α_0 is classical separation factor. The classic ingredient ln α_0, where α_0 is a classic isotope separation factor for the isotope exchange system composed of A and B exchanging substances is expressed as follows:

$$\ln \alpha_0 = \ln \beta(A) - \ln \beta(B) \tag{4a}$$

$$\ln \beta \cong (kT)^{-2}\Delta Sp(GF), \tag{4b}$$

where $\Delta Sp(GF)$ is the isotope increment in Spur of the product of the kinetic energy G matrix and that of the potential energy F matrix.

This interpretation is not unique but it correctly distinguishes the principal physical basis for all three anomalies observed in ASAHI reaction coefficients by attributing them to those nuclear properties that do not depend on the mass.

Table 1 presents the comparison of results reported by Bigeleisen (4) with relative values of $\delta\langle r^2\rangle_{ij}$ taken from King (8). As seen, the ln α_{fs} values appear to be proportional to $\delta\langle r^2\rangle_{ij}$ values. It is essential that ln α_{fs} values have an opposite sign in respect to ln α_0 values for the ASAHI system that reduces the efficient value of ln α by 40%. For example, the ratio ln α(236–238)/ln α_{fs}(236–238) = 7.3 $\cdot\ 10^{-4}/12.3 \cdot 10^{-4} \approx 0.59$. This compensation is caused by the combination of

Table 1. Equilibrium Characteristics of ASAHI Process

Uranium Isotope Pair	Relative Field Shift	Relative Difference* $\delta\langle r^2\rangle_{ij} = \langle r^2\rangle_i - \langle r^2\rangle_j$	ln α × 10^4	ln α_{fs} × 10^4	ln α_0 ×10^4
236–238	0.599	1.00	7.30	12.32	−5.02
235–238	1.000	1.67	13.00	20.56	−7.56
234–238	1.194	1.99	14.42	24.54	−10.12
233–238	1.561	2.59	19.39	32.09	−12.70

*Charge radius increments of uranium isotopic nuclei taken from King (8). Adapted from Bigeleizen (4).

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

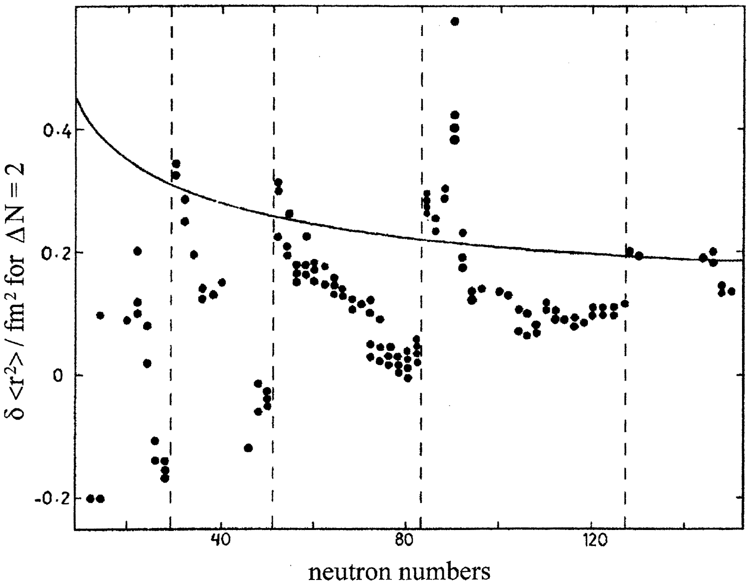

Figure 1. Isotopic shifts ($\delta\langle r^2\rangle$) plotted against neutron number of heavier isotope. All results are given for even neutron numbers. Points correspond to stable isotopes or to those that lie close to stability region on Segre chart (8).

signs of $\delta\langle r^2\rangle_{ij}$ and $\Delta\rho(0)$. On the contrary to the classic effect where heavy isotope has always a less zero vibration energy than the light one, in case of interaction of isotopic nuclei with electron clouds, the light nuclei are commonly located at a lower energy state having as a rule a less charge radii. Furthermore two differences in the ASAHI system, namely the difference of $\Delta Sp(GF)$ and $\Delta\rho(0)$, have the same signs. In other words, $\Delta Sp(GF)$ and $\Delta\rho(0)$ are bigger for U(6+) in $UO_2(OH)_{5-n}L_n$ than the same values for U(3+) in U^{+3}_{aq}. The right-hand part of Eq. (2) shows the dependence of $\Delta E_{fs}(i,j)$ on three factors that can be considered as independent parameters.

Let us consider first $\delta\langle r^2\rangle_{ij}$ factor. As shown in Table 1, the non-linear dependence of ln α on isotopic mass increments, or more exactly, on the reciprocal isotopic mass increments, $\Delta\mu = \mu_i - \mu_j$, is fully determined by the shifts of $\delta\langle r^2\rangle_{ij}$. The latter cannot be measured directly in physical experiments but can be calculated by using semi-empirical relations describing optic or X-ray isotopic shifts (8). As seen in Fig. 1, $\delta\langle r^2\rangle_{ij}$ quantities can substantially vary remaining within a narrow range. They change their absolute value periodically according to the neutron magic numbers. For the elements behind krypton $\delta\langle r^2\rangle_{ij}$ values are mostly positive whereas they are always positive for the elements after La.

As shown in Fig. 2, the dependence of the second factor $z^{-1}f(z)$ on z is stronger than exponential. This is developed through the shift of the classic vibra-

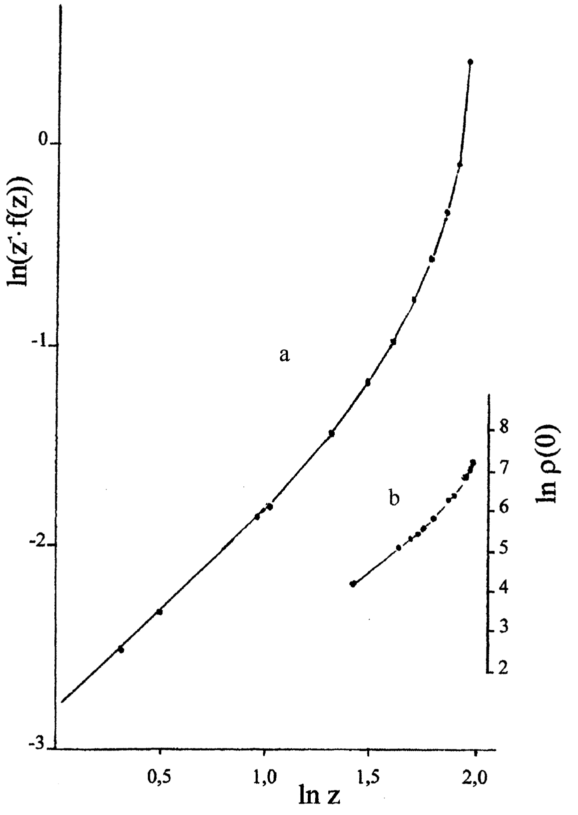

Figure 2. Change of function $z^{-1}f(z)$ plotted against nucleus charge z in bilogarithmic coordinates. Recalculated from data adapted from Ref. 8, pp. 42–43 (a). Values for uranium are obtained by extrapolation. Nucleus electron density changes according to data adapted from Ref. 10 (b).

tion component of the equilibrium effects to the secondary plan for the heaviest elements.

The third factor, the increment of electron density of $\Delta\rho(0)$, is the sole chemical variable, which should be selected somehow. Due to the favorable choice of $\Delta\rho(0)$ parameters, CHEMEX and ASAHI processes became the most important achievement in separation of U isotopes.

The increment of electron density depends on the chemical nature of compounds interacting in a chemical exchange system. The nucleus electron density, being an essential characteristic of a chemical compound, should be included in the extended partition function ratio of isotope species. In other words, the classic $\ln(s/s')f$ value must be complemented with the $(\mathrm{RT})^{-1}\rho\,(0)z^{-1}f(z)\delta\langle r^2\rangle_{ij}$ factor.

NUCLEAR-QUADRUPLE EFFECT

The potential interaction energy of the nucleus quadruple with the molecular field is described by the following equation:

$$E_Q = e^2 q_{zz} Q \tag{5}$$

where e is the electron charge; eq_{zz} is the tension gradient equal to $e\,\partial^2\varphi/\partial z^2$; φ is the electrostatic potential, and Q is an averaged quadruple moment of the nucleus. Tension gradient eq_{zz} is determined in the point of the nucleus location on the z-axis, along which the non-uniformity of the molecular field is maximal.

The even nuclei are spherical, and their quadruple moments equal zero. The majority of odd nuclei have the shape of an elongated ellipsoid. They are characterized by positive quadruple moments. However, flattened nuclei having negative Q values have also been found. Absolute Q values are higher and are more frequently met in the second half of the periodic system (6–9).

For a random chemical exchange system consisting of A and B compounds, where two different isotopes i and j have non-zero quadruple moments Q_i and Q_j, the separation factor must include the component $(\mathrm{RT})^{-1}\Delta E_Q(i,j)$, where

$$\begin{aligned} \Delta E_Q(i,j) &= e\Delta(eq_{zz})(Q_i - Q_j), \\ \Delta(eq_{zz}) &= eq_{zz}^{(A)} - eq_{zz}^{(B)} \end{aligned} \tag{6}$$

Therefore, the quadruple contribution is determined by the difference of quadruple moments $(Q_i - Q_j)$ and that of the field tension gradients in compounds. Tension gradients of electrostatic fields at the point of nucleus location are controlled by bonds and by the geometry of their arrangement in the compound. For the central symmetry compounds, a full compensation and reduction of eq_{zz} to zero may occur due to the vector summation of bond components.

Up to now, the only known nuclear-quadruple effect has been reported by Knyazev et al. (5). This effect was determined as a part of the isotope separation factor for U(235, 238) isotopes and amounts to nearly 10 % of the nuclear size and shape effect for CHEMEX process reactions. There is no reason to assert that the electrostatic fields tension gradients on the U nuclei in $\mathrm{U(3+)_{aq}}$ and $\mathrm{U(4+)_{org}}$ ions are close to the maximum. Therefore, one can expect even more significant manifestations of this effect. The types and properties of the bonds, as well as the peculiarities of the compound geometry, that are capable of increasing E_Q, are known (to some extent) and can be predicted (9,15).

However, it seems unlikely that this effect will be used as a tool to select systems for isotope separation of heavy elements due to numerous factors weakening its significance. Its value is probably less than that of the nucleus size and shape effect and occurs only in asymmetric compounds with specific bonds. Moreover the nuclear-quadruple effect exists only in nuclei with high Q values. However, when selecting systems for separation of heavy element isotopes, one needs to account for the possibility of its manifestation. Hence, estimation of this possibility along with forecasting of this effect are of particular importance.

POSSIBILITY OF PROGNOSIS AND PROSPECTS FOR APPLICATION OF HEAVY NUCLEI EFFECTS

More than a 50-year-long history of attempts to find a suitable chemical system for uranium isotope separation brought about a very impressive outcome—the CHEMEX and ASAHI processes. It is important to emphasize that the development of both processes is the result of persistent and wide empirical research rather than that of strict theoretical prediction.

The isotope field uranium effect substantially exceeds the classical one and it is probably the case for other heavy elements. Both estimation of the field isotope effects attainable by different elements and the purposeful search of the systems with high isotope separation factors are possible only because of the thorough analysis and elucidation of factors, which can be used to control this effect. Such analysis is pending and this work is only an attempt to trace possible routes for the solution of this task.

In the product of the right-hand part of Eq. (2), the multiplier $z^{-1}f(z)$ is identical to any of the isotope nuclei with charge z, whereas the multiplier $\delta\langle r^2\rangle_{ij}$ characterizes the pair of isotopes i and j. These parameters are fixed and cannot be controlled. The third multiplier $\Delta\rho(0)$ depends on the chemical nature of the compounds composing a chemical exchange system. Hence, it can be an objective of the purposeful search and optimization of chemical exchange systems. Since $\Delta\rho(0)$ can be used as a controlling tool to run the chemistry of the process, the task is then reduced to the search of factors that permit governing this parameter.

At present, several big databases are accessible for analysis to achieve the above goal. Each of them is characterized by certain peculiarities, which are specified below:

1. Experimental measurements of ΔE_{fs} values are almost exclusively performed for free atoms and sometimes for ions. These data are the source of precise information about $\delta\langle r^2\rangle_{ij}$ and may be used to evaluate the accuracy of parameter $z^{-1}f(z)$ (or its equivalents) and to determine $\Delta\rho(0)$ values. The ΔE_{fs} values of some electron transitions for free atoms of most elements have been measured, but the field isotope shifts for heavy elements have been extensively studied for only a few of them (8). The results of measurements of ΔE_{fs} in chemical compounds are available only in some cases.
2. Theoretical possibilities used to calculate $\rho(0)$ in chemical compounds are limited by low accuracy and time-consuming computation procedures. These calculations are scarce, and the accuracy of the best calculations of $\rho(0)$ even for free atoms and ions needs to be confirmed.

Most probably, the accurate theoretical calculations of $\Delta\rho(0)$ characterizing discrepancies of chemical compound with uncertainty of $10^{-5} - 10^{-4}$ of $\rho(0)$ value will not be achievable in the near future (10–13).

3. The Messbauer spectroscopy is a potential source of accurate $\rho(0)$ values for compounds (10–13). Nevertheless, the actual accuracy of this technique is still not sufficient due to the lack of precise calibration methods. In particular, the correlations between isomeric shifts of compounds with different formal oxidation states of the elements and the electron densities of free ions cannot be associated so far with real $\rho(0)$ values.

Further on, we use the same working hypothesis as in the analysis of classical effects (16). We assume that the distribution functions of $\ln \alpha_{fs}$ and ΔE_{fs} values are more or less similar to distribution functions of $\gamma = \ln \alpha / \ln \beta_{\max}$ of classical equilibrium isotope effects, which is typical for the majority of chemical isotope exchange reactions.

Statistical sets of $\ln \alpha_{fs}$ for different elements can decompose into subsets, in which some factors have a dominant influence on $\ln \alpha_{fs}$. These subunits, like a general set of reactions of a given element (or groups of elements) can have their own distribution functions of $\gamma_{fs} = \ln \alpha_{fs}/\ln \beta_{fs}$, where $\ln \beta_{fs}$ is the standardizing or scaling-up value specific for each element.

In contrast to $\ln \beta_{\max}$ values for classical effects, it is impossible (at least now) to find the normalizing value of $\ln \beta_{fs}$ because the variability limits of $\ln \alpha_{fs}$ values are yet unknown. At the same time, it is obvious that $\ln \beta_{fs} = \ln \alpha_{\max}$ because uranium is probably only several times higher than $\ln \alpha$ for the CHEMEX process. In this situation, the scaling-up values of $\ln \alpha_{fs}$, ΔE_{fs} and $\Delta\rho(0)$ (but not the normalizing ones) can be used to provide the closeness of γ_{fs} to unity, although they do not ensure that the experimental $\ln \alpha_{fs}$ values lie within the interval $0 \leq \gamma_{fs} \leq 1$. Such a scale-up allows carrying out the statistical analysis and comparison of $\ln \alpha_{fs}$ values for different elements. To make a well-grounded choice of technique suitable for $\ln \alpha_{fs}$, $\Delta\rho(0)$, and γ_{fs} determination, it seems reasonable to discuss the possibilities of Messbauer spectroscopy with respect to the variability of $\Delta\rho(0)$ and to the factors controlling its value as well as those for ΔE_{fs} and $\ln \alpha_{fs}$.

The values of $\Delta\rho(0)$ measured in respect to standards are the main object of study in Messbauer spectroscopy. The available data comprise 38 elements with atomic weights of over 100, i.e. provides full information in the field of interest. The basic equation connecting the isomeric changes of S (mm/s) with the electron density increments $\Delta\rho(0)$ of the compound is written as follows:

$$S = 2/3\pi e^2 z \delta\langle R^2\rangle(\Delta\rho(0)_{\text{substance}} - \rho\ (0)_{\text{standard}}) \qquad (7)$$

where z is the element nucleus charge, and $\delta\langle R^2\rangle$ is the change of an average square of nucleus radius in its resonant excitation. Note that this value does not coincide by sense with $\delta\langle R^2\rangle$ in Eqs. (1) and (2). The compounds with well reproducible parameters are used as a standard. The error of S determination varies from 100 to 10% and in some cases (but rarely) to a several or more percentage for small S values. Sometimes $\delta\langle R^2\rangle$ values are measured with an error percentage. The $\rho(0)$ values for the standard cannot be accurately estimated as mentioned earlier.

For many elements, big databases on S values have been accumulated. This information is systematized and analyzed to find the factors controlling $\rho(0)$ values of compounds. From the viewpoint of possible application of these data to forecast the equilibrium values of $\ln \alpha_{fs}$, the following main results seem to be of particular interest:

1. The following (and same) generalized chemical parameters strongly influence both the classical isotope effects, $\Delta\rho(0)$, and ΔE_{fs} values: the oxidation state, the ligand type (or the type of donor atom of the ligand), and configuration of the coordination sphere of element.
2. The correlation between S and $\Delta\rho(0)$ values of free ion in a formal oxidation state corresponding to its position in a compound are reported in numerous publications. The correlations between S and a formal oxidation state can also be found in the literature. It is important to keep in mind, that the growth of the oxidation state n is accompanied by the growth of $\rho(0)$ for free ion. This has been unambiguously confirmed by calculations of $\rho(0)$ for atoms and ions. The type of ligand or less precisely the type of donor atom of the ligand shown for the spectrochemical series, according to their influence on S and $\Delta\rho(0)$ are ranked in similar series. Ligand contributions to $\Delta\rho(0)$ can be described with the help of additive partial increments, but on the whole, the ligand type affects $\Delta\rho(0)$ in a far weaker manner than the oxidation state. The data obtained for tin allow the assumption that $\Delta\rho(0)$ for configuration transitions is far less than $\Delta\rho(0)$ for ligand substitution, but this conclusion should be regarded as a preliminary one. Figure 3 shows the general influence of oxidation state, ligand type, and configuration on the isomer shifts in neptunium compounds. As seen, the influence of the three factors above on the field effects are different, which makes the difference between field and classical effects, because for classical isotope exchange effects all of the three factors noted above have comparable influence on $\ln \alpha_0$.
3. The nucleus electron density is highly sensitive to all parameters, which either increase or decrease the screening of s-electrons. The screening of p-, d- or f-electrons is less manifested. On the whole, the field effects markedly depend on the Coulomb parameters weakly influencing the classical effects. These second-order parameters include ions of the outer sphere of coordination compounds in the crystalline state, the packing characteristics of crystal lattices, phase state of the compounds, the nature of solvents and solvent particles (e.g., aggregates), and pressure.

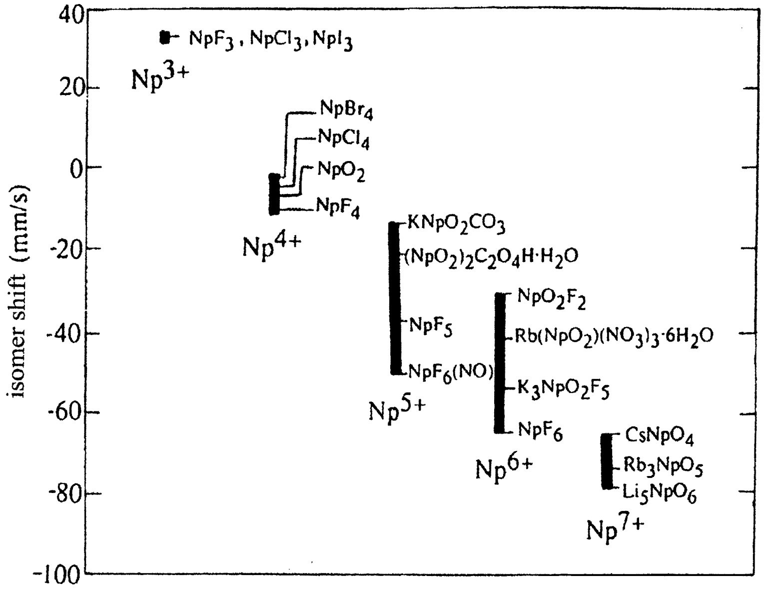

Figure 3. Isomer shifts in neptunium compounds. Isomer shift for $NpAl_2$ is taken as zero-point (see Ref. 11, pp. 481–506).

The total effect of these numerous and insufficiently studied factors is difficult to predict. It is even more difficult to study these factors under real conditions corresponding to the processes used for separation of metal isotopes. For example, both extraction CHEMEX and ion exchange ASAHI processes involve the treatment of highly concentrated aqueous and/or non-aqueous solutions.

In summing up, one can conclude that the current situation with available information shows that attention must be focused upon the main chemical factor affecting $\Delta\rho(0)$, namely, on the oxidation state as the basic variable of field effects.

Table 2 shows the results of theoretical calculations of $\rho(0)$ values on nuclei and values of $\Delta\rho(0)$ corresponding to the consecutive ionization states of free ions (10–13). For convenience, these results along with some additional data are also shown in Figs. 2–6. For the choice and evaluation of the scaling $\ln \alpha_{fs}$ values of interest, the following points are important:

1. Both function $z^{-1}f(z)$ and $\rho(0)$ grow quickly with the charge of nucleus z. In bilogarithmic coordinates both dependencies are non-linear and deviate from the linear pattern toward increase of the influence of z (see Fig. 2).
2. The differences of $\Delta\rho(0)$ corresponding to electron splitting with an increase of z and $\rho(0)$ grow symbatically to $\rho(0)$. The ratios $\tau = \Delta\rho(0)/\rho(0)$ vary within a rather narrow range.

Table 2. Nucleus Electron Densities $\rho(0)$ (in Atomic Units, a.u.), Increments of $\Delta\rho(0)$ for Free Ions, and Ratio Intervals of $\tau = \Delta\rho(0)/\rho(0)$ for Number of Elements*

Element, $\rho(0) \times 10^{-5}$, a.u. $\tau \times 10^5$	Charges of Free Ions	$\Delta\rho(0)$, a.u.	Element, $\rho(0) \times 10^{-5}$, a.u. $\tau \times 10^5$	Charges of Free Ions	$\Delta\rho(0)$, a.u.
^{26}Fe			^{66}Dy		
$\rho(0) = 0.153$	3+/2+	2.83	—	3+/2+	50.5
$\tau = 1.8; 3.0$	4+/3+	4.63	—	4+/3+	60.1
^{44}Ru			^{77}Ir		
$\rho(0) = 1.15$	3+/2+	5.10	$\rho(0) = 21.49$	3+/2+	25.66
$\tau = 4.4; 9.4$	4+/3+	7.96	$\tau = 1.2; 2.9$	4+/3+	34.63
	5+/4+	9.18		5+/4+	43.31
	6+/5+	10.83		6+/5+	52.56
^{50}Sn				7+/6+	61.33
$\rho(0) = 1.86$	0/1−	5.64	^{92}U		
$\tau = 2.2; 3.2$	1+/0	5.88	$\rho(0) = 61{,}29$	4+/3+	154.1
	2+/1+	6.39	$\tau = 2.5; 2.8$	5+/4+	182.4
	3+/2+	7.09		6+/5+	244.0
	4+/3+	4.13	^{93}Np		
^{53}I			$\rho(0) = 66.67$	4+/3+	167.4
$\rho(0) = 2.41$	0/1−	9.95	$\tau = 2.5; 4.3$	5+/4+	198.1
$\tau = 3.3; 6.1$	1+/0	10.39		6+/5+	224.3
	2+/1+	10.95		7+/6+	286.9
	3+/2+	11.70	^{95}Am		
	4+/3+	12.65	$\rho(0) = 78.82$	3+/2+	155.6
	5+/4+	13.65	$\tau = 2.0; 3.6$	4+/3+	200.0
	6+/5+	14.77		5+/4+	229.4
	7+/6+	7.98		6+/5+	260.8
^{61}Pr				7+/6+	286.9
—	3+/2+	34.7			
—	4+/3+	43.2		estimate	
^{63}Eu			^{82}Pb		
$\rho(0) = 5.89$	3+/2+	41.4	—	4+/2+	200 ± 20
$\tau \cong 7.0$	—	—	—	—	—

* Data adapted from Refs. 10 and 11.

3. The differences of $\Delta\rho(0)$ grow monotonously in almost all cases with the growth of $n+$ charge of the free ion. For d- and f-metals, the values of $\Delta\rho(0)$ are approximately proportional to $(2n + 1)/2$. For p-elements, the dependence on n are markedly weaker, and they are monotonous up to the removal of the last but one valent electron.
4. It follows from Fig. 6 that at higher oxidation states the isomeric shifts S deviate from the linear dependence on n toward its weakening, which

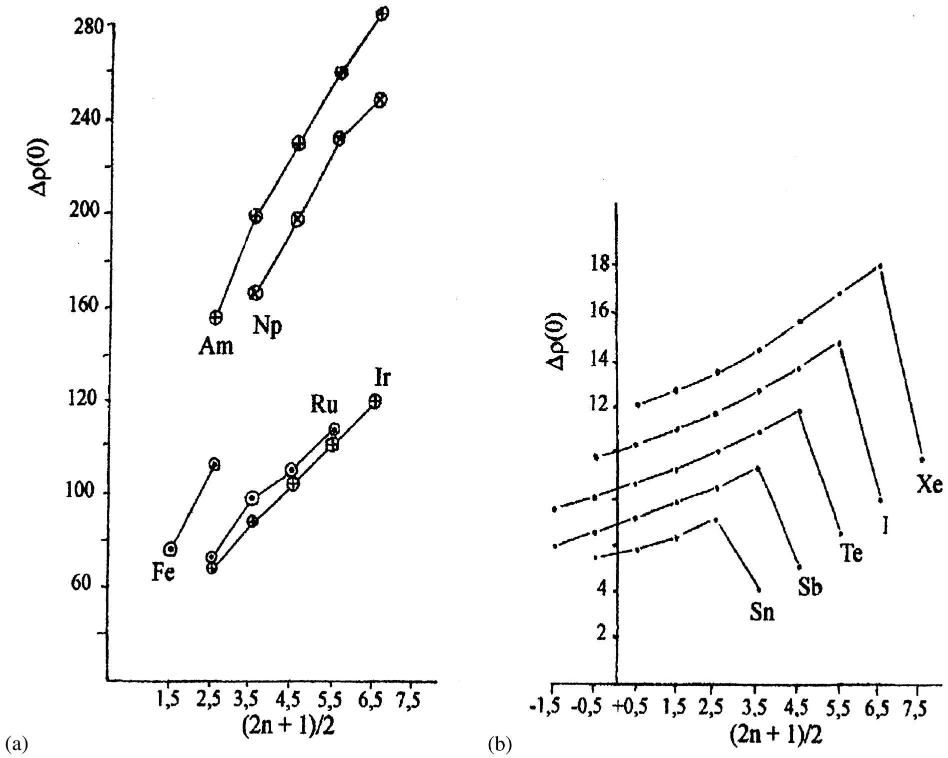

Figure 4. Dependencies of increments Δρ(0) on value of factor $(2n + 1)/2$ for free ions: transition metals (a); p-elements (b). Recalculated from data adapted from Ref. 10 (pp. 617–659).

is usually attributed to the decrease of bond ionization. The plot shown in Fig. 6 clearly demonstrates the difference of the actual electron densities from the densities of free ions.

The latter conclusion emphasizes once again the fact that the required objective information on Δρ(0) for compounds is lacking. Nevertheless, the available material allows $\ln \alpha_{fs}$ evaluations to be made. Such evaluation is based on the assumption that Δρ(0) for a pair of free ions is the upper limit of Δρ(0) values corresponding to the same ions within compounds, and they are, probably, several times higher. Since the compounds differing by one or two units in oxidation states in chemical systems for isotope separation can easily coexist, two variants of calculation have been performed.

If the chemistry of an element is characterized by low oxidation states, then it seems rational to estimate ΔE_{fs} and $\ln \alpha_{fs}$ by Δρ(0) values corresponding to Δn

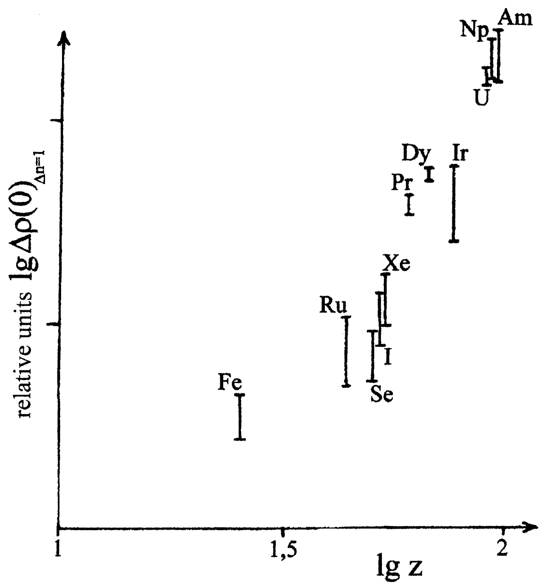

Figure 5. Interrelation between $\Delta\rho(0)$ values corresponding to $\Delta n = 1$ and nucleus charge z plotted in bilogarithmic coordinates. Bar heights denote intervals of known values of $\Delta\rho(0)$ for different element compounds.

= 1. If, as in the ASAHI process, the compounds with high oxidation degrees are compatible and are able to exchange electrons and isotopes, then one needs to account for the ΔE_{fs} and ln α_{fs} values corresponding to $\Delta n = 2$. Figure 6 allows for the conclusion that in this case both ΔE_{fs} and ln α_{fs} values were to be decreased twice as much, but this seems reasonable only with regard to compounds with very high oxidation states and is not likely to be applicable to other elements. Therefore ln α_{fs} values have been calculated for the cases corresponding to $\Delta n = 2$ and, particularly, to those n combinations that could be considered compatible based on the chemistry of a particular element (Table 3).

Before calculation of ln α_{fs} ($\Delta n = 1$) and ln α_{fs} ($\Delta n = 2$) values, it was necessary to solve the problem of the proper selection of the isotope pairs under study, i.e. to reduce $\delta\langle r^2\rangle_{ij}$ values to standard (see Eqs. (1) and (2)). The scattering of $\delta\langle r^2\rangle_{ij}$ values for even–even neutron isotopic pairs is evidently large (see Fig. 1), and it is not less for even–uneven neutron pairs. The problem is complicated because the isotopic pleiades are large for many elements whereas the others have only one stable isotope. Therefore, we have found it reasonable to calculate ln α_{fs} for the conventional difference $\delta\langle r^2\rangle_{ij} = 0.0868$ corresponding to the half of ln α_{fs} for uranium isotopes (238 and 236). This choice allows for the comparison of calculation results with respective experimental data on separation of uranium isotopes and, at the same time, simplifies the comparison of ln α_{fs} with ln $\beta_{\max}$ values for classical effects calculated for the difference of isotopic masses of $\Delta m = 1$.

The role of the datum mark point allowing the theoretically calculated values of $\Delta\rho(0)$ to be adjusted to the actual experimental data (see Fig. 7) was assigned to a precisely measured isotope shift in the optical spectrum of samarium. This shift, corresponding to the isotopic pair of Sm (148 and 154) and to the electron transition 4f6s → 4f6s6p exactly, related to the electron density difference $\Delta\rho(0)$ of free ions Sm^{3+}/Sm^{2+} (14). The ln α_{fs} values shown in Table 3 have been obtained by recalculation from $\Delta\rho(0)$ of respective oxidation degrees (indicated in this table) and $\Delta\rho(0)$ for Sm^{3+}/Sm^{2+} by using the function $z^{-1}f(2)$ in Eqs. (1) and (2).

Estimates of ln α_{fs} presented in Table 3 correspond to the principal requirement: both of them lie either close to or not so far from virtual upper limits of ln α_{fs}, which can be obtained from their expected relationships with classical effects. In the area of average masses, they are three or four orders of magnitude lower than 1n $\beta_{\max}$ values and in the range of uranium isotope masses they are almost ten times higher.

Table 4 shows a comparison of ln α_{fs} and ln $\beta_{\max}$ values with the best results on experimental determination of α for values in the most completely characterized chemical exchange systems involving heavy metals such as, samarium,

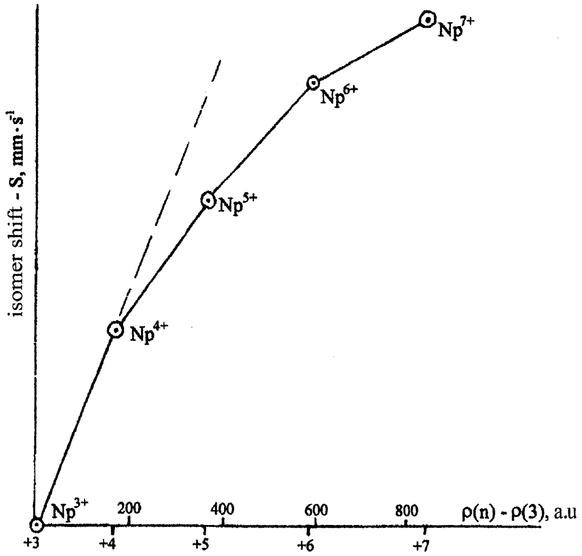

Figure 6. Relation between isomer shift of S Mossbauer spectra of fluorides NpF_3, NpF_4, NpF_5, NpF_6, and $\rho(0)$ for free neptunium ions. Point Np^{7+} corresponds to the shift for Li_5NpO_6 [see Ref. 10, p. 493]. Dashed line corresponds to assumption of pure ionic character of bonds in NpF_3 and NpF_4.

Table 3. Estimates of ln α_{fs} Values for Chemical Systems with Differences in Oxidation States of $\Delta n = 1$ and $\Delta n = 2$ Obtained by Using Data Adapted from Refs. 10 and 11. All ln α_{fs} Values Are Obtained for Virtual Isotopic Pair Using $\delta\langle r^2\rangle_{ij} = 0.0868$ fm^2 and 300 K. The ln $\beta_{\max}$ Values of Sm, Dy, Yb Are Considered to Equal to That of La. Estimation for Pb Is Obtained from $\Delta\rho(0)$ of Hg and Sn.

Elements	^{26}Fe	^{44}Ru	^{50}Sn	^{53}I	^{62}Sm	^{66}Dy	^{70}Yb	^{76}Os	^{77}Ir	^{82}Pb	^{92}U
$z^{-1}f(z)$	0.0523	0.130	0.174	0.197	0.316	0.389	0.479	0.662	0.700	0.927	~1.65
Least chemically stable oxidation states with $\Delta n = 1$	2+/3+	2+/3+	2+/3+	1−/0	2+/3+	2+/3+	2+/3+	—	3+/4+	—	3+/4+
$\Delta\rho(0)$ increments for free ions in the above oxidation states and $\Delta n = 1$, a.u.	2.83	5.10	7.09	9.95	34.1	46.5	58.9	—	34.6	—	154.1
Chemically stable oxidation states differing in $\Delta n = 2$	2+/4+	2+/4+	2+/4+	1−/1+	—	2+/4+	—	4+/6+	4+/6+	2+/4+	3+/5+
$\Delta\rho(0)$ increments for free ions in the above oxidation states and $\Delta n = 2$, a.u.	7.46	13.1	11.2	20.3	—	106.5	—	91.1	97.9	200 ± 20	336
ln $\alpha_{fs} \times 10^3$ $\Delta n = 1$	0.0020	0.0089	0.016	0.026	0.14	0.24	0.38	—	0.32	—	3.4
ln $\alpha_{fs} \times 10^3$ $\Delta n = 2$	0.0052	0.023	0.026	0.054	—	0.56	—	0.80	0.91	2.5	7.4
ln $\beta_{\max} \times 10^3$ $\Delta m = 1$	9.3	3.6	2.1	2.5	1.6	1.6	1.6	1.3	1.3	0.86	0.60

lead, and uranium. As seen, the results of this comparison provide a direct confirmation of what might be expected. Indeed, for example, in samarium ln $\alpha_{\exp}$ values are far smaller than both ln α_{fs} and ln $\beta_{\max}$ values. The following reasons can be taken into account to explain this effect: the chemical compounds under comparison have identical donor atoms and slightly different effective force fields. The field nuclear shift is still small and cannot be manifested yet in a randomly

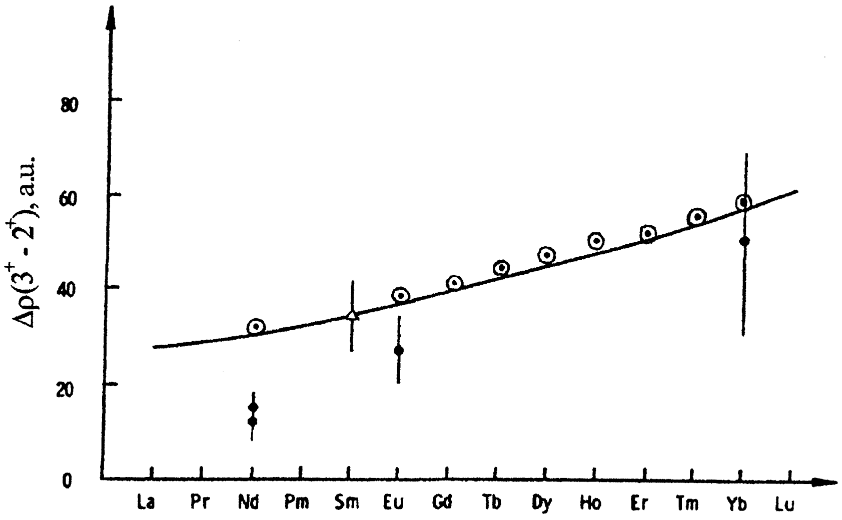

Figure 7. Electron density differences for divalent and trivalent rare earth ions (•) determined from respective optical isotope shifts (14). Solid line was obtained by extrapolation from value deduced for SmI additional points with bars were obtained by using Dirak-Fock approximation (see Refs. 14, pp. 111–201, and 15).

Table 4. Comparison of Calculated ln α_{fs}^{300} Values with Δm ln β_{max} and Experimental ln α Values Obtained by Thoroughly Studying Heavy Element Systems; $T = 300$ K; $\Delta m = m_i - m_j$, According to Data Adapted from Refs. 1, 3, 4, and 17

Element, Isotopic Mass	System, Heavy Isotpe Concentrates in First Compound (Medium)	Oxidation Degrees	$\delta\langle r^2\rangle_{ij}$, fm^2	$\Delta\rho(0)$, a.u.	ln α_{fs} $\times 10^3$	ln α_{exp} $\times 10^3$	ln β_{max} $\times \Delta m$ $\times 10^3$
Sm (144–154)	HOB* Sm^{3+} − Sm^{3+}_{aq}	3+/3+	1.47	10.8	1.20	0.19	16
Pb (206–208)	NTA* Pb^{2+} − Pb^{2+}_{aq}	2+/2+	0.11	200 ± 20	2.8 ± 0.3	0.47	1.7
	U^{3+}_{aq} (HCl) − TBP* U^{4+}_{org}	3+/4+		154	0.84	3.0	
U (235–238)	$NOUF_6$(HF) − UF_6 (FC*)	5+/6+	0.29	206	1.12	1.6	1.8
	$U^{4+}_{aq} - UO_2{}^{2+}_{aq}$ (IE*)	4+/6+		389	2.11	1.30	

* HOB = hydroxybutyrate; NTA = nitrilotriacetate; TBP = tributylphosphate; FC = fluorocarbon; IE = ion exchanger.

chosen system with identical oxidation states of both compounds. On the contrary, the isotopic effects of lead (3) are already comparable to both ln α_{fs} and Δm ln $\beta_{\max}$ values whereas uranium effects are markedly determined by nuclear field shifts.

In conclusion, we emphasize that the estimate of the role played by the field nuclear shifts presented in this study is, naturally, of a semi-quantitative character. It seems evident that the search of new possibilities to use the above factor for chemical separation of heavy elements needs to be more widely and elaborately explored. In this context, one of the most essential problems to be investigated deals with identification of the class of systems, in which the reciprocal compensation of the classical and field effects could be avoided.

LIST OF SYMBOLS

i,j	two arbitrary isotopes of element with masses m_i and m_j
$\delta\, T_{fs}(i,j)$	energy shift of either basic or any excited state of nucleus, cm^{-1} or J/mol
$\lvert\Psi(0)\rvert^2 a_0 = \rho(0)$	nucleus electron density (charge is expressed in atomic units)
$z^{-1}f(z)$	charge (z) function characterizing nucleus of element being the same for all isotopic nuclei, atomic units
$\Delta E_{fs}(i,j)$	difference in isotopic shifts of basic state energies for two components, cm^{-1} or J/mol
$\Delta\rho(0)$	difference of nucleus electron density of two compounds of element (charge is expressed in atomic units)
$\delta\langle r^2\rangle_{ij}$	isotopic shift of nucleus effective charge radius in square for given pair of isotopes i and j
α_0	classical equilibrium isotope separation factor for chemical exchange reaction
$\ln\beta = \ln(s/s')f$	reduced partition function ratio
G	kinetic energy matrix (inverse mass, D^{-1})
F	potential energy matrix, 10^5 dyne·cm
E_Q	potential interaction energy of nucleus quadrupole with molecular electrostatic field, J/mol
eq_{zz}	tension gradient that is equal to $e\delta^2\varphi/\delta z^2$ of electrostatic potential φ, $10^{-18}\ \mathrm{V\cdot cm^{-1}}$
Q	averaged quadrupole moment of nuclei (can be different for isotopes i and j), $10^{-24}\ \mathrm{cm}^2$
$\delta\langle R^2\rangle$	change of average nucleus radius in square in its resonant excitation
S	Mossbauer isotopic shift, cm s^{-1}

REFERENCES

1. Kakihana, H.; Oi, T. In *Proceedings of International Symposium on Isotope Separation and Chemical Exchange Uranium Enrichment,* Tokyo, Japan, October 29–November 1, 1990; pp. 18–24.
2. Dujardin, T.; Lonchamp, G. In *Proceedings of International Symposium on Isotope Separation and Chemical Exchange Uranium Enrichment,* Tokyo, Japan, October 29–November 1, 1990; pp. 161–170.
3. Jardy, A.; Rosset, R.; Deson, J.; Foned, H. Separation des isotopes du plomb au moyer de resines echangeuses de cations. Bull. Soc. Chim. France, **1969**, *12*, 4576–4590.
4. Bigeleizen, J. Nuclear size and shape effects in chemical reactions: Isotope chemistry of the heavy elements. J. Am. Chem. Soc. **1996**, *118*(15), 3676–3680.
5. Knyazev, D.A.; Semin, G.K.; Bochkarev, A.V. Nuclear quadrupole contribution to the equilibrium isotope effects. Polyhedron **1999**, *18/20*, 2579–2582.
6. Grigoriev, I.S.; Meilikhova, E.Z., Eds. *Handbook of Physical Quantities*; Energoatomizdat: Moscow, 1992; 846 pp. (in Russian)
7. Wegener, H. *Der Mossbauer Effect und Seine Anwendungen in Physik und Chemie;* Mauncheim, 1965; Cited by Goldansky, V.I.; Makarov, E.F. *Chemical Applications of Messbauer Spectroscopy*, Khimia: Moscow, 1978; 43–44. (in Russian)
8. King, W.H. *Isotope Shift in Atomic Spectra;* Plenum Press: New York, 1984.
9. Semin, G.K.; Babushkina, T.A.; Yakobson, G.G. *Application of Nuclear Quadruple Resonance in Chemistry*; Khimia: Leningrad, 1972. (in Russian)
10. Shenoy, G.K.; Wagner, F.E., Eds. *Mossbauer Isomer Shifts*; North-Holland: Amsterdam, 1978.
11. Long, G.J., Ed. *Mossbauer Spectroscopy Applied to Inorganic Chemistry*; Plenum Press: New York, 1984.
12. Dickson, D.P.E.; Berry, F.J., Eds. *Mossbauer Spectroscopy*; Cambridge University Press: Cambridge, London, 1986.
13. Thosaret, B.V., Ed. *Advances of Mossbauer Spectroscopy Application to Physics, Chemistry and Biology*; Elsevier: Amsterdam, 1983.
14. Hufner, S. Electron densities from isotope shifts. In *Mossbauer Isomer Shifts*; Shenoy, G.K., Wagner, F.E., Eds.; North-Holland: Amsterdam, 1978; 203–220.
15. Freeman, A.J.; Ellis, D.E. Calculation of charge and spin densities of solids. In *Mossbauer Isomer Shifts*; Shenoy, G.K., Wagner, F.E., Eds.; North-Holland: Amsterdam, 1978; 111–201.

16. Knyazev, D.A.; Ivlev, A.A.; Bantish, A.N.; Dobiza, E.V. Uber die moglichkeit der Trennung von isotopen mittelschwerer und schwerer elemente durch chemischem austausch. Kernenergie **1968**, *11* (9), 229–238.
17. Aaltonen, J. Separation of alkaline earth metal isotope by ion exchange. Part 1. Studies on magnesium and calcium. Suomen Kemistilenti **1971**, *44* (1), 1–4.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded At: 10:46 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS100104758