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QUANTUM-STATISTICAL AND PHENOMENOLOGICAL ANALYSIS OF EQUILIBRIUM ISOTOPE EFFECTS

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ABSTRACT

This article discusses theoretical consequences of quantum-statistical representations of logarithm of isotopic reduced partition function ratio (ln β). Among the effects being under consideration are the localization of equilibrium isotope effect on the molecular structural elements in the vicinity of the site of isotopic substitution, distribution of increments of ln β, relationship between ln β values for the substitution of different atoms, and the influence of anharmonicity. The review also presents the phenomenological analysis of ln β for more than 2000 compounds as well as the classification of equilibrium isotope effects according to the causes of their appearance. Methods for the quantitative statistical estimation of the maximum possible isotope separation factors and criteria for the purposeful search for chemical exchange systems applicable for the practical separation of isotopes are also given.

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INTRODUCTION

For more than 60 years the major interest toward chemical isotope effects was determined by the possibility of their use for separation of isotope. An imposing development in this field during the last decades resulted in the design of two chemical processes for separation of uranium isotopes (1,2). Stable isotopes of light elements produced by chemical methods are widely used in scientific researches of complex systems as one of the best instruments for compound identification since they do not perturbate the intra- and intermolecular force fields. They also do not distort the properties of chemical, biological, and ecological systems and successfully compete with radioactive isotopes first and foremost in life sciences. The second direction is the use of natural chemical isotope effects as a method to study intermolecular forces, chemical bonds and structures, which is widely applied in many fields of chemistry, biological chemistry and earth sciences.

The general theoretical basis of all of these pragmatic aspects is quantum-statistical theory of chemical isotope effects. This review comprises three parts. The first part presents the main results obtained by the authors in developing the general theory of equilibrium effects during the last 15 years (3). The second part describes the thermodynamics of isotope effects. The main purpose of this part is to numerically estimate the attainable values of isotope separation factors for the majority of chemical elements and to formulate the principles for prediction of systems with high isotope effects. In the third part, we made an attempt to compare the energy consumption in chemical and physical methods for isotope separation.

THERMODYNAMICS OF ISOTOPE EXCHANGE REACTIONS

General Theory

Equilibrium Characteristics

In the general case, a chemical compound can contain an element undergoing isotope substitution in several different non-equivalent positions. Non-equivalent atoms are characterized by different equilibrium and kinetic isotope effects, whereas equivalent atoms have identical effects.

Let us consider the equilibrium in the isotope exchange of an element X between two compounds AX_n and BX_m by following the procedure described by Varshavskii and Vaisberg (4). The first compound contains n atoms X capable of isotope substitution in given equivalent positions. The remainder of the molecule A may contain exchangeable atoms of the element X but in other equivalent positions, which are disregarded in the present treatment. Similarly, in the molecule BX_m only the exchange of m equivalent atoms of the element X is accounted for.

If the numbers n and m are not unity, the exchange of isotopes X and X' will proceed through a series of stages. Each stage can be formulated as follows:

$$AX_{n-i+1}X'_{i-1} + BX_{m-j}X'_j \leftrightarrows AX_{n-i}X'_i + BX_{m-j+1}X'_{j-1} \tag{1}$$

where $i = 1,2, \ldots, n$ and $j = 1,2, \ldots, m$.

The equilibrium constant K_{ij} for this stage can be expressed in terms of the concentrations of the isotopic forms:

$$K_{ij} = \frac{[AX_{n-i}\,X'_i][BX_{m-j+1}\,X'_{j-1}]}{[AX_{n-i+j}\,X'_{i-1}][BX'_{m-j}\,X_j]} \tag{2}$$

In general, reaction (1) proceeds through $n \times m$ independent stages described by equilibrium constants defined by Eq. (2) type. Their sequence (from the first to the last) corresponds to the overall exchange reaction between the fully substituted isotopic forms:

$$mAX_n + nBX'_m \leftrightarrows mAX'_n + nBX_m \tag{3}$$

with equilibrium constant K_Σ equal to the product of K_{ij} constants:

$$K_\Sigma = \prod_{i=1}^{n} \prod_{j=1}^{m} K_{ij} \tag{4}$$

The real equilibrium includes all nm stages and is characterized by the isotope separation factor α, which can be measured experimentally:

$$\alpha = \frac{[X'_{AX_n}]/[X_{AX_n}]}{[X'_{BX_m}]/[X_{BX_m}]} \tag{5}$$

where $[X]$ and $[X']$ are the overall mole fractions of the isotopes X and X' in the compounds AX_n and BX_m.

The quantities K_{ij}, $K_{\Sigma,}$ and α are interrelated with each other and with the symmetry numbers, σ, of the isotopic forms of molecules AX_n and BX_m through the following expressions:

$$\begin{aligned} K_{ij} &= \alpha\,\frac{\sigma(AX_{n-i+1}X'_{i-1})\sigma(BX_{m-j}X'_j)}{\sigma(AX_{n-i}X'_i)\sigma(BX_{m-j+1}X'_{j-1})}, \\ K_\Sigma &= \alpha^{nm} \end{aligned} \tag{6}$$

General Equations of Statistical Thermodynamics

Statistical thermodynamics express the equilibrium constant K_{ij} in terms of the partition functions Q of the isotopic forms of compounds AX_n and BX_m:

$$K_{ij} = \frac{Q'_{AX_n}/Q_{AX_n}}{Q'_{BX_m}/Q_{BX_m}} \tag{7}$$

where the prime refers to AX_n and BX_m forms, containing the larger number of atoms of the X' isotope. In the ideal gas approximation, usually used for chemical equilibrium, one neglects the dependence of the partition functions on the phase state of the given substance, which makes it possible to calculate these quantities from the molecular spectra and molecular constants disregarding interactions between molecules. A further simplification is achieved by using the Born-Oppenheimer approximation concerning the subdivision of the internal energy of molecules into the electronic, spin-nuclear, vibrational, rotational, and translation components (5). For the majority of isotope equilibria, this approximation is also the only one possible, since more accurate calculations require far more detailed information about the molecular force field. The calculation of thermodynamic isotope effects does not require calculating the electronic and spin-nuclear components of the partition function. The electronic component does not differ from the statistical weight of the electronic ground state for the vast majority of molecules in the temperature range between 0 and 2000 K, since the excited electronic levels are usually much higher than the ground levels. For the rare molecules where there is a possibility of thermal excitation of even one electronic level, the total partition functions must be calculated for each level separately because the excitation is accompanied by a strong variation of the vibrational characteristics and a very significant change in the rotational characteristics of the molecules (6,7). An analogous situation also exists for the spin-nuclear component, which plays a significant role only for molecular hydrogen where it must be taken into account by calculating separately the partition functions for the ortho- and para-forms (8).

The exclusion of the electronic and spin-nuclear components reduces the task of finding the thermodynamic isotope effects to the calculation of the vibrational, rotational, and translation partition functions or, in the refined version, to the calculation of the vibrational-rotational and translation partition functions.

In the most accurate studies the vibrational-rotational component is calculated taking into account the anharmonicity of the vibrations, the centrifugal stretching effect, and the effects associated with vibration-rotation interactions (9,10). However, the information required for this purpose is available for very few molecules, and in the calculation of the isotope effects of all elements except hydrogen, one therefore uses simplified models of the vibrational and rotational motions, which are assumed to be independent. The simplest and most widely used harmonic oscillator-rigid rotator model neglects the above corrections and makes it possible to resolve completely the rotational and vibrational partition functions (11,12).

The calculation of the thermodynamic isotope effects is not required to separately determine the partition functions for each isotopic form of the compound. It is more rational to calculate the ratio of the partition functions of the isotopic forms (RPFR) of the given molecule. In terms of the “rigid rotator-harmonic oscillator” approximation, the RPFR , also denoted by f, can be formulated as follows (13,14):

$$f = \frac{\sigma}{\sigma'}\left(\frac{M'}{M}\right)^{3/2}\left(\frac{I'_A I'_B I'_C}{I_A I_B I_C}\right)^{1/2}\exp\left[\frac{hc}{2kT}\left(\sum_i d_i\omega_i - \sum_i d'_i\omega'_i\right)\right] \frac{\prod_i [1 - \exp(\omega_i hc/kT)]^{d_i}}{\prod_i [1 - \exp(\omega'_i hc/kT)]^{d'_i}} \tag{8}$$

where M is the molecular weight; $I_A I_B I_C$ is the product of the moments of inertia of the molecule relative to the three (principal) Cartesian axes; ω_i is the ith harmonic vibration frequency, and d_i is the multiplicity of its degeneracy. The primes denote the same isotopic forms as in Eq. (7). If isotopic forms with primes contain a greater number of heavy isotope atoms involved in exchange while those without prime are assigned to forms with a greater number of light isotope atoms, then Eq. (8) leads to a convenient specific relation: $f\sigma'/\sigma \geq 1$.

Equation (8) can be significantly simplified by using the Teller-Redlich theorem (15,16), which allows for connecting the moments of inertia, the vibration frequencies, the molecular weights M and M', and the masses of isotopes m and m' in the isotopic forms differing in the isotopes of a single element:

$$\left(\frac{m}{m'}\right)^{3n}\left(\frac{M'}{M}\right)\left(\frac{I'_A I'_B I'_C}{I_A I_B I_C}\right)\prod_i\left(\frac{\omega}{\omega'}\right)^2 = 1 \tag{9}$$

Substitution of Eq. (9) in Eq. (8) leads to the following relation:

$$f = \frac{\sigma}{\sigma'}\left(\frac{m'}{m}\right)^{3n/2} \frac{\prod_i \{\omega'_i \exp(-\omega'_i hc/2kT)[1 - \exp(-\omega'_i hc/2kT)]^{-1}\}^{d'_i}}{\prod_i \{\omega_i \exp(-\omega_i hc/2kT)[1 - \exp(-\omega_i hc/2kT)]^{-1}\}^{d_i}} \tag{10}$$

The multiplier $(m'/m)^{3n/2}$ determined by the masses of the pair of isotopes under consideration, stands in all RPFR referring to this pair of isotopes. In calculation of isotope effects, it is usually disregarded and here it is also omitted. In most studies the ratio σ/σ', which equals RPFR when all isotope distributions are equally probable, is transferred to the left side of Eq. (10). The so-called reduced frequencies, $\omega_i hc/kT$, are usually designated by u_i. When accounting for these conventional procedures and notations, Eq. (10) can be rewritten in the following form:

$$\left(\frac{\sigma'}{\sigma}\right)f = \frac{\prod_i \{u'_i \exp(-u'_i/2)[1 - \exp(-u'_i)]^{-1}\}^{d'_i}}{\prod_i \{u_i \exp(-u_i/2)[1 - \exp(-u_i)]^{-1}\}^{d_i}} = \frac{\prod_i [sh(u_i/2)/ui]^{d_i}}{\prod_i [sh(u'_i/2)/u'_i]^{d'_i}} \tag{11}$$

Simplifying Relations

The difficulty in determining the quantities $(\sigma/\sigma')f$ by Eq. (11) depends on the number of atoms in the molecule and on the symmetry of the isotopic forms under consideration. The symmetry numbers σ and the degree of degeneracy of the vibration classes, d_i and d_I', depend on the latter. The decrease of the symmetry of a given form results in the decrease of the degrees of degeneracy that increases, in turn, the orders of the submatrices of the secular equations of vibrational motion. The latter implies an increase of the number of non-identical cofactors in the products in the numerator and denominator of Eq. (11). In the limiting case, the products can have 3N-6 cofactors but the main difficulties in the application of Eq. (11) do not depend on the large number of cofactors. A large number of non-identical frequencies imply a sharp increase of the difficulty of their calculation, because the frequencies of isotopic forms are usually unknown and are found by solving the secular equations using particular models of the potential energy of the molecules.

It is obvious that the number of different isotopic forms $AX_{n-i}X_i'$ of the compound AX_n is $n + 1$. Therefore, to fully characterize the thermodynamic non-equivalence of these forms, it is necessary and sufficient to calculate n independent RPFR values. For equilibrium between the molecules of AX_n and BX_m, the calculation of the isotope effects requires the determination of $n + m$ RPFR values, and as shown above, each of these determinations can be very complicated. A successive radical simplification of the calculation of isotope effects is achieved by replacing the RPFR for all possible pair combinations of the isotopic forms for any molecule by the simplest functions of a single RPFR referring to the fully substituted forms AX_n and AX_n'. This replacement greatly reduces the number of RPFR required for the consideration of the equilibrium (two instead of $n + m$), and also maximally simplifies the very calculation of these two necessary RPFR values, since the high and identical symmetries of the fully substituted forms reduce to a minimum the number of different vibration frequencies.

The "rules of the sums of isotopic frequencies" first obtained by Sverdlov (17,18) and Decius and Wilson (19) and subsequently modified by Broderson (20) follow from the theory of the vibrations of polyatomic molecules(15,21,22). These rules can be represented by the following formula

$$\sum_{i}^{3N-6} \omega_i^{2p}\,(AX_{n-j}\,X_j') - \sum_{i}^{3N-6} \omega_i^{2p}\,(AX_{n-(j+k)}\,X_{j+k}') = \sum_{i}^{3N-6} \omega_i^{2p}\,(AX_{n-l}\,X_l') - \sum_{i}^{3N-6} \omega_i^{2p}\,(AX_{n-(l+k)}\,X_{l+k}') \tag{12}$$

where the symbols X and X' refer to the light and heavy isotopes of the element X, respectively, and p is any integer.

Using Eq. (12) with $p = 1{,}2$, Bigeleisen (23,24) showed that, for the values of ln $f(\sigma'/\sigma)$ referring to different members of the isotope-homologous series $AX_{n-j}X_j$, the "geometrical mean rule" holds with an adequate degree of approximation. This rule can be written in the general form

$$\frac{1}{j-k}\ln\Big[\frac{\sigma'}{\sigma}f(AX_{n-j}\,X'_j/AX_{n-k}X'_k)\Big] = \text{const} \qquad (13)$$

This rule, first discovered empirically in an early study by Urey (14), has been frequently subjected to numerical tests (23,24,25), which invariably confirms its adequate accuracy (the deviation of $\ln(f\sigma'/\sigma)$ from the rule does not exceed 1.0%).

When the isotopic equilibrium of a specific pair of isotopes is considered, the geometrical mean rule makes it possible to characterize the entire set of isotopic homologues by a single RPFR value. This establishes an unambiguous (isomorphous) correlation between the chemical compound (molecule, ion) and the characteristics of its ability for isotope separation. Varshavskii and Vaisberg (4) suggested the β-factor concept (related to f) to be used for this purpose. If RPFR refers to the fully substituted forms AX_n and AX'_n containing n equivalent X atoms capable of isotope substitution, then, regardless of the complexity of the compounds and the n value, the following very simple relation holds:

$$\ln\beta = \frac{1}{n}\ln f\,(AX_n/AX'_n) \qquad (14)$$

Equation (14) defines unambiguously the degree of thermodynamic non-equivalence of two isotopes in a given molecule whereas RPFR includes in addition the equally probable distribution factor, which is equal to the ratio of the symmetry numbers. The expression for the β-factor can be written in the following form:

$$\ln\beta = \frac{1}{n}\sum_i d_i \ln\,\{[sh(u_i/2)/u_i]/[sh(u_i^*/2)/u_i^*] \qquad (15)$$

Equation (15) has become the main working relation in most studies devoted to the thermodynamics of isotope exchange and kinetic isotope effects, although the necessary stipulations concerning its application are made in just a few works. Brodskii (26) and Varshavskii and Vaisberg (4) showed in the general case that when accounting for the equal probabilities of the distributions of isotopes between all isotopic forms of substances AX_n and BX_m, the isotope separation factor α, corresponding to the equilibrium in the entire set of type (1) reactions, is given by the very simple equation:

$$\alpha = \beta_{AX_n}/\beta_{BX_m} \qquad (16)$$

The simplicity of Eq. (16) is an additional confirmation of superiority of the β-factor concept over the RPFR-based approach. Due to the difference in significance of these two concepts, it seems essential to confine only one of them in the present review, namely the β-factor. Nevertheless, to simplify and facilitate the exposition, both terms are used in the text further. Unless otherwise stated, here the significance of the term "RPFR" is always identical with that of the term "β-factor."

It seems important to note that according to the results by Bigeleisen (27), if the nuclei have non-zero quadruple moment (i.e., non-spherical shape), they may have different sizes and shapes for different isotopes of a given element. Because s-electrons have non-zero electronic density near the nuclei, interaction between nuclei and s-electrons may result in isotopic difference of the order of 1 cm^{-1}. For light and moderate elements, this difference is rather small compared with the difference in vibrational frequencies directly caused by isotopic mass shift. But this increment ("nuclear form and shape effect") does not decrease with the increase of mass and for heavy elements becomes comparable with increment of molecular vibrations. For example, according to the estimate by Bigeleisen for uranium, this increment is three times greater than the difference of ln β and has an opposite sign. Therefore, for heavy elements, the ln α value calculated from ln β should be corrected by adding the value of increment of nuclear shape and size effect, $\ln K_{fs}$. It is evident that the calculation of ln β is still necessary. Moreover, by now the term $\ln K_{fs}$ may be estimated only as the difference between experimental ln α values and calculated values of ln β. Hence, the importance of precise calculation of ln β becomes even greater than before.

Accuracy of Statistical Thermodynamics Calculations

By taking the logarithm of Eq. (16), we obtain $\ln \alpha = \ln \beta_{AXn} - \ln \beta'_{AXm}$. As seen, the ln α value is determined as a small difference between two comparatively large quantities that makes the precision of β calculation particularly important. This problem depends on two factors: 1) accuracy of harmonic oscillator-rigid rotator model, which is quite satisfactory (see Appendix), and 2) limited accuracy of vibrational frequencies. The isotope frequency values are determined either in experiment or from calculation by using the theory of molecular vibrations. The experimental frequencies usually have known error limits that simplify the calculation of error on ln α determination. But for real systems under interest, such calculations are scarce. Usually the frequency values used are the calculated ones. Hence, their accuracy is determined by the precision of calculation of intramolecular force constants. In this context, the theory of vibrations of polyatomic molecules appears to be an instrument to analyze nearly all theoretical problems of chemical exchange equilibrium.

Elements of Theory of Molecular Vibrations

From the viewpoint of mechanics, n-atom molecule is a system of n material points each of mass m_i, kept together by elastic forces. This system has $3n$ degrees of freedom and $N = 3n\text{-}6$ of them are the vibrations ($N = 3n\text{-}5$ in the linear molecule case). In the harmonic approximation, the frequencies of these vibrations are described by the following matrix equation:

$$\mathrm{GFL} = \mathrm{L}\Lambda \tag{17}$$

where G is the kinetic energy matrix expressed in terms of generalized momenta, and F is the potential energy matrix in generalized coordinates. The elements of matrix G (the so-called kinematic coefficients) can be calculated if both the geometry of the molecule (the length of the bonds, values of valent, and dihedral angles) and the masses of atoms are known. The elements of matrix F (the force constants) are the second derivatives of the potential energy in generalized coordinates at a point corresponding to the equilibrium geometrical configuration of the molecule. Matrix L is the diagonal matrix of the eigenvalues of matrix GF, which is equal (up to a coefficient) to the squares of the vibration frequencies ($\lambda_i = C\nu_i^2$, C is a constant dependent on the chosen units). Matrix L (the so-called matrix of "forms of vibrations") is both the matrix of eigenvectors of matrix GF and the transition matrix from the generalized coordinates to the normal coordinates. The so-called "natural" vibration coordinates, i.e., deviations from the geometric parameters of the molecule (bond lengths, valent, and dihedral angles) are commonly used as generalized coordinates to solve equation (17).

To allow best for the symmetry and specificity of the molecule, the natural coordinates corresponding to all bonds and valent angles of the molecule (the complete system of natural coordinates) are used. The number of coordinates may exceed here the number of vibrational degrees of freedom. While solving the vibration problem, zero frequencies corresponding to the extra degrees of freedom occur. The natural vibrational coordinates make it possible to establish a relationship between the vibrational and spectroscopic properties of the molecule and the concepts of the classical theory of molecular structure such as, the chemical bond, molecular fragments and their properties, etc. In particular, the force constants expressed in terms of natural coordinates show transferability, that is, they change little in series of similar molecules.

In high approximation in isotopic substitution, the potential energy of molecule and, hence, the matrix of force constants remains unchanged only when the kinematic coefficients depend on the atom masses change. In the course of substitution for heavier isotope, the vibration frequencies can only decrease.

While the kinematic coefficients may be calculated on the basis of geometry and masses of the molecule, it is usually difficult to find force constants (elements of *F* matrix). This problem ("inverse vibrational problem") is the most difficult for inorganic compounds because the transferability of force field does not work in this case. The precise characteristics of force fields can be found in the literature only for few polyatomic inorganic molecules. They were determined with the help of additional information such as, frequencies of different isotopic forms, Coriolis constants, etc. (28).

In the literature devoted to the vibrational spectra of inorganic compounds, the "precise force field" (i.e., firmly determined) is used to evaluate the validity of numerous models of force fields. These models are based on some assumptions, but in many cases they give a good approximation of force fields for groups of inorganic compounds. For most molecules calculated in this work, the Urey-Bradley-Shimanouchi and the general valent forces models were used. The previous studies made it clear that these models give an acceptable level of error (error of $\ln \beta$ is about 2% for simple molecules and high-symmetrical ions). For the complexes with polyatomic ligands, the error is two to three times higher, which makes it impossible to calculate small $\ln \alpha$ values from these results. Nevertheless, but in many instances, these results appear to be of use in studies of the changeability of $\ln \beta$.

Methods of Interpretation

Polynomial Representations for RPFR

An accurate expansion in a variable sign power series with Bernoulli coefficient B_{2j-1} was obtained by Bigeleisen (23) for the range $u_{\max} < 2\pi$:

$$\ln \beta = \sum_{j=1}^{\infty} \frac{(-1)^{j+1} B_{2j-1}}{2j(2j)!} \sum_{i=1}^{3N-6} \delta(u_i^{2j}) = \sum_{j=1}^{\infty} \frac{(-1)^{j+1} B_{2j-1}}{2j(2j)!} \left(\frac{hc}{kT}\right)^{2j} \Delta tr\,(GF)^j \qquad (18)$$

The condition for the convergence of this series ($u_{\max} < 2\pi$) holds only for molecules with comparatively weak bonds or at relatively high temperatures.

This limitation as well as the low rate of convergence of series (18) stimulated the derivation of approximate expressions for $\ln \beta$ over an arbitrary range of u values. Considerable efforts were wasted in the search for ways to achieve a sufficiently accurate mathematical description of $\ln \beta$ with the aid of finite orthogonal Jacobi polynomials (29–31). Analysis of different versions of this description by Bigeleisen and Ishida (30) led to the conclusion that the following approximate expression, in which the terms of series (18) are modulated by finite first-order Chebyshev polynomials, is best:

$$\ln \beta = \sum_{j=1}^{n} T(n, j, u_{\max}) \frac{(-1)^{j+1} B_{2j-1}}{2j(2j)!} \left(\frac{hc}{kT}\right) \Delta tr(GF) \qquad (19)$$

The accuracy provided by the Bigeleisen-Ishida expansion (19) is determined by the order n of the modulating Chebyshev function $T(n,j,u_{\max})$ and the required range of values $u \in [0,u_{\max}]$. The accuracy of Eq. (19) is higher, the higher the order n and the narrower the required range of values of u. The marked increase of the error of this approximate expression with increase of u necessitates the application of a (third-fourth)-order function $T(n,j,u_{\max})$ and the introduction into $T(n,j,u_{\max})$ of exact values of $u_{\max}$ corresponding to the maximum frequency of the vibrations of the molecule in the "light isotope" form.

Nemeth et al. (32) used the minimax method to expand the components of ln β into a finite polynomial that resulted in the following approximate expression:

$$\ln \beta = \sum_{j=1}^{n} a(n, j, u_{\max}) \sum_{i}^{3N-6} \delta(u_i/u_{\max})^{2j} = \sum_{j=1}^{n} a(n, j, u_{\max}) \left(\frac{hc}{kT}\right)^{2j} \Delta tr\,(GF)^j \quad (20)$$

where $a(n,j,u_{\max})$ are the modulating polynomials analogous to $T(n,j,u_{\max})$. Their numerical values have been tabulated in (32).

The difference between Eqs. (20) and (19) is in far better fit of polynomials $a(n,j,u_{\max})$ to the components of ln β even over a wide range of u values. Although the accuracy of Eq. (20) is ultimately comparable to that of Eq. (19), the weak dependence of the error of the former equation on u makes it possible to employ the same numerical values with $a(n,j,u_{\max})$ for large sets of molecules over a wide temperature range. This converts Eq. (20) into an algebraically simple expression and greatly facilitates the mathematical analysis of the relation between the RPFR and all its intramolecular characteristics.

Equation (20) was used in a series of studies (25,33–38) to investigate in detail the relationship between the RPFR and the force constants. The following example provides an idea about the complexity of the resulting specific relations (35): the overall form of the expression for $\Delta tr(GF)^3$ for a non-linear triatomic molecule has 113 terms. If it is necessary to estimate the scale of significance of various constants, this makes numerical analysis of specific molecules preferable and lowers the generality of the conclusions.

Estimation of the contribution of various force constants to ln β by using equations of type (20) represents a difficult task for the following reasons: replacement of the real (numerical) value of force constant by zero has the physical significance in case of 1) bond rupture (dealing with the valence constant); 2) complete elasticity of the valence angle (zero deformation constant for the angle); and 3) the cessation of the interaction between unlike coordinates. Such substitution can influence the coefficients of the characteristic polynomial to such an extent that certain vibration frequencies of the molecule "modified" in this way can prove to be imaginary. A special method has therefore been proposed (37) to extrapolate ln β in terms of the force constants from the region where all frequencies of the "modified" molecule retain positive values to zero values of the force constant. This method must be used in estimating the contributions of the valence and deformation constants, which are the largest. On the other hand, the constants for interaction between unlike coordinates can be estimated directly through the use of Eq. (20).

This exact analysis of the approximate relations and empirical correlations confirms the dominant role of valence force constants and the secondary role of the deformation constants. A far smaller influence of constants of f_{rr}, $f_{r\alpha}$, and $f_{\alpha\alpha}$ type reflects the interactions of unlike internal coordinates of the molecule. It has been shown (37) that contributions of the valence constants to ln β_H, characterizing polyatomic deuterium-substituted hydrides, are nearly additive at normal temperatures (300 K) and are rigorously additive at higher temperatures. The isotope effects of oxygen and in general of any element whose atoms play the role of terminal atoms are similarly almost additive and cumulative with respect to the force constants (33,38). On the other hand, the additivity rule is not valid for elements of carbon type, which form numerous bonds and play the role of central atoms (33).

A deficiency of Eqs. (19), (20), and other polynomial expansions of ln β in terms of the parameters $\Delta tr(GF)^j$ is the algebraic complexity (see above) of the increments in the traces of the matrix GF, which constitutes a significant obstacle in the mathematical analysis of the relations between the RPFR and the characteristics of the molecules. In this respect, a definite step forward was made by the simplification achieved by using Waring's formula (39). Their application replaces the parameters $\Delta tr(GF)^j$ by$\Delta\sigma_j$ (isotopic increments in the coefficients of the characteristic polynomial for molecular vibrations):

$$\begin{aligned}\sigma_1 &= 4\pi^2c^2\sum_i \omega_i^2,\\ \sigma_2 &= (4\pi^2c^2)^2\sum_{i\neq k}\omega_i^2\omega_k^2, \qquad (21)\\ \sigma_3 &= (4\pi^2c^2)^3\sum_{i\neq k\neq l}\omega_i^2\omega_k^2\omega_l^2.\end{aligned}$$

This replacement of the expansion parameters reduces Eqs. (19) and (20) to the form:

$$\ln\beta = \sum_j b_j\Delta\sigma_j + \sum_{j,k} b_{j,k}\Delta\sigma_j\Delta\sigma_k + \sum_{j,k,l} b_{j,k,l}\Delta\sigma_j\Delta\sigma_k\Delta\sigma_l + \ldots. \qquad (22)$$

where b_j, b_{jk}, and b_{jkl} are the functions of σ_j of different orders depending on the choice of modulating polynomials. If functions b_j, b_{jk}, and b_{jkl} are found by the method proposed by Nemeth et al. (32) from the polynomials $a(n,j,u_{\max})$, then their form is significantly simpler than in the case when $T(n,j,u_{\max})$ is used for the same purpose (see Table 1).

The advantages of Eq. (22) over Eqs. (19) and (20) are as follows: despite its apparent greater complexity, Eq. (22) has a simpler structure and converges more rapidly. Table 2 shows that the contribution of even the second sum on the

Table 1. Functions b_j According to Nemeth et al. (32)

N	Function b_j
1	$b_1 = B_1$
2	$b_1 = B_1 + 2B_2\sigma_1$
	$b_2 = -2B_2$
3	$b_1 = B_1 + 2B_2\sigma_1 + 3B_3\sigma_1^2 - 3B_3\sigma_2$
	$b_2 = -2B_2 - 3B_3\sigma_1$
	$b_3 = 3B_3$
4	$b_1 = B_1 + 2B_2\sigma_1 + 3B_3\sigma_1^2 - 3B_3\sigma_2 + 4B_4\sigma_1^3 - 8B_4\sigma_1\sigma_2 + 4B_4\sigma_3$
	$b_2 = -2B_2 - 3B_3\sigma_1 - 4B_4\sigma_1^2 - 4B_4\sigma_2$
	$b_3 = 3B_3 + 4B_4\sigma_1$
	$b_4 = -4B_4$

Here $B_j = (3.55559 \times 10^{-6}/T^2u_{\max})^{2j}$, and n is the degree of polynomial.

right side of Eq. (22) is comparable to the error of approximation and can therefore be neglected together with higher terms. The first sum has a convenient structure. In contrast to the variable-sign sums on the right sides of Eqs. (19)and (20), it includes only positive terms in which absolute magnitude decreases rapidly. As seen in Table 2, the first term with $\Delta\sigma_1$ amounts to 70–90% of ln β.

The contribution of the second term with $\Delta\sigma_2$ is 10-30%, and that of the term with $\Delta\sigma_3$ is about 1% of ln β, i.e., it is comparable to the error of the approximation. This enables us to talk about the relative contribution of each term to ln β, while a similar statement does not make such clear sense in relation to the terms of the variable-sign sums (19) and (20). Furthermore, the first sum $\sum b_j\Delta\sigma_j$ consists of simple functions. Table 1 shows that b_j values are power functions of coefficients σ_j of the characteristic polynomial. These coefficients refer to an isotopically unperturbed molecule and can be readily expressed not only in terms of the frequencies but also in terms of the matrices *G* and *F*.

Table 2. Structure of Contributions of Terms of Expansion (22) to ln β at 300 K (Degree of Polynomial Fitted $n = 3$, $n' =$ Degree of Secular Equation)

Molecule	ln β	n'	$\sum b_j\Delta\sigma_j$	$b_1\Delta\sigma_1$	$b_2\Delta\sigma_2$	$b_3\Delta\sigma_3$
NO_2	0.0976	2 + 1	0.0997	0.0737	0.0254	0.0006
NOF	0.0823	2 + 1	0.0838	0.0718	0.0119	0.0001
NOCl	0.0761	2 + 1	0.0775	0.0704	0.0070	0.0001
CO_2	0.1719	1 + 1 + 1 + 1	0.1678	0.1215	0.0450	0.0013
COF_2	0.1811	3 + 3	0.1840	0.1517	0.0317	0.0006
HCO	0.1773	3 + 3 + 3	0.1797	0.1290	0.0492	0.0015

The values of σ_j are equal to the sums of products of the principal minors of order j of the matrices G and F. The isotopic increments $\Delta\sigma_j$ can be expressed quite similarly. The properties of σ_j and $\Delta\sigma_j$ make it possible to separate (quite easily) the influence of both force characteristics and the geometry and mass of the molecules on ln β. This makes Eq. (22) convenient to interpret isotope effects and to search the desired relations.

An example of useful applications of Eq. (22) is the derivation of the quantitative coupling relations between the isotope effects of different elements and the frequency characteristics of the molecules (40). Thus, for reaction

$$\mathrm{HCO_3^-} = \mathrm{CO_2} + \mathrm{OH^-} \tag{23}$$

four isotope exchange processes are possible between all three substances and there can be four equilibrium isotope effects with respect to three elements:

$$\begin{aligned}
&\mathrm{H\overset{*}{C}O_3^-} + \mathrm{CO_2} = \mathrm{HCO_3^-} + \mathrm{\overset{*}{C}O_2};\ \alpha_\mathrm{C} = \beta_{\mathrm{CO_2}}/\beta_{\mathrm{HCO_3^-}},\\
&\mathrm{\overset{*}{H}CO_3^-} + \mathrm{OH^-} = \mathrm{HCO_3^-} + \mathrm{O\overset{*}{H}{}^-};\ \alpha_\mathrm{H} = \beta_{\mathrm{OH-}}/\beta_{\mathrm{HCO_3^-}},\\
&\mathrm{HCO\overset{*}{O}{}_2^-} + \mathrm{CO_2} = \mathrm{HCO_3^-} + \mathrm{C\overset{*}{O}_2};\ \alpha_\mathrm{O}^{(1)} = \beta_{\mathrm{CO_2}}/\beta_{\mathrm{HCO_3^-}},\\
&\mathrm{HC\overset{*}{O}O_2^-} + \mathrm{OH^-} = \mathrm{HCO_3^-} + \mathrm{\overset{*}{O}H^-};\ \alpha_\mathrm{O}^{(2)} = \beta_{\mathrm{OH^-}}/\beta_{\mathrm{HCO_3^-}}.
\end{aligned} \tag{24}$$

The coupling relation for Eq. (24) or (what is the same) for reaction (23) is as follows:

$$\begin{aligned}
&\frac{\mu_\mathrm{C}}{\Delta\mu_\mathrm{C}} \ln \alpha_\mathrm{C} + \frac{\mu_\mathrm{H}}{\Delta\mu_\mathrm{H}} \ln \alpha_\mathrm{H} + 2\frac{\mu_\mathrm{O}}{\Delta\mu_\mathrm{O}} (\ln \alpha_\mathrm{O}^{(1)} + \ln \alpha_\mathrm{O}^{(2)})\\
&\qquad = \sum_j jb_j\,(\mathrm{CO_2})\sigma_j\,(\mathrm{CO_2}) + \sum_j jb_j\,(\mathrm{OH^-})\sigma_j\,(\mathrm{OH^-})\\
&\qquad\qquad - \sum_j jb_j\,(\mathrm{HCO_3^-})\sigma_j\,(\mathrm{HCO_3^-})
\end{aligned} \tag{25}$$

The coupling relations of type (25) permit 1) to estimate the isotope effects which have not been investigated experimentally, 2) to test the reliability of the results, and 3) to determine the characteristics of the transition complexes.

Perturbation Theory Approximation

Another approach was proposed by Wolfsberg et al. (41). It is based on application of the perturbation theory to the calculation of ln β. The quantity taken as the 0th approximation ln β_0 is obtained by neglecting all the non-diagonal terms in the matrices G and F. The basic idea of the method is that ln β_0 is represented as the sum of contributions with respect to the "0th" frequencies ν_0 and ν_0^*, each of which (since the matrix of the 0th approximation G_0F_0 is diagonal) can be associated with a corresponding vibrational coordinate (bond, angle, etc.). Thus, 0th approximation gives a clear representation, suitable for interpretation. For this, naturally, the values of the 0th approximation ln β_0 must be close to the exact value of ln β (that is the matrix *GF* must not contain significant non-diagonal elements).

This closeness, however, takes place in some cases only, and for many molecules one has to use the second-order approximation of perturbation theory. The second-order approximation gives the accuracy of about a few percent, but the representation of ln β in this case loses algebraic simplicity.

Representation of RPFR as Infinite Transcendental Series

An accurate representation of ln β in the harmonic approximation as the sum of the terms of an infinite series of functions, which are clearly and simply determined by the force constants, the geometry and the masses of the atoms of the isotopic forms of the molecule has heen proposed by the authors of the present review (42,43). The representation has the following form:

$$\begin{aligned} \ln \beta &= \sum_{p=1}^{\infty} \ln \beta_p \\ &= \sum_{p=1}^{\infty} \frac{1}{l} \ln\left[1 + \frac{(\kappa/p)^2\, \Delta\sigma_1 + (\kappa/p)^4\, \Delta\sigma_2 + \ldots + (\kappa/p)^{2N}\, \Delta\sigma_N}{1 + (\kappa/p)^2\, \sigma_1^* + (\kappa/p)^4\, \sigma_2^* + \ldots + (\kappa/p)^{2N}\, \sigma_N^*}\right] \end{aligned} \tag{26}$$

The quantities σ_p equal to the sums of all principal minors of pth order of the matrix *GF*, $\sigma_i = \sigma_i^* + \Delta\sigma_i$, $\kappa = h/4\pi^2 kT$.

To obtain representation (26) one has to present the function *sh(x)* into an infinite product and then to take the logarithm of this product by using the Varing's formulae. The evident advantage of (26) over the above-mentioned series is that the expansion (26) converges for all positive u_i. The existence of a simple equation for estimating the error for restricted number of terms taken into account, the fact that the signs of the logarithmic terms are constant, and the rapid decrease in the contributions of these terms with increase in p all distinguishes the expansion (26) from familiar approximate expansions. The drawback of (26) is its algebraic complicity, particularly for substitution of hydrogen isotopes. Nevertheless, (26) appears to be very useful to analyze the regularities of ln β behavior in cases when the convergence is the main factor.

Representation of RPFR as Sum of Contributions of Structural Elements of Molecule

A clear and accurate representation of the ln β as the sum of contributions with respect to the vibrational coordinates corresponding to the structural elements of the molecule may be easily obtained on the basis of similar representation of the differences in the thermodynamic functions proposed by the authors (44). To construct this representation we note that the logarithm of the β-factor, with an accuracy corresponding to an additive constant, is the difference, divided by kT, between the free energies for two isotopic forms of the molecule AX_i and AX_i^*, calculated for one atom being replaced:

$$\ln \beta_{AX_i^*/AX_i} = \frac{1}{l}\left[\frac{F_{AX_i} - F_{AX_i^*} + F_X - F_{X^*}}{kT}\right] \tag{27}$$

Here $(F_X - F_{X^*})/kT$ is the difference between the free energies of the isotopes of the hypothetical monatomic gas X (which is constant for a given type of isotopic substitution).

For the difference between the internal energies of the isotopic forms we can write:

$$\Delta U = U_{X^*} - U_X = kT^2\left(\frac{\partial \ln(Q_{X^*}/Q_X)}{\partial T}\right) \tag{28}$$

where Q is the partition function. Adopting the Born-Oppenheimer approximation and the harmonic oscillator-rigid rotator approximation, we have $Q = Q_{tr}Q_{rot}Q_{vibr}$, (subscripts: tr = translational, rot = rotational, $vibr$ = vibrational motion). Because the translational and rotational motions do not contribute to the isotopic difference of the energies, the difference in the internal energies of the isotopic forms is equal to the difference in the vibrational energies.

Substituting in Eq. (28) the expression for Q_{vibr} by accounting for the energy of the zero-point vibrations gives

$$\Delta U = \sum_{i=1}^{N}\left[\frac{hc\upsilon_i^*}{2}\, cth\, \frac{hc\upsilon_i^*}{2kT} - \frac{hc\upsilon_i}{2}\, cth\, \frac{hc\upsilon_i}{2kT}\right] \tag{29}$$

Let us introduce now the system of natural vibrational coordinates corresponding to the above structural elements of the molecule. The vibrational energy of the molecule can be represented as follows (28):

$$U_{vibr} = tr \sum F \tag{30}$$

where F is the force constant matrix, and Σ is the matrix of the mean-square amplitudes of the vibrations (in this particular case it is more convenient to represent mean square amplitudes in natural coordinates).

According to the Binet-Cauchy theorem (45), the trace of the product of two matrices A and B is equal to the sum of the paired products of the corresponding elements $\sum_{(i,j)} a_{ij}\, b_{ij}$. Then one obtains:

$$U_{vibr} = tr\Sigma F = \sum_{(i,j)} \sigma_{ij} F_{ij} \tag{31}$$

where σ_{ij} represents the elements of the matrix of the mean-square amplitudes in natural coordinates, and F_{ij} are the force constants.

The relationship (31) can be represented in the following clear form. We write the matrix A_{Uvibr}, whose elements are the products of the corresponding elements of the matrices Σ and F:

$$A_{U_{vibr}} = \begin{pmatrix} \sigma_{11}F_{11} & \sigma_{12}F_{12} & \dots & \sigma_{1N}F_{1N} \\ \sigma_{12}F_{12} & \sigma_{22}F_{22} & \dots & \sigma_{2N}F_{2N} \\ \dots & \dots & \dots & \dots \\ \sigma_{1N}F_{1N} & \sigma_{2N}F_{2N} & \dots & \sigma_{NN}F_{NN} \end{pmatrix} \tag{32}$$

This matrix is obviously symmetrical. According to Eq. (31), the sum of all the elements of the matrix (32) is equal to the vibrational energy U_{vibr} of the molecule. The term at the intersection of the *i*th column and the *j*th row of matrix (32) represents the contribution of interaction of the *i*th and *j*th vibrational coordinates to the vibrational energy. In particular, the terms on the diagonal of matrix (32) represent the contributions due to the interaction of each vibrational coordinate with itself (the "increment of the structural element").

Matrix (32) readily gives the representation of the isotopic difference in the energies as the sum of contributions of structural elements. Thus $\Delta U = \Delta tr\Sigma F = tr(\Delta\Sigma)F$, since the matrix F remains unchanged in the isotopic substitution (here, $\Delta\Sigma$ is the matrix $\Sigma^* - \Sigma$). On the other hand, we can write the matrix made up of the elements $\Delta\sigma_{ij}F_{ij}$:

$$A_{\Delta U} = A^*_{U_{vibr}} - A_{U_{vibr}} \tag{33}$$

where the term at the intersection of the *i*th column and the *j*th row represents the contribution made to the isotopic difference in the energies by the interaction of the *i*th and *j*th vibrational coordinates. The sum of all elements of matrix (33) is equal to ΔU.

To obtain the corresponding expansion with respect to vibrational coordinates for the difference in the heat capacities, ΔC_{vibr}, one needs to differentiate matrix (33) by temperature. This can easily be done by representing the matrix Σ as $\Sigma = L\Delta\tilde{L}$, where L is the matrix of the modes of the vibrations, the tilde above the letter denotes transposition of the matrix, and Δ is the diagonal matrix with the elements $\delta_{ii} = [h/8\pi^2 c\nu_i]cth[hc\nu_i/2kT]$ (28). From this one obtains:

$$\Delta C_{vibr} = C^*_{vibr} - C_{vibr} = \left(\frac{\partial \Delta U}{\partial T}\right)_{vibr} = tr\left(\frac{\partial \Sigma^*}{\partial T} - \frac{\partial \Sigma}{\partial T}\right)F \tag{34}$$

where $\partial\Sigma^*/\partial T = L^*(\partial\Delta^*/\partial T)\tilde{L}^*$, and $\partial\Sigma/\partial T = L(\partial\Delta/\partial T)\tilde{L}$. Here $(\partial\Delta/\partial T)$ is the diagonal matrix with elements

$$\mathrm{d}\delta_{ii}/\mathrm{dT} = h^2/\{16\pi^2 T^2 k\, sh^2[hc\nu_i/2kT] \tag{35}$$

Using the Binet-Cauchy theorem, we can represent the trace of the product of two matrices in Eq. (34) as the matrix $A_{\Delta Cvibr} = A^*_{Cvibr} - A_{Cvibr}$, whose *(i,j)*th element is the product of the *(i,j)*th element of the matrix $(\partial\Sigma^*/\partial T - \partial\Sigma/\partial T)$ and the *(i,j)*th element of the matrix F. The matrices A_{Cvibr} and $A_{\Delta Cvibr}$ are the representations of the vibrational heat capacity and the isotopic difference in the total heat capacities, respectively, as the sum of contributions with respect to the structural elements of the molecule.

For the isotopic difference in the entropies we have

$$\Delta S = (S_0^* - S_0) + \int_0^T \frac{(C^*_{vibr} - C_{vibr})}{T}\,dT = (S_0^* - S_0) + tr\left[\int_0^T \left(\frac{\partial\Sigma^*}{\partial \mathrm{T}}\right)\frac{\partial T}{T} - \int_0^T \left(\frac{\partial\Sigma}{\partial T}\right)\frac{\partial T}{T}\right]F,\ \int_0^T \left(\frac{\partial\Sigma}{\partial T}\right)\frac{\partial T}{T} = L\left\{\int_0^T \left(\frac{\partial\Delta}{\partial T}\right)\frac{\partial T}{T}\right\}\tilde{L} \qquad (36)$$

Here $\int_0^T (\partial\Delta/\partial T)\ \partial T/T$ is the diagonal matrix with elements on the diagonal $[hc\nu_i/2T]cth[hc\nu_i/2kT] - k\ \ln(\mathrm{sh}[hc\nu_i/2kT])$. The corresponding matrix $A_{\Delta Svibr}$ is easily obtained from the second term in Eq. (36) in the same manner as matrices $A_{\Delta Cvibr}$ and $A_{\Delta \mathrm{U}}$ were constructed.

Let us introduce the matrix

$$A_{\ln\beta_{vibr}} = -\frac{A_{\Delta F_{vibr}}}{kT} = -\frac{A_{\Delta U} - TA_{\Delta S_{vibr}}}{kT} \qquad (37)$$

The matrix obtained is symmetrical, and the term at the intersection of its *i*th row and *j*th column represents the contribution of the interaction of the *i*th and *j*th vibrational coordinates to ln β. The sum of all the elements of matrix (37) is connected with ln β by the following formula:

$$\ln\beta = \Omega + \ln\beta_{vibr} = \Omega + \sum_{(i,j)} a_{i,j} \qquad (38)$$

where a_{ij} denotes the *(i,j)*th element of matrix (37), and $\Omega = 1/2\ \ln \det G^*/\det G$. The Teller-Redlich term Ω is determined by the geometry and the mass distribution over the whole molecule. Still, it is not difficult to make a precise representation of the Teller-Redlich term and so the complete value of ln β as a matrix of contributions of interactions of the structural elements of the molecule, similar to matrix (37). To make this representation one needs to account for that $\lim_{T\to\infty}(\ln\beta) = 0$. Because the Teller-Redlich term does not depend on temperature, one obtains from formula (38):

$$\lim_{T\to\infty}(\ln\beta_{vib}) = -\Omega \qquad (39)$$

The representation for the Teller-Redlich term (matrix A_Ω) through the aim matrix is as follows:

$$A_{\Omega} = -\lim_{T \to \infty} A_{\ln\beta_{vibr}} = \begin{pmatrix} \lim\limits_{T \to \infty} a_{12} & \lim\limits_{T \to \infty} a_{12} & \cdots & \lim\limits_{T \to \infty} a_{1N} \\ \lim\limits_{T \to \infty} a_{22} & \lim\limits_{T \to \infty} a_{22} & \cdots & \lim\limits_{T \to \infty} a_{2\mathrm{N}} \\ \vdots & \vdots & \ddots & \vdots \\ \lim\limits_{T \to \infty} a_{2N} & \lim\limits_{T \to \infty} a_{2N} & \cdots & \lim\limits_{T \to \infty} a_{NN} \end{pmatrix} \tag{40}$$

The matrix representation for the full value of ln β can now be easily obtained:

$$A_{\ln\beta} = A_{\ln\beta vibr} + A_{\Omega} \tag{41}$$

where each element of matrix $A_{\ln\beta}$ is the sum of corresponding elements of matrices $A_{\ln\beta vibr}$ and A_{Ω}. Representation (41) is accurate and makes it possible to analyze ln β and consequently the isotopic effect in terms of vibrational coordinates, but not the vibrational frequencies.

General Relations

Mathematical representations described in Section 1.2 can be used to study the dependencies that determine the general properties of ln β. In this section, we present the results of this study.

Equivalent and Non-Equivalent Atoms

In some cases the molecule may contain hydrogen atoms within different non-equivalent groups. For instance, the molecule of propionic acid CH_3CH_2COOH has three groups containing hydrogen atoms: three atoms in the methyl group, two in the methylene group and one in the carboxyl group. Hydrogens of these groups show different chemical behavior and each group should be characterized by its individual ln β value. In principle, the occurrence of intramolecular (intrastructural) isotopic effects is possible, i.e., the isotopic enrichment of separate groups within one molecule by means of intramolecular exchange. The intrastructural effects are of large value in cases when the real equilibrium has been established (for instance, in some systems of geological interest). If the real equilibrium in several non-equivalent groups of the same molecule is established, the concept of the "total beta-factor β_{Σ}" of the molecule suggested by Galimov can be used to evaluate the isotope separation factor. The method of calculation of β_{Σ} on the basis of β-factor values for different groups has been described (46).

But even the molecule contains only one group of substituted atoms (i.e., all substituted atoms are equivalent), the equilibrium exchange constants of every atom can be different. As stated above, the application of the β-factor concept is based on the fact that the isotope separation coefficient does not depend on the concentration of isotopes in the isotopic mixture. The sufficient condition thereof is observed when the following rule is met (47,48): if a group of l equivalent atoms (H) is present in the molecule then in their successive substitution for isotope atoms we obtain

$$\ln \beta = \frac{1}{x} \ln f(AX_x^{*} X_{l-x}/AX_l) = \frac{1}{l} \ln f(AX_l^{*}/AX_l) \tag{42}$$

where f is the reduced partition function ratio of the isotopic forms indicated in brackets.

As seen from Eq. (42), the geometric mean rule states the independence of the ln β value on the number of substituted atoms x. The precision test of this rule was carried out in the above cited studies and in some other publications. Thus, in Eq. (49) a theoretical analysis of possible deviations from the rule (42) was conducted with the use of representation (26). It was shown that for all isotopic equilibria, except those in which molecular hydrogen participates, deviations from Eq. (42) are less than 2% at room temperature and can be ignored (see Table 3). Deviations of about 2% are only possible for small molecules of the H_lB type. In this case the substituted hydrogen atoms are bound with one central atom B. Hence, all vibrations of the molecule are those of hydrogen atoms vibration modes and undergo a strong shift in the isotopic substitution. The described molecules include H_2O, H_2S, and NH_3 that are of practical interest for chemical exchange. As for organic molecules (except CH_4), their deviations from Eq. (42) are negligibly small. As seen from Table 3, for isotopic equilibrium systems with participation of molecular hydrogen deviations from Eq. (42) are noticeable. They are particularly important for the systems involving hydrogen (gas) and metal hydrides (solid) (50,51).

Dependence of RPFR upon Δμ and μ

This problem can be studied precisely with the use of ln β representation discussed above. However, in most cases (except hydrogen substitution) the linear approximation appears to be sufficient.

Table 3. Deviations from Geometrical Mean Rule in Substitution of Hydrogen Isotopes, %

T, K	$D_2CO/HDCO/H_2CO$	$H_2O/HDO/D_2O$	$H_2O/HTO/T_2O$	$T_2/HT/H_2$	$D_2/HD/H_2$
30	0.79	1.37	2.08	14.19	9.23
100	0.69	1.22	1.84	13.79	9.00
300	0.37	0.77	1.10	12.52	8.99

The relative simplicity of the theoretical relations between chemical isotope effects and the intramolecular characteristics has already been mentioned. The simplest relation whereby one can obtain to estimate the influence of various factors on ln β, is the linear Bigeleisen-Mayer approximation, which is valid at high temperatures (52):

$$\ln \beta = \frac{1}{24n} \sum_i [u_i^2 - (u_i')^2] = \frac{1}{24n} \left(\frac{h}{kT}\right)^2 \Delta trGF \tag{43}$$

where $\Delta trGF$ is the isotopic increment in the trace of the product of the kinematic coefficient matrix G and the force constants matrix F.

Bearing in mind that the stretching vibration (highest) frequencies make the main contribution to ln β, Bigeleisen proposed a modification of Eq. (43) which is suitable in the region of all usual temperatures. This is achieved by introducing a correction coefficient $\gamma_s(u_s)$ determined by the reduced frequency u_s of the symmetrical stretching vibration (23,53):

$$\ln \beta = \frac{\gamma_s}{24n} \left(\frac{h}{kT}\right)^2 \Delta trGF \tag{44}$$

At room temperatures Eqs. (43) and (44) cannot be used for the case of substitution of hydrogen isotopes because the relative error may exceed 30%. But for other elements, one may consider these equations as a good approximation.

Equations (43) and (44) reveal the principal intramolecular parameters, which have an influence on the values of ln β that constitutes their analytical value. These parameters are the force constants, geometrical characteristics, and atomic masses in the molecule. Analysis of $\Delta trGF$ term makes it possible to estimate the relative role of each of three groups of factors and the relative contributions of different components within these groups. In terms of their influence on ln β, the above groups can be arranged in the following sequence. The influence of the masses of atoms capable of undergoing the isotope substitution is the strongest. That of the force constants is weaker, and the influence of molecular geometry is the weakest. However, one needs to bear in mind that this subdivision of molecular parameters into groups is conditional, since the characteristics of the force fields of the molecules in which the element is included depend on the nature of each other, and the force constants and molecular geometry are interrelated to an even greater extent.

In other words, the analysis of the relations between ln β and intermolecular parameters implies the existence of certain indirect conditions (interrelations) between these parameters themselves. These interrelations are determined by the quantum mechanics and are not generally known. Therefore, these interrelations must be accounted for by using empirical experimental results.

Analysis of ΔtrGF revealed a virtually rigorous proportionality of the quantity ln β, and hence, also ln α, to the square of the reciprocal of atomic weight of the element involved in isotope substitution,μ. This explained very rapid decrease of the chemical isotope effects with the increase of atomic weight (52):

$$\Delta trGF = \Delta\mu \sum_{ij} a_{ij} f_{ij} = \frac{\Delta m}{m(m - \Delta m)} \sum_{ij} a_{ij} f_{ij} \tag{45}$$

where $\Delta m = m' - m$; m and m' are the atomic weights of the isotopes of the given element; μ and μ' are the reciprocals of the atomic weights of the isotopes, a_{ij} are coefficients in the elements g_{ij} of the matrix G, which depend solely on the molecular geometry, and f_{ij} are the elements of the force constants matrix F.

Equation (45) permits a rough estimate of the degree of diminution of the chemical isotope effects when moving from the first element of the periodic system (hydrogen) to the last ones such as, for example, uranium. The quantities ln β and ln α recalculated in terms of a single increment in the mass difference Δm, should then diminish by a factor of $(2\text{–}3) \times 10^4$. In reality, the scale of the decrease of the effects is somewhat smaller (54) owing to the influence of the second cofactor on the right side of this equation. Nevertheless, it imposes very stringent limitations on the overall scope of both chemical isotope separation methods and applications of isotope effects as a research method. The first (and the main) factor on the right side of Eq. (45) determines the limits of the development of these fields (at least at the present time) and shows that they are applicable to the set of relatively light polyisotopic elements.

Other important results that follow from Eq. (45) are the direct proportionality between ln β (and ln α) and the difference of inverse masses Δμ. The results obtained by studying the hydrogen substitution (55,56) demonstrate that the ratio

$$\xi = \ln \beta_{\mathrm{T/H}} / \ln \beta_{\mathrm{D/H}} \tag{46}$$

is nearly constant for almost all molecules. A detailed analysis of Eq. (46) has shown that ξ depends on the same factors as ln β (see above): geometry of the molecule, masses of its atoms, and the force field (that is on its "nature"), and temperature. By varying the parameters of a molecular model, it is possible in principle to obtain the maximum and minimum theoretical limits of ξ (lower limit of 1.33, and the upper one of l.44). It should be emphasized that the published observation about approximate constancy of ξ value for the real molecules is related not to the properties of Eq. (46) but to the fact that the values of atom masses and force constants in real molecules lie in fairly narrow ranges.

The analysis of the behavior of the ratio ξ for a representatively large number of molecules has established that ξ is highly characteristic with respect to the type of bond (that is to the nature of the atom directly joined to the hydrogen being replaced). The ξ value also increases with the increase of the number of equivalent atoms being replaced. The influence of other factors is insignificant.

Since ξ is the characteristic, the most correct method to find ln $\beta_{T/H}$ is its direct calculation from ln $\beta_{\mathrm{D/H}}$ by using relationship (46). The recommended values

Table 4. Recommended ξ Values for Molecules of Different Types

	T, K			
Molecule	100	200	300	400
H*F	1.435	1.429	1.423	1.416
H*Cl	1.436	1.427	1.417	1.407
H*Br	1.436	1.426	1.414	1.402
H*I	1.436	1.424	1.41	1.396
HOH*	—	1.412	1.407	1.400
CH_3OH^*	1.418	1.410	1.402	1.396
CH_3SH^*	1.419	1.407	1.396	1.386
H_2^*O	1.434	1.426	1.418	1.418
H_2^*S	1.419	1.407	1.396	1.385
H_2^*Se	1.442	1.428	1.415	1.402
H*CN	1.417	1.409	1.403	1.396
$C_2H_4^*$	1.418	1.407	1.397	1.389
NH_3^*	1.432	1.422	1.413	1.404
PH_3^*	1.433	1.418	1.405	1.394
AsH_3^*	1.432	1.415	1.401	1.388
SbH_3^*	1.428	1.409	1.394	1.381
CH_4^*	1.421	1.409	1.398	1.388
SiH_4^*	1.419	1.402	1.388	1.377
GeH_4^*	1.42	1.402	1.388	1.376
SnH_4^*	1.42	1.401	1.386	1.373

of ξ for molecules of different types are given in Table 4 compiled by using literature data.

The contributions of individual frequencies to ln β do not necessarily satisfy Eq. (46). Moreover, Eq. (46) can be used as a criterion of the correctness of regarding molecular fragments as individual molecules, and also for verifying the reliability of data on the vibrational frequencies of *D*- and *T*-forms. Thus the use of Eq. (46) makes it possible (for isolated molecules) to restrict the study to only deuterium or tritium equilibrium isotope effect. The masses of other atoms (except those substituted by the isotope) do not enter into the expression for $\Delta tr(GF)$, so that RPFR values and ln α depend only slightly on them (57).The influences of the masses of other elements linked to those involved in the isotope substitution are appreciable only in hydrides, where protium can be substituted by deuterium and tritium, which are two and three times as heavy.

Equation (45) makes it possible to separate the influence of the isotopic masses from the influence of the force constants and molecular geometry within ln β. The role of the last two factors can be seen from Table 5, which presents the algebraic expressions for the sums $\Sigma_{ij}\, a_{ij}\, F_{ij}$ for isotope substitutions of the central

Table 5. Algebraic Expressions for $\Delta trGF/\Delta\mu$ for XY_n and $X(YZ)_n$ Types of Molecules with Linear Ligands YZ

Molecule type (asymmetry)	$\sum_{ij} a_{ij}F_{ij} = \Delta tr(GF)/\Delta\mu$
$XY_2(\mathrm{D}_{\infty h})$	$2(f_r - f_{rr}) + 8\,f_\alpha$
$X(YZ)\ (\mathrm{D}_{\infty h})$	$2(f_r - f_{rr}) + 8f_\alpha - 16\sqrt{\frac{R}{r}}f_{\alpha\beta} + 4\left(\frac{R}{r}\right)(f_\beta + f_{\beta\beta})$
$XY_2(\mathrm{C}_{2\mathrm{v}})$	$2(f_r + \cos\alpha f_{rr}) - 4sin\alpha \quad f_{rr} + 2(1 - \cos\alpha)f_\alpha$
$X(YZ)_2(\mathrm{C}_{2\mathrm{v}})$	$2(f_r + \cos\alpha f_{rr}) - 4\,sin\alpha \quad f_{rr} + 2\,(1 - \cos\alpha)f_\alpha - 4\sqrt{\frac{R}{r}}\,(1 + \cos\alpha)f_{\alpha\beta} + 2\left(\frac{R}{r}\right)(f_\beta + f_\theta - \cos\alpha f_{\beta\beta} - f_{\theta\theta})$
$XY_3(\mathrm{D}_{3h})$	$3(f_r - f_{rr}) - 6\sqrt{3}(f_{r\alpha} - f'_{r\alpha}) + 9(f_\alpha - f_{\alpha\alpha}) + 9f_\gamma$
$X(YZ)_3\ (\mathrm{D}_{3h})$	$3(f_r - f_{rr}) - 6\sqrt{3}(f_{r\alpha} - f'_{r\alpha}) + 9(f_\alpha - f_{\alpha\alpha}) + 9\,f_\gamma - 6\sqrt{\frac{R}{r}}f_{\alpha\beta} + \frac{27}{2}\sqrt{\frac{R}{r}}\,(f_{\gamma\theta} + f'_{\gamma\theta}) + 3\left(\frac{R}{r}\right)(f_\beta + f_\theta + f_{\beta\beta} - 2f_{\theta\theta})$
$XY_4\ (\mathrm{D}_{4h})$	$4(f_r - f'_{rr}) - 16(f_{r\alpha} - f'_{r\alpha}) + 8(f_\alpha - f'_{\alpha\alpha}) + 8(f_\gamma - f_{\gamma\gamma})$
$X(YZ)_4\ (\mathrm{D}_{4h})$	$4(f_r - f'_{rr}) - 16(f_{r\alpha} - f'_{r\alpha}) + 8\,(f_\alpha - f'_{\alpha\alpha}) + 8(f_\gamma - f_{\gamma\gamma}) - 16\sqrt{\frac{R}{r}}\,(f_{\alpha\beta} + f_{\alpha\theta}) + 4\left(\frac{R}{r}\right)(f_\beta + f_\theta - 2f_{\beta\beta} - f_{\theta\theta})$
$XY_4\ (\mathrm{T}_d)$	$4(f_r - f_{rr}) - 16\sqrt{2}(f_{r\alpha} - f'_{r\alpha}) + 16(f_\alpha - f'_{\alpha\alpha})$
$X(YZ)_4\ (\mathrm{T}_d)$	$4(f_r - f_{rr}) - 16\sqrt{2}(f_{r\alpha} - f'_{r\alpha}) + 16(f_\alpha - f'_{\alpha\alpha}) - 16\sqrt{\frac{R}{r}}\,(f_{\alpha\beta} + f'_{\alpha\beta}) + 24\sqrt{\frac{R}{r}}\,(f''_{\alpha\beta} + f''_{\alpha'\beta}) + 8\left(\frac{R}{r}\right)(f_\beta + f_{\beta\beta} - 3f'_{\beta\beta})$
$XY_6\ (\mathrm{O}_h)$	$6(f_r - f'_{rr}) - 48f_{r\alpha} + 24(f_\alpha + 2f_{\alpha\alpha} - f'_{\alpha\alpha})$
$X(YZ)_6\ (\mathrm{O}_h)$	$6(f_r - f'_{rr}) - 48f_{r\alpha} + 24(f_\alpha + 2f_{\alpha\alpha} - f'_{\alpha\alpha}) - 48\sqrt{\frac{R}{r}}\,(f_{\alpha\beta} + f'_{\alpha\beta} + 2f''_{\alpha\beta}) + 12\sqrt{\frac{R}{r}}\,(f_\beta + f_{\beta\beta} - f'_{\beta\beta})$

Here r and R are the XY and YZ distances; $\alpha = YXY$ angle; $\beta = XYZ$ angle in the YXY plane; $\beta = XYZ$ angle in the plane orthogonal to the YXY plane; γ is the angle defining the displacement of the XY bond from the plane; f_r is XY bond force constant; f_{rr} and f'_{rr} are the force constants for the interaction of the adjacent and opposite XY bonds; f_α is the YXY valence angle force constant; $f_{\alpha\alpha}$ and $f'_{\alpha\alpha}$ are the force constants for the interaction of adjacent and opposite angles; f_β, $f_{\beta\beta}$, $f'_{\beta\beta}$ etc. are defined analogously atoms X in compounds of the XY_n and $X(YZ)_n$ types (58). Both the force constants f_{ij} and the coefficients a_{ij}, which are determined by the molecular geometry, are derivatives of the characteristics of the potential energy of the molecule, and their effects can be separated only by convention. Nevertheless, analysis of expressions in Table 5 shows that formally such subdivision can be readily achieved.

Localization of Isotope Effect

Isotopic substitution is a perturbation of the kinematics of the molecule (considerable in the case of substitution of hydrogen atom). This perturbation involves the whole molecule but is manifested to different degrees at its different parts, and it decreases with the distance growth of the vibration coordinates from the substituted atom. For the calculation of isotope effects, particularly in complex molecules, fragmentary models are often used. In some cases this is the only possible approach. The values of errors introduced by this approximation should be known. Specifically, it is necessary to know whether the occasional resonance of the vibration of substituted atom with the vibration of remote coordinates (due to their close frequencies) exerts any significant effect on the $\ln \beta$ value.

This problem with respect to the equilibrium isotope effect was examined by Knjazev et al. (59) both with the use of direct calculations of $\ln \beta$ of fragmentary models and with the use of theoretical representation of β-factor as an infinite product (see Eq. 26). To solve the problem, a four-atom molecular model shown in Fig. 1 was analyzed. The following natural coordinates were introduced: changes of bond lengths r_1, r_2, and R, changes of valent angles φ_1 and φ_2, the out-of-plane twisting coordinate χ. In the calculation process, the force constants and geometric parameters typical for saturated hydrocarbons were chosen.

To generate the fragmentary model from the initial "molecule", matrix G of kinematic coefficients was left unchanged while the rows and columns of the force constants matrix F of initial molecular model were multiplied by the weighting factor x, if these rows and columns corresponded to the natural coordinate containing the atom being removed.

The calculation was performed for two cases: 1) the atom three bonds away from the substituted one (the "third neighbor") was "broken away" (x was accepted to be equal to 0), and 2) the atom two bonds away from the substituted one (the "second neighbor") got "broken away" together with that one.

The effect of "breaking away" of the "second" and "third" neighbors are essentially different. Namely, the breaking off of the atom three bonds away from the substituted one introduces a small error of not more than 2%. As to the effect of the atom two bonds away from the substituted one, it cannot be ignored.

Upon multiplication by x (see above) of the force constants of the removed coordinates and after substitution of these values in representation (26), we obtain

$$\ln \beta = \ln \beta_0 + \text{correction}(x) \tag{47}$$

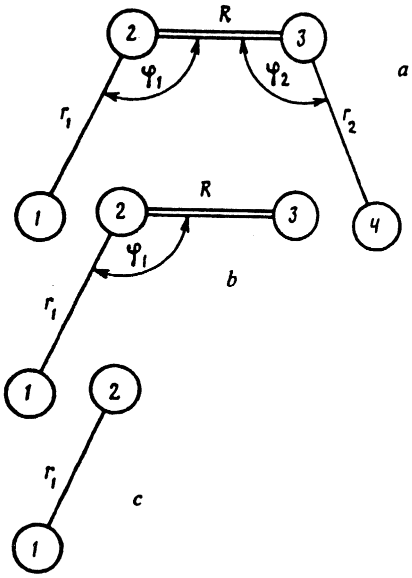

Figure 1. Fragmentary models.

Here the term ln β_0 in the right part contains only the force constants and geometrical parameters of the remaining part of the molecule (i.e., of the fragmentary model) and is the main part of ln β (contribution of the nearest environment of the substituted atom). The second term in the right part of Eq. (47) depends on x and when $x = 1$ is the correction presenting the contribution of the remote fragments of the molecule.

The analysis of formula (47) conducted in (59) shows the isotopic effect to be localized at the center of substitution, i.e., the correction in formula (47) is minor. As the temperature decreases the correction grows and at 30 K its value is comparable with the ln β value. This reflects the increasing delocalization of the isotope effect at decreasing temperature. It should be also mentioned that representation (47) allows for solution of the problem of ln β representation as a sum of contributions of the first, second, and higher environments of the substituted atom (59).

Analysis of the case of resonance of vibrations of substituted atom with remote coordinates having close frequencies showed that this resonance exerts no effect on the ln β. Although the "forms" of normal vibrations (matrix L elements) appear to be dramatically disturbed during the resonance. This outcome can be understood very easily keeping in mind that neither the individual frequencies nor matrix L elements adequately describe the vibration of an individual isotopic atom within the molecule. The notion "the ith normal vibration of jth atom" is no more than a mathematic abstraction. Indeed, in reality each atom undergoes a complicated three-dimensional vibrational movement, which can be *mathematically* represented as a linear combination of idealized normal vibrations. The quantity that most clearly describes the real physical vibrational motion of the atom in the molecule is the mean square amplitude σ in the Cartesian coordinates where the set of amplitudes $(\sigma_j^{\Delta x},\sigma_j^{\Delta y},\sigma_j^{\Delta z})$, of each jth atom can be represented by an ellipsoid. The mean square amplitude depends on temperature and is changed in isotopic substitution. In case of resonance when one of the frequencies of the vibration of part of the molecule remote from the substituted atom occasionally becomes close to some other frequency, the form of the ellipsoid (physical values) is not significantly affected. Nevertheless, the resonance dramatically changes the form of mathematical representation of the real vibrational picture as a linear combination of normal vibrations.

The localization of isotope effect makes it possible to use it as a tool to study electronic effects of substituents in organic molecules. Indeed, localization means that if substituent is introduced in the molecule at the place removed from the site of isotopic substitution and $\ln \beta$ value changes, all changes are due to the electronic influence of this particular substituent. On the other hand, localization of course seriously restricts the possibilities of isotope effects as an instrument of research. Namely, from the data on isotope equilibrium one can obtain information about masses, force field (and sometimes geometry) of only the local neighborhood of substituted atom.

Relationship Between RPFR and Parameters of Molecular Structure

Isotope Effect of End Atom (Using Hydrogen as an Example)

Analysis of the RPFR of the normal molecular hydrides. It is well known empirically that the values of the β-factor of the molecule is determined primarily by the nature of the atom directly joined to the atom being replaced. To study this relationship it is natural to consider the set of so-called normal molecular hydrides of the s- and p-elements (i.e., hydrides of the general formula EH_n). The normal hydrides can serve as a model to examine more complex compounds containing both hydrogen and other monoatomic ligands.

Attempts have been made to obtain a phenomenological description of $\ln \beta$ for normal hydrides (4), and also to interpret $\ln \beta$ in terms of the force field using the approximate methods of interpretation and correlations described above (54,60,61). Among these works, the recent work by Bigeleisen (60) is worth mentioning. As follows from this work, the contribution of each ith vibrational coordinate to $\ln \beta$ is proportional to $(f_{ii}\Delta g_{ii})^{1/2}$, where f_{ii} is a diagonal element of the force constants matrix, and $\Delta g_{ii} = g_{ii} - g_{ii}^*$ is the difference in the diagonal elements of the matrices of the kinematic coefficients for light and heavy isotopic forms of the molecule. It should be noted, however, that although the contribution made to ln β by the bond coordinates is in fact approximately linearly dependent on $(f_{ii}\Delta g_{ii})^{1/2}$, this correlation is not completely satisfactory for the angle coordinates, particularly for the normal hydrides of groups IV and V.

The representation (41) has been used by Knjazev et al. (61) to analyze the behavior of ln β for normal hydrides. Figures 2 and 3 give the force constants and the contributions of different coordinates to ln β. In the analysis of these data, it should first be noted that the Teller-Redlich term, which depends on the geometry and the masses, changes little and does not determine the behavior of ln β for normal hydrides. The decisive factor is the variability of the vibrational contribution. For all normal hydrides, a predominant part is played by the contribution made to ln β by the H—E valence bond coordinate. This contribution increases regularly in each period together with the force constant F—E by moving from group I to group VII, and decreases regularly in each group with the increase of the atomic number of the element.

The contribution of the angular coordinates depends both on the magnitude of the contribution of an individual valence angle and on the total number of valence angles. This number equals 3 for the hydrides of the group IV elements, 2 for group V, and 1 for group VI. Moving from group VI to group IV, the contribution made by one angle (see Fig. 3) decreases, whereas the total contribution from the angular coordinates increases due to the rise of the total number of angles. The role of the number of angles is extremely significant, and the total contribution made to ln β by the angular coordinates is the greatest for the normal hydrides of the elements of group IV. This contribution does not exist for diatomic molecules, because ln β for the hydrogen halides is smaller than that for the hydrides of the elements of groups V and VI, despite the larger force constant and the corresponding larger contribution of the H—E bond to ln β.

Data for ln $\beta_{D/H}$ are shown in Fig. 3. It should be emphasized that due to the localization of isotopic effect these conclusions are valid not only for the normal hydrides but for their derivatives as well, and therefore the majority of normal hydrides form the basic set for the evaluation of ln β of various compounds.

Dependence of ln β on number, type and remoteness of substituents. Undoubtedly, the substitution of hydrogen atoms joined to carbon is of principal significance. However, the substitution of hydrogen joined to oxygen and nitrogen in biogenic compounds is also of great practical importance. It seems reasonable to discuss the reasons for ln β value changeability on the basis of the numeric representation of ln β as the sum of contributions of the structural elements. Besides the nature of the hydride-forming element discussed above, a significant effect on the ln β value is exerted by the origin and number of substituents at the atom immediately connected with the substituted atom. The dependence of ln β on the nature and number of substituents is strong and its range is comparable with the ln β dependence on the nature of the hydride-forming atom. For instance, in the case of

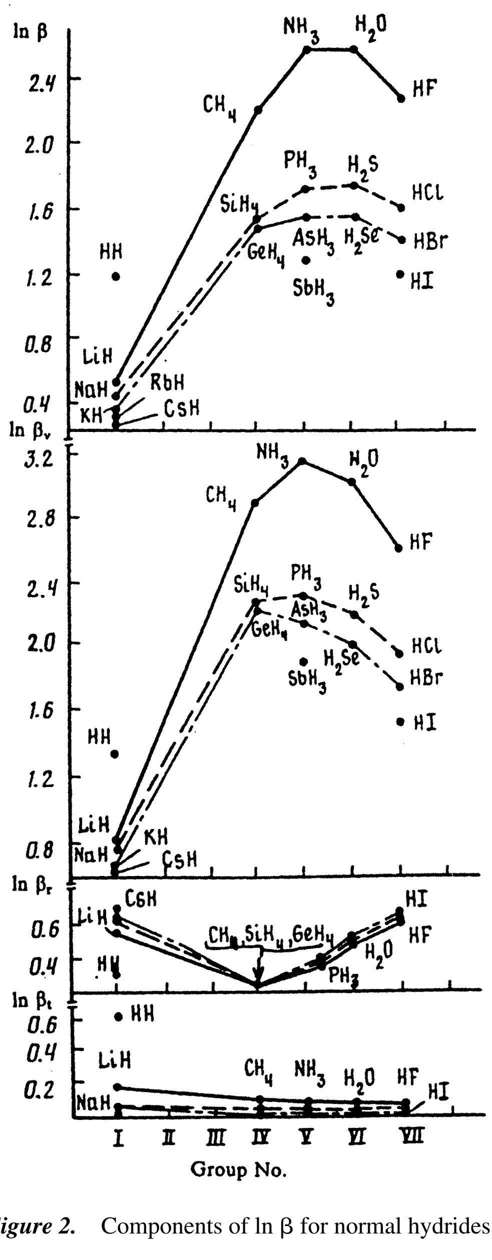

Figure 2. Components of ln β for normal hydrides.

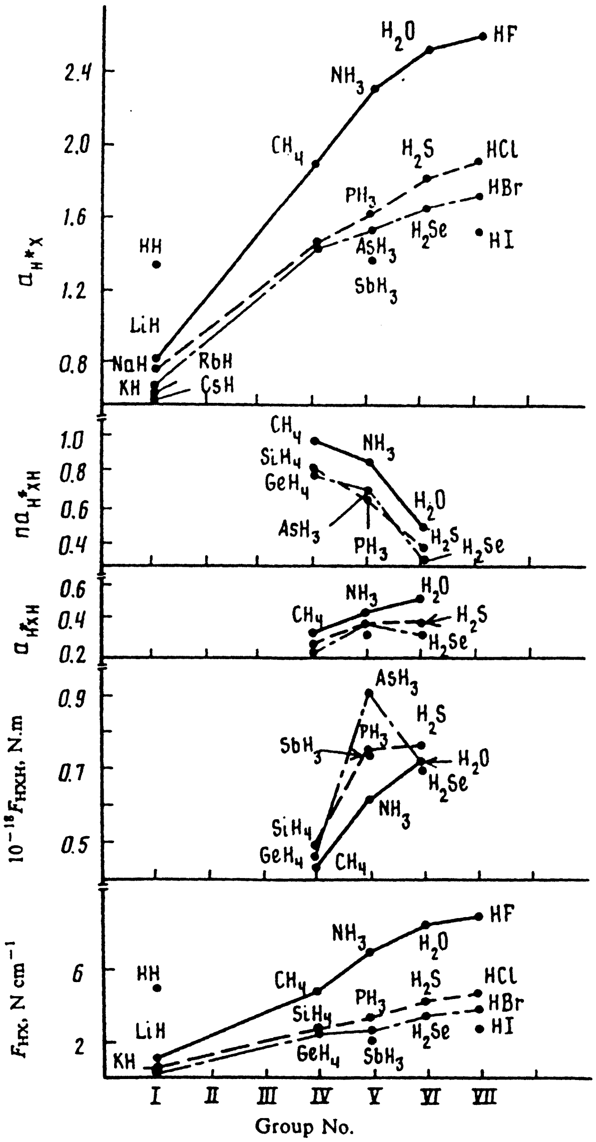

Figure 3. Contributions of different structural elements to ln β for normal hydrides. a_{H*X} is contribution of H*—X bond, a_{H*XH} is contribution of valence angle H*XH, and na_{H*XH} is contribution of valence angles with allowance for their multiplicity; F_{HX} and F_{HXH} are bond and valence angle force constants, respectively.

carbon, even without hybridization the change for CH_3 X compounds, the ln $\beta_{D/H}$ value can change from 3.49 ($X = OCOCH_3$) to 3.16 (X = H), which almost coincides with the changeability range of ln β of period II normal hydrides from group IV to group VII. The number of substituents exerts the same strong influence.

By using Eq. (41) the contribution into ln β of different types of vibrational coordinates for molecules of the $CH_{4\text{-}n\text{-}m}Y_n X_m$ (X, Y = F, Cl, Br, and J) type can be calculated. This set is rather representative for the analysis of the ln β dependence on the number and the type of substituents. Table 6 shows some results of these calculations. As follows from this table, the main contribution into ln $\beta_{D/H}$ is that of the C—H bond. This increment retains its approximate constancy and changes by no more than 5% over the whole set of the molecules under study (here and below the mark * shows the atom substituted for isotope). This changeability range is much smaller than the changeability of the ln β value but larger than the changeability of the force constant F_{CH} in this set. This is partly accounted for by the fact that the vibrational coordinate of variation of C—H bond length (below denoted by CH) has a considerable dynamic connection with the valent angle coordinates. This is particularly so for the fluorine-containing molecules, and therefore, the value of its contribution to ln β cannot be determined only by the force constant of this single coordinate. The contribution of valent angles to ln β calculated on the basis of force fields has a rather large force spread and is noncharacteristic. The spread of these contributions for the same molecule estimated from the force fields by different authors exceeds very often even the spread of ln β values.

This is not strange as the numerical ln β value is only determined by the frequencies unambiguously obtained from the force field whereas the values of contributions of particular coordinates are determined by the force field ambiguously calculated from experimental frequencies. In other words, a larger spread of force constant values may correspond to a smaller spread of frequencies or even to the same set. The difference (inaccuracy) of force fields causes emergence of the spread in the values of contributions.

The changeability of the ln β of methyl group with a given substituent X primarily depends on the contribution of the HCX angle and, to a smaller degree, on the effect of the substituent on the force constants of the C—X and C—H bonds. These factors can act in opposite directions. For instance, in the transition from CH_3F to CH_3J the force constant of angle (F_{HCX} /r_{CH}) changes from 0.900 to 0.651 N/cm, predetermining the change of ln $\beta_{D/H}$ from 3.44 to 3.25. The force constant of the C—X bond also drops from 5.535 to 2.338 N/cm in the F—J transition, but this factor exerts less influence on ln β. The F_{CH} constant in this series changes in the opposite direction, though not significantly (from 4.878 N/cm in CH_3F to 5.002 N/cm in CH_3J).

Dependence of ln β on the geometry of the molecule. Upon comparison of ln β for compounds with the sp_3-, sp_2-, and sp-hybridization of the hydride-form-

Table 6. ln $\beta_{D/H}$ Values for Halomethanes and $CH_2(C{\equiv}N)_2$ at $T = 300$ K

Molecule	ln $\beta_{D/H}$	Σ	C—H* bond	H*—C*X* angles	
CHF_3	2.67 ± 0.03 (E)				
$CHClF_2$	2.7	0.07	1.97	2 × 0.57	(HCF)
				0.51	(HCCl)
$CHBrF_2$	2.65	−0.25	1.93	2 × 0.67	(HCF)
				0.63	(HCBr)
CH_2F_2	2.64	−0.39	1.94	2 × 0.79	(HCF)
				0.4	(HCH)
$CHCl_2F$	2.64	−0.03	1.98	0.63	(HCF)
				2 × 0.50	(HCCl)
CH_2Cl_2	2.52 ± 0.02 (E)				
$CHBr_2F$	2.62	−0.08	1.94	0.76	(HCF)
				2 × 0.50	(HCBr)
CH_2FCl	2.62	−0.2	1.95	0.74	(HCF)
				0.67	(HCCl)
				0.38	(HCH)
$CHBrClF$	2.61	0.03	1.95	0.58	(HCCl)
				0.56	(HCF)
				0.5	(HCBr)
$CHCl_3$	2.54 ± 0.02 (E)				
CH_2BrF	2.58	−0.18	1.95	0.8	(HCF)
				0.55	(HCBr)
				0.38	(HCH)
$CHBrCl_2$	2.56	−0.03	1.94	2 × 0.57	(HCCl)
				0.52	(HCBr)
$CHBr_2Cl$	2.51	−0.1	1.93	0.68	(HCCl)
				2 × 0.51	(HCBr)
CH_2BrCl	2.57 ± 0.06 (E)				
	Calculated value:				
	2.51	−0.1	1.95	0.67	(HCCl)
				0.55	(HCBr)
				0.38	(HCH)
$CHBr_3$	2.55 ± 0.03 (E)				
CH_2Br_2	2.47 ± 0.05 (E)				
CH_2ICl	2.48	−0.07	1.94	0.6	(HCl)
				0.6	(HCCl)
				0.36	(HCH)
CH_3Br	2.33 ± 0.04 (E)				
CH_2IBr	2.44	−0.1	1.95	0.62	(HCBr)
				0.57	(HCl)
				0.35	(HCH)
$CH_2(C{\equiv}N)_2$	2.43				

Note: Letter "E" marks the value obtained from experimental frequencies; the contributions of vibration coordinates are only shown for the molecules for which the most reliable data concerning their force constants in natural coordinates are available; Σ is the sum of total contribution of unlike coordinates interactions and the contribution of the bonds and angles not carrying substituted atom.

ing carbon atom a total decrease of the ln β value for sp_2- and sp-hybridization as compared with sp_3-hybridization is observed, despite force constants and, consequently, the contributions of F bond into ln β are maximal for sp-hybridized and minimal for sp_3-hybridized molecules. The reason for smaller ln β compared with sp_3-hybridization is the decreased number of vibrational coordinates contributing to ln β. To confirm this conclusion, let us analyze the contributions of vibrational coordinates into the ln β of single-substituted ethane, ethylene, and acetylene shown in Fig. 4. As seen, the number of coordinates closest to the substituted atom decreases in the ethane-ethylene-acetylene series, which results in the drop of ln β in spite of the increase of force constants and, consequently, of the contributions into ln β by each separate vibrational coordinate.

It should be taken into account that in the substitution of ethylene at positions R_2 and R_3 the substituent is three bonds away from the substituted hydrogen. In this connection, the effect of substituent at positions R_2 and R_3 is weaker than that at position R_1 but stronger than similar effects observed in the methyl group. Besides, for ethylene considerable contribution to ln β is made by out-of-plane coordinates that are strongly dependent on the substituent. The influence of substituents R_2 and R_3 on ln β is much stronger than in the methyl group case. In fact, atoms R_2 and R_3 enter the out-of-plane torsion coordinate χ (the rotation of the CHR_1 and the CR_2R_3 planes around the C=C bond in different directions) that has a large force constant and makes a significant contribution into ln β. In this case atoms R_2 and R_3 cannot be regarded as remote neighbors. This remark should be taken into account in all cases of substitution of compounds with a double bond.

Aldehydes and ketones present another group of carbon compounds with sp_2-hybridization that may be regarded as substituted formaldehydes. The above reasoning about β-factors of ethylene compounds are also valid in this case except the vibration coordinate χ is absent in substituted formaldehydes. Therefore, the ln β value of formaldehyde is low. In carbonyl compounds, the electronic effects of the substituents play a greater role. Upon introduction of electron acceptor groups such as —OH and —F, the H—C bond becomes stronger, resulting in growth of its contribution and, consequently, in ln β increase.

The ln β values of acetylene compounds show a very small variability, depending on the type of substituents, which is accounted for by larger remoteness of the latter. The ln β of these molecules decreases in the presence of heavy substituents because of a smaller contribution of the angle coordinates.

Alicyclic molecules, compared with the open ones, have smaller ln β values, which only slightly increase with the rise of strength (rigidity) of the cycle due to the growing H—C—C angle values (compared with the tetrahedral angle) that leads to their weakening and decrease of their contribution to ln β. On the other hand, the ln β of benzene is unexpectedly large for the formal sp_2-hybridization. This is attributed to the rigid structure of benzene cycle and considerable contribution of a large number of out-of-plane coordinates. Many vibrations

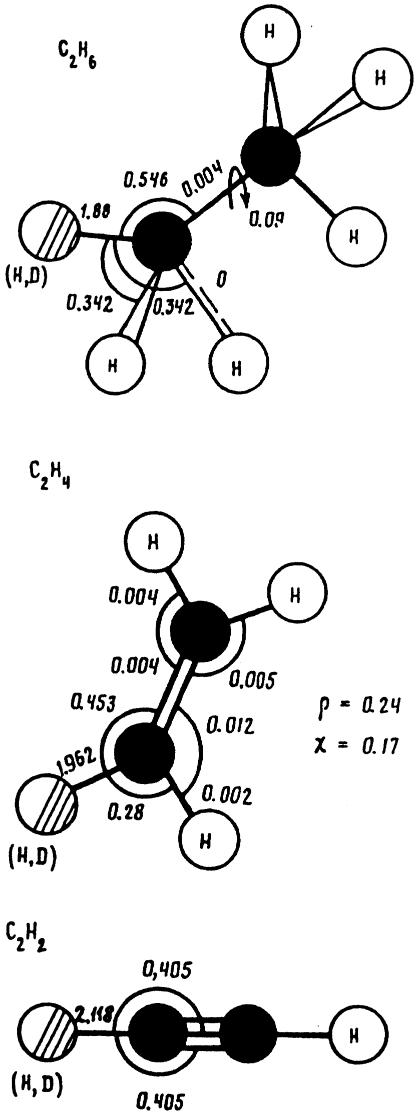

Figure 4. Dependence of ln $\beta_{D/H}$ on hybridization; change in contributions of vibrational coordinates in series: ethane − ethylene − acetylene; only non-zero contributions are given; ln $\beta_{D/H}$ values correspond: 2.372 (ethane), 2.334 (ethylene), and 2.105 (acetylene).

of the benzene ring cannot be assigned to one definite bond or angle. Therefore, similar to halogen-substituted methanes, it is reasonable to view the benzene ring as a whole, without distinguishing therein some “closer” or “remote” fragments.

ln β values of hydrogen compounds with nitrogen and oxygen. Rules describing the variation of ln β value for nitrogen and oxygen compounds are similar to those for the carbon compounds. All of the above conclusions about dependence of ln β on the hybridization type, the number, origin, and remoteness of substituents are also valid for these molecules. However, unlike carbon compounds, experimental data on considerably fewer numbers of nitrogen and oxygen compounds are available in the literature. The ln β values of nitrogen compounds with sp_3 hybridization behave similar to methyl group with the same substituents. However, their numerical value is higher by approximately 0.3. For nitrogen compounds with sp_2 hybridization, the ln β values are, as might be expected, lower than for sp_3 hybridization compounds. The ln β values characterizing oxygen compounds (with O–H bond) are on the level of those typical for N—H bonds.

The influence of protonation and hydrogen bond formation. Practically all compounds containing NH^- and OH^- groups are capable of hydrogen bond formation, which leads to the changing of the closest environment of the substituted atom and the force constants and affects the ln β value. At the same time, the influence of hydrogen bond formation on the $\ln \beta_H$ is weak and might be ignored. This conclusion follows from low values of hydrogen isotopic effects of vapor pressure reported by Rabinovich (62). Knjazev et al. (63) have shown that upon the formation of hydrogen bond the contribution of the disappearing and reappearing degrees of freedom into the isotope effect is compensated and this fact accounts for the weak effect of this association type on the β-factor in substitutions of hydrogen.

Along with the hydrogen bond formation, some other special protonation process for the amino group may occur, for example, in aqueous solutions of amino acids. The protonation of the amino group results in an increase of $\ln \beta_{H/T}$ value (for tritium substitution) by approximately 0.35 due to the growing number of involved vibrational degrees of freedom. It should be emphasized that, unlike hydrogen bond formation, protonation dramatically affects ln β. Besides, protonation is accompanied by a strong change of the force field of the molecule and can result in variation of ln β in any direction. For instance, unlike nitrogen, protonation of oxygen and fluorine atoms causes a significant drop of ln β. It follows from data on separation factors of hydrogen isotopes between H_3O^+ and H_2O (64,65) that the $\ln \beta_{D/H}$ of hydroxonium ion is smaller than the ln β of H_2O by approximately 0.3. Different electron structure of O and N atoms, and, as a result, the protonation of water molecule or electron separation from it, leads to the bond weakening and dramatic decrease of force constants. All this results in decrease of ln β. The dramatic changes of ln β due to the protonation may be significant in the processes of isotope fractionation in biological systems.

Isotope Effect of Central Atom (Using Carbon as an Example)

Substitution of the central atom is an even more interesting case for the isotope separation than the substitution of an end atom, because most elements behave as acceptors of electron pairs and are able to attach many donor atoms or polyatomic ligands. Analysis of the isotope effect (ln β) of the central atom on the basis of structural element representation must be much more complex than that for the end atom. It is evident from the fact that the number of internal coordinates involved increases in comparison with the case of substitution of end atom. By using the representation of ln β as a sum of increments of structural elements developed (66,67) we studied the comparative contribution of structural elements of different types in ln β_C ($^{13}C/^{12}C$) for molecules of type $CH_{4-n-m}Y_nX_m$, where X and Y = F, Cl, Br, J. The values of ln β_C for these molecules and their representations as sums of increments of structural elements are presented in Table 7. For the sake of clarity, representation for CHFClBr molecule is presented in matrix form in Table 8.

The analysis of data presented in Table 7 shows that the increments to ln β_C are scattered and not characteristic both for valent bonds and valent angles. Again, similar to the end atom substitution, the reason for such behavior is inaccuracy of determination of force field used for calculation. Force fields of halogen-substituted methanes were determined by different authors. Moreover, quite different approaches to solving the inverse vibrational problem were used in those works. This leads to force fields that cannot be compared and used in a series of molecules. Solution of the inverse vibrational problem gives the most inaccurate results for force constants of valent angles and non-diagonal force constants of all types. The incomparability of initial force fields is the main reason of inaccuracy in the values of increments. This makes it impossible to estimate the degree of regularity of increments of the same type in the series of molecules due to the impossibility of distinguishing the real variation of increments in the presence of great scatter of data determined with low accuracy. Indeed, although mean square amplitudes (diagonal elements of Σ matrix) may be calculated from the force constants quite confidently, off-diagonal elements of mean square amplitudes matrix Σ are all badly determined from the mathematical point of view. Errors in force field lead to a very inaccurate estimate of off-diagonal elements. This, in turn, does not allow for precise estimation of off-diagonal increments to ln β.

At the same time, it is obvious that the physically correct solution for the force field is unique. Moreover, from its physical significance the scale of the variation in the contributions for a set of molecules should not exceed the scale of the variation of ln β. It is therefore reasonable to solve the inverse problem, that is to find the values of the contributions of the coordinates by solving the over-

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Table 7. Representation of ln β_C of Halogen-Substituted Methanes as Sum of Contributions of Structural Elements of Molecule

Molecule	Ref.	ln β_C	Bond Increments		Angle Increments		Sum of Non-diagonal Increments
CHF_3	(4)	0.1858	0.0198	(CH)	3 × 0.0284	(HCF)	−0.0598
			3 × 0.0630	(CF)	3 × 0.0161	(FCF)	
CHF_3	(5)	0.1807	0.0179	(CH)	3 × 0.0163	(HCF)	−0.0624
			3 × 0.0662	(CF)	3 × 0.0247	(FCF)	
$CHClF_2$	(6)	0.1568	0.0196	(CH)	2 × 0.0164	(HCF)	−0.0692
			2 × 0.0714	(CF)	0.0104	(HCCl)	
			0.0502	(CCl)	2 × 0.0214	(ClCF)	
					0.0269	(FCF)	
CH_2F_2	(7)	0.1522	2 × 0.0235	(CH)	0.0091	(HCH)	−0.0964
			2 × 0.0705	(CF)	4 × 0.0218	(HCF)	
					0.0396	(FCF)	
$CHBrF_2$	(8)	0.1436	0.0221	(CH)	2 × 0.0195	(HCF)	−0.1246
			2 × 0.0741	(CF)	0.0173	(HCBr)	
			0.053	(CBr)	0.0423	(FCF)	
					2 × 0.0241	(BrCF)	
$CHCl_2F$	(6)	0.1359	0.0188	(CH)	0.0168	(HCF)	−0.0663
			0.0698	(CF)	2 × 0.0122	(HCCl)	
			2 × 0.0571	(CCl)	2 × 0.0217	(ClCF)	
					0.0176	(ClCCl)	
CHBrClF	(9)	0.1306	0.0198	(CH)	0.0164	(HCF)	−0.0667
			0.0623	(CF)	0.0128	(HCCl)	
			0.053	(CCl)	0.0112	(HCBr)	
			0.0499	(CBr)	0.029	(ClCF)	
					0.0246	(BrCF)	
					0.0236	(ClCBr)	
CH_4	(10)	0.1147	4 × 0.0207	(CH)	6 × 0.0090	(HCH)	0.0075
CH_2Cl_2	(11)	0.1116	2 × 0.0231	(CH)	0.012	(HCH)	−0.0509
			2 × 0.0541	(CCl)	4 × 0.0127	(HCCl)	
					0.0255	(ClCCl)	
CH_4	(12)	0.1114	4 × 0.0239	(CH)	6 × 0.0117	(HCH)	−0.0247
$CHBr_2F$	(13)	0.1075	0.0235	(CH)	0.0244	(HCF)	−0.1227
			0.0786	(CF)	2 × 0.0139	(HCBr)	
			2 × 0.0611	(CBr)	0.027	(BrCBr)	
					2 × 0.0199	(BrCF)	
$CHCl_3$	(5)	0.1065	0.0193	(CH)	3 × 0.0140	(HCCl)	−0.074
			3 × 0.0563	(CCl)	3 × 0.0188	(ClCCl)	
CH_3Br	(14)	0.1038	3 × 0.0232	(CH)	3 × 0.0120	(HCH)	−0.0376
			0.0589	(CBr)	3 × 0.0111	(HCBr)	

(*continued*)

Table 7. Continued

Molecule	Ref.	ln β_C	Bond Increments		Angle Increments		Sum of Non-diagonal Increments
$CHBrCl_2$	(15)	0.1018	0.0197	(CH)	2 × 0.0144	(HCCl)	−0.1023
			2 × 0.0607	(CBr)	0.0144	(HCBr)	
			0.0569	(CCl)	2 × 0.0237	(BrCCl)	
					0.0243	(ClCCl)	
$CHBr_2Cl$	(16)	0.1016	0.0187	(CH)	0.0167	(HCCl)	−0.1058
			0.061	(CCl)	2 × 0.0145	(HCBr)	
			2 × 0.0598	(CBr)	2 × 0.0249	(BrCCl)	
					0.0239	(BrCBr)	
CH_2BrCl	(17)	0.1003	2 × 0.0243	(CH)	0.0118	(HCH)	−0.0754
			0.0584	(CBr)	2 × 0.0157	(HCCl)	
			0.0585	(CCl)	2 × 0.0127	(HCBr)	
					0.0251	(BrCCl)	
CH_2Br_2	(18)	0.0991	2 × 0.0210	(CH)	0.0112	(HCH)	−0.0673
			2 × 0.0623	(CBr)	4 × 0.0132	(HCBr)	
					0.0226	(BrCBr)	
CH_2Br_2	(19)	0.0954	2 × 0.0228	(CH)	0.0132	(HCH)	−0.08
			2 × 0.0635	(CBr)	4 × 0.0130	(HCBr)	
					0.0241	(BrCBr)	
$CHBr_3$	(5)	0.0922	0.0198	(CH)	3 × 0.0122	(HCBr)	−0.0836
			3 × 0.0614	(CBr)	3 × 0.0162	(BrCBr)	
CH_2Br_2	(20)	0.0861	2 × 0.0243	(CH)	0.0151	(HCH)	−0.1128
			2 × 0.0671	(CBr)	4 × 0.0158	(HCBr)	
					0.0243	(BrCBr)	

Table 8. Representation of ln β_C ($\times 10^3$) of CHFClBr as Sum of Contributions of Structural Elements of Molecule

CBr	CCl	CF	CH	ClCBr	BrCF	ClCF	BrCH	ClCH	FCH	
49.9	−5	−7		−3			−1			CBr
	53	−3				−7		2		CCl
		62.3							−5	CF
			19.8				0.7			CH
				23.6		−0.02				ClCBr
					24.6					BrCF
						29				ClCF
							11.2		0.01	BrCH
								12.8		ClCH
									16.4	FCH

determined system of linear equations by the least squares method for a sufficiently representative set of molecules using known ln β values. For example, for the molecules of CH_2XY type such equation has the form:

$$2\mathrm{CH} + \mathrm{C}X + \mathrm{C}Y + \mathrm{HCH} + 2\mathrm{HC}X + 2\mathrm{HC}Y + X\mathrm{C}Y = \ln \beta_{\mathrm{CH2}XY} \qquad (48)$$

Here CH, HCH, etc. denote the increments of corresponding structural elements. The values of contribution of structural elements obtained in this way may serve as an additional criterion of the physical correctness of the force fields.

It is evident that the system of Eq. (48) would be overestimated if one tries to find physically correct values of increments. The least squares method with singular decomposition can be used for this purpose (68). However, in our opinion the best estimate of accuracy of the additive scheme is given by the comparison between initial ln β values and the values obtained as the sums of increments determined from system (48). The errors of approximation of ln β values by this additive scheme are given in Table 9. As seen, the calculation gives quite acceptable results.

Low accuracy of force fields of complex molecules leads also to the following situation. The study of sets of complex molecules by means of coordinate analysis is not feasible at the moment. Because of this we restricted our consideration in the first part of the review by a simple set of halogen-substituted methanes. In the second part, we give the analysis of the isotope effect of central atom on the basis of semiempirical and empirical relationships that may give practical valuable results.

Table 9. Results of Independent Determination of ln β Increments by Solving System of Linear Equations for Substitution of Central Atom Case

Molecule	Relative Error of Approximation, %	Molecule	Relative Error of Approximation, %
CHF_3	0	$CHBr_2Cl$	−0.64
CHF_3	−0.12	CH_2BrCl	1.94
$CHClF_2$	1.25	CH_2Br_2	−3.56
CH_2F_2	0	CH_2Br_2	−1.62
$CHBrF_2$	−0.87	$CHBr_3$	−0.06
$CHCl_2F$	0	CH_2Br_2	3.27
CHBrClF	−2.62	$CHBr_2F$	2.32
CH_4	−1.27	$CHCl_3$	−0.13
CH_2Cl_2	−1.02	CH_3Br	0.99
CH_4	0.9	$CHBrCl_2$	1.21

CHARACTERISTICS OF VARIABILITY OF ISOTOPES EFFECTS

Relations between RPFR and Force Fields of Molecules

Considerable effort has been made to search the simplest linear relationships connecting ln β values and intramolecular force field characteristics. Discovery of linear correlations will signify the possibility of adequate interpretation and quantitative prognosis for RPFR without expensive spectroscopic studies. The detailed knowledge of hydrogen isotope effects along with sufficient accuracy of higher ln β_H values made hydrides a good model to study regulations and correlations of general type applicable to describe the isotopic effects of other elements. A considerable progress (though partial) has been made (41,54,57,69–72) in this direction.

At the same time, these studies show that ln β values do not always linearly correlate with available and convenient characteristics of chemical bonds. Moreover, hydrogen effects, which are simpler than effects of multiply linked atoms, shift the problem of well-known and applied empirical correlations into another plane that requires explanation of the existence of similar linear links, and definition of the boundaries of their existence.

The final paragraphs of the first part of the review show that the contributions by non-diagonal elements of the force constant matrix are not negligible and all numerous interactions of differently named coordinates should be considered. These interactions are too plentiful and it is, therefore, natural to try to simplify their analysis by taking into account the most important complex total characteristics of intramolecular forces.

Conditions and Parameters of Linearization of Correlations

The possibilities for efficient empirical comparison of RPFR values with characteristics of compounds are usually limited by some specific features of mathematic representation of ln β as a function of the force field, the molecule geometry and by the properties of reduced frequencies u_i.

If reduced frequencies u_i and isotopic shifts Δu_i are large, one must take into account the square and larger powers of expansions (22) and the like, if required. This means the impossibility of existence of dense linear correlation in large sets of heterogeneous molecules that narrows the working range of graphic correlations by limiting their applicability to small sets of strictly similar compounds.

The very first studies on the theoretical analysis of isotopic effects have shown that at low temperatures ln β values must linearly depend on the isotope shift sums of frequencies $(1/n)\ \Sigma\ \Delta u_i$ and at high temperatures on their sums

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$(1/n)\,\Sigma\,\Delta u_i^2$. But in reality, both sums can hardly be used as linearizing arguments. Correlations of large hydrogen ln β_H values with these sums leave no doubts about this. As clearly follows from Fig. 5, even at 20 K the dependence ln $\beta_H - (1/n)\,\Sigma\,\Delta u_i$ is not linear for both diatomic molecules and polyatomic hydrides. As seen in Fig. 6, a good correlation for diatomic and polyatomic hydrides with the same line can be similarly achieved in coordinates ln $\beta_H - (1/n)\,\Sigma\,\Delta u_i^2$ only at temperatures higher than 1000 K. Thus, both figures demonstrate a splitting of the set of hydrides into smaller subsets with more or less simple regular change of ln β values close to the normal temperature range (300 K), which presents the largest practical interest.

At 300 K, the 1300 cm^{-1} frequency is the upper boundary of series convergence (22). Although many compounds other than hydrides possess markedly

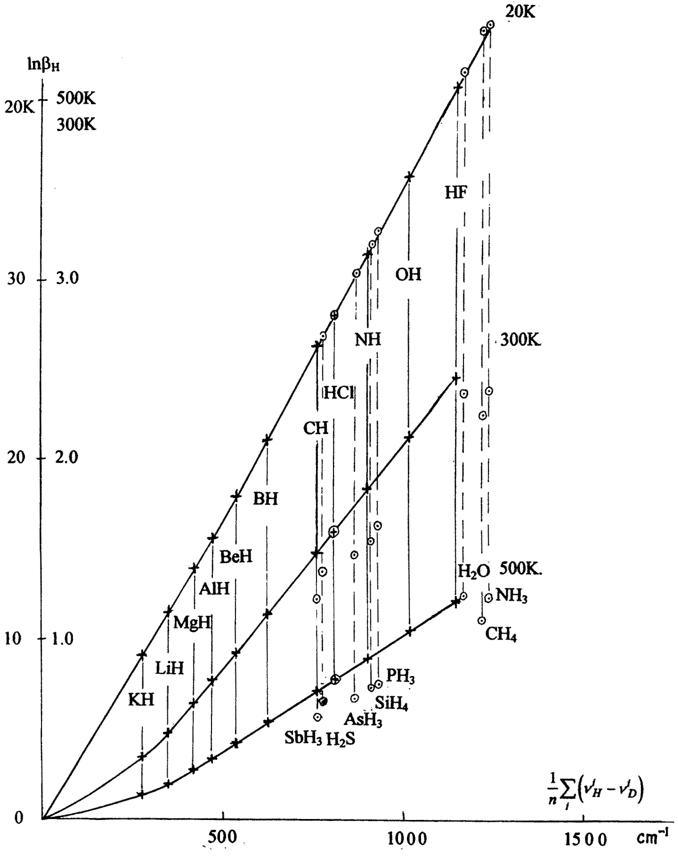

Figure 5. Correlations of ln β_H and sums of differences $(\nu^i_H - \nu^i_D)$ at $T = 20$ K.

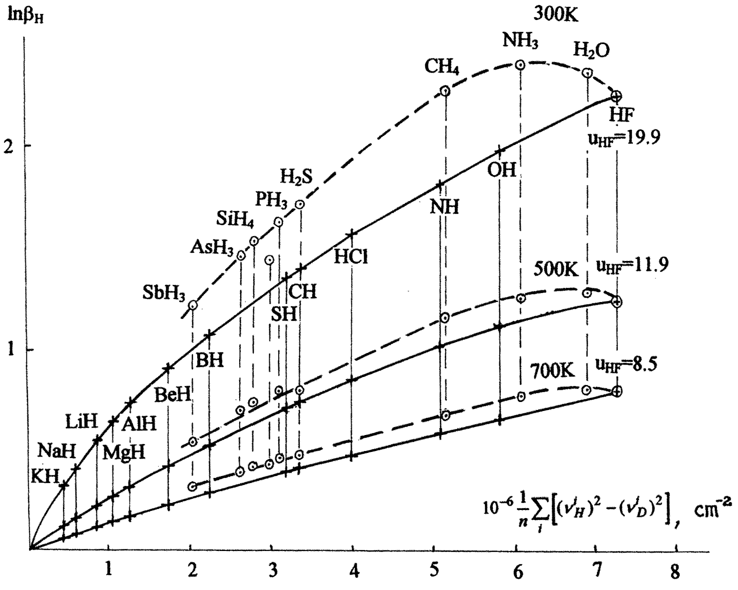

Figure 6. Correlations of ln βH and sums of differences $(v^i_{\mathrm{H}})^2 - (v^i_{\mathrm{D}})^2$.

larger valence frequencies, the linearization of correlations can only be attained if a function well approximating the strict representation of ln β values is used as an argument. Figure 7 shows a correlation between ln β values normalized according to the isotopic shift of the reverse mass and the similarly normalized sums of the two first components of the expansion (22). As seen, the correlation is dense and linear.

Correlations between RPFR and Δtr(GF)

Simplification of linearizing arguments provides a practically required condition to apply ln β correlations as simple interrelations when the data are limited. Consideration of only the first term of Eq. (22) and transfer to the correlation ln $\beta_x/\Delta\mu_x - \Delta tr(GF)/\Delta\mu_x$ is accompanied by a splitting of the interrelation into individual linear dependencies of closely related molecules, see Fig. 8.

This splitting may be related to the difference of algebraic forms of $\Delta tr(GF)_x/\Delta\mu_x$ for molecules of different geometry. Table 5 shows the forms of $\Delta tr(GF)_x/\Delta\mu_x$ that correspond to substitutions of central atoms of symmetrical molecules XY_n and $X(YZ)_n$. Solely valent constants f_r, have simple coefficients, which are equal to the number of valent bonds n. The coefficients of deformation constants f_α and constants of different coordinates all include the trigonometric functions. Hence, the sums of all minor terms are roughly proportional to $n(f_r - f_{rr})$ only for molecules of fixed geometry.

Correlations between RPFR and Valent Force Constants

A further simplification of the argument through exclusive retention of the dominating value $\Delta tr(GF)$ - valence constant force f_r does not always help to preserve the linearity of correlations, see Fig. 9. For instance, the linearity of the ln $\beta_x / \Delta\mu_x - f_r$ interrelation is observed in the series AlF_6^{3-}, SiF_6^{2-}, PF_6^-, SF_6, and ClF_6^+ but for tetrahalogenides CY_4 and SiY_4 this correlation appears to be non-linear.

Definite relations exist between the f_r quantities and other molecular force constants (f_α, f_{rr}, f_r , $f_{\alpha\alpha}$) or between their simple combinations (elements of the F-matrix) (58,73,74) for the series of related compounds of identical geometry. The force constants for deformation of bonds, f_r, deformation of valence angles,

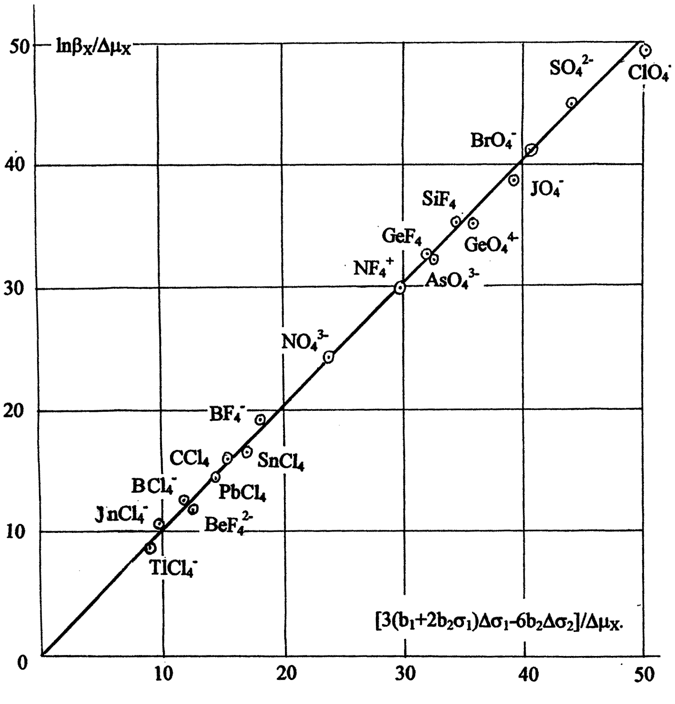

Figure 7. Correlation ln $\beta X/\Delta\mu\, X$ − polynom $[3(b1 + 2b2\sigma1)\Delta\sigma1 - 6b2\Delta\sigma2]/\Delta\mu\, X$.

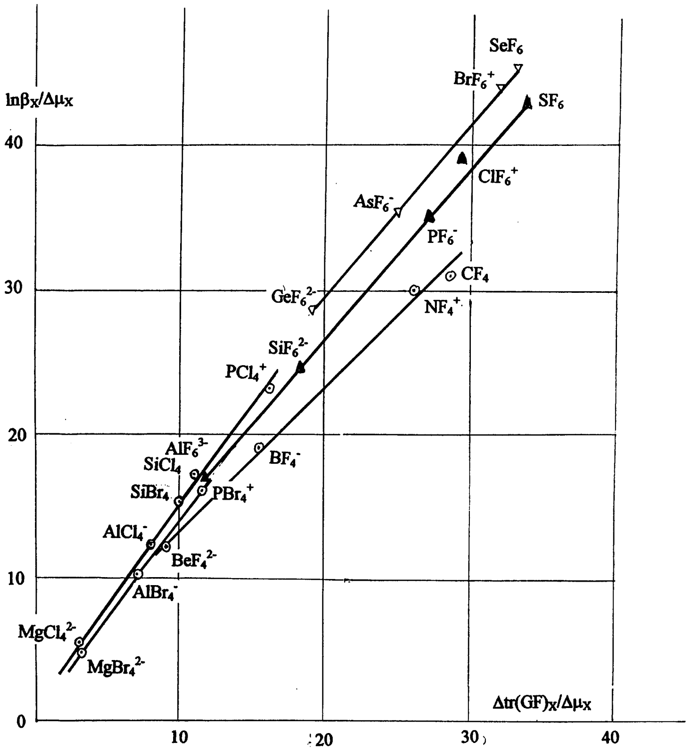

Figure 8. Correlation ln $\beta X/\Delta\mu\, X - \Delta tr(GF)X/\Delta\mu\alpha$ for halogenides and oxoanions.

f_α, interaction of bonds, f_{rr}, interaction of bonds and angles $f_{r\alpha}$, and interaction of angles with each other $f_{\alpha\alpha}$ decrease in a specific sequence (75):

$$f_r \gg f_\alpha \gg f_{rr} \geq f_{\alpha\alpha} \geq f_{r\alpha} \tag{49}$$

This means that the main contribution to $\Delta tr(GF)$ is due to the $(f_r - f_{rr})$ combination multiplied by the coefficients a_{ii}, which are equal to the number, n, of attached atoms Y or atomic groups YZ. Despite the far higher numerical values of a_{ij} coefficients of other constant combinations, the fraction of this contribution does not fall below 60% of $\Delta tr(GF)$ value and is in the range 80–90% for the vast majority of molecules. Thus, the force constants f_r and their number n introduce the main contribution to $\Delta tr(GF)$ (52,75). This permits selection of the valence force constants f_r as the main argument in studying the RPFR correlations. For polyatomic molecules, dense linear ln $\beta - f_r$ and ln $\beta - (f_r \pm f_{rr})$ correlations are observed for sets of geometrically similar compounds. Moreover, the sum $f_r + f_{rr}$ gives a better linear graphic correlation than the difference $f_r - f_{rr}$ due to the dropping down of points related to the rigid molecules containing either fluorine or oxygen donor atoms.

A phenomenological feature of the compounds in such sets usually deals with the nature of the donor atom attached to the atom undergoing the isotope substitution. Examples of such correlations are presented in Figs. 10 and 11 (76–80). In the series of XY_n and $XY_iY'_{n-i}$ types, where Y and Y' are different halogens, hydrogen, oxygen, and chalcogens, these correlations are so close that the methods used for comparative calculation of the RPFR become justified. For example, this

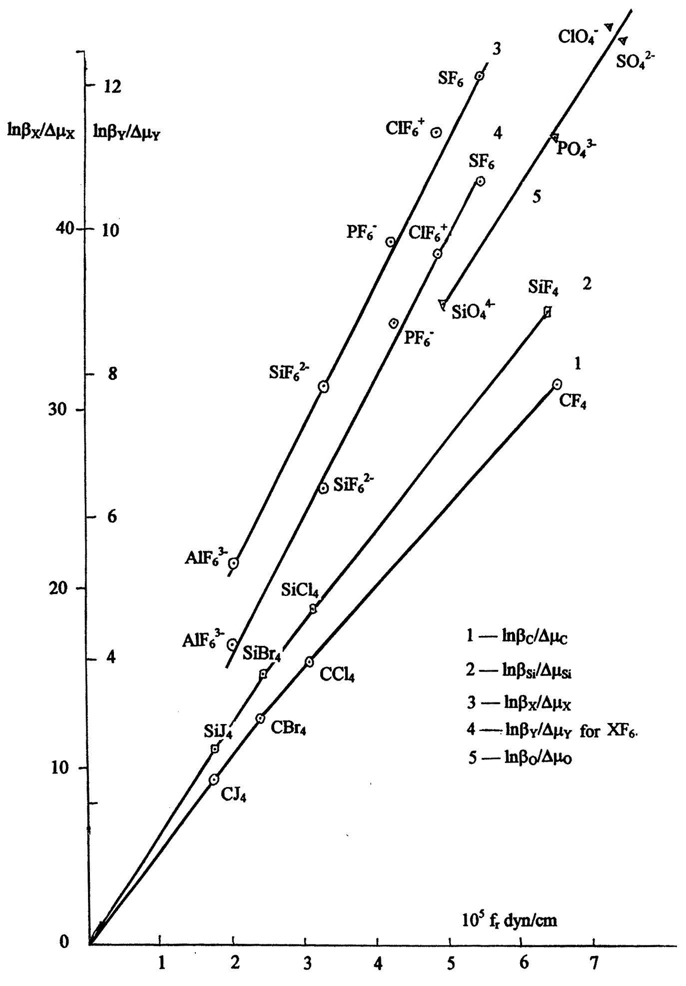

Figure 9. Correlation ln $\beta X/\Delta\mu$ X and ln $\beta Y/\Delta\mu$ Y with valent force constant f_r.

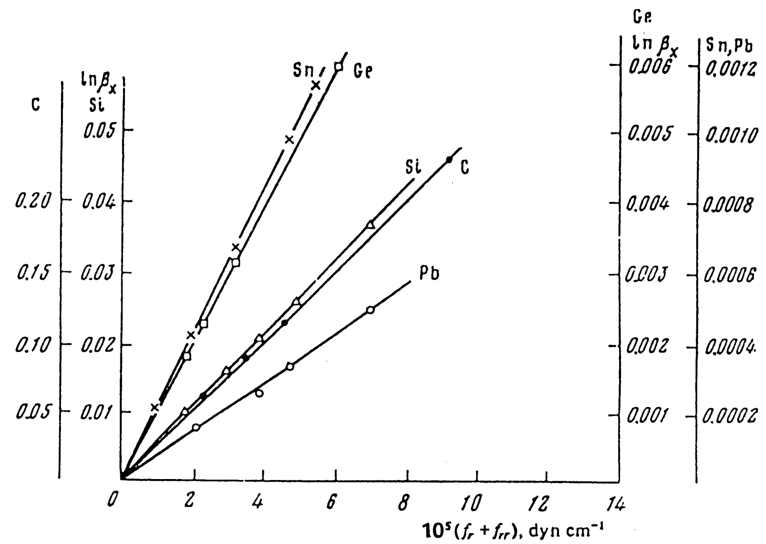

Figure 10. Dependence of ln β_X on combination of constants $f_r + f_{rr}$ at 300 K for tetrahalides XY_4 of elements of carbon subgroup.

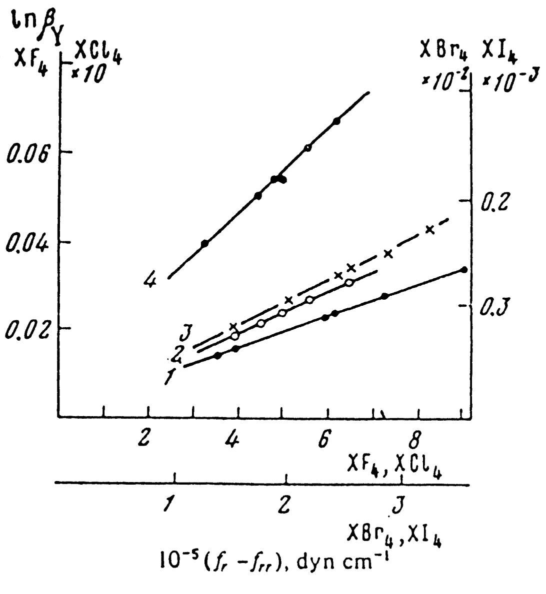

Figure 11. Dependence of $\beta_Y - 1$ on combination of force constants $f_r + f_{rr}$ at 300 K for terminal atoms Y in tetrahalides XY_4 of elements of carbon subgroup: (1) XF_4; (2) XCl_4; (3) XBr_4; (4) XJ_4.

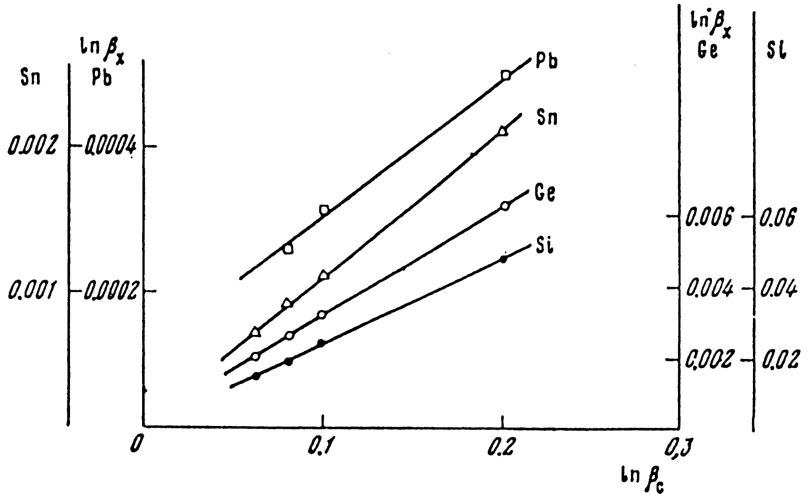

Figure 12. Correlation between ln β_X for silicon, germanium, tin, and lead tetrahalides and ln β_C.

concerns those based on the linear relations of the ln β_x − ln $\beta_{x'}$ type (see Fig. 12) (80). For a molecule of the $XY_1Y_2 \ldots Y_i \ldots Y_n$ type, in which atom X involved in the isotope substitution is linked to different atoms or groups Y_i, the dominant component of $\Delta tr(GF)$ is the sum $\Sigma(f_r)_{ij}$.

According to the transferability of force constants concept (75), the bond deformation force constants for a series of related molecules have the same numerical value or change comparatively slightly. Along with above considerations, this justifies the treatment of ln β quantities as sums of certain constant increments

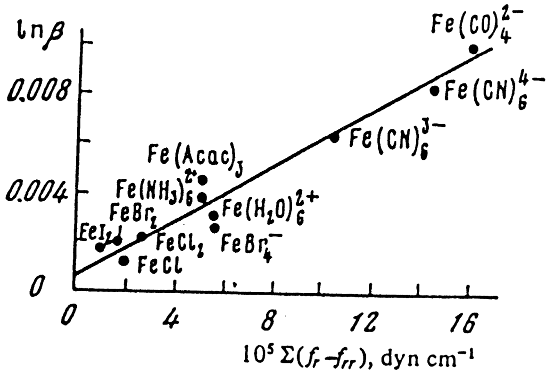

Figure 13. Correlation between ln β_{Fe} and $\Sigma(f_r - f_{rr})$.

corresponding to each bond. It has been shown (74,78) that in the isostructural series of the following type: CH_4, CH_3F, CH_2F_2, CHF_3, CF_4 or BF_3, BF_2Cl, $BFCl_2$, and BCl_3 the additivity of the ln β values for the central carbon and boron atoms holds with a high degree of accuracy. However, the additivity rule is generally not valid. The additivity of RPFR has the same accuracy as that obtained in the calculation of all thermodynamic functions by the additive schemes. The applicability of each specific scheme for RPFR calculation must be defined by the desired accuracy. This point usually requires special studies.

The correlations between ln β and $\Sigma(f_r + f_{rr})$ for a set of compounds with different geometry have a much smaller density. For such sets, the correlation coefficients are approximately 0.8. This is the result of the influence of $\Delta tr(GF)$ component, which is not proportional to Σf_r and reflects the differences associated with the geometrical variety of molecules (Fig. 13).

The existence of close correlations between ln β and the valence force constants seems to make it rational to use the quantum mechanical values of f_r. This route was examined by Hanshmann (81,82) to show this consistently theoretical method MNDO to yield 10 to 20% overrating of ln β. Such relative errors are several times as high as in the cases when well selected model force fields are used. Therefore, the empirical methods of f_r approximation and graph plotting still remain most preferable.

Correlations between RPFR and Empirical Equivalents of Valent Force Constants

Since valence force constants f_r characterize the bond strength and correlate with other bond properties, the ln β values must quite closely correlate with both bond and atom and molecule (forming these bonds) parameters. The density of such correlations and, hence, their reliability and usefulness are determined both by the selected method of expressing the bond strength and by the nature of compounds for which the correlations are constructed. For example, for simple diatomic molecules (76,83,84) the observed relations are so close and simple that the RPFR can be expressed analytically as a function of properties of atoms forming the molecule.

The force constants are the second derivatives of the bond energy E with respect to the internuclear distances corresponding to equilibrium distance r_e. Therefore, the relations of the ln β-E or ln β-E_i types can be expected to be fairly simple. However, even for the sets of related diatomic compounds such expectations are not realized in practice (76,83,84). For polyatomic molecules, the above relations are also not so simple (80). A much better correlation is observed between ln β and the argument $\eta E/r_e = \eta_0(I_X I_Y / I_X^0 I_Y^0)^{1/2} E/r_e$, where η_0 is a constant, I_X and I_Y are the first ionization potentials of atoms X and Y forming the molecule, I_X^0 and I_Y^0 are the first ionization potentials of the alkali metals belonging to the same periods as X and Y, and r_e is the interatomic distance. The use of this argument (see Fig. 14) is based on the known empirical relation $f_r = cE/r_e$ generalized by Lippincott (85). The above relation has been confirmed to be valid for a fairly large set of compounds (86).

Among numerous other methods used for fitting approximate expressions to the sum of valence force constants, we may mention the empirical relations by Gordy (87), Guggenheimer (88), Ferreira (89), Varshni (90), and Somayajulu (91), which have made it possible to obtain linear correlations between ln β and the internuclear distances, electronegativities, numbers of valence electrons in the atoms, and other characteristics (76–80,83,84) (see Figs. 15 and 16). Hanschmann supplements these probabilities with RPFR correlations and effective charges on carbon, nitrogen, and oxygen atoms.

Often only the stretching vibration frequencies (symmetric or anti-symmetric) are known for the compounds of interest. The knowledge of these frequencies is virtually equivalent to the knowledge of one of the combinations ($f_r + f_{rr}$). The squares of the stretching vibration frequencies can therefore be used as bond characteristics for compounds where the central atom is linked to monatomic ligands. Such correlations are equally well applicable to sets containing elements of a single group or a single period. It is also necessary to exclude the influence of masses by introducing the corresponding multiplier (see Fig. 17).

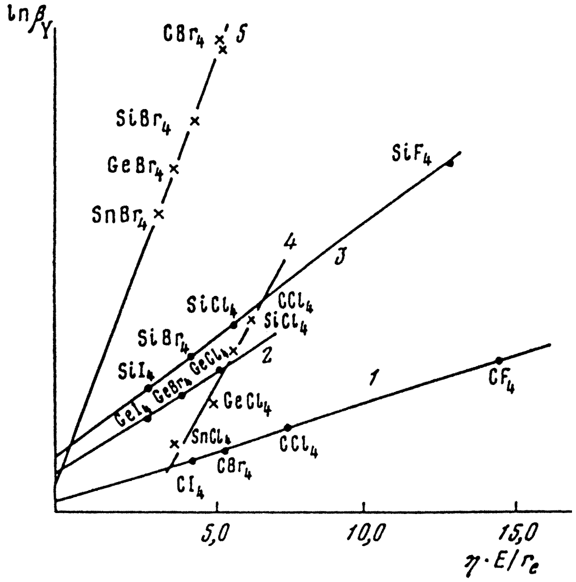

Figure 14. Dependence of ln β on ηE/r_e: (1)–(3), for C, Ge, and Si; (4) and (5), for Cl and Br.

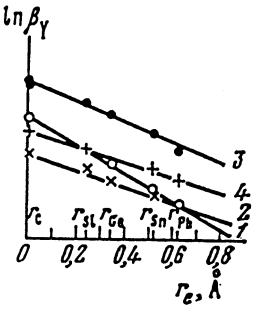

Figure 15. Correlation between ln β_Y and r_e for tetrahalides XY_4 of elements of group IV: (1) fluorides; (2) chlorides; (3) bromides; (4) iodides.

Phenomenological Relations between RPFR and Characteristics of Chemical Substances

This concept includes correlations that can be observed by comparing the isotope effects of one or several elements with generally accepted chemical concepts such as the degree of element oxidation, the type of donor atom or ligand,

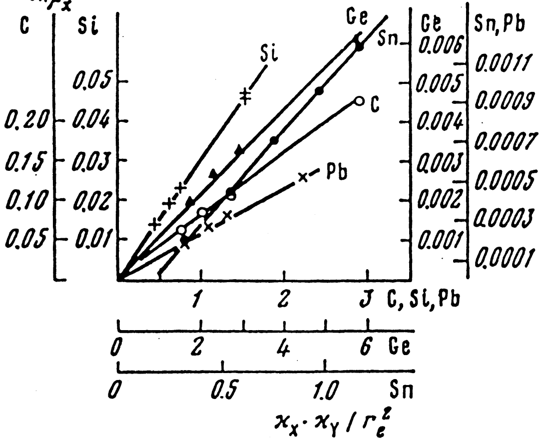

Figure 16. Correlation between ln β_X and Gordy-Ferreira factor $\kappa_X\kappa_Y/r_e^2$ for tetrahalides XY_4 of elements of group IV. κ_X and κ_Y are atomic electronegativities; r_e is internuclear distance.

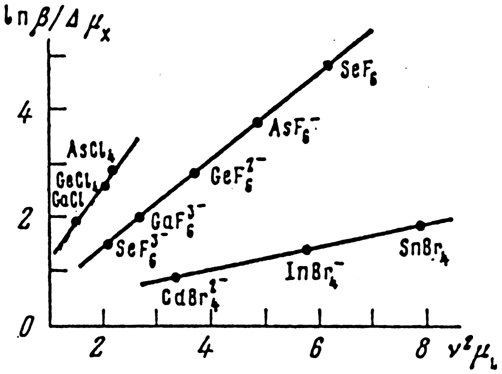

Figure 17. Dependence of ln β_X on $v^2\mu_L$, where v is stretching frequency and μ_L is reduced mass [$\mu_L = m_L m_X/(m_L + m_X)$]: (1) cyanides; (2) acetylacetonates.

and the configuration of coordination sphere of the element involved in isotope substitution. The choice of these features of the chemical compound as the phenomenological equivalent of the intramolecular force field is justified by the possibility of a direct comparison of the isotope effects with a wide variety of chemical data (75,77).

The oxidation state of an element, the type of ligand, and the type of configuration sphere are interrelated discrete parameters. Although the others are kept constant, each can vary only within narrow limits. To extend the range of values of the given parameter, it is necessary to adjust the isotope effects of different elements to a single scale and to include them in an overall analysis. This is achieved in two ways. First, to compare the isotope effects of different elements, one needs to use the effects corresponding to a unit increment in isotopic masses. All numerical values of ln β and ln α quoted in this review satisfy this condition. Second, if one needs to exclude the influence not only of Δm but also of the atomic mass m of an element involved in isotope substitution, then the quantities ln $\beta/\Delta\mu$ should be analyzed. In conformity with the significance of Eqs. (22) and (49), these quantities can be referred to as the effective force fields in which the atoms in the molecule involved in isotope substitution are located.

Relations between RPFR and Degrees of Oxidation

The influence of the degree of oxidation of the central atom on its ln β can be most readily followed for the sequence of compounds formed by elements with the same donor atom or ligand. The variation of the effective field ln $\beta/\Delta\mu$ is simplest for the sequence of isoelectronic-isostructural compounds of p-elements. Figures 18, 19, and 20 present relations between ln $\beta/\Delta\mu$ and the formal oxidation state of the central atom in a series of isoelectronic molecules. They show that the values of ln $\beta/\Delta\mu$ in certain limits are linear functions of the formal oxidation state in the series of tetraoxo-anions and tetra-, and hexa-halogeno complexes of both *p*- and *d*-elements in the highest oxidation states.

The increase of oxidation degree of *p*-elements is coupled with a change in the number of attached ligands, the type of hybridization of the valence orbitals, and the configurations of the compounds. A monotone increase of the effective force fields observed in such sequences (see Table 10) must be attributed to the increase of degree of oxidation, since the configuration can be regarded as derived from the oxidation state and the type of ligand. The monotone variation of ln β_X for sequences of this type does not imply their simplicity. These sequences are characterized by a change of both the type of hybridization and the number of nonbonding electron pairs. A more flexible and exact equivalent of the oxidation degree concept is the sum of bond orders, which exhibits a closer correlation with ln β (see Fig. 21). Relations with charges on atoms are analogous. For isostructural series of transition metals compounds the variation of ln $\beta/\Delta\mu$ with increasing degree of oxidation remains monotonic (see Table 11). For σ-donor and ($\sigma - \pi$)-donor ligands, ln $\beta/\Delta\mu$ increases, while for σ-donor and π-acceptor ligands it diminishes with degree of oxidation.

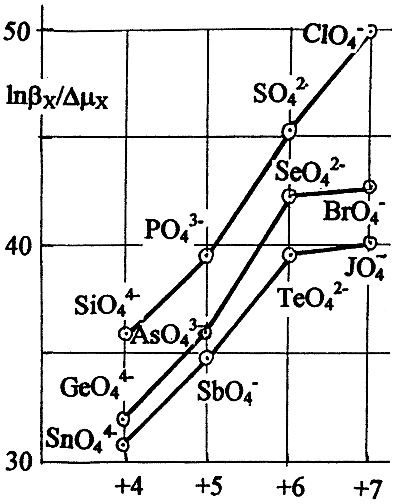

Figure 18. Oxygen and fluorine effects in oxo- and fluoro-anions (see text).

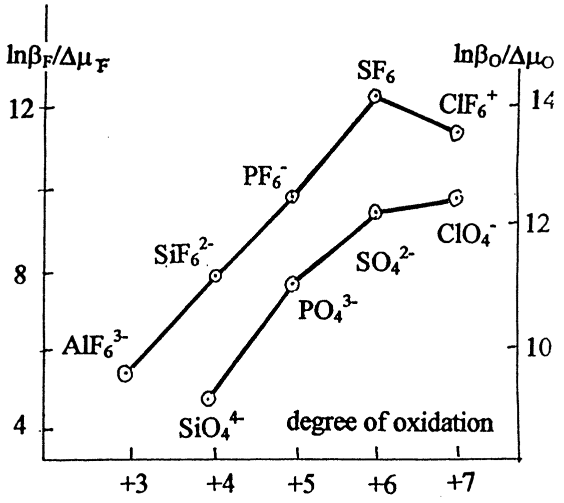

Figure 19. Central isotope effects in oxoanions of p-elements.

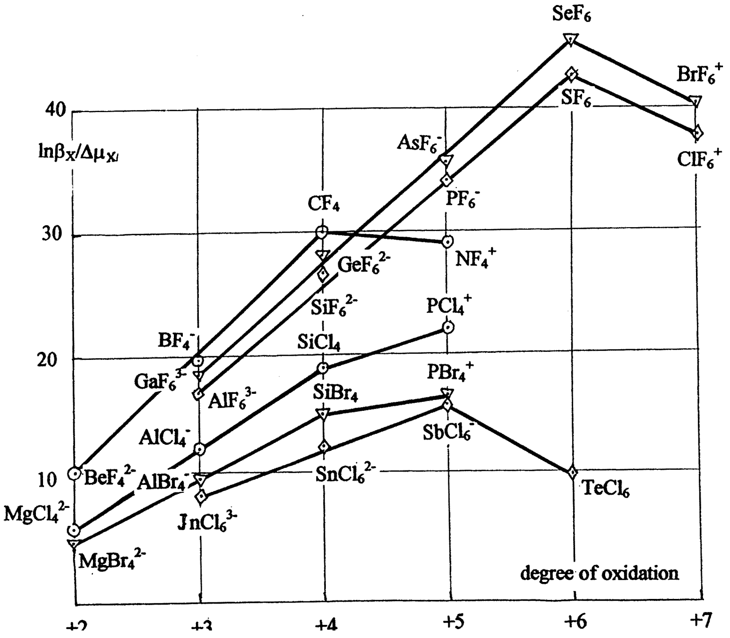

Figure 20. Central isotope effects in hexa- and tetrahalocompounds.

Table 10. ln β_X Values for Oxides and Fluorides of p-Elements of VI-A Group, 300 K

SF_2	0.00940	SeF_2	0.00174	TeF_2	0.00067
SO	0.00862	SeO	0.00130	TeO	0.00043
SO_2	0.00240	SeO_2	0.00347	TeO_2	0.00126
SO_3^{2-}	0.00267	SeO_3^{2-}	0.00377	TeO_3^{2-}	0.00145
SF_6	0.00403	SeF_6	0.00741	TeF_6	0.00297
SO_4^{2-}	0.00427	SeO_4^{2-}	0.00678	TeO_4^{2-}	0.00177

Relations between RPFR and Characteristics of Donor Atoms and Ligands

The study of relations between the RPFR and the nature of ligands and donor atoms is complicated because ln β values are currently known mainly as compounds with the simplest monoatomic ligands. Table 6 shows that in the series of isostructural compounds formed by donor atoms of elements of a single group of the Periodic Table, a remarkable decrease of ln β for donor elements with an increasing atomic number (within the same group) is observed. Fairly rigorous relations of the following type:

$$\ln \beta_{(XYn)}/\ln \beta_{(XY'n)} = t \cong \text{const} \tag{50}$$

are observed between ln β values for halides, oxides, and chalcogenides. The t values appear to be close to the ratios of the electronegativities of donor elements Y and Y'. Compounds with different oxidation states of the central atom and ligands belonging to the same period ($F^-$and O^{2-}, $Cl^-$and S^{2-}, $Br^-$and Se^{2-}) have approximately the same RPFR values of the central atoms (see Tables 10, 12, and 13).

The following factors determine the dependence of the RPFR on the nature of the ligand: 1) occurrence of donor atom of the ligand in a definite period, 2) chemical individuality of the donor atom, and 3) influence of atomic environment (in the ligand) on the donor atom. The available data for different complex-forming ligands permit the conclusion that the first factor is of the greatest importance, although the influence of two others is far less. In addition, the general charge of the coordination sphere probably has an essential influence because high negative charge relax the valent force constant f_r. As seen from Table 13, the RPFR increases with the positive charge and decreases with the negative charge of coordination sphere if donor atom relates to the same row of the Periodic Table ($F^-$and O_2^-, Cl^-, and S_2^-, etc.).

Relations between RPFR and Geometrical Configuration of Molecule

The relation between the RPFR and configurations of coordination spheres of an element in the compound under consideration can be traced only for a few

Table 11. Relation between $\beta_X - 1$ and Oxidation State of Central Atom

Isostructural σ-complexes											
VF_6		CrF_6		RuF_6		ReF_6		MnO_4		RuO_4	
−3	0.00550	−3	0.00720	−3	0.00177	−2	0.00065	−3	0.00711	−2	0.00296
−2	0.00860	−2	0.00762	−2	0.00234	−1	0.00087	−2	0.00987	−1	0.00334
−1	0.01066	0	0.01450	0	0.00363	0	0.00129	−1	0.01173	0	0.00396
Isostructural π-complexes											
$Cr(CN)_6$		$Mn(CN)_6$		$Fe(CN)_6$		$Cr(C_6H_6)_2$		$Fe(C_5H_5)_2$			
−3	0.00586	−3	0.00583	−3	0.00634	+1	0.00271	+1	0.00313		
−4	0.00678	−4	0.00694	−4	0.00852	0	0.00324	0	0.00506		

Table 12. Relationship between ln β_X and Type of Monoatomic Ligand, 300K

Y	LiY	BeY_2	BY_3	CY_4	PY_3	PY_5	SnY_6^{2-}
F	0.0727	0.274	0.2110	0.205	0.0273	0.0454	0.00207
Cl	0.0457	0.106	0.1392	0.0991	0.0125	0.0219	0.00099
Br	0.0328	0.101	0.1084	0.0804	0.0108	—	0.00070
J	0.0215	0.083	0.0880	0.0629	0.0098	—	0.00047
Y	CY_2	CY_3^{2-}	PY_4^{3-}	VY_4^{3-}	AsY_4^{3-}	MoY_4^{2-}	WY_4^{2-}
O	0.1729	0.1902	0.0390	0.0125	0.00586	0.00407	0.00123
S	0.1054	0.0939	0.0178	0.0069	0.00292	0.00208	0.00062
Se	0.0897	0.0830	—	0.0050	—	0.00184	0.00053

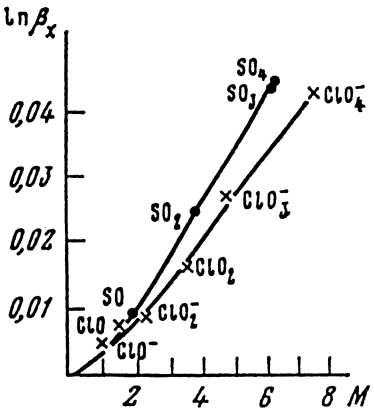

Figure 21. Correlation between ln β of sulfur and chlorine oxides and sum of bond orders M.

Table 13. ln β_X Values for Isostructural-Isoelectron Pairs of Compounds of *p*- and *d*-Elements Influence of the Charge of Coordination Sphere

NF_4^+	SiF_4	PF_4^+	TiF_4	PCl_4^+	$AsCl_4^+$
0.1446	0.0437	0.0457	0.0118	0.0226	0.00349
NO_4^-	SiO_4^{4-}	PO_4^-	TiO_4^{4-}	PS_4^{3-}	AsS_4^{3-}
0.1180	0.0390	0.0389	0.0109	0.0178	0.00292
$SbCl_4^+$	MoF_6	TeF_6	WF_6	ReF_6^+	
0.000117	0.00379	0.00295	0.00104	0.00156	
SbS_4^{3-}	MoO_6^{6-}	TeO_6^{6-}	WO_6^{6-}	ReO_6^{5-}	
0.000102	0.00321	0.00222	0.00075	0.00075	

Table 14. Isotope Effects, ln β_X of Configurational Changes, 300 K

Effects with Change of Hybridization and Variation of Number of Ligands					
BF_3	BF_4^-	CO_2	CO_3^{2-}	NO_2^+	NO_3^-
0.2110	0.1760	0.1729	0.1902	0.1342	0.1398
BCl_3	BCl_4^-	CS_2	CS_3^{2-}		
0.1392	0.0998	0.1054	0.0939		
BBr_3	BBr_4^-	CSe_2	CSe_3^{2-}		
0.1084	0.0889	0.0897	0.0830		
SiF_4	SiF_6^{2-}	TiF_4	TiF_6^{2-}	SnF_4	SnF_6^{2-}
0.0437	0.0318	0.0118	0.0089	0.00208	0.00258
$SiCl_4$	$SiCl_6^{2-}$	$TiCl_4$	$TiCl_6^{2-}$	$SnCl_4$	$SnCl_6^{2-}$
0.0256	0.0085	0.0070	0.0041	0.00119	0.00089
Effects without Change of Hybridization of Central Atom but with Variation of Number of Ligands					
NH_3	NH_4	$PdCl_4$	$PdCl_6$	$PtCl_4$	$PtCl_6$
0.0535	0.0821	0.00098	0.00142	0.00035	0.00058
PH_3	PH_4	$PdBr_4$	$PdBr_6$	$PtBr_4$	PtF_6
0.0104	0.0132	0.00083	0.00111	0.00031	0.00043

types of configuration transitions (see Tables 14 and 15). Examples of such transitions, associated with an increase in the number of added donor atoms and a change in the type of hybridization of the electronic orbitals of the atom involved in isotope substitution, are provided by transitions of the following types:

$CO_2(D_{\infty h})$	CO_3^{2-} (D_{3h});
$BF_3(D_{3h})$	BF_4^- (T_d);
$SiF_4(T_d)$	SiF_6^{2-} (O_h).

Table 15 shows that in the majority of instances these transitions are accompanied by a decrease of ln β. This can be explained by substantial decrease of

Table 15. Isotope Effects ln β_X in Configuration Transitions

Y	$CY_2(D_{\infty h})$	$CY_3^{2-}(D_{3h})$	Y	$BY_3(D_{3h})$	$BY_4^-(T_d)$
O	0.1888	0.2095	OH	0.278	0.247
S	0.1111	0.0985	F	0.2435	0.213
Se	0.0938	0.0865	Cl	0.1364	0.106
Y	$SiY_4(T_d)$	$SiY_6^{2-}(O_h)$	Y	$SnY_4(T_d)$	$SnY_6^{2-}(O_h)$
F	0.0475	0.0323	F	0.00208	0.00207
Cl	0.0259	0.0085	Cl	0.00119	0.00099
Br	—	—	Br	0.000954	0.000996

f_r in such transitions. However, the configuration transitions caused by the addition of electron-deficient species and by delocalization of the nonbonding electron pair of the atom can be accompanied by an appreciable increase of ln β. An example of such transitions is $NH_3(C_{2v}) \rightarrow NH_4^+(T_d)$ (78).

SYSTEMATIZATION AND PROGNOSIS OF EQUILIBRIUM CHEMICAL ISOTOPE EFFECTS

Two problems must be solved in applications of isotope effects for both separation of stable isotopes and as the basis of a research technique: 1) determination of applicability limits of corresponding method, and 2) prediction of systems and situations where these methods are most effective. These problems can be reformulated as follows: a) statistical estimation of isotope effects for various elements of the Periodic System; b) methodological search for a rational classification of isotope exchange reactions as the basis for a systematic treatment of isotope effects, and c) determination of principles permitting the prediction of systems with large isotope effects on the basis of general chemical information. The results obtained by solving the above problems (92–97) will be considered briefly in this section.

Statistical Evaluation of Equilibrium Isotope Effect of Different Elements

The sets of possible chemical exchange systems of different elements are quantitatively non-equivalent. Although the number of such systems usually equals several thousand, the number of compounds of each element for which RPFR values are known is in most cases small. The sets of systems with calculated isotope separation factors susceptible to a statistical treatment are also small. For the majority of elements, the sets of possible systems are insufficiently representative. The lack of information can be compensated by extending the framework of the treatment by combining the systems of different elements in a single set. However, both ln β and ln α values primarily depend on the atomic weight of an element. Hence, such combination requires the normalization of ln α values, i.e., they must be adjusted to a single scale.

For this purpose, the γ-factor concept has been introduced. The γ-factor is defined as the ratio of the absolute ln α value for a specific chemical exchange system (of a given element) to the maximum possible ln α value (ln β_{max}) for the same element. α_{max} numerically is equal to the separation factor for a hypothetical system, in which the exchange proceeds between the compound with the maximum possible β value, β_{max}, and the non-bonded atomic form for which $\beta = 1$, i.e.,

$$\gamma = \left|\ln \alpha\right| / \ln \beta_{max} \tag{51}$$

For any element, γ varies in the same range $0 \leq \gamma \leq 1$. The regularities of RPFR variation were accounted for to establish a basic system of β_{max} values (at 300 K). The basis for this are also the agreement and absence of any contradictions between the laws of ln β change and available experimental data on isotope separation coefficients for s-, p- and d-elements, and also the data hitherto collected on the vibrational spectroscopic characteristics of these element compounds (98).

The obtained ln β_{max} values are grouped in Table 15. They cannot be regarded as a set of exact upper limits of ln β variability for each of the s-, p- and d-elements as all values contain an uncertain relative error varying from element to element. Most probably, this error for the majority of elements is within the range of 10–20 %, although in some cases it may be extended. The choice of ln β_{max} for each element is determined by the available set of compounds with well-known RPFR, which also satisfies the following requirements: 1) they are to be fluorine or oxygen compound either coordinately unsaturated or with coordination structure close to saturation, in which the element (central atom) exhibits the highest oxidation degree, and 2) the compound must not bear any large negative charge markedly decreasing the valence force constants of the coordination sphere bonds of the central atom. If RPFRs of the proper compounds were unknown, these requirements had to be softened by choosing compounds with N- and C-bonds with valence force constants markedly lower on the whole, compared with F- and O-bonds. Sometimes when necessary, compounds with the largest ln β values were chosen. For s-elements the ln β values of crystalline fluorides and oxides of LiF and MgO type have been chosen.

Table 16 exemplifies the possibility to select β_{max} for nitrogen compounds. There are seven known compounds of this element (including the dimer O_2N-NO_2), which meet the above criteria. In this fairly rare case, ln β_{max} as the upper limit is established rather reliably because the types of coordination sphere formation with F- and O-bonds have been almost exhausted and no compound can be expected to be found with RPFR exceeding that of NF_4^+. For the majority of p- and d-elements, the sets of fluoride and oxide compounds with known RPFR include from one to three. Besides, it is unlikely that for elements of the 6th and the 7th periods specific compounds with high coordination numbers and higher RPFR can be discovered.

This situation has resulted from a long-term empirical elaboration of the industrial process for uranium isotope process by chemical isotope exchange method. Analysis of ln β values undertaken by Bigeleisen (99) and Kakihana (100) using experimental separation factors leads to ln $\beta_{max} \cong 0.0018$ for uranium. This value exceeds ln β_{max} estimates for d-elements closest to uranium and

Table 16. ln β Values for Nitrogen and Uranium, 300 K

Oxidation States						
+2	+3	+4	+5			
NF_2	NF_3			NF_4^+		
0.0592	0.0859			0.1446		
	NOF			NOF_3	NO_2F	
	0.0823			0.1250	0.1368	
NO	NO_2^-	NO_2	NO_2^+	NO_3^-	NO_4^-	HNO_3
0.0617	0.1017	0.0962	0.1342	0.1398	0.1180	0.1123
	N_2	$ON^* - {}^*NO_2$		$ON - NO$		
	0.0775	0.1053		0.1292		
	NOCl			NO_2Cl		
	0.0720			0.1172		

Oxidation States				
+3	+4	+6		
U_{aq}^{3+}	$U(OH_2)_8^{4+}$	$UO_2(OH_2)_5^{2+}$	UF_6	$NOUF_6$
0.00177	0.0011	0.00063–0.00067	0.00067	0.0012

refers to U^{3+} aqua-complex and not to fluoride, UF_6 (see Table 16). It is now difficult to state what accounts for this situation: some unknown specificity of f-element bonds or the general scarce knowledge of vibration-spectroscopic characteristics of coordination compounds of heavy metals. Let us suppose that central U^{3+} ion in the aqua-complex possesses a coordination similar to that of the crystalline UF_3 (coordination number is 11). Then an average value of the force constant of U-OH_2 bond appears to be close to 4.105 dyne/cm. So high constants of metal-ligand bonds are presently unknown (101).

Table 15 shows both compounds possessing ln β_{max} and their effective fields. As seen, ln $\beta_{max}/\Delta\mu$ values regularly grow throughout the periods. The higher the element numbers the larger effective fields. These characteristics show a tendency to a slight increase with the growth of the mass of element.

Uranium has nearly a two times larger effective field related to U_{aq}^{3+} than the nearest d-elements. A similar strange situation existed for a long period for lithium isotope separation factors. Any system including Li^+ complex with uramyl-*N*-*N*-diacetate has an unusually high separation factor (102). Only relatively recent studies of systems with crown ethers exposed the reason for that: an extraordinary form of the potential energy surface of such complexes, where cations are located in a big cavity inside the crown (103). These episodes (both with uranium and lithium) illustrate a possibility of a considerable increase of chemical exchange separation factors.

The separation factors for each element can assume different values within the range from 1 to β_{max}. The frequency of the appearance of larger and smaller α values can be different. The concept of attainable α values has the significance for maximum values, in which appearance probability remains acceptably high from the practical viewpoint. A direct empirical estimate of probability of the existence of different α is mathematically equivalent to the construction of statistical distribution functions for α.

The conversion of statistical distribution functions for α into statistical distribution functions for γ makes it possible to compare directly the functions for different elements, to estimate the degree of their similarity, and to solve the problem of the possibility of employing average (generalized) distribution functions for γ to estimate the attainable values of α for those elements for which the direct analysis of the problem is either difficult or impossible.

The γ distribution function is determined by the nature of the set of systems for which it is constructed. It is possible to distinguish hypothetical random sets formed by pair combinations of all the compounds with known β-factors; the sets of thermodynamically compatible systems; the sets of systems with a high (or practically acceptable) rate of isotope exchange. The γ-functions of three types have been investigated for eleven elements (H, B, C, N, O, F, Fe, Co, Ni, Zn), see Table 17. It has been found that in general the γ-functions of each type differ slightly from each other despite the remarkable difference in chemical individuality elements under consideration. Therefore, the estimation of attainable α values for different elements can be achieved by using averaged γ -functions.

However, the set of systems satisfying both thermodynamic and kinetic requirements can be constructed in different ways. For example, it is possible to investigate a set of all systems with known α values by taking into account the different abundance of different system classes (see set 1 in Table 18). The γ distribution function for such a set will reflect the probability of a random selection or discovery of systems with particular γ values. Then one can investigate the γ-functions for each class of systems (see below). The averaging of such functions without taking into account the abundance of the classes leads to γ-functions accounting for an element of specificity in the search for systems (see set 2 in Table 18). Finally, one can study the γ-function for a set of experimentally investigated systems (set 3 in Table 18). Evidently, all three types of γ-functions are suitable to estimate the attainable values of α.

As seen from Table 18, the probability of obtaining high γ values is the highest for the function that does not take into account the abundance of systems of different classes. The lowest probability is observed for the function that accounts for this factor. The function of experimentally investigated systems occupies an intermediate position, which is evidently a consequence of low specificity of the empirical search for systems to be used in isotope separation. At the same time, all three functions are generally quite similar. This shows that their use for the estimation of the attainable values of α is fairly reliable.

Table 17. Distribution Functions Created from "Random", "Thermodynamical", and "Kinetical" Sets for Elements H, B, C, N, O, F, Fe, Co, Ni, Zn

Number of Systems in Initial Set	H 1009	B 486	C 1280	N 349	O 664	F 256	Fe 1225	Co 220	Ni 232	Zn 595	mean
0–0.1	26.9	33.2	27.0	24.6	33.7	34.1	27.3	25.3	30.0	25.4	28
0.1–0.2	21.6	12.7	23.7	20.4	28.8	25.1	25.6	27.5	22.1	22.5	23
0.2–0.3	20.2	8.9	19.5	16.1	18.5	18.4	19.0	20.9	13.8	17.5	17
0.3–0.4	16.9	16.2	13.3	12.0	11.3	9.2	12.1	15.4	15.9	15.8	13
0.4–0.5	7.8	9.8	8.4	10.0	3.9	6.6	7.9	6.6	9.1	10.0	8
0.5–0.6	3.9	6.4	4.5	8.3	2.2	4.0	4.2	6.4	6.5	4.2	5
0.6–0.7	2.1	7.3	2.3	6.3	0.8	2.1	1.7	—	2.5	3.7	2
0.7–0.8	0.3	5.2	0.9	2.3	0.8	0.5	1.5	—	—	0.6	1
0.8–0.9	—	0.3	0.2	—	—	—	0.7	—	—	0.3	0
0.9–1.0	—	—	—	—	—	—	—	—	—	—	—
Relative Volume of Thermodynamic Set	0.86	0.90	0.49	0.29	0.95	0.82	0.39	0.58	0.18	0.16	
0–0.1	28.4	67.5	34.5	29	33.7	39.3	39.1	40.8	51.0	45.1	40
0.1–0.2	21.9	20.4	30.0	27	28.6	28.6	30.3	36.7	26.4	32.6	28
0.2–0.3	20.8	5.6	19.3	19	18.5	15.5	12.1	15.0	15.8	9.1	15
0.3–0.4	16.7	6.0	10.4	10.0	11.2	8.4	9.9	6.1	5.3	4.8	8
0.4–0.5	7.6	0.6	3.8	10	4.1	5.4	4.9	1.4	1.5		
0.5–0.6	3.8	—	1.9	3	2.4	2.4	3.3	—	—	4	1
0.6–0.7	0.9	—	—	2	0.8	0.2	0.4	—	—	2.4	0
0.7–0.8	—	—	—	—	0.8	—	—	—	—	—	0
0.8–1.0	—	—	—	—	—	—	—	—	—	—	—
Relative Volume of Kinetic Set	0.05	0.05	0.02	0	0.12	0.2	0.23	0.18	0.13	0.30	
0.0–0.1	28	39	55.5	24	48	36.5	47	38.4	51	53.5	42
0.1–0.2	28	61	37	18	26	29.2	38.5	33.4	26.4	35.5	33
0.2–0.3	17.5	—	7	24	17	15.4	9	13.8	15.8	6	12
0.3–0.4	15.5	—	0.5	18	4.5	10.8	3.5	8.3	5.3	3.5	6
0.4–0.5	6.5	—	—	12	4.5	4.9	2	5.4	1.5	0.5	3
0.5–0.6	4.5	—	—	6	—	3.2	—	1.5	—	0.5	1
0.6–1.0	—	—	—	—	—	—	—	—	—	—	

Classification of Equilibrium Isotope Exchange Reactions

The main requirement for classification of chemical exchange systems is in its interpretative and predictive ability. For this reason this classification must cover fairly completely the entire range of equilibrium chemical isotope effects and must constitute a flexible means to combine a specific and general chemical information. The choice of 1) oxidation state (OS) of the element, 2) the type of coordinated ligand (CL), and 3) configuration of the coordination sphere (CCS) of the compound can be used for this purpose.

Allowance for the above three features of each compound implies that each chemical exchange system is to be described by six features and that in each pair of like features two can be either identical or different. Hence, the entire set of isotope exchange reactions can be subdivided into eight classes. Table 19 defines different classes and presents examples of the corresponding reactions. All classes can be subdivided into four groups: class I, the class of homomolecular exchange reactions, for which the isotope separation factors are mathematically and rigorously equal to unity; three "simple" classes II, III, and IV, in which the number of differing features of the compounds is unity; three classes V, VI, and VII with two differing features of the compounds; and class VIII, in which the number of distinguishing features of the compounds is maximum and is equal to three. Each class can be subdivided, in turn, into subclasses corresponding to a specific combination of both variable and invariant features. However, the available data are insufficient for a detailed investigation of the subclasses, and in the main, only the classes as a whole are so far susceptible to analysis. Analysis of the experimentally investigated systems does not allow a comparison of the possibilities of different classes, because the vast majority of systems investigated refer to class VII. Isolated systems in classes III, IV, VI, and VIII have been studied.

Table 20 illustrates the distribution functions for seven classes with $\gamma \neq 0$ obtained as a result of the interpretation of calculated theoretical data (93). As seen, an average γ value (γ_{av}) for a given class increases by increasing the number of differing features. The difference between the influences of individual variable features on γ_{av} can also be clearly traced. The classes of systems with a variable OS have higher γ_{av} values than the classes with variable CCS, whereas the classes with different CL have the lowest values of γ_{av}. This is associated with the stepwise substitution of ligands and predominance of the O- and N-donor ligands among those investigated. The most complex class, class VIII, in which all three

Table 18. Distribution Functions γ (Probabilities of Finding Systems in Different Ranges of γ Values)

Type*	No. of System	Ranges of γ Values						Mean γ
		0–0.1	0.1–0.2	0.2–0.3	0.3–0.4	0.4–0.5	0.5–0.6	
1	1081	0.573	0.238	0.094	0.063	0.025	0.007	0.126
2	—	0.381	0.281	0.172	0.091	0.061	0.014	0.171
3	161	0.410	0.349	0.138	0.058	0.025	0.010	0.150

* 1, set taking into account the abundance of different classes; 2, set not taking into account the abundance of different classes; 3, set of experimentally investigated systems.

Table 19. Classification of Isotope Exchange Reactions. Examples of Kinetically Acceptable Reactions Belonging to Different Classes (290–300 K) (95,96)

Class (see text)	System	Kinetic Parameters	Theory ($\Delta m = 1$)	Exper. ($\Delta m = 1$)	γ Values of Reaction
II. Identical CCS and CL, different OS	$Fe(CN)_6^{3-} + Fe(CN)_6^{4-}$	$k = 3.5 \times 10^2$ $L{\cdot}mol^{-1}s^{-1}$	1.00216	—	0.24
	$Mo(CN)_8^{3-} + Mo(CN)_8^{4-}$	$K = 355$ $L{\cdot}mol^{-1}s^{-1}$	1.00075	—	0.19
III. Identical OS and CCS, different CL	$HDS + H_2O$	HETS = 10 cm	2.20	2.38	0.27
	$BF_3 + BF_3$ anyzol	rapid exch.	—	1.028	0.21
	$LiF(s) + Li^+(aq.)$	slow exch.	—	1.0068	0.04
IV. Identical OS and CL, different CCS	$NH_3 + NH_4^+$	$k = 24.6$ mol s	1.034	1.035	0.25
	$BF_3 + BF_4{}^-$	rapid exch.	1.036	1.04	0.32
V. Identical CCS, different OS and CL	$V(H_2O)_6 + V(CN)_6^{3-}$	rapid exch.	1.0012	—	0.08
	$Mn(H_2O)_6^{3+} + Mn(CN)_6^{4-}$	rapid exch.	1.0008	—	0.07
VI. Identical CL, different OS and CCS	$NO + NO_3^-$	rapid exch.	1.079	—	0.54
	$NO + NO_2$	rapid exch.	1.035	1.028	0.24
VII. Identical OS, different CCS and CL	$CO_2 + H_2O$	HETS = 13 cm	1.021	1.021	0.18
	$SO_2 + HSO_3$	rapid exch.	—	1.010	0.22
	$UF_6 + NOUF_6$	moderate exchange	—	1.00053	0.30
VIII. Different CCS, OS and CL	$Li(Hg) + Li(H_2O)_4^+$	HETS = 10 cm	1.050	1.055	0.72
	$U^{3+}(aq) + U^{4+}(TBP)$	HETS = 2–3 cm	—	1.00077	0.30

HETS, height equivalent to theoretical separation stage; TBP, tributylphosphate in organic solvent.

features of the contrasted compounds forming the systems are different, has the highest value of γ_{av}.

Principles of Prognosis of Chemical Exchange Systems with High Equilibrium Isotope Separation Factors

For both isotope separation and research, chemical isotope effects are more suitable the higher their absolute value. The problem of prediction therefore usually involves the search for systems with large effects. The principles of predic-

Table 20. Distribution Functions for Different Classes (Probabilities of Finding Systems in Different Ranges of γ Values)

		Ranges of γ Values					
Class	γ_{av}	0–0.1	0.1–0.2	0.2–0.3	0.3–0.4	0.4–0.5	0.5–0.6
II	0.174	0.30	0.35	0.22	0.11	0.02	0.00
III	0.079	0.85	0.14	0.00	0.00	0.01	0.00
IV	0.105	0.48	0.30	0.16	0.04	0.05	0.00
V	0.198	0.28	0.38	0.24	0.03	0.07	0.00
VI	0.282	0.08	0.34	0.22	0.12	0.18	0.02
VII	0.124	0.55	0.31	0.09	0.05	0.00	0.00
VIII	0.310	0.16	0.16	0.29	0.24	0.16	0.08

tion must be formulated as *the most rational method for finding such systems on the basis of the entire available information about chemical systems.* Direct theoretical calculation and correlation estimates of α values are the most reliable means for such a search. However, the computational method of prediction is limited by the lack of required initial data. The knowledge of thermodynamic characteristics of isotope exchange can to some extent compensate for this deficiency and can play a role as the main guiding principle.

Nevertheless, the broadest base for a rational search and for a comprehensive analysis of systems is provided by the above classification of chemical exchange systems (see Table 19). Indeed, it is derived not only from the common causes of the occurrence of isotope effects but also ensures the possibility of employing the most readily available general chemical information.

Isotope effects should be predicted by accounting for the specific purpose of the systems sought. In relation to the specific search for chemical exchange systems suitable for isotope separation on the basis of the classification described above, the principles of the selection of systems with high isotope separation factors can be formulated as follows:

1. One of two compounds of the system must be formed by an element in its highest OS.
2. CL coordinated by the element must contain donor atoms belonging to the Second Period (the σ-donor or σ-π-donor atoms F, O, and N) and must form an unsaturated coordination sphere.
3. Other compounds must contain the given element in the lowest possible OS, and the ligands coordinated by this element must contain the elements of higher Periods as donor atoms (σ-π-donor ligands with weak π-acceptor properties).
4. The coordination sphere must be either completely or nearly saturated.

These principles conflict with other requirements. Apart from a high separation factor, the “promising” chemical system must also have thermodynamic stability, satisfactory kinetics of isotopic exchange, the ease of separation of juxtaposed chemical forms between contacting phases, and simplicity of the interconversion of coexisting chemical forms. Since the thermodynamic classification of chemical exchange systems takes into account the general chemical unity of different classes, it can serve as the basis for general analysis of the possibilities of different classes, including the above specific requirements.

GENERAL PROSPECTS OF CHEMICAL METHODS FOR SEPARATION OF ISOTOPES

Comparison of Energy Consumption of Reversible and Irreversible Separation Processes

The estimation of general prospects for chemical exchange techniques in isotope separation can only be made through the comparison of these methods with each other, although their number is not small. If we limit the comparison to a most evident choice it will require less time. Nevertheless, the analysis to be done is complicated due to the following reasons:

1. Chemical exchange can be applied to all or almost all of the 63 polyisotopic elements; in other words, the problem has the same number of objects.
2. Efficient physical methods, namely gas diffusion and centrifugation, have been developed mainly for special purposes. Their applicability to large groups of elements has not played a significant role.
3. Considerable differences exist at the scientific levels of their development and realization.

The short review of 1990 (104) considers 17 prospective isotope separation methods. Only nine of them are really used and 15 are being studied and developed in application to one element only. Table 21 shows the convolution of (1), which reflects the following main tendency: aspiration to decrease the energy consumption has resulted in special attention given to reversible (chemical) and partly reversible (centrifuge) methods. Gradually, more and more elements have been involved, and this fact becomes apparent from the development of the two uranium enrichment processes based on the chemical exchange technique (100,101). The intention to use large laser isotope effects for the majority of elements has the same implication. In cases when small amounts of isotopes are needed, laser separation tends to gradually substitute electromagnetic isotope separation.

Laser methods have not hitherto been described in detail since they are not yet well developed. Our estimation of prospects of chemical methods is based

Table 21. Estimation of Isotope Separation Methods by Number of Elements for Which Their Application Is Considered as Prospective (104)

Type	Irreversible			Intermediate		Reversible	
Methods	EMIS	GBD	LIS	GCNT	TD	CHEX	DIST
Production	48	1	0	3	9	8	6
R & D	0	0	60	14	1	15	6

EMIS, electromagnetic isotope separation; GBD, gaseous barrier diffusion; LIS, atomic vapor and molecular laser isotope separation; GENT, gas centrifuge; TD, gaseous and liquid thermal diffusion; CHEX, chemical exchange, ion exchange, chromatographic separation; DIST, distillation.

on their comparison with industrial processes such as gas barrier diffusion and gas centrifugation. Like chemical exchange, both of them are characterized by low separation factors $\alpha \cong 1$. Hence, the elementary act of isotope separation needs multiplication by means of big cascades. Using big cascades always requires large energy consumption (EC). The nearer to unity the separation factor is, the larger this consumption. For this reason, enrichment factors $\varepsilon = \alpha - 1 \cong \ln \alpha$ and characteristics of EC provide the criteria for evaluation of methods. The former is defined by α value and by a specific feature of the elementary separation act.

Understanding the fundamental difference between a reversible chemical method and completely (diffusion) or partly irreversible (centrifuge) methods requires the answer to the following question. *For what purpose is the main part of the energy consumed?* In reversible processes, the energy is mainly spent for the flow reversal. In irreversible processes, the energy seems to be mostly consumed to accomplish each elementary separation act. Therefore, the theory of cascades has given two essentially different solutions of reversible and irreversible processes. Rectangular cascades account for the former and "ideal cascades" of some particular configuration with a minimized sum of EC of all the separation units for the latter.

In our comparison of chemical exchange, gas diffusion, and centrifugation, we proceed from numerous minor parameters, which show specific character in different processes. To simplify the analysis, we will consider only the EC in both reversion forms in reversible processes and only the EC proportional to the number of separation units in irreversible processes. For the comparison to be as correct as possible, we will additionally introduce the following approximations: let us assume that EC for initial concentration of the product plays the prevalent role. Rather arbitrarily, let us choose the degree of the initial product (P) concentration to be = 5 and the degree of waste (W) extraction to be $\Gamma = 0.5$ with $Q_p = 0.555$ corresponding to this one. With $Q_p = 3$ or 10 and $\Gamma = 0.6$ or 0.7, the computer simulation has shown a small influence on the results.

We did not consider the extraction part of reversible cascade processes and the flow reduction for them, because both made no significant contribution in the EC for flow reversal. We assume that the initial concentration of the purpose isotope X_0 is very small, so that $X_W < X_0 < X_p << 1$. Therefore the degree of separation for initial concentration and extraction have the following forms: $Q_p = X_p/X_0$; $Q_W = X_W/X_0$. Two structurally very similar equations for EC can be written as follows (105,106):

Ideal cascades, irreversible processes:

$$E_{irrev} = \frac{1+\varepsilon}{\varepsilon_2} C_{irrev}\left(\ln Q_p + \frac{W}{P}\ln Q_W\right) \tag{52}$$

Rectangular cascades, reversible processes:

$$E_{revers} = \frac{1}{\varepsilon} C_{revers}(Q_p - 1) \tag{53}$$

The typical constants C_{irrev} and C_{revers} reflect the specifics of the isotope separation process and its current technological level. For gas barrier diffusion, gas centrifugation and chemical exchange, the values C-GBD, C-GCNT, and C-CHEX may be found in the literature. Table 21 shows the data adapted from Bigeleisen et al. (99,100). By using these results, it appears possible to obtain a numerical evaluation of their intervals. These numerical evaluations are appropriate for the construction of the dependence E vs. lgε for all three processes under comparison (see Table 22 and Fig. 22).

The wide and tight-shaded stripes in Fig. 22 show possible intervals of the specific coefficients C_{revers} and $C_{irrevers}$. As seen, GBD, GCNT, and CHEX show different values of ln α for the same energy consumption.

The tight stripes for centrifuges show differences in C_{centr} obtained from the diverse information sources. Another situation is observed for chemical methods.

Table 22. Comparison of Different Isotope Separation Methods

Method	Working Phases	Number of Elements for which Method is Prospective	Energy Consumption per Unit of Work of Separation, kWh/mol	Productivity	Substance Delay in Unit Element
GBD	molecular gas	>1	570	high	medium
GCNT	molecular gas	>16	12–24	medium	low
LIS	atomic vapor	>11	25–5	medium	low
	molecular gas	>45	25–35	medium	low
CHEX	gas, liquid, ion exchangers	≈50	10–90	high	low or medium

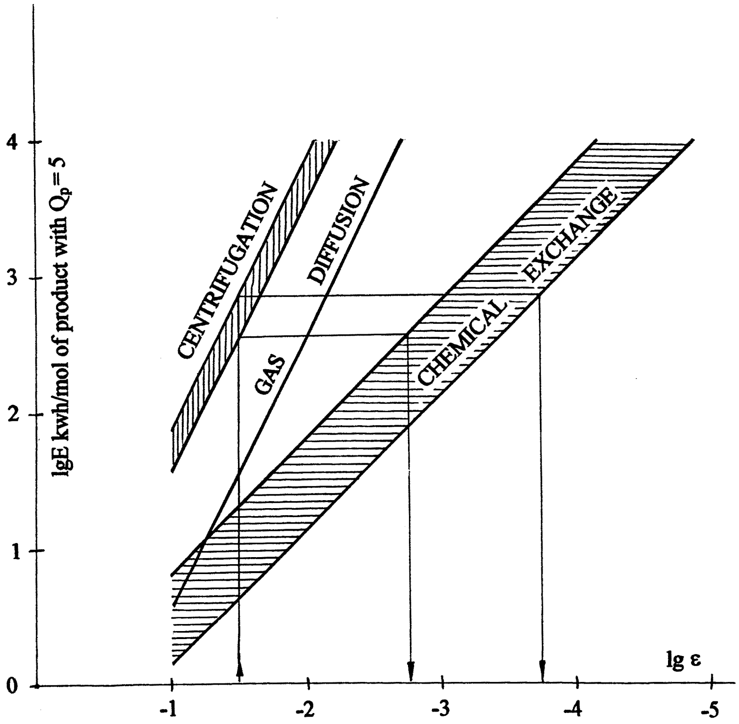

Figure 22. Relation between energy consumption and ε values for different methods of isotope separation at general separation factor $Qp = 5$ and degree of extraction $T = 0.5$

Chemical exchange is a reversible method and specific constants C_{chem} give small-scale production expenses acceptable at the moment. Only in Japan and France, the chemical exchange uranium enrichment processes are successfully applied, which conforms the estimation of C_{chem} to economic sense. It seems interesting that the EC in ACEP is half as much compared with the CHEMEX-process because of the regeneration of the chemical reducing agent, Ti(III), used for flow reversal. Table 23 shows EC data for several chemical isotope separation processes. The EC values of processes 1 and 2 are the highest, although they can produce other valuable products besides isotopes. For example, process 1 may be included in the production technology of NH_4NO_3, whereas process 2 may be used to manufacture highly pure NO and H_2SO_4. Therefore, process 3 with one-electron electrochemical flow reversal reaction may be regarded as a conditional upper limit of wide stripe for chemical exchange. This limit can probably be decreased. The EC in processes 4 and 5, approximating the energy (heat) required

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Table 23. Energy Consumption Required for Flow Reversal per 1 mol of Substance Flow, kWh

Type of Flow (Phase) Reversal	Energy Equivalent for Flow Reversal, kWh Per Mole of Substance Flow
Chemical	
1. $NH^{+}_{4\,(solv)} + OH^{-}_{(solv)} \rightarrow NH_{3(gas)} + H_2O_{(liq)}$ $NH_{3(gas)} + H^{+}_{(solv)} \rightarrow NH_4{}^{+}{}_{(solv)}$	0.9
2. $2HNO_{3(solv)} + 3SO_{2(gas)} + 2H_2O_{(liq)}$ $\rightarrow 2NO_{(gas)} + 3H_2SO_{4(solv)}$	2.4
Electrochemical	
3. $Li^{+}_{(solv)} + e + Hg_{(liq)} \rightarrow Li(Hg)_{(liq)}$	0.17
Thermal	
4. $BF_3.anisole_{(liq)} \xrightarrow{heating} BF_{3(gas)} + anisole_{(gas)}$	0.036
5. $2NO_{(gas)} \xrightarrow{cooling} N_2O_{2(liq)}$	0.04

for flow reversal by rectification, can provide the lower limit. An additional decrease of EC in this is usually achieved through heat recuperation.

Comparison of Separation Factors for Physical and Chemical Methods of Isotope Separation

Figure 23 shows the dependence of separation factors $\ln \alpha \cong \varepsilon$ ($\Delta m = 1$) on elements atomic masses in bilogarithmical coordinates for three methods: centrifugation, gas diffusion, and chemical exchange (99,105,106). The first two methods are used for industrial isotope production and may be regarded as realistic standards for comparison. The α values for gas diffusion are calculated as square roots from relations of molecular masses of the isotope form of volatile halogenides and hydrides. The values of α for centrifugation are found by a peripheral speed selected to be 400 and 500 meters per second. Two groups of results describing chemical exchange are shown in Fig. 23. The statistical estimation of separation factors, $\ln \alpha$, for the $\gamma \in [0.2; 0.4]$ interval with the corresponding probability of 0.157 (see Table 18, set 1) is shown as an undergoing periodic change stripe. In addition, the largest experimental $\ln \alpha$ values for studied elements are designated as points by $\Delta m = 1$.

As shown in Fig. 22, the same amount of EC is required to obtain one mole of product with $Q_p = 5$ by using the following $\varepsilon \cong \ln \alpha$ values of different separation methods:

1. centrifugation, $\ln \alpha = 0.033$;
2. chemical exchange, electrochemical flow reversal, $\ln \alpha = 0.0017$;
3. chemical exchange, thermoreflux (thermal flow reversal), $\ln \alpha = 0.00017$.

If we translate these results on Fig. 23, we will see that this range (interval) of $\ln \alpha$ contains all the elements with atomic masses over 100 and, consequently, uranium. Not many elements can be found below this range (interval). Taking into

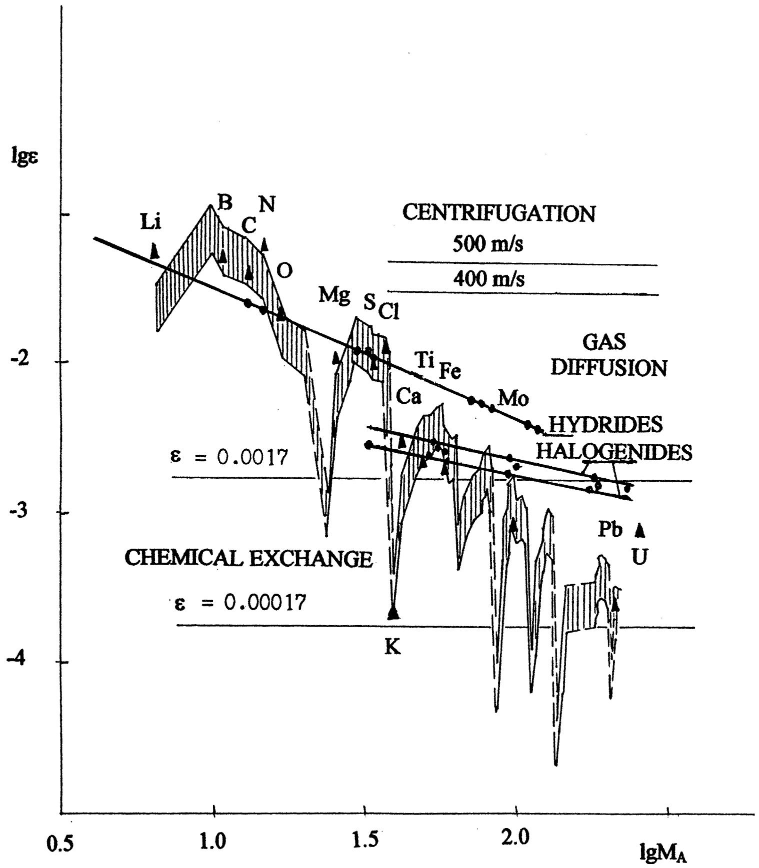

Figure 23. Relation between elementary separation factor ε and atomic mass MA for different isotope separation methods.

consideration the isotope separation factors α for uranium, reported by French and Japanese researchers, the optimistic result for our analysis of the general prospects for chemical methods may be considered as well confirmed and sufficiently careful.

APPENDIX: RELATIONS OF QUANTUM- STATISTICAL THEORY OF EQUILIBRIUM ISOTOPE EFFECTS

Refined Quantum-Statistical Relations

The “harmonic oscillator-rigid rotator” approximation ensures sufficient accuracy of the RPFR calculation for the majority of practical problems in the thermodynamics of isotope exchange. Here we will consider the refinements and corrections that follow from improved models and are necessary in certain special situations. At the same time, such treatment should indicate the limits of the accuracy of approximations used.

Real molecules are anharmonic oscillators and non-rigid rotators. Different vibrations of polyatomic molecules are not independent. The same applies to the vibrational and rotational motions of the molecule as a whole. Furthermore, the energies of states with zero vibrational quantum numbers differ from the quantity $hc\omega_i/2$. Finally, account must be taken of the effects of the internal rotation of groups in the molecule and (at low temperatures) of the difference between the rotational partition functions and their classical values (quantization effects). The influence of these factors on the RPFR decreases approximately in the following sequence.

1. anharmonicity and interaction between the vibrations;
2. quantum effects of the rotation;
3. hindered internal rotation;
4. non-rigidity of the rotators (centrifugal stretching);
5. interaction between rotation and vibrations.

All these corrections are introduced in the form of the corresponding multipliers of the quantity β_{harm} in terms of the “harmonic oscillator-rigid rotator” approximation:

$$\beta_{exact} = \beta_{harm} C_1 C_2 C_3 C_4 C_5 \qquad (54)$$

The correction for anharmonicity C_1 includes simultaneously the effect of the deviation of the shape of the potential energy surfaces of the molecules from the parabolic form and the interaction of different normal vibrations (9,107,108).

The vibrational energy levels of po1yatomic molecules are usually specified by the following expression (12):

$$E_{vibr} = \sum_i hc\omega_i\left(v_i + \frac{1}{2}\right) + \sum_i hcx_{ii}\left(v_i + \frac{1}{2}\right)^2 + \sum_{i<j} hcx_{ij}\left(v_i + \frac{1}{2}\right)\left(v_j + \frac{1}{2}\right) + \ldots \qquad (55)$$

where v_i and v_j are the vibrational quantum numbers of the vibrations i and j and x_{ii} and x_{ij} are the anharmonicity constants. Since the forms of the potential energy surfaces have been little studied, we will confine ourselves to the first terms of the expansion of E_{vibr} in Eq. (55). In terms of this approximation, the correction for anharmonicity is as follows (107,108):

$$C_1 = \exp\left[\frac{hc}{4kT}\sum(x'_{ij} - x_{ij})d_i d_j\right]\left\{1 + \frac{hc}{kT}\sum d_i(d_i + 1) \times \left[\frac{x'_{ii}\exp(u'_i)}{(\exp(u'_i) - 1)^2} - \frac{x_{ii}\exp(u_i)}{(\exp(u_i) = 1)^2}\right] + \frac{hc}{kT}\sum d_i d_j \times \left[\frac{x'_{ij}(\exp(u'_i) + \exp(u'_j))}{(\exp(u'_i) - 1)(\exp(u'_j) - 1)} - \frac{x_{ij}(\exp(u_i) + \exp(u_j))}{(\exp(u_i) - 1)(\exp(u_j) - 1)}\right]\right\} \qquad (56)$$

The first term in this expression, which reflects the influence of anharmonicity on the zero-point energy, makes the main contribution. The expression in braces corresponds to the thermal excitation of the vibrational levels and at the usual temperatures hardly differs from unity. Taking this factor into account, the correction for anharmonicity can be rewritten in the following form:

$$C_1 = \exp\left[\frac{hc}{4kT}\sum(x'_{ij} - x_{ij})d_i d_j\right] \qquad (57)$$

According to the Darling-Dennison rule (109), we have for fully substituted isotopic forms

$$x'_{ij}/x_{ij} = \omega'_i\,\omega'_j/\omega_i\,\omega_j \qquad (58)$$

Equation (57) transforms into (108)

$$C_1 = \exp\left[\frac{hc}{4kT}\sum_{i<j} d_i d_j\left(\frac{\Delta\omega_i}{\omega_i} + \frac{\Delta\omega_j}{\omega_j}\right)\right], \qquad \Delta\omega_i = \omega'_i - \omega_i \qquad (59)$$

Wolfsberg (110–112) showed that the correction to zero-point energy for anharmonicity, expressed by equations of type (55), suffers from a significant inaccuracy, because it does not take into account the component of the zero-point energy that is independent of the vibrational quantum numbers. A more accurate expression for the vibrational levels should include the constant terms G_0, which converts Eq. (57) into the following expression:

$$C_1 = \exp \frac{hc}{kT}\left[(G_0' - G_0) = \sum_{i<j} \frac{d_i d_j}{4}(x_{ij}' - x_{ij})\right] \tag{60}$$

Allowance for the constant terms G_0 introduces a contribution to the correction for anharmonicity, which is comparable to the correction itself (112,113). Using the Morse potential function, Ishida (114) expanded the analysis of the correction for anharmonicity and tabulated the increments in partition functions corresponding to it as functions of u and x.

The presence of a single hindered rotation in a molecule implies a decrease of the number of vibrational degrees of freedom by unity, a decrease of the number of cofactors in the expression for the partition function ratio, and hence, an appreciable decrease of the ratio. The vanishing cofactor is replaced by the ratio of the internal rotation partition functions, which in the general case differs very little from unity (115). This correction (C_2) amounts to several tenths of a percent of $\ln \beta$ at the usual temperatures for the protium-deuterium substitution and falls to hundredths of a percent for heavier elements.

The correction C_3 due to the quantization of the rotational motion (9,10,116) is significant in the protium-deuterium substitution at low temperatures, whereas in other cases it is insignificant. The corrections for the centrifugal stretching of the bonds in the molecules (9,10,117) (C_4) and for the interaction of vibrational and rotational motions (9,118,119) (C_5) are always negligible at temperatures above 100 K.

In studies (120,121) the accuracy of the initial Born-Oppenheimer approximation itself was analyzed in relation to diatomic molecules. A correction for its inaccuracy can be introduced by means of a correction coefficient C_6. In the examples examined (121), the contribution of this correction to $\ln \beta$ does not exceed 0.1%.

Approximate Relations

The quite satisfactory accuracy of the “rigid rotator-harmonic oscillator” approximation, the low availability of more detailed information about the energy states of the molecules, and the applicability of the geometrical mean rule make Eq. (11) the main mathematical relation of the thermodynamics of isotope effects.

Despite its simplicity, its practical application is quite laborious. A number of attempts have been made to reduce it to forms more suitable for calculations.

The method of Bigeleisen and Mayer (52) is widely used for this purpose. They expressed RPFR as the following function of reduced frequencies and their isotopic shifts:

$$\begin{aligned} &\beta = 1 + \sum G(u_i)\Delta u_i; \quad \Delta u_i = u_i - u_i'; \\ &G(u_i) = 1/2 - 1\big/u_i + 1\big/(\exp(u_i) - 1). \end{aligned} \tag{61}$$

Equation (61) significantly reduces the values of ln β; the relative error of the calculation reaches 15–17%. Despite this, Eq. (61) is frequently employed as a simple means to estimate the contributions of different vibrational frequencies to RPFR and as a means of interpreting the different overall variations of RPFR due to the absolute values of u_i and Δu_i.

Another expansion of β, in terms of functions of u_i and Δu_i, is sufficiently accurate for computational purposes (117)

$$\begin{aligned} &\ln\beta = \sum G(u_i)\left[1 + \frac{S(u_i)}{2G(u_i)}\left(\frac{\Delta u_i}{u_i}\right) + \frac{C(u_i) - 2S(u_i)}{6G(u_i)}\left(\frac{\Delta u_i}{u_i}\right)^2\right]\Delta u_i, \\ &G(u_i) = 1/2 - 1\big/u_i + 1\big/(\exp(u_i) - 1), \\ &S(u_i) = 1\big/u_i - u_i \exp(u_i)/(\exp(u_i) - 1)^2; \\ &C(u_i) = 2u_i^2 \exp(2u_i)/\,(\exp(u_i) - 1)^3 - u_i\,(u_i + 2)\exp(u_i)/(\exp(u_i) - 1)^2. \end{aligned} \tag{62}$$

The functions $G(u_i)$, $S(u_i)$, and $C(u_i)$, as well as their derivatives with respect to u, have been tabulated using small steps in u (52,122).

As mentioned in the Introduction, the theory of chemical isotope effects has two complementary aspects: the use of isotope effects as a research technique and the consequent problem of the analysis and interpretation of the measured effects, and the prediction of effects in order to select chemical systems for the separation of isotopes or to devise a research technique. Both problems involve the same mathematical procedures and differ solely in their formulation and the preference given to different methods of solution.

Depending on the means used for the analysis and prediction, it is possible to distinguish three levels in these problems:

1. the level of the rigorous theory of the vibrations of polyatomic molecules;
2. the level of semiempirical relations using the correlation between the isotope effects with separate exact or approximate characteristics of the molecular force field; and

3. the phenomenological level, operating with concepts such as the degree of oxidation of the element, the type of geometrical configuration of the compound or its fragment, and the type of donor atom or ligand attached to the element.

The first level is naturally of key importance, since a rigorous treatment of α and β values in terms of the theory of vibrations makes it possible to isolate the most important determining groups of molecular characteristics, which can then be expressed approximately in terms of the other two levels. Nevertheless, the first level is used nowadays solely for the interpretation of isotope effects (in consequence of the complexity of the mathematical relations for this level and the existence of simpler but accurate procedures, which make it possible to calculate the isotope effect directly); it is therefore the level of the rigorous interpretation of isotope effects.

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