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Thermodynamics of Isotope Exchange Reactions

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The present state of the theory of the equilibrium chemical isotope effect is examined and the methods for the approximate and exact calculation of the partition functions of the isotopic forms of polyatomic molecules are analysed. Also analysed is the possibility of employing the chemical isotope effect for the interpretation of the force fields of molecules of transition complexes; relations between the isotope effects associated with the stepwise substitution of isotopes, coupled isotope effects, etc, are considered.
The relations between the isotope effects and the structural and general chemical phenomenological characteristics of compounds are discussed and a systematic treatment of chemical isotope effects together with the methods for the statistical prediction of the magnitude of these effects are considered.
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I. INTRODUCTION

For a long time the interest in chemical isotope effects was concentrated on the possibility of using them for the separation of the isotopes of light elements. During the last 10–12 years, much more attention has been devoted to them but largely for other reasons. It was found that the measurement of isotope effects is useful for research in many fields of chemistry, biochemistry, and geochemistry. For example, the kinetic hydrogen and carbon isotope effects have been used successfully to study the mechanisms and activated complexes of organic reactions; the hydrogen, carbon, and sulphur effects have been employed to predict the presence of petroleum and natural gas in geometrical regions, the oxygen and hydrogen effects have been used in paleogeothermometry, and the effects of biogenic elements have found applications in the study of the mechanisms of cell metabolism.

The value of isotope effects as sources of information in research is due to one specific feature of their theory. Statistical thermodynamics reveals a relation, of rare simplicity, between the isotope effects and the characteristics of intramolecular force fields. This feature makes it possible to infer intramolecular characteristics directly from changes in macroscopic quantities—the isotope concentrations, but not conversely, which is in general characteristic of the applications of the molecular-statistical theory. Hence follows the possibility of securing information about the force fields not only of simple stable molecules, which can be studied by other

methods, but also of investigating short-lived compounds and fragments of large molecules, which play an important role in chemical, biochemical, and geochemical systems and mechanisms.

The general, extensive literature on chemical isotope effects has been reflected systematically in frequently published reviews, specialised compilations, and monographs. Being unable to analyse the state of the problem in fields adjoining chemistry, we shall indicate the reviews and monographs dealing with various aspects of the applications of isotope effects in biochemistry[1-5] and geochemistry[6-13]. Compilations and review articles have been devoted to chemical isotope exchange reactions used for the separation of stable isotopes of light, medium, and heavy elements (ranging from hydrogen to uranium inclusive)[14-20]. The results of the study of isotope effects[18-22] and their applications to the study of molecular structures[14-24], reaction kinetics and mechanisms[21,24-29], phase exchange[14,24,30], solutions, and the behaviour of solvents[14,24,30] are reflected in the reviews and monographs quoted above.

However despite their relatively large number, the aim of the review articles published in the last decade was to inform the reader about fairly narrow questions and they consisted too often of handbooks and bibliographic compilations. Owing to their specialist characteristics, both the reviews and monographs are concerned either only with the main features or only with special features of the general theory, so that a general picture of the scope of the theory is not built up.

Nevertheless, in many of the fields indicated, the interpretation of chemical isotope effects is invariably based on the thermodynamics of isotope exchange reactions. This is because the methods for the analysis of kinetic and equilibrium isotope effects are fundamentally the same and are based on the general theoretical apparatus of statistical thermodynamics and the theory of the vibrations of polyatomic molecules. Significant new theoretical results, which make it an effective weapon in the hands of research chemists, biochemists, and geochemists, have not as yet been described in one publication. Nor has any attempt been made to carry out a combined analysis of isotope effects which would reflect their relation to the chemical nature and specific features of the elements. The aim of the present review is to fill these gaps to some extent.

II. THERMODYNAMICS OF ISOTOPE EXCHANGE REACTIONS

1. General Theory

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

Following the procedure of Varshavskii and Vaisberg[31], we shall consider the equilibrium in the isotope exchange of an element X between two compounds AX_n and BX_m. The first contains n atoms X capable of isotope substitution in the given equivalent positions. The remainder of the molecule of A may contain exchangeable atoms of the element X, but in other equivalent positions, which are not taken into account in the present treatment. Similarly in the molecule BX_m account is taken only of the exchange of m equivalent atoms of the element X. 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:

$$AX_{n-i+1}X'_{i-1} + BX_{m-j}X'_j \rightleftarrows AX_{n-i} + X'_i + BX_{m-j+1}X'_{j-1}, \quad (1)$$

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:

$$K_{ij} = \frac{[AX_{n-i}X_i]\ [BX_{m-j+1}X'_{j-1}]}{[AX_{n-i+j}X'_{i-1}]\ [BX_{m-j}X_j]}. \quad (2)$$

In all there are nm independent stages in the reaction under consideration with equilibrium constants of the type defined by Eqn.(2). Their sequence, from the first to the last, corresponds to the overall exchange reaction between the fully substituted isotopic forms:

$$mAX_n + nBX_m' \rightleftarrows mAX'_n + nBX_m \quad (3)$$

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

$$K_\Sigma = \prod_{i=1}^{n}\prod_{j=1}^{m} K_{ij}. \quad (4)$$

The real equilibrium includes all nm stages and is characterised by the isotope separation factor α measured experimentally:

$$\alpha = \frac{[X'_{AX_n}]/[X_{AX_n}]}{[X'_{BX_m}]/[X_{BX_m}]}, \quad (5)$$

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_Σ, and α are related to one another and to the symmetry numbers of the isotopic forms of the molecules AX_n and BX_m by the following expressions:

$$K_{ij} = \alpha \frac{\sigma(AX_{n-i+1}X'_{i-1})\,\sigma(BX_{m-j}X'_j)}{\sigma(AX_{n-i}X'_i)\,\sigma(BX_{m-j+1}X'_{j-1})}, \quad (6)$$

$$K_\Sigma = \alpha^{nm}. \quad (7)$$

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

$$K_{ij} = \frac{Q'_{AX_n}/Q_{AX_n}}{Q'_{BX_m}/Q_{BX_m}}, \quad (8)$$

where the prime refers to forms AX_n and BX_m containing the larger number of atoms of the X′ isotope.

In the ideal gas approximation, usually employed 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 molecular spectra and molecular constants without taking into account the interactions of the molecules. A further simplification is achieved by employing the Born–Oppenheimer approximation concerning the subdivision of the internal energy of molecules into the electronic, spin-nuclear, vibrational, rotational, and translational components[32]. For the majority of isotope equilibria, this approximation is also the only one possible, since more accurate calculations require much more detailed information about the molecular force field.

In the calculation of thermodynamic isotope effects there is no necessity to calculate 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 range 0–2000 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 excitation is accompanied by a sharp change in the vibrational characteristics and a very significant change in the rotational characteristics of the molecules[33,34]. An analogous situation obtains also 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[35].

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 translational partition functions or, in the refined version, to the calculation of the vibrational-rotational and translational 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[36,37]. 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 employs 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 three corrections enumerated above, and makes it possible to resolve completely the rotational and vibrational partition functions[38,39].

The calculation of the thermodynamic isotope effects does not require the separate determination of 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 (RPFIF) of the given molecule.

In terms of the "rigid rotator–harmonic oscillator" approximation, the RPFIF, also denoted by f, can be formulated as follows[27,40]:

$$f = \frac{\sigma}{\sigma'}\left(\frac{M'}{M}\right)^{3/2}\left(\frac{I'_A I'_B I'_C}{I_A I_B I_C}\right)^{1/2}\exp\left[\frac{hc}{2kT}\left(\sum_i d_i\omega_i - \sum_i d'_i\omega'_i\right)\right]\frac{\prod_i [1-\exp(\omega_i hc/kT)]^{d_i}}{\prod_i [1-\exp(\omega'_i hc/kT)]^{d'_i}}, \quad (9)$$

where M is the molecular weight, $I_A I_B I_C$ the product of the moments of inertia of the molecule relative to the three (principal) Cartesian axes, ω_i the ith harmonic vibration frequency, and d_i the multiplicity of its degeneracy; the primes refer, as in Eqn.(8), to isotopic forms containing a greater number of atoms of the isotope X′. If the prime is attributed to isotopic forms of molecules containing a greater number of heavy isotope atoms involved in exchange while the symbols without prime are assigned to forms with a greater number of light isotope atoms, then Eqn.(9) leads to a convenient specific relation: $f\sigma'/\sigma \geq 1$.

Eqn.(9) can be significantly simplified by the application of the Teller–Redlich theorem[41,42], which relates the moments of inertia, the vibration frequencies, the molecular weights M and M', and the masses of the isotopes m and m' in the isotopic forms, which differ in the isotopes of a single element:

$$\frac{I'_A I'_B I'_C}{I_A I_B I_C}\left(\frac{M'}{M}\right)\left(\frac{m}{m'}\right)^{3n}\prod_i\left(\frac{\omega}{\omega'}\right)^2 = 1. \quad (10)$$

Substitution of Eqn.(10) in Eqn.(9) leads to the following relation:

$$f = \frac{\sigma}{\sigma'}\left(\frac{m'}{m}\right)^{3n/2}\frac{\prod_i \{\omega'_i \exp(-\omega'_i hc/2kT)[1-\exp(-\omega_i hc/2kT]^{-1}\}^{d'_i}}{\prod_i \{\omega_i \exp(-\omega_i hc/2kT)[1-\exp(-\omega_i hc/2kT]^{-1}\}^{d_i}}. \quad (11)$$

The multiplier $(m'/m)^{3n/2}$, determined by the masses of the pair of isotopes under consideration, enters into all the RPFIF referring to this pair of isotopes; in the calculation of isotope effects it always cancels out and is therefore omitted. In most studies the ratio σ/σ', which is equal to RPFIF when all isotope distributions are equally probable, is transferred to the left-hand side of Eqn.(11). The so-called reduced frequencies $\omega_i hc/kT$ are in general designated by u_i. When account is taken of these conventional procedures and notations, Eqn.(11) can be put in the form

$$\left(\frac{\sigma'}{\sigma}\right)f = \frac{\prod_i \{u'_i \exp(-u'_i/2)[1-\exp(-u'_i)]^{-1}\}^{d'_i}}{\prod_i \{u_i \exp(-u_i/2)[1-\exp(-u_i)]^{-1}\}^{d_i}} = \frac{\prod_i [\mathrm{sh}(u_i/2)/u_i]^{d_i}}{\prod_i [\mathrm{sh}(u'_i/2)/u'_i]^{d'_i}}. \quad (12)$$

The difficulty of the determination of the quantities $(\sigma'/\sigma)f$ by Eqn.(12) 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. With decrease of the symmetry of the given form, the degrees of degeneracy diminish and the orders of the submatrices of the secular equations of vibrational motion increase. The latter implies an increase of the number of non-identical cofactors in the products in the numerator and denominator of Eqn.(12). In the limit one of the products can have $3N-6$ cofactors, but the main difficulties in the application of Eqn.(12) do not depend on the fact that the number of cofactors can be large. A large number of non-identical frequencies implies 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.

Evidently the number of different isotopic forms $AX_{n-i}X'_i$ of the compound AX_n is $n+1$; in order to characterise fully the thermodynamic non-equivalence of these forms, it is necessary and sufficient to calculate n independent values of the RPFIF.

For equilibrium between the molecules of AX_n and BX_m, the calculation of the isotope effects requires the determination of $n+m$ values of the RPFIF, and, as just shown, each of these determinations can be very complicated. A successive radical simplification of the calculation of isotope effects is achieved by replacing the RPFIF for all possible pair combinations of the isotopic forms for any molecule by the simplest functions of a single RPFIF referring to the fully substituted forms AX_n and AX'_n. This replacement not only greatly reduces the number of RPFIF required for the consideration of the equilibrium (two instead of $n+m$), but also simplifies to the maximum extent the very calculation of these two necessary values of the RPFIF, 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[45,46] and Decius and Wilson[47] and subsequently modified by Broderson[48], follow from the theory of the vibrations of polyatomic molecules[42–44]. These rules can be represented by the formula

$$\sum_i^{3N-6}\omega_i^{2p}(AX_{n-j}X'_j) - \sum_i^{3N-6}\omega_i^{2p}(AX_{j+k}X'_{n-(j+k)}) = \sum_i^{3N-6}\omega_i^{2p}(AX_{n-l}X'_l) - \sum_i^{3N-6}\omega_i^{2p}(AX_{n-(l+k)}X'_{l+k}), \quad (13)$$

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

Using Eqn.(13) with $p = 1,2$, Bigeleisen[17,49] 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", which assumes the general form

$$\frac{1}{j-k}\ln\left[\frac{\sigma'}{\sigma}f(AX_{n-j}X'_j/AX_{n-k}X'_k)\right] = \text{const}. \quad (14)$$

holds with an adequate degree of approximation. This rule, first discovered empirically in an early study by Urey[40], has been frequently subjected to numerical tests[15,17,49,50], which invariably confirmed its adequate accuracy [the deviation from the rule does not exceed 1.0% of $\ln(f\sigma'/\sigma)$].

When the isotopic equilibrium of a specific pair of isotopes is considered, the geometrical mean rule makes it possible to characterise the entire set of isotopic homologues by a single value of the RPFIF, which establishes an unambiguous (isomorphous) correspondence between the chemical compound (molecule, ion) and the characteristics of its possibilities as regards isotope separation. Varshavskii and Vaisberg[31] suggested that the concept of the β-factor, which is related to f, be used for this purpose. If the RPFIF refers to the fully substituted forms AX_n and AX'_n containing n equivalent atoms of X capable of isotope substitution, then, regardless of the complexity of the compounds and the value of n, the following very simple relation holds:

$$\ln\beta = \frac{1}{n}\ln f\,(AX_n/AX'_n). \tag{15}$$

The advantage of the concept of the β-factor over the RPFIF thus consists in the fact that it defines unambiguously the degree of thermodynamic non-equivalence of two isotopes in the given molecule, while the RPFIF 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 form

$$\ln\beta = \frac{1}{n}\sum_i d_i \ln\left\{\frac{u'_i \exp(-u'_i/2)\,[1-\exp(-u'_i/2)]^{-1}}{u_i \exp(-u_i/2)\,[1-\exp(-u_i/2)]^{-1}}\right\} \tag{16}$$

or

$$\ln\beta = \frac{1}{n}\sum d_i \ln\left[\frac{\mathrm{sh}\,(u_i/2)}{\mathrm{sh}\,(u'_i/2)}\Big/\frac{u_i}{u'_i}\right] \tag{17}$$

Eqn.(16) 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 the conditions governing its application are not made in many investigations.

Brodskii[51] and Varshavskii and Vaisberg showed in the general case[31] that, when account is taken of the equal probabilities of the distributions of isotopes between all the isotopic forms of substances AX_n and BX_m, the isotope separation factor α, corresponding to the equilibrium in the entire set of type (2) reactions, is given by the very simple equation

$$\alpha = \beta_{AX_n}/\beta_{BX_m}. \tag{18}$$

The simplicity of Eqn.(18) constitutes yet another piece of evidence demonstrating the superiority of the concept of the β-factor compared with that of RPFIF.

In view of the difference in the significance of these concepts, we thought it essential to confine ourselves to only one of them in the present review, namely the β-factor. Nevertheless, in order to simplify and facilitate the exposition, both terms are used in the text below. Unless otherwise stated, here the significance of the term "RPFIF" is always identical to that of the term "β-factor".

2. Refined Quantum-Statistical Relations

The "harmonic oscillator–rigid rotator" approximation, to which Eqns.(12), (16), and (17) correspond, ensures an accuracy of the calculation of the RPFIF sufficient for the majority of practical problems in the thermodynamics of isotope exchange. Here we shall consider the refinements and corrections which follow from improved models and which are necessary in certain special situations. At the same time, such treatment should indicate the limits of the accuracy of Eqn.(12), (16), and (17).

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 (quantisation effects). The influence of these factors on the RPFIF 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} found by Eqns.(12), (16), or (17) in terms of the "harmonic oscillator–rigid rotator" approximation:

$$\beta_{exact} = \beta_{harm}\,C_1C_2C_3C_4C_5. \tag{19}$$

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[36,52,53]. The vibrational energy levels of polyatomic molecules are usually specified by the expression[39]

$$E_{vibr} = \sum_i hc\omega_i\left(v_i+\frac{1}{2}\right) + \sum_i hcx_{ii}\left(v_i+\frac{1}{2}\right)^2 + \sum_{i<j} hcx_{ij}\left(v_i+\frac{1}{2}\right)\left(v_j+\frac{1}{2}\right) + \ldots, \tag{20}$$

in which v_i and v_j are the vibrational quantum numbers of the vibrations i and j and x_{ii} and x_{ij} are anharmonicity constants. Since the forms of the potential energy surfaces have been little studied, we shall confine ourselves to the first terms of the expansion of E_{vibr} in Eqn.(20). In terms of this approximation, the correction for anharmonicity is[52,53]

$$C_1 = \exp\left[\frac{hc}{4kT}\sum (x'_{il}-x_{ij})\,d_id_j\right]\cdot\left\{1+\frac{hc}{kT}\sum d_i(d_i+1)\times\right. \tag{21}$$
$$\left.\times\left[\frac{x'_{ii}\cdot e^{u'_i}}{(e^{u'_i}-1)^2}-\frac{x_{ii}e^{u_i}}{(e^{u_i}-1)^2}\right]+\frac{hc}{kT}\sum d_id_j\left[\frac{x'_{ij}(e^{u_i}+e^{u_j})}{(e^{u'_i}-1)(e^{u'_j}-1)}-\frac{x_{ij}(e^{u_i}+e^{u_j})}{(e^{u_i}-1)(e^{u'_j}-1)}\right]\right\}$$

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 in relation to Eqns.(16) and (17) is expressed thus:

$$C_1 = \exp\left[\frac{hc}{4kT}\sum d_id_j\,(x_{ij}-x_{ij})\right]. \tag{22}$$

According to the Darling–Dennison rule[54], we have for fully substituted isotopic forms

$$x_{ij}'/x_{ij} = \omega_i'\omega_j'/\omega_i\omega_j. \tag{23}$$

Eqn.(22) transforms into[53]

$$C_1 = \exp\left[\frac{hc}{4kT}\sum_{i<j} d_id_j\left(\frac{\Delta\omega_i}{\omega_i}+\frac{\Delta\omega_j}{\omega_j}\right)\right];\quad \Delta\omega_i = \omega_i'-\omega_i. \tag{24}$$

Wolfsberg[24,55,56] showed that the correction to zero-point energy for anharmonicity, expressed by equations of type (20), suffers from a significant inaccuracy, because it does not take into account the component of the zero-point energy which is independent of the vibrational quantum numbers. A more accurate expression for the vibrational levels should include

the constant terms G_0, which converts Eqn.(22) into the following expression:

$$C_1 = \exp\frac{hc}{kT}\left[(G_0' - G_0) + \sum_{i<j}\frac{d_i d_j}{4}(x_{ij}' - x_{ij})\right]. \qquad (24')$$

Allowance for the constant terms G_0 introduces a contribution to the correction for anharmonicity which is comparable to the correction itself[56,57]. Using the Morse potential function, Ishida[58] 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[59]. This correction (C_2) amounts to several tenths per cent of $\ln\beta$ at the usual temperatures for the protium–deuterium substitution and falls to hundredths per cent for heavier elements.

The correction C_3 due to the quantisation of the rotational motion[36,37,60] is significant in the protium–deuterium substitution at low temperatures, while in other cases it is insignificant. The corrections for the centrifugal stretching of the bonds in the molecules[36,37,61] (C_4) and for the interaction of the vibrational and rotational motions[36,62,63] (C_5) are always negligible at temperatures above 100 K.

In a series of recent studies[64,65] the accuracy of the initial Born–Oppenheimer approximation itself was analysed in relation to diatomic molecules. A correction for its inaccuracy can be introduced into Eqn.(19) by means of a correction coefficient C_6. In the examples examined[65] the contribution of this correction to $\ln\beta$ does not exceed 0.1%.

3. 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 Eqn.(16) the main mathematical relation of the thermodynamics of isotope effects. Despite its simplicity, its practical application is quite laborious. In order to develop computer programs for its calculation, a number of attempts have been made to reduce it to forms more suitable for calculations.

The method of Bigeleisen and Mayer[66] is widely used. They expressed RPFIF as the following function of reduced frequencies and their isotopic shifts:

$$\beta = 1 + \Sigma G(u_i)\Delta u_i; \quad \Delta u_i = u_i - u_i'; \qquad G(u_i) = 1/2 - 1/u_i + 1/(e^{u_i} - 1). \qquad (25)$$

Eqn.(25) significantly reduces the values of $\ln\beta$—the relative error of the calculation reaches 15–17%. Despite this, Eqn.(25) is frequently employed as a simple means of estimating the contributions of different vibrational frequencies to RPFIF and as a means of interpreting the different overall variations of RPFIF 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[61]:

$$\ln\beta = \Sigma G(u_i)\left[1 + \frac{S(u_i)}{2G(u_i)}\cdot\left(\frac{\Delta u_i}{u_i}\right) + \frac{C(u_i) - 2S(u_i)}{6G(u_i)}\left(\frac{\Delta u_i}{u_i}\right)^2\right]\Delta u_i,$$
$$G(u_i) = 1/2 - 1/u_i + 1/(e^{u_i} - 1); \quad S(u_i) = 1/u_i - u_i e^{u_i}/(e^{u_i} - 1)^2; \quad C(u_i) = 2u_i^2 e^{2u_i}/(e^{u_i} - 1)^3 - u_i(u_i + 2)e^{u_i}/(e^{u_i} - 1)^2. \qquad (26)$$

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[66,67].

III. METHODS FOR THE INTERPRETATION OF CHEMICAL ISOTOPE EFFECTS

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 in order 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: the level of the rigorous theory of the vibrations of polyatomic molecules; the level of semiempirical relations using the correlations between the isotope effects with separate exact or approximate characteristics of the molecular force field; 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 the values of α and β 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.

1. Approximate Relations

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 a general estimate of the influence of various factors on $\ln\beta$, is the linear Bigeleisen–Mayer approximation, which is valid at high temperatures[66]:

$$\ln\beta = \frac{1}{24n}\sum_i [u_i^2 - (u_i')^2] = \frac{1}{24n}\left(\frac{h}{kT}\right)^2 \Delta\,\mathrm{Sp}\,(GF), \qquad (27)$$

where $\Delta\mathrm{Sp}(GF)$ is the isotopic increment in the trace of the product of the kinematic coefficients matrix G and the force constants matrix F.

Bearing in mind that the stretching vibration frequencies make the main contribution to $\ln\beta$, Bigeleisen proposed a modification of Eqn.(27) which is suitable in the region of all of the 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[68,69]:

$$\ln\beta = \frac{\gamma_s}{24n}\left(\frac{h}{kT}\right)^2 \Delta\,\mathrm{Sp}\,(GF); \quad \gamma_s = 12G(u_s)/u_s. \qquad (28)$$

Subsequently he described[23] a method whereby one can fit to γ a finite Chebyshev polynomial as a function of u_{max}—the maximum stretching vibration frequency of the molecule. It has been shown[70] that, instead of u_S and u_{max}, it is more desirable to employ the weighted-mean frequency using the isotopic increments in the squares of the frequencies themselves as the weighting factors.

A simpler method has been proposed[71] for the determination of γ from the u_{as} (asymmetric stretching vibration frequencies) and $\Delta Sp(GF)$ whereby an expression can be fitted to $\ln\beta$ with a relative error of ±2% and the necessity to take into account the isotopic shifts of all the frequencies of the molecule is eliminated. The values of γ_{as} have been tabulated[71] as functions of u_{as} and the ratio of the isotope shift Δu to u.

The analytical value of Eqns.(27) and (28) consists in the fact that they reveal the principal intramolecular parameters which determine the values of $\ln\beta$. These are the force constants, geometrical characteristics, and atomic masses in the molecule. Analysis of $\Delta Sp(GF)$ makes it possible to estimate the relative role of each of the three groups of factors and the relative contributions of different components within these groups. In terms of their influence on $\ln\beta$, the above groups can be arranged in the following sequence. The influence of the masses of the atoms capable of undergoing isotope substitution is strongest, that of the force constants is weaker, and that of molecular geometry is weaker still. However, one should bear in mind that this subdivision of molecular parameters into groups is conventional, since the atomic weight of the element and the characteristics of the force fields of the molecules in which it is included depend on one another, and the force constants and molecular geometry are interrelated to an even greater extent.

Analysis of $\Delta Sp(GF)$ revealed a virtually rigorous proportionality of the quantity $\ln\beta$ and hence also $\ln\alpha$ to the square of μ, the reciprocal of the atomic weight of the element involved in isotope substitution, and explained the very rapid decrease of the chemical isotope effects with increasing atomic weight[66]:

$$\Delta Sp\,(GF) = \Delta\mu \sum_{ij} a_{ij} f_{ij} = \frac{\Delta m}{m\,(m+\Delta m)} \sum_{ij} a_{ij} f_{ij} \qquad (29)$$

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.

Eqn.(29) permits a rough estimate of the degree of diminution of the chemical isotope effects on passing from the first element in the Periodic System (hydrogen) to the last—for example, uranium. The quantities $\ln\beta$ and $\ln\alpha$, recalculated in terms of a single increment in the mass difference Δm, should then diminish by a factor of $(2-3)\times 10^4$. Although in reality the scale of the decrease of the effects is somewhat smaller[72] owing to the influence of the second cofactor on the right-hand side of Eqn.(29), this equation imposes very stringent limitations on the overall scope of both chemical isotope separation methods and the applications of isotope effects as the basis of a research technique. The first factor on the right-hand side of Eqn.(29) is in fact the main factor, which determines the limits of the development of these fields at the present time and shows that they are applicable to the set of relatively light polyisotopic elements.

Another corollary of Eqn.(29) is the proportionality of the isotope effects to the difference between the isotopic masses Δm or, more precisely, the direct proportionality of $\ln\beta$ and $\ln\alpha$ to the increment in the reciprocal of the mass of the isotope Δu. This relation is responsible for the large magnitude of the isotope effects and the ease of their measurement and application in those cases where $\Delta m > 1$. At the same time it can be used to test the accuracy of the experimental determination of the effects, when the latter have been measured in relation to three or more isotopes of the given element.

The masses of other elements (incapable of isotopic substitution) do not enter into the expression for $\Delta Sp(GF)$, so that the values of RPFIF and $\ln\alpha$ depend only slightly on them[73]. The influences of the masses of other elements linked to those involved in isotope substitution are appreciable only in hydrides, where protium can be substituted by deuterium and tritium which are twice and three times as heavy.

Table 1. Algebraic expressions for $\Delta Sp(GF)/\Delta\mu$ for certain types of molecules XY_n and $X(YZ)_n$ with linear ligands (YZ) (r and R = XY and YZ distances; α = YXY angle; β = XYZ angle in the YXY plane; θ = XYZ angle in the plane orthogonal to the YXY plane; γ = angle defining the displacement of the XY bond from the plane; f_r = XY bond force constant; f_{rr} and f'_{rr} = force constants for the interaction of the adjacent and opposite XY bonds; f_α = YXY valence angle force constant; $f_{\alpha\alpha}$ and $f'_{\alpha\alpha}$ = force constants for the interaction of adjacent and opposite angles; f_β, $f_{\beta\beta}$, $f'_{\beta\beta}$, etc. are defined analogously).

Type of molecule and its symmetry	$\sum_{ij} a_{ij} f_{ij} = \Delta Sp\,(GF)/\Delta\mu$
$XY_2\,(D_{\infty h})$	$2\,(f_r - f_{rr}) + 8 f_\alpha$
$X(YZ)\,(D_{\infty h})$	$2\,(f_r - f_{rr}) + 8 f_\alpha - 16\sqrt{\frac{R}{r}} f_{\alpha\beta} + 4\left(\frac{R}{r}\right)(f_\beta + f_{\beta\beta})$
$XY_2\,(C_{2v})$	$2\,(f_r + \cos\alpha f_{rr}) - 4\sin\alpha f_{r\alpha} + 2\,(1-\cos\alpha)\,f_\alpha$
$X(YZ)_2\,(C_{2v})$	$2\,(f_r + \cos\alpha f_{rr}) - 4\sin\alpha f_{r\alpha} + 2\,(1-\cos\alpha)\,f_\alpha - 4\sqrt{\frac{R}{r}}(1+\cos\alpha)\times$ $\times f_{\alpha\beta} + 2\left(\frac{R}{r}\right)(f_\beta + f_\theta - \cos\alpha f_{\beta\beta} - f_{\theta\theta})$
$XY_3\,(D_{3h})$	$3\,(f_r - f_{rr}) - 6\sqrt{3}\,(f_{r\alpha} - f'_{r\alpha}) + 9\,(f_\alpha - f_{\alpha\alpha}) + 9 f_\gamma$
$X(YZ)_3\,(D_{3h})$	$3\,(f_r - f_{rr}) - 6\sqrt{3}\,(f_{r\alpha} - f'_{r\alpha}) + 9\,(f_\alpha - f_{\alpha\alpha}) + 9 f_\gamma - 6\sqrt{\frac{R}{r}}\times$ $\times f_{\alpha\beta} + \frac{27}{2}\sqrt{\frac{R}{r}}(f_{\gamma\theta} + f'_{\gamma\theta}) + 3\left(\frac{R}{r}\right)(f_\beta + f_\theta + f_{\beta\beta} - 2 f_{\theta\theta})$
$XY_4\,(D_{4h})$	$4\,(f_r - f'_{rr}) - 16\,(f_{r\alpha} - f'_{r\alpha}) + 8\,(f_\alpha - f'_{\alpha\alpha}) + 8\,(f_\gamma - f_{\gamma\gamma})$
$X(YZ)_4\,(D_{4h})$	$4\,(f_r - f'_{rr}) - 16\,(f_{r\alpha} - f'_{r\alpha}) + 8\,(f_\alpha - f'_{\alpha\alpha}) + 8\,(f_\gamma - f_{\gamma\gamma}) -$ $- 16\sqrt{\frac{R}{r}}(f_{\alpha\beta} + f_{\alpha\theta}) + 4\left(\frac{R}{r}\right)(f_\beta + f_\theta - 2 f_{\beta\beta} - f_{\theta\theta})$
$XY_4\,(T_d)$	$4\,(f_r - f_{rr}) - 16\sqrt{2}\,(f_{r\alpha} - f'_{r\alpha}) + 16\,(f_\alpha - f'_{\alpha\alpha})$
$X(YZ)_4\,(T_d)$	$4\,(f_r - f_{rr}) - 16\sqrt{2}\,(f_{r\alpha} - f'_{r\alpha}) + 16\,(f_\alpha - f'_{\alpha\alpha}) - 16\sqrt{\frac{R}{r}}\times$ $\times (f_{\alpha\beta} + f'_{\alpha\beta}) + 24\sqrt{\frac{R}{r}}(f''_{\alpha\beta} + f'''_{\alpha\beta}) + 8\left(\sqrt{\frac{R}{r}}\right)(f_\beta + f_{\beta\beta} -$ $- 3 f'_{\beta\beta})$
$XY_6\,(O_h)$	$6\,(f_r - f'_{rr}) - 48 f_{r\alpha} + 24\,(f_\alpha + 2 f_{\alpha\alpha} - f'_{\alpha\alpha})$
$X(YZ)_6\,(O_h)$	$6\,(f_r - f'_{rr}) - 48 f_{r\alpha} + 24\,(f_\alpha + 2 f_{\alpha\alpha} - f'_{\alpha\alpha}) - 48\sqrt{\frac{R}{r}}(f_{\alpha\beta} + f'_{\alpha\beta} +$ $+ 2 f''_{\alpha\beta}) + 12\left(\sqrt{\frac{R}{r}}\right)(f_\beta + f_{\beta\beta} - f'_{\beta\beta})$

In terms of the range of its accuracy, Eqn.(29) makes it possible to separate the influence of the isotopic masses from the influence of the force constants and molecular geometry within $\ln\beta$. The role of the last two factors can be seen from Table 1, which presents the algebraic expressions for the sums $\sum_{ij} a_{ij} f_{ij}$ for isotope substitutions of the central atoms X in compounds of the type XY_n and $X(YZ)_n$.[74] 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 surface of the molecules and their effects can be separated only by convention. Nevertheless, inspection of the expressions in Table 1 shows that formally such subdivision can be readily achieved and this makes it possible to separate the influence of bond strength from the influence of molecular geometry. We shall take into account the fact that the force constants for the deformation of bonds f_r, the deformation of valence angles f_α, the interaction of bonds $f_{rr'}$, the interaction of bonds and angles $f_{r\alpha}$, and the interaction of angles with one another $f_{\alpha\alpha}$ decrease in a specific sequence[75,76]:

$$f_r \gg f_\alpha \gg f_{rr'} \geqslant f_{\alpha\alpha} \geqslant f_{r\alpha}. \qquad (30)$$

This means that the main contribution to $\Delta\mathrm{Sp}(GF)$ comes invariably from $(f_r - f_{rr'})$ combinations multiplied by the coefficients a_{ii}, equal to the number n of attached atoms Y or atomic groups YZ. Despite the much greater numerical values of the coefficients a_{ij} of other combinations of constants, the fraction of this contribution does not fall below 60% of $\Delta\mathrm{Sp}(GF)$ and is in the range 80–90% for the vast majority of molecules. Thus the force constants f_r for the deformation of bonds and their number n make the main contribution to $\Delta\mathrm{Sp}(GF)$.[66,76] If one is dealing with a molecule of the type $XY_1Y_2\ldots Y_i\ldots Y_n$ in which the atom X involved in isotope substitution is linked to different atoms or groups Y_i, then the dominant component of the sum $\sum_{ij} a_{ij}f_{ij}$ is $\sum_i f_{ri}$.

According to the concept of the transferability of force constants[75,76], the bond deformation force constants for series of related molecules have the same numerical value or change comparatively slightly. Together with the considerations described above, this justifies the treatment of the quantities $\ln\beta$ as sums of certain constant increments corresponding to each bond. It has been shown[74,77] that in isostructural series of the type CH_4, CH_3F, CH_2F_2, CHF_3, CF_4 or BF_3, BF_2Cl, $BFCl_2$, BCl_3 the additivity of the values of $\ln\beta$ for the central carbon and boron atoms holds with a high degree of accuracy. However, even for an approximate maintenance of the additivity of $\Delta\mathrm{Sp}(GF)$, numerous conditions must hold, which are partly outside the scope of the concept of transferability of the force constants[78]. The next section of this review will show that the rigorous additivity of $\ln\beta$ is incompatible with the rigorous additivity of the higher terms of the expansion of $\ln\beta$ in series in terms of the quantities $\Delta\mathrm{Sp}(GF)^j$ even for series of geometrically similar molecules. The assumption of the additivity of the thermodynamic isotope effects of carbon for arbitrary sets of organic compounds[7,79] is therefore erroneous.

2. Exact Relations

Eqns.(28)–(29) make it possible to interpret the values of $\ln\beta$ only to within a correction factor γ. Although in most cases the latter lies within a narrow range of values, the corrections which it introduces can reach 30% of the true value of $\ln\beta$. This is a result of the failure to take into account the non-linear terms of the expansion of $\ln\beta$ in terms of the characteristics of the force field.

An accurate expansion in a variable-sign power series with Bernoulli coefficients B_{2j-1} was obtained by Bigeleisen[68] for the range $u_{\max} < 2\pi$:

$$\ln\beta = \sum_{j=1}^{\infty} \frac{(-1)^{j+1} B_{2j-1}}{2j\,(2j)!} \sum_{i=1}^{3N-6} \delta\,(u_i^{2j}) = \sum_{j=1}^{\infty} \frac{(-1)^{j+1} B_{2j-1}}{2j\,(2j)!} \left(\frac{hc}{kT}\right)^{2j} \Delta\,\mathrm{Sp}\,(GF)^j. \qquad (31)$$

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 (31) stimulated the derivation of approximate expressions for $\ln\beta$ over an arbitrary range of values of u. Considerable efforts were wasted in the search for ways of achieving a sufficiently accurate mathematical description of $\ln\beta$ with the aid of finite orthogonal Jacobi polynomials[14,23,80]. Analysis of different versions of this description by Bigeleison and Ishida[23] led to the conclusion that the following approximate expression, in which the terms of series (31) are modulated by finite first-order Chebyshev polynomials, is best:

$$\ln\beta = \sum_{j=1}^{n} T\,(n, j, u_{\max}) \frac{(-1)^{j+1} B_{2j-1}}{2j\,(2j)!} \left(\frac{hc}{kT}\right) \Delta\,\mathrm{Sp}\,(GF). \qquad (32)$$

The accuracy ensured by the Bigeleisen–Ishida expansion (32) 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 Eqn.(32) is higher the higher the order n and the narrower the required range of values of u. The marked increase of the error of the approximate expression (32) 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.[81] used the minimax method in order to expand the components of $\ln\beta$ into a finite polynomial; the resulting approximate expression is

$$\ln\beta \simeq \sum_{j=1}^{n} a\,(n, j, u_{\max}) \cdot \sum_{i}^{3N-6} \delta\,(u_i/u_{\max})^{2j} = \sum_{j=1}^{n} a\,(n, j, u_{\max}) \cdot \left(\frac{hc}{kT}\right)^{2j} \Delta\,\mathrm{Sp}\,(GF)^j, \qquad (33)$$

where $a(n,j,u_{\max})$ are modulating polynomials analogous to $T(n,j,u_{\max})$, and their numerical values have been tabulated[81].

The difference between Eqn.(33) and (32) is that the $\ln\beta$ polynomials $a(n,j,u_{\max})$ fit much better the components of $\ln\beta$ and over a wide range values of u. Although the accuracy of Eqn.(33) is ultimately comparable to that of Eqn.(32), 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 Eqn.(33) into an algebraically simple expression and greatly facilitates the mathematical analysis of the relations between the RPFIF and all its intramolecular characteristics.

Having used the perturbation technique, Singh and Wolfsberg[82] obtained a new relation expressing the RPFIF directly in terms of the force constants, masses, and geometrical parameters of the molecule. To a second approximation, this method ensures an error in the fitting of an expression to $\ln\beta$ at the level of several per cent. The resulting expression is not algebraically simple[83] and has not as yet been subjected to a general analysis from the standpoint of the possibility of using it for the investigation of the structural characteristics of the thermodynamics of isotope exchange.

Eqn.(32) has been used in a series of studies[50,83–88] in order to investigate in detail the relations between the RPFIF and the force constants. The following example provides an idea about the complexity of the resulting specific relations[85]: the overall form of the expression for $\Delta\mathrm{Sp}(GF)^3$ for a non-linear triatomic molecule has 113 terms. If it is necessary to estimate the scale of the significance of various constants, this makes numerical analysis of specific molecules preferable and lowers the generality of the conclusions.

The estimation of the contributions of various force constants to $\ln\beta$ with the aid of equations of type (32) involves a significant difficulty: the replacement of the real (numerical) value of the force constant by zero has the physical

significance of either bond rupture (if one is dealing with the valence constant), or the complete elasticity of the valence angle (zero deformation constant for the angle), or 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[87] for the extrapolation of $\ln\beta$, in terms of the force constants, from the region where all the frequencies of the "modified" molecule retains 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 largest. On the other hand, the constants for the interaction between unlike coordinates can be estimated directly with the aid of Eqn.(32).

This exact analysis confirmed the dominant role of the valence force constants f_r (which follows from the analysis of the approximate relations and empirical correlations), the secondary role of the deformation constants f_α, and the much smaller influence of constants of the type f_{rr}, $f_{\alpha\alpha}$, and $f_{r\alpha}$, which reflect the interaction of unlike internal coordinates of the molecule. It has been shown[87] that the contributions of the valence constants to $\ln\beta_H$, characterising polyatomic deuterium-substituted hydrides, are almost 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[83,88]. On the other hand, additivity breaks down significantly for elements of the type of carbon, which form numerous bonds and play the role of central atoms[83].

Expansion (32) has been used[50] to test the accuracy of Eqn.(14), which postulates the thermodynamic equivalence of all the stages of the isotope substitution of equivalent atoms. In contrast to earlier studies, it was found that the corrections to the geometrical mean rule are appreciable and can amount to 0.1–1% of $\ln\beta$.

Table 2. The functions b_j in Eqn.(35) [$B_j = (3.55559\times 10^{-6}/T^2u_{max})^{2j}$, $a_ja_j = a(n,j,u_{max})$ according to Nemeth et al.[81] and n = degree of polynomial].

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

A deficiency of Eqns.(32), (33), and other polynomial expansions of $\ln\beta$ in terms of the parameters $\Delta\mathrm{Sp}(GF)^j$ is the algebraic complexity, already mentioned, of the increments in the traces of the degrees of the matrix (GF), which constitutes a significant obstacle in the mathematical analysis of the relations between the RPFIF and the characteristics of the molecules. A definite advance in this respect was made by the simplification achieved using Waring's formulae[89,90]. Their application replaces the parameters $\Delta\mathrm{Sp}(GF)^j$ by $\Delta\sigma_j$ (isotopic increments in the coefficients σ_j of the characteristic polynomial for molecular vibrations):

$$\sigma_1 = 4\pi^2c^2\sum_i \omega_i^2,$$
$$\sigma_2 = (4\pi^2c^2)^2\sum_{i\neq k}\omega_i^2\omega_k^2, \qquad (34)$$
$$\sigma_3 = (4\pi^2c^2)^3\sum_{i\neq k\neq l}\omega_i^2\omega_k^2\omega_l^2.$$

This replacement of the parameters of the expansion reduces Eqns.(32) and (33) to the form

$$\ln\beta = \sum_j b_j\Delta\sigma_j + \sum_{j,k} b_{jk}\Delta\sigma_j\Delta\sigma_k + \sum_{j,k,l} b_{jkl}\Delta\sigma_j\Delta\sigma_k\Delta\sigma_l + \ldots, \qquad (35)$$

where b_j, $b_{j,k}$, and $b_{j,k,l}$ are functions of σ_j of different orders, which depend on the choice of modulating polynomials. If the functions b_j, $b_{j,k}$, ... are found by the method of Nemeth et al.[81] from the polynomials $a(n,j,u_{max})$, then their form is significantly simpler than in the case where $T(n,j,u_{max})$ is used for the same purpose (Table 2).

The advantages of Eqn.(35) compared with Eqns.(32) and (33) are as follows. Despite its apparent greater complexity, Eqn.(35) has a simpler structure and converges more rapidly, but Table 3 shows that the contribution of even the second sum on the right-hand side of Eqn.(35) is comparable to the error of the approximation and can therefore be neglected together with higher terms. The first sum $\sum_j b_j\Delta\sigma_j$ has a convenient structure. In contrast to the variable-sign sums on the right-hand sides of Eqns.(32) and (33), it includes only positive terms whose absolute magnitude decreases rapidly. Table 3 shows that the first term with $\Delta\sigma_1$ amounts to 70–90% of $\ln\beta$, 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 $\ln\beta$, i.e. is comparable to the error of the approximation. This enables us to speak of the relative contribution of each term to $\ln\beta$, while a similar statement does not have such a clear-cut significance in relation to the terms of the variable-sign sums (32) and (33).

Table 3. The structure of the contributions of the terms of expansion (35) to $\ln\beta$ at 300 K (degree of polynomial fitted $n = 3$, n' = degree of secular equation).

Molecule	$\ln\beta_{harm}$ [Eqn.(16)]	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

Furthermore, the first sum $\sum_j b_j\Delta\sigma$ consists of simple functions. Table 2 shows that the values of b_j are power functions of the 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 [Eqn.(34)] but also in terms of the matrices G and F. 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.[91] The isotopic increments $\Delta\sigma_j$ can be expressed quite similarly.

Overall, the properties of σ_j and $\Delta\sigma_j$ make it possible to separate relatively simply the influence on $\ln\beta$ of force characteristics, on the one hand, and of the geometry and mass of the molecules, on the other. This makes Eqn.(35) convenient for the interpretation of isotope effects and for the search for relations.

An example of useful applications of Eqn.(35) is the derivation of the quantitative coupling relations between the isotope effects of different elements and the frequency characteristics of the molecules[92]. For the reaction

$$HCO_3^- \rightleftarrows CO_2 + OH^- \qquad (36)$$

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

$$\begin{aligned} &H\overset{*}{C}O_3^- + CO_2 \rightleftarrows HCO_3^- + \overset{*}{C}O_2; \quad \alpha_C = \beta_{CO_2}/\beta_{HCO_3^-},\\ &\overset{*}{H}CO_3^- + OH^- \rightleftarrows HCO_3^- + \overset{*}{O}H^-; \quad \alpha_H = \beta_{OH^-}/\beta_{HCO_3^-},\\ &HCO\overset{*}{O}_2^- + CO_2 \rightleftarrows HCO_3^- + C\overset{*}{O}_2; \quad \alpha_O^{(1)} = \beta_{CO_2}/\beta_{HCO_3^-},\\ &HC\overset{*}{O}O_2^- + OH^- \rightleftarrows HCO_3^- + \overset{*}{O}H^-; \quad \alpha_O^{(2)} = \beta_{OH^-}/\beta_{HCO_3^-}. \end{aligned} \qquad (37)$$

The coupling relation for Eqns.(37) or, what amounts to the same thing, for reaction (36), is as follows:

$$\begin{aligned} &\frac{\mu_C}{\Delta\mu_C}\ln\alpha_C + \frac{\mu_H}{\Delta\mu_H}\ln\alpha_H + 2\frac{\mu_O}{\Delta\mu_O}(\ln\alpha_O^{(1)} + \ln\alpha_O^{(2)}) =\\ &= \sum_j jb_j(CO_2)\,\sigma_j(CO_2) + \sum_j jb_j(OH^-)\,\sigma_j(OH^-) - \sum_j jb_j(HCO_3^-)\,\sigma_j(HCO_3^-). \end{aligned} \qquad (38)$$

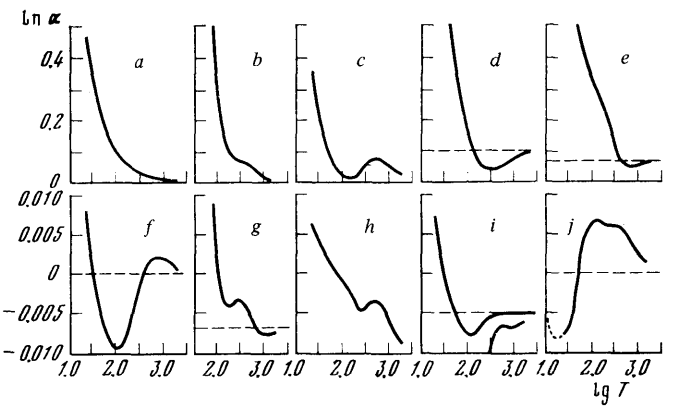


Figure 1. Types of temperature variations of theoretically calculated isotope separation factors for oxygen, carbon, and hydrogen in terms of the variables $\ln\alpha$ and $\lg T$ in the following systems: *a*) $^{18}OCS/CH_3CH^{18}O$; *b*) $Br_2C^{18}O/H^{18}OCO_2$; *c*) $CH_3{}^{13}CHO/H^{13}COO^-$; *d*) $CH_3CHDCH_3/DCOOH$; *e*) $CH^{18}OCH_3/Cl_2C^{18}O$; *f*) $CH_2{}^{13}CO/H^{13}COO^-$; *g*) $DONO_2$/*trans*-DONO; *h*) $^{13}CO_2/CH_3COCH_3$; *i*) $DONO_2/HCOOD$; *j*) $CH_2DCOCH_3/CH_2DCH_2CH_3$.

With the aid of coupling relations of type (38), it is possible to estimate isotope effects which have not been investigated experimentally, to test the reliability of the results, and to determine the characteristics of the transition complexes.

3. Temperature Variation of Isotope Effects

The most complete theoretical treatment of the nature of the temperature variation of $\ln\beta$ and $\ln\alpha$ has been achieved by Denisov et al.[71] and by Stern and coworkers[93,94]. The analysis was based on the study of the $\ln\beta_i$ components of the RPFIF corresponding to different vibration frequencies ω_i [see Eqn.(17)]. Each component $\ln\beta_i$ can be effectively fitted at low temperatures by a linear relation in terms of the reciprocal of the absolute temperature and at high temperatures by a quadratic relation. The transition from the first type of relation to the second occurs at higher temperatures for each frequency the higher the frequency. In the general case the resultant value of $\ln\beta$ in the region of moderate temperatures therefore depends on temperature in a complex way and, while obeying the linear and quadratic relations at low and high temperatures, always exhibits a monotonic decrease with increase of temperature. In contrast to $\ln\beta$, the values of $\ln\alpha$, which are equal to differences between the $\ln\beta$, can vary non-monotonically with increase of temperature. It has been shown[71,93,94] that there are several types of temperature variation of $\ln\alpha$, which include relations with inversion of the sign of $\ln\alpha$, with a maximum, with a minimum, and with points of inflection (Fig.1).

IV. CHARACTERISTICS OF THE VARIABILITY OF ISOTOPE EFFECTS

1. Semiempirical Structural Relations

The study of the correlations between the RPFIF and the exact or approximate characteristics of molecular force fields leads to the possibility of estimating the RPFIF with the aid of extremely limited spectroscopic or non-spectroscopic information. Conversely, measurement of isotope effects makes it possible to find the approximate values of the force constants, the stretching vibration frequencies, and other molecular parameters.

As shown above, the valence force constants f_r, corresponding to the longitudinal deformation of the valence bonds involving the atom undergoing isotope substitution, make the dominant contribution to the values of $\ln\beta$. In series of related compounds there are definite relations between the quantities f_r and other force constants of the molecules (f_α, f_{rr}, $f_{r\alpha}$, $f_{\alpha\alpha}$) or their simple combinations (elements of the *F*-matrix)[74,75,95,96], which permits a definite selection of the valence force constants f_r as the main argument in the study of RPFIF correlations. Since the valence force constants f_r are characteristics of the bond strength and there are many other bond properties correlated with them, the quantities $\ln\beta$ should exhibit fairly close correlations with many parameters of both the bonds themselves in the molecules and of the atoms involved in the bonds.

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 the set of compounds for which such correlations are constructed For example, for simple sets such as those of diatomic molecules[97-99], the observed relations are so close and simple that the RPFIF can be expressed analytically as a function of the properties of the atoms forming the molecule. On the other hand, for the set of hydrides of different elements, it has been possible merely to conclude that the variation of the RPFIF is periodic[31]. In the general case of polyatomic molecules dense linear $\ln\beta - \Sigma f_r$ and $\ln\beta - \Sigma(f_r \pm f_{rr})$ correlations

are observed for sets formed by geometrically similar compounds. A variable phenomenological feature of the compounds in such sets is usually the nature of the donor atom attached to the atom undergoing isotope substitution. Examples of such correlations are presented in Figs. 2 and 3.[100-103] In series of the type XY_n and $XY_iY'_{n-i}$, where Y and Y' are different halogens, hydrogen, oxygen, and chalcogens, etc, these correlations are so close that methods of comparative calculation of the RPFIF become justified, for example, those based on the linear relations of the $\ln\beta_X - \ln\beta_{X'}$ type (Fig. 4).[103]

In compounds $XY_iY'_{n-i}$, where the geometry of the coordination sphere of the atom involved in isotope substitution is retained, $\ln\beta_X$ is nearly additive: the values of $\ln\beta_X$ can be obtained as the sums of certain increments for the X–Y and X–Y' bonds. As shown above, this is a consequence of the transferability of the force constants in such series of molecules.

The correlations between $\ln\beta$ and $\Sigma(f_r \pm f_{rr})$ for a set of compounds with different geometries have a much smaller density. For such sets (Fig. 5), the correlation coefficients are approximately 0.8. This is a natural consequence of the influence of the component of $\Delta Sp(GF)$, which is not proportional to Σf_r and reflects the differences associated with the geometrical variety of molecules.

Frequently only the stretching vibration (symmetric or anti-symmetric) frequencies are known for the compounds of interest. The knowledge of these frequencies is virtually equivalent to the knowledge of one of the combinations $(f_r \pm f_{rr})$ and the squares of the stretching vibration frequencies ν 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 the elements of a single Group or a single Period. It is also necessary to exclude the influence of masses by introducing the corresponding multiplier (Figs. 6 and 7).

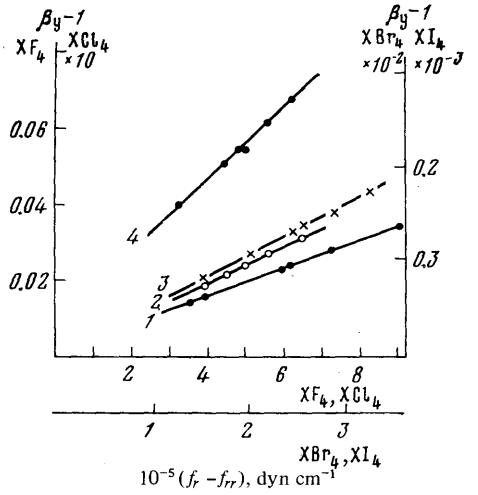


Figure 3. Dependence of $\beta_Y - 1$ for the terminal atoms Y in the tetrahalides XY_4 of the elements in the carbon subgroup on the combination of force constants $f_r + f_{rr}$ at 300 K; 1) XF_4; 2) XCl_4; 3) XBr_4; 4) XI_4.

The force constants are second derivatives of the bond energies E with respect to internuclear distances corresponding to equilibrium distances r_e. It is therefore natural to expect that relations of the type $\ln\beta - E$ or $\ln\beta - \sum_i E_i$ should be fairly simple. However, even for sets of related diatomic compounds such expectations are not borne out in practice[97-99]. For polyatomic molecules, the above relations are

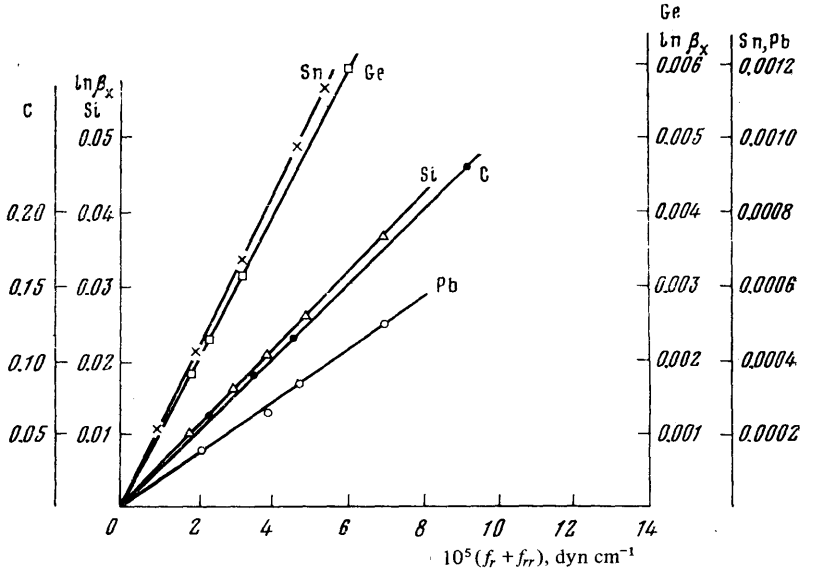


Figure 2. Dependence of $\ln\beta_X$ for the tetrahalides XY_4 of the elements in the carbon subgroup on the combination of constants $fr + f_{rr}$ at 300 K.

also not simple[103]. A much better correspondence is observed between $\ln\beta$ and the argument $\eta_0(y_X y_Y / y_X^0 y_Y^0)^{1/2} E/r_e$, where η_0 is a constant, y_X and y_Y are the first ionisation potentials of the atoms X and Y forming the molecule, and y_X^0 and y_Y^0 are the first ionisation potentials of the alkali metals belonging to the same Periods as X and Y. The use of this argument (Fig.7) is based on the familiar empirical relation $f_r = cE/r_e$, which Lippincott generalised[104]. The above relation has been confirmed for a fairly large set of compounds[105].

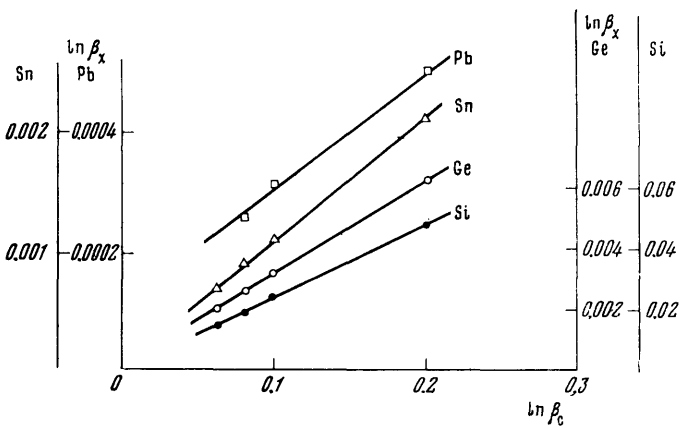


Figure 4. Correlation between the $\ln\beta_X$ for silicon, germanium, tin, and lead tetrahalides and $\ln\beta_C$.

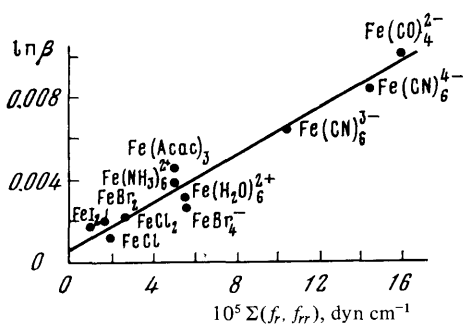


Figure 5. Correlation between $\ln\beta_{Fe}$ and $\Sigma(f_r, f_{rr})$.

Among the numerous other methods for fitting approximate expressions to the sum of valence force constants, we may note the empirical relations of Gordy[106], Guggenheimer[107], Ferreira[108], Varshni[109], and Somayajulu[110], which made it possible to obtain linear correlations between $\ln\beta$ and the internuclear distances, electronegativities, the numbers of valence electrons in the atoms, and other characteristics[97-103] (Figs.8 and 9).

For hydrogen isotope effects, the influences exerted on the H–X bond by other atoms linked to the hydride-forming element are significant. Characteristics such as the electronic charge of the bond, the electron density at the bond, the electronegativity of the substituting group, and the Taft and Hammett constants are fairly closely correlated with $\ln\beta_H$ for the corresponding sets of hydrides[101,102] (Figs.10–12).

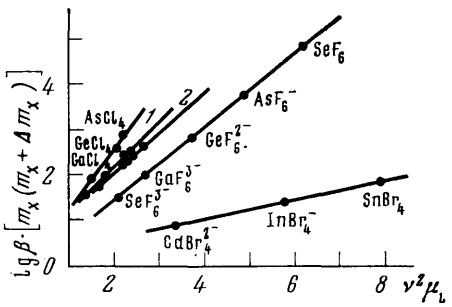


Figure 6. Dependence of $\lg\beta[m_X(m_X + \Delta m_X)]$ on $\nu^2\mu_L$, where ν is the stretching frequency and μ_L the reduced mass $[\mu_L = m_L m_X/(m_L + m_X)]$: 1) cyanides; 2) acetylacetonates.

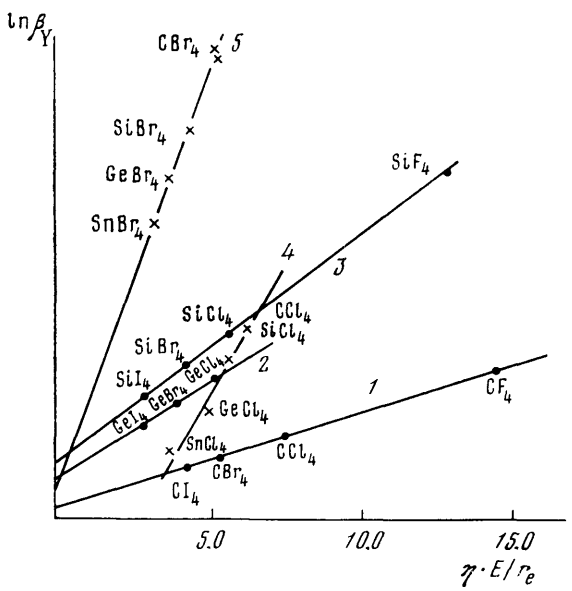


Figure 7. Dependence of $\ln\beta$ on $\eta E/r_e$: 1)–3) for C, Ge, and Si; 4) and 5) for Cl and Br.

2. Phenomenological Relations

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

and the configuration of the 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[76,100,111].

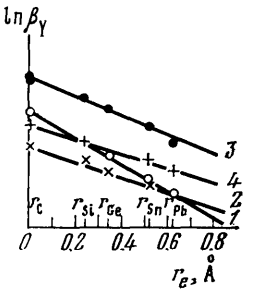


Figure 8. Correlation between $\ln\beta_Y$ and r_e for the tetrahalides XY_4 of Group IV elements: 1) fluorides; 2) chlorides; 3) bromides; 4) iodides.

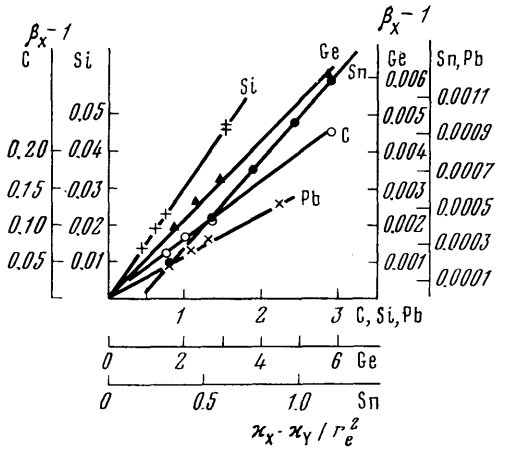


Figure 9. Correlation between $\beta_X - 1$ and the Gordy–Ferreira factor $\kappa_X\kappa_Y/r_e^2$ for the tetrahalides XY_4 of Group IV elements; κ_X and κ_Y = atomic electronegativities; r_e = internuclear distance.

The oxidation state of the element, the type of ligand, and the type of configuration sphere are interrelated discrete parameters. While the others are kept constant, each can vary only within narrow limits. In order 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. Firstly, if one needs to compare the isotope effects of different elements, then one should use effects corresponding to a unit increment in isotopic masses. All the numerical values of $\ln\beta$ and $\ln\alpha$ quoted in this review satisfy this condition. Secondly, if one needs to exclude the influence not only of Δm but also of the atomic mass m of the element involved in isotope substitution, then the quantities $\ln\beta/\Delta\mu$ should be analysed. In conformity with the significance of Eqns. (28) and (29), these quantities can be referred to as the effective force fields in which the atoms in the molecule involved in isotope substitution are located.

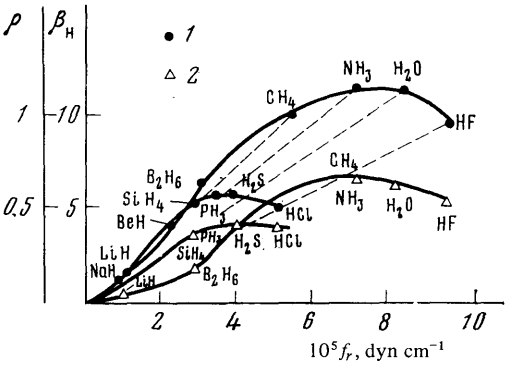


Figure 10. Dependence of β_H (*1*) and electron density ρ (*2*) of the H–X bond on the force constant f_r.

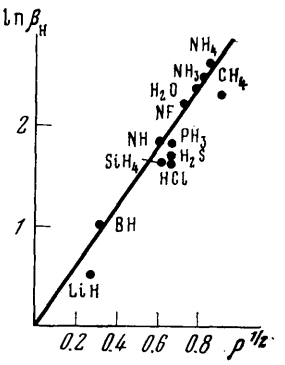


Figure 11. Correlation between $\ln\beta_H$ and the bond electron density ρ.

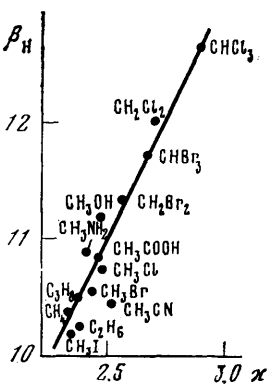


Figure 12. Correlation between β_H and the electronegativity κ of the hydrogen-substituting groups.

The influence of the degree of oxidation of the central atom on its $\ln\beta$ 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. Fig. 13 shows that the values of $\ln\beta/\Delta\mu$ 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. For transition metals in isostructural series of compounds the variation of $\ln\beta/\Delta\mu$ with increasing degree of oxidation remains monotonic (Table 4). For σ-donor and (σ−π)-donor ligands, $\ln\beta/\Delta\mu$ increases, while for σ-donor and π-acceptor ligands it diminishes with increasing degree of oxidation.

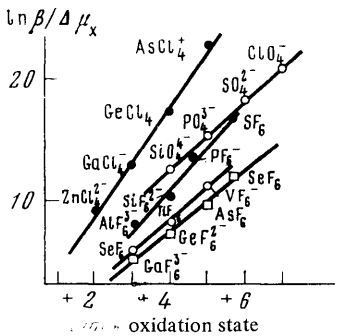


Figure 13. Relation between $\ln\beta_X/\Delta\mu_X$ and the formal oxidation state of the central atom in series of isoelectronic molecules.

Table 4. Relation between $\beta_X - 1$ and the oxidation state of the central atom.

n	β_X-1	*n*	β_X-1	*n*	β_X-1	*n*	β_X-1	*n*	β_X-1	*n*	β_X-1
Isostructural σ-complexes											
	VF_6^n		CrF_6^n		RuF_6^n		ReF_6^n		MnO_4^n		RuO_4^n
−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											
	$Cr(CN)_6^n$		$Mn(CN)_6^n$		$Fe(CN)_6^n$		$Cr(C_6H_6)_2^n$		$Fe(C_5H_5)_2^n$		
−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		

The increase of the degree of oxidation of *p* elements is coupled with a change in the number of attached ligands, the type of hybridisation of the valence orbitals, and the configurations of the compounds. The monotonic increase of the effective force fields observed in such sequences (Table 5) must be attributed to the increase of the degree of oxidation, since the configuration can be regarded as derived from the oxidation state and the type of ligand. The monotonic variation of $\ln\beta/\Delta\mu$ for sequences of this type does not imply their simplicity. In these sequences there is a change of both the type of hybridisation and of the number of non-bonding electron pairs. A more flexible and exact equivalent of the concept of the degree of oxidation proves to be the sum of bond orders, which exhibits a closer correlation with $\ln\beta$ (Fig. 14).

Table 5. The values of $\beta_X - 1$ for the fluorides and oxides of Group VI *p* elements.

Compound	β_X-1	Compound	β_X-1	Compound	β_X-1
SF_2	0.00944	SeF_2	0.00174	TeF_2	0.000676
SO	0.00866	SeO	0.00130	TeO	0.000433
SF_3^+	0.019	SeF_3^+	0.0028	TeF_3^+	0.0011
SO_2	0.0243	SeO_2	0.00348	TeO_2	0.00126
SO_3^{2-}	0.0271	SeO_3^{2-}	0.00378	TeO_3^{2-}	0.00145
SF_6	0.0411	SeF_6	0.00718	TeF_6	0.00285
SO_3	0.0430	SeO_3	—	TeO_3	—
SO_4^{2-}	0.0428	SeO_4^{2-}	0.00680	TeO_4^{2-}	0.00177

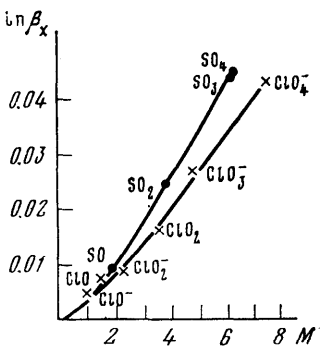


Figure 14. Correlation between $\ln\beta$ of sulphur and chlorine oxides and the sum of bond orders *M*.

The study of the relations between the RPFIF and the nature of the ligands and donor atoms is complicated by the fact that at the present time the values of $\ln\beta$ are known mainly only for compounds with the simplest monatomic ligands. Table 6 shows that, in series of isostructural compounds formed by donor atoms of the elements of a single Group of the Periodic Table, there is a marked decrease of $\ln\beta_X$ with increase of the atomic number of the donor element in the Group. Fairly rigorous relations of the type

$$\ln\beta(XY_n)/\ln\beta(XY_n') = t \simeq \text{const.} \qquad (39)$$

are observed between the values of $\ln\beta_X$ for halides, oxides, and chalcogenides. The values of *t* are then close to the ratios of the electronegativities of the donor elements Y and X. 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 values of the RPFIF of the central atoms.

For octahedral complexes of doubly- and triply-charged metal ions belonging to the first transition Period, the following sequence, corresponding to the variation of $\ln\beta_X$ with the nature of the ligand, apparently holds:

$$CN^->Acac>F^->H_2O\simeq NH_3\geqslant O^{2-}{}_X. \qquad (40)$$

Table 6. Relation between $\beta_X - 1$ and the type of monatomic ligands.

Y	LiY	BeY_2	BY_3	CY_4	PY_3	PY_5	SnY_6^{2-}
F	0,0754	0.1139	0.2435	0.2251	0.0277	0.0465	0.00207
Cl	0.0468	0.0634	0.1364	0.1042	0.0126	0.0219	0.00099
Br	0.0333	0.0486	0.1157	0.0837	0.0109		0.00070
I	0.0217	0.0358	0.0975	0.0649	0.0098		0.00074

Y	CY_2	CY_3^{2-}	PY_4^{3-}	VY_4^{3-}	AsY_4^{3-}	MoY_4^{2-}	WY_4^{2-}
O	0.1888	0.2059	0.03974	0.01253	0.00616	0.00402	0.00121
S	0.1111	0.0985	0.02289	0.00698	0.00298	0.00257	0.00072
Se	0.0938	0.0865	—	—	—	0.00159	0.00047

Overall, there are three factors which determine the dependence of the RPFIF on the nature of the ligand: the occurrence of the donor atom of the ligand in a definite Period, the chemical individuality of the donor atom, and the influence on the donor atom by the remaining atoms of the ligands. The available data for different complex-forming ligands permits the conclusion that the first factor is of greatest importance, while the individuality of the donor atom has less influence and the latter is comparable to the influence of the remaining part of the ligand. There is a satisfactory correspondence between the sequence based on the variation of $\ln\beta$ and the familiar simple sequence of donor elements:

$$C\geqslant N\geqslant O\geqslant F>S\geqslant Cl>Br>I. \qquad (41)$$

The variation of $\ln\beta$ with the degree of oxidation of the element and with the nature of the donor atom or ligand added to it follows the analogous variation of the valence force constants f_r. This correspondence is confirmed by numerous empirical relations between f_r and both phenomenological features of the compound specified above and is caused by the relation between $\ln\beta$ and f_r already discussed.

The relation between the RPFIF and the configurations of the coordination spheres of the element in the compound can be traced only for a few types of configurational transitions. Examples of such transitions are provided by transitions of the following types:

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

Table 7 shows that in the majority of instances such transtions, associated with an increase in the number of added donor atoms and a change in the type of hybridisation of the electronic orbitals of the atom involved in isotope substitution, are accompanied by a decrease of $\ln\beta$. This can be explained by the marked decrease of f_r in such transitions. However, the configurational transitions caused by the addition of electron-deficient species and by the delocalisation of the non-bonding electron pair of the atom can be accompanied by an appreciable increase of $\ln\beta$. An example of such transitions is $NH_3(C_{3v}) \rightarrow NH_4(T_d)$.[101]

V. SYSTEMATIC TREATMENT OF CHEMICAL ISOTOPE EFFECTS AND THEIR PREDICTION

In both applications of isotope effects—in the separation of stable isotopes and in the employment of such effects as the basis of a research technique—it is necessary to solve the following problems: the determination of the limits of applicability of the corresponding methods and prediction of the systems and situations in which these methods are most effective. In other words, the problems can be formulated in the following way: (a) statistical estimation of the isotope effects for various elements of the Periodic System; (b) the search for a method of rational classification of isotope exchange reactions as the basis for a systematic treatment of isotope effects; (c) the determination of the principles governing the prediction of systems with large isotope effects on the basis of general chemical information. The above problems have been solved[111-117] and the results will be considered briefly in this section.

Table 7. Isotope effects $\beta_X - 1$ in configurational transitions.

Y	$CY_2(D_{\infty h}) \rightarrow CY(D_{3h})$		Y	$BY_3(D_{3h}) \rightarrow BY_4(T_d)$	
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	$SiY_4(T_d) \rightarrow SiY_6^{2-}(O_h)$		Y	$SnY_4(T_d) \rightarrow SnY_6^{2-}(O_h)$	
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

1. Statistical Estimation of the Isotope Effects of Different Elements

The sets of possible chemical exchange systems of different elements are quantitatively non-equivalent but their number is always at least several thousands. On the other hand, the number of compounds of each element for which the values of the RPFIF are known is almost always small. The sets of systems with calculated isotope separation factors α susceptible to a statistical treatment are also small and for the majority of elements the sets of possible systems are insufficiently representative. The deficiency of information can be compensated by extending the framework of the treatment by combining the systems of different elements in a single set. However, the values of $\ln\beta$ and $\ln\alpha$ depend to the greatest extent on the atomic weight of the element and such combination requires the normalisation of the $\ln\alpha$, i.e. they must be adjusted to a single scale.

For this purpose, the concept of the γ-factor has been introduced; it is defined as the ratio of the absolute value of $\ln\alpha$ for a specific chemical exchange system of a given element to the maximum possible value $\ln\alpha_{max}$ for the same element. α_{max} is numerically equal to the separation factor for a hypothetical system in which the exchange takes place between the compound with the maximum possible value β_{max} and the non-bonded atomic form for which $\beta = 1$:

$$\gamma = |\ln\alpha|/\ln\beta_{max}. \qquad (42)$$

For any element, γ varies in the same range $0 \leq \gamma \leq 1$. The available information about the characteristic features and limits of variation of β is sufficient to create a reference system of maximum values β_{max} for the majority of elements of the Periodic Table. Compounds in which the element exhibits the highest oxidation state, coordinates ligands with donor atoms of elements in the Second Period (C,N,O, and F), and has a nearly saturated coordination sphere have the highest values of β. For a large number of elements, it is possible to indicate directly compounds whose β-factors should be extremely close to the upper limit; for others, the β_{max} were estimated by correlation methods[112]. Comparison of the β_{max} for different elements reveals a periodicity in their variation with increase of the atomic number of the element in the Periodic Table.

Table 8. The γ distribution functions (the probabilities of finding systems in different ranges of γ values).

Type	Characteristic of set	No. of systems	Ranges of γ values						
			0—0.1	0.1—0.2	0.2—0.3	0.3—0.4	0.4—0.5	0.5—0.6	$\gamma_{cp.}$
I	Set taking into account the abundances of different classes	1081	0.573	0.238	0.094	0.063	0.025	0.007	0.126
II	Set not taking into account the abundances of different classes	—	0.381	0.281	0.172	0.091	0.061	0.014	0.171
III	Set of experimentally investigated systems	161	0.410	0.349	0.138	0.058	0.025	0.010	0.150

The separation factors for each element can assume different values within the range $[1; \beta_{max}]$. The frequency of the appearance of larger and smaller values of α can be different. The concept of attainable values of α has the significance of maximum values, the probability of the appearance of which remains acceptably large from the practical point of view. A direct empirical estimate of the 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 (generalised) distribution functions for γ in order to estimate the attainable values of α for those elements for which direct analysis of the problem is impossible or difficult.

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 rate of isotope exchange or a rate satisfactory for practical purposes. The γ distribution functions of the three types have been investigated in the case of eleven elements (H,B,C,N,O,F,Fe,Co,Ni,Zn). It has been established that overall the γ-functions of each type differ little despite the marked chemical individuality of each of the elements enumerated. Hence it follows that the estimation of the attainable values of α for different elements can be achieved with the aid of averaged γ-functions.

However, the set of systems satisfactory in both thermodynamic and kinetic respects can be constructed in different ways. It is possible to investigate the set of all the systems with known values of α in which account is taken of the different abundances of different classes of systems (set I, Table 8). The γ distribution function for such a set will reflect the probability of a random selection or discovery of systems with particular values of γ. One can investigate the γ-functions for each class of systems (see below). The averaging of such functions without taking into account the abundances of the classes leads to γ-functions taking into account the element of specificity in the search for systems (Set II). Finally, one can investigate the γ-function for the set of experimentally investigated systems (set III). Evidently all three types of functions are suitable for the estimation of the attainable values of α.

Table 8 presents the γ distribution functions corresponding to the three specified methods of construction of the initial sets. The probability of obtaining high values of γ is highest for the function which does not take into account the abundance of systems of different classes and is lowest for the function which does take this factor into account. The

Table 9. The values of $\ln \beta_{max}$ at 300 K (the formula of the compound with β_{max} is indicated).

Li_2O 0.117	BeF_2 0.124	BF_3 0.214	CF_4 0.202	NO_3^- 0.150	NO_2^+ 0.115	CF_4 0.0309			
NaF 0.00467	MgF_2 0.0160	AlF_3 0.0257	SiF_4 0.0473	PO_4^{3-} 0.0382	SO_4^{2-} 0.0428	ClO_4^- 0.00406			
KF 0.00121	CaF_2 0.00347	ScF_6^{3-} 0.00704	TiF_6^{2-} 0.00911	VO_4^{3-} 0.0122	CrF_6 0.0133	MnO_4^- 0.0117	$Fe(CO)_4^{2+}$ 0.0104	$Co(CN)_6^{3-}$ 0.00745	NiF_6^{2-} 0.0101
CuF_2 0.00274	ZnF_2 0.00235	GaF_6^{3-} 0.00551	GlF_4 0.00605	AsF_6^- 0.00677	SeF_6 0.00719	BrF_5 0.00449			
RbF 0.000259	SrF_2 0.000661	YF_6^{3-} 0.00223	ZrF_4 0.00302	NbF_6^- 0.00373	MoF_6 0.00429	TcF_6 0.00423	RuF_6 0.00394	RhF_6 0.00385	PdF_6 0.00355
AgF 0.000303	CdF_2 0.000707	InF_6^{3-} 0.00163	SnF_4 0.00220	SbF_6 0.00266	TeF_6 0.00285	IF_6 0.00251			
CsF 0.000102	BaF_2 0.000241	LaF_6 0.000924	HfF_4 0.000980	TaF_6^- 0.00110	WF_6 0.00136	ReF_6 0.00135	OsF_6 0.00129	IrF_6 0.00128	PtF_6 0.00123
AuF 0.000141	HgF_2 0.000269	TlF_6^{3-} 0.000431	PbF_4 0.000493	BiF_4 0.00070	UF_6 0.000642				

function of experimentally investigated systems occupies an intermediate position, which is evidently a consequence of the low specificity of the empirical search for systems to be used in isotope separation. At the same time all three functions are on the whole similar. This shows that their use for the estimation of the attainable values of α is fairly reliable.

Table 9 presents the estimates of the attainable values of α at 300 K, obtained for all the elements in the Periodic Table, with the exception of the lanthanides, actinides, and the noble gases.

2. Classification of Isotope Exchange Reactions

In order to serve as an effective instrument for interpretation and prediction, the classification of chemical exchange systems must cover fairly completely the entire region of equilibrium chemical isotope effects and must constitute a flexible means of combining specific information with general chemical information. The set of features defining the systematic classification must meet these requirements. The choice of the state of oxidation of the element, the type of coordinated ligand, and the configuration of the coordination sphere of the compound as features of this kind is satisfactory in this respect.

Allowance for the three features of each compound implies that each chemical exchange system is described by six features and that in each pair of like features the two can be either identical or different. Hence follows the subdivision of the entire set of isotope exchange reactions into eight classes. Table 10 defines the different classes and presents examples of the corresponding reactions. All the classes can be subdivided into four groups: class I—the class of homomolecular exchange reactions for which the isotope separation factors are mathematically 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; class VIII, in which the number of differing features of the compounds is a maximum and equal to three. Each class can be subdivided in its 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, VIII have been studied, while classes II and V have not been studied at all.

Table 11. The γ distribution functions for different classes (probabilities of finding systems in different ranges of γ values).

Class	γ_{av}	Ranges of γ values					
		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

Table 11 illustrates the γ distribution functions for seven classes with $\gamma \neq 0$ obtained as a result of the interpretation of calculated theoretical data[113]. Table 11 shows that the average value γ_{av} for a given class increases with increasing

Table 10. Classification of isotope exchange reactions. Examples of kinetically satisfactory isotope exchange reactions belonging to different classes (290–300 K)[115,116].

Class	System	Kinetic characteristic	α_{theor} ($\Delta m = 1$)	α_{exp} ($\Delta m = 1$)	γ for reaction
Class II Configuration and ligand identical, oxidation states different	$Fe(CN)_6^{3-} + Fe(CN)_6^{4-}$	$k = 3.5 \times 10^2$ litre mol^{-1} s^{-1}	1.00216	—	0.24
	$Mo(CN)_8^{-3} + Mo(CN)_8^{4-}$	$k = 355$ litre mol^{-1} s^{-1}	1.00075	—	0.19
Class III Oxidation state and configuration identical, ligands different	$HDS + H_2O$	HETS = 10 cm	2.20	2.38	0.27
	$Mn(CN)_6^{4-} + Mn(H_2O)_6^{+}$	rapid exchange	1.0032	—	0.21
	$ZnI_4^{2-} + ZnI_3F^{2-}$	very rapid exchange	1.00052	—	0.16
Class IV Oxidation state and ligand identical, configurations different	$NH_3 + NH_4^{+}$	$k = 24.6$ mol s	1.034	1.035	0.25
	$SiF_6^{2-} + SiF_4$	rapid exchange	1.0150	—	0.32
	$HgCl_2 + HgCl_4^{2-}$	rapid exchange	1.00005	—	0.20
Class V Configurations identical, oxidation states and ligands different	$V(H_2O)_6^{2} + V(CN)_6^{3-}$	rapid exchange	1.0012	—	0.08
	$Mn(H_2O)_6^{3+} + Mn(CN)_6^{4-}$	rapid exchange	1.0008	—	0.07
Class VI Ligands identical, configurations and oxidation states different	$NO + NO_3^{-}$	rapid exchange	1.079	—	0.54
	$NO + NO_2$	rapid exchange	1.035	1.028	0.24
Class VII Oxidation states identical, configurations and ligands different	$CO_2 + H_2O$	HETS = 13 cm	1.021	1.021	0.18
	$SO_2 + HSO_3$	rapid exchange		1.010	0.22
	$Zn(H_2O)_6^{2+} + ZnI_4^{2-}$	rapid exchange	1.0007	—	0.30
Class VIII Configurations, oxidation states, and ligands different	Li(amalgam) + $Li(H_2O)_6^{+}$	HETS = 10 cm	1.050	1.055	0.72
	$NO + HNO_3$	HETS = 2–3 cm		1.065	0.43
	Mg (amalgam) + $Mg(H_2O)_6^{2+}$	rapid exchange	1.0105	1.0105	0.43

*HETS = height equivalent to the theoretical stage.

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 valence state have higher values of γ_{av} than the classes with variable configurations of the coordination spheres, while the classes with different types of ligands have the lowest values of γ_{av} (this is associated with the stepwise nature of the substitution of the ligands and the predominance of the O- and N-donor ligands among those investigated). The most complex class VIII, in which all three features of the contrasted compounds, forming the systems, are different, has the highest value of γ_{av}.

3. Principles of the Prediction of Systems with High Isotope Effects

Both as a means for isotope separation and as the basis for a research technique, chemical isotope effects are more suitable the higher their absolute value. The problem of the prediction therefore usually involves the search for systems with large effects. On the other hand, the principles of the prediction 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 the values of α are the most reliable means used in such search. However, the computational method of prediction is limited by the small availability of the required initial data. The knowledge of the thermodynamic characteristics of isotope exchange can to some extent compensate for this deficiency and can play the role of the main guiding principle.

However, the broadest base for a rational search and for a comprehensive analysis of systems is provided by the above classification of chemical exchange systems, since 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 taking into account 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 principle of the selection of systems with high isotope separation factors can be formulated as follows. One of the two compounds of the system should be formed by an element in its highest oxidation state and the ligands coordinated by the element must contain donor atoms belonging to the Second Period (the σ-donor or $\sigma\pi$-donor atoms F, O, and N) and must form an unsaturated coordination sphere. The other compound must contain the given element in the smallest possible oxidation state; the ligands coordinated by this element must contain the elements of higher Periods as donor atoms ($\sigma\pi$-donor ligands with weak π-acceptor properties) and the coordination sphere must be saturated.

This principle conflicts with other requirements. Apart from a high separation factor, the "promising" chemical system must have specific qualities, namely thermodynamic stability, satisfactory kinetics of isotopic exchange, ready separability of the juxtaposed chemical forms between the juxtaposed phases, and simplicity of the interconversion of the juxtaposed chemical forms. Since the thermodynamic classification of chemical exchange systems takes into account the general chemical unity of different classes, it can serve as a basis for a general analysis of the possibilities of different classes, including also the series of specific requirements enumerated.

The prediction of isotope effects in systems which can be fruitful objects of study using the isotope effects themselves constitutes a more difficult problem which awaits solution.

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