<center>CHEMICAL THERMODYNAMICS
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Calculation of the Ratios between the Reduced Partition Functions of Isotopic Forms (β-Factors) for Ionic Crystals

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Abstract—The cluster approach to calculations of the ratio between the partition functions of isotopic forms (β-factors), which was earlier applied to molecules and covalent and metallic crystals, was extended to ionic crystals. It was shown that, as distinguished from molecular crystals and crystals of the other types, crystal lattice fragments cut from real ionic crystals could not be used in calculations as a satisfactory approximation because of the long-range nature of Coulomb forces. Correct calculation data on β-factors coinciding with those obtained by the other methods can be attained if ionic clusters are calculated taking into account their real equilibrium geometry. Various approaches to modeling short-range interatomic interactions in ionic crystals were studied, including *ab initio* quantum-chemical methods and the method of empirical interatomic pair potentials. It was shown that, among the empirical interatomic potentials, the Born–Mayer exponential potential was the best one for calculating β-factors. The β-factors were calculated for several ionic crystals with NaCl-type lattices.

INTRODUCTION

Isotope effects offer much promise for studying solvation and crystallization in solid–liquid systems, in particular, in isotopic geochemistry. Of the greatest importance in this field is the ability to calculate the β-factors of solids.

Consider element X isotope exchange between substance AX in solution and BX in the solid state,

$$AX^*(sln) + BX(s) = AX(sln) + BX^*(s).$$
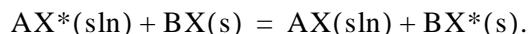
According to the general theory of chemical isotope exchange, the isotope separation coefficient in this reaction is given by

$$\alpha_{X^*/X} = \frac{\{[X^*]/[X]\}_A}{\{[X^*]/[X]\}_B}.$$

Here, X^* is the heavy isotope of X, $[X^*]$ and $[X]$ are the total equilibrium concentrations of isotopic atoms, and $\{[X^*]/[X]\}_i$ is their ratio in the *i*th substance. The equilibrium isotope separation coefficient can be calculated theoretically as the ratio

$$\alpha_{X^*/X} = \beta_{AX^*/AX}/\beta_{BX^*/BX},$$

where $\beta_{AX^*/AX}$ is the so-called ratio between the partition functions of isotopic forms, or the β-factor [1, 2],

$$(\beta_{AX^*/AX})^N = \left\{\frac{Z_{AX}^{quant}}{Z_{AX}^{class}}\right\}\bigg/\left\{\frac{Z_{AX^*}^{quant}}{Z_{AX^*}^{class}}\right\}. \qquad (1)$$

Here, Z are the partition functions of the AX and AX* isotopic forms and N is the number of equivalent X atoms that are replaced by X^*. The *quant* and *class* indices label the quantum and classical partition functions, respectively. Whereas the isotope separation coefficient α is a characteristic of a particular isotope exchange reaction, the β-factor characterizes a certain substance, and its value determines the ability of the substance to concentrate the heavy isotope in chemical isotope exchange reactions. Knowledge of β-factor values for a group of compounds allows us to calculate the isotope separation coefficients for all possible reactions between them. Precisely for this reason, the β-factor is considered a fundamental property of compounds. This property characterizes their behavior in isotope exchange reactions and plays the key role in the theory of equilibrium chemical isotope exchange.

For an arbitrary gaseous or liquid compound, the β-factor can be calculated with an error of ~2% if the vibrational frequencies of the isotopic forms of the compound are known.[1] The equation for calculating β-factors can be written as [1, 2]

$$\ln\beta = \frac{1}{N}\sum_{j=1}^{N'}\ln\left\{\frac{\sinh[u_j/2]}{\sinh[u_j^*/2]}\left[\frac{u_j^*}{u_j}\right]\right\}. \qquad (2)$$

Here, N' is the number of vibrational frequencies; $u_j = hc\nu_j/kT$ are the dimensionless, so-called reduced frequencies; ν_j are the vibrational frequencies in cm^{-1}; h is the Planck constant; k is the Boltzmann constant;

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[1] Of course, if fairly accurate frequency values are known. In addition, the error increases to 5% if hydrogen isotope substitution is considered, or if the atom undergoing replacement is linked with hydrogen.

c is the velocity of light; and *T* is the absolute temperature.

Calculations of β-factors for solids, especially for crystals, encounter serious difficulties. Calculations by (2) require knowledge of all frequencies (of the density distribution of phonon states) for both the initial and isotope-substituted crystals. As the density function of phonon states is never determined from experimental data completely, this requirement in reality means that we must use force field models that allow the dynamic matrix to be constructed and the dependence of frequencies on the wave vector to be calculated. The $\ln\beta$ value is then calculated by Eq. (2), which, for a crystal, reduces to the integral over the first Brillouin zone. Such calculations were performed for LiF in [3], where the integration was replaced by the summation over a limited number of points.

The absence of phonon spectrum data for several practically important (especially for geochemistry) crystals has led to the development of methods for calculating β-factors that do not use interatomic force models [4–6]. These methods in essence reduce to expressing the thermodynamic functions of a crystal directly through its heat capacity without invoking the phonon spectrum and to the use of experimental heat capacities and their temperature dependences for calculating β-factors.

All these methods necessarily use crystal lattice symmetry; therefore, they can only be applied to calculate the β-factors of perfect crystals. At the same time, studies of natural objects and, especially, isotope separation during crystallization require using methods applicable to calculate the β-factors of atoms in amorphous substances with developed surfaces of crystallization nuclei and, especially, the surfaces of solids at the instant of their formation. The required approach, well-known in isotope effect theory, is the cluster approach based on calculations of fragmentary models of molecules that include the nearest environment of the atom involved in exchange. The purpose of this work was to adapt this approach to calculations of the β-factors of ionic crystals.

CLUSTER MODEL CALCULATIONS OF THE β-FACTORS OF IONIC CRYSTALS

The simplest approach to calculating $\ln\beta$ is the cluster method; that is, calculations of the normal vibration frequencies of clusters, or fragments of a molecule or a solid including the nearest environment of the atom involved in exchange. This approach is based on the well-known concept of the localization of isotope effects, according to which the $\ln\beta$ value is only determined by the nearest (sometimes also next-nearest) environment of the atom replaced by its isotope [7]. In practice of applying the cluster approach to solids, this reduces to calculating the normal vibration frequencies of small fragments of a solid, that is, clusters, by the

methods of the theory of normal vibrations of molecules [8]. As $\ln\beta$ only depends on the nearest environment of the atom being replaced, the $\ln\beta$ parameter calculated for a cluster should rapidly converge to its value for the real solid as the number of atoms in the cluster increases. Our calculations for metals showed that, in the majority of cases, even the smallest possible cluster (a three-dimensional harmonic oscillator) gave $\ln\beta$ values comparable with those obtained using more complex models [9].

Unfortunately, this approach cannot be directly transferred to ionic crystals because Coulomb forces act at large distances. The dynamic matrix (GF matrix) of ionic crystals cannot therefore be considered quasi-diagonal for ionic crystals as distinguished from molecules and crystals of the other types. The off-diagonal constants corresponding to Coulomb forces decrease approximately proportionally to $1/n^3$, where *n* is the number of the matrix subdiagonal. At the same time, the number of these constants increases as n^2. Our preliminary calculations showed that the β-factor of a crystal calculated using the force constants transferred from an infinite crystal lattice converges very slowly as the size of the cluster increases. In practice, this approach either substantially overestimates β-factors or, for attaining convergence, requires calculating clusters of such a size that the use of the cluster method becomes inexpedient or even impossible. This prompted us to check the convergence of $\ln\beta$ values for ionic clusters obtained by a method different from mechanically cutting a fragment from a lattice, namely, by constructing clusters from ions in such a way that they had the real geometry of a cluster of a given size. It is shown in this work that the $\ln\beta$ values for these clusters rapidly converge to those obtained by other independent methods. In all probability, the reason for the fast convergence is the balancing of the divergence of the lattice sums by the relaxation of lattice parameters (first and foremost, internuclear distances) in clusters.

CALCULATION OF FORCE CONSTANTS FOR IONIC CRYSTAL LATTICES

With crystals, the use of natural vibrational coordinates (interatomic distance and valence angle variations) becomes very inconvenient, because these parameters cannot be defined unambiguously. For this reason, we use Cartesian displacements of atoms from their equilibrium positions as vibrational coordinates. The Cartesian displacement Δx_L of atom L along *x* is defined as

$$\Delta x_L = x_L(t) - x_L^0,$$

where $x_L(t)$ is the instantaneous x_L value at time *t* and x_L^0 is the x_L value at equilibrium.

Below, we also denote Cartesian displacements by q_L (Δx_L, Δy_L, or Δz_L). Force constants *F* in the harmonic approximation are the second derivatives of the poten-

tial energy U_{tot} of the cluster with respect to vibrational coordinates calculated at the point of equilibrium (that is, at the point where all Cartesian displacements $q = 0$). For an ionic crystal, a force constant can conveniently be represented as the sum

$$F = F_{\text{rep}} + F_{\text{Coul}},$$

where F_{rep} is the contribution of repulsion, which is determined by short-range repulsive forces, and F_{Coul} is the contribution of Coulomb electrostatic forces that act between charged ions in the crystal lattice.

Calculations of Force Constants for a Generalized Pair Potential

The energy of a system of particles whose interaction is described by a pair potential is written in the most general form as

$$U_{\text{tot}} = \frac{1}{2} N \sum_{M \neq L} u_{\text{LM}},$$

where u_{LM} depends on r_{LM}, which is the distance between arbitrarily selected L and M atoms. The factor 1/2 prevents doubly taking into account interactions within each pair of atoms twice.

The first derivative of energy U_{tot} with respect to coordinate Δx_{L} is

$$\frac{\partial U_{\text{tot}}}{\partial \Delta x_{\text{L}}} = \sum_{I \neq L} \left(\frac{\partial u_{\text{LI}}}{\partial r_{\text{LI}}} \right) \left(\frac{\partial r_{\text{LI}}}{\partial \Delta x_{\text{L}}} \right). \tag{3}$$

The expressions for the force constants are obtained as the second derivatives of U_{tot} with respect to q_{L}, q_{M} at equilibrium $q = 0$. Following the terminology accepted in the theory of molecular vibrations, we apply the term "diagonal" to those force constants that refer to only one coordinate each and are therefore the diagonal elements of the F force constant matrix. The force constants for different coordinates, which describe their dynamic interaction, will be called "off-diagonal."

For a diagonal force constant, we have

$$\left(\frac{\partial^2 U_{\text{tot}}}{\partial \Delta x_{\text{L}}^2} \right) = \sum_{I \neq L} \left[\left(\frac{\partial^2 u_{\text{LI}}}{\partial r_{\text{LI}}^2} \right) \left(\frac{\partial r_{\text{LI}}}{\partial \Delta x_{\text{L}}} \right)^2 + \left(\frac{\partial u_{\text{LI}}}{\partial r_{\text{LI}}} \right) \left(\frac{\partial^2 r_{\text{LI}}}{\partial \Delta x_{\text{L}}^2} \right) \right], \tag{4}$$

where r_{LI} is the distance between atoms L and I.

Consider off-diagonal force constants. If two unlike coordinates involve one atom L, that is, correspond to its displacements in different directions, we have

$$\left(\frac{\partial^2 U_{\text{tot}}}{\partial \Delta x_{\text{L}} \partial \Delta y_{\text{L}}} \right) = \sum_{I \neq L} \left[\left(\frac{\partial^2 u_{\text{LI}}}{\partial r_{\text{LI}}^2} \right) \left(\frac{\partial r_{\text{LI}}}{\partial \Delta x_{\text{L}}} \right) \left(\frac{\partial r_{\text{LI}}}{\partial \Delta y_{\text{L}}} \right) \right.$$
$$\left. + \left(\frac{\partial u_{\text{LI}}}{\partial r_{\text{LI}}} \right) \left(\frac{\partial^2 r_{\text{LI}}}{\partial \Delta x_{\text{L}} \Delta y_{\text{L}}} \right) \right]. \tag{5}$$

If two coordinates refer to different atoms M and L, then

$$\left(\frac{\partial^2 U_{\text{tot}}}{\partial \Delta x_{\text{L}} \partial \Delta y_{\text{M}}} \right) = \left(\frac{\partial^2 u_{\text{LM}}}{\partial r_{\text{LM}}^2} \right) \left(\frac{\partial r_{\text{LM}}}{\partial \Delta x_{\text{L}}} \right) \left(\frac{\partial r_{\text{LM}}}{\partial \Delta y_{\text{M}}} \right)$$
$$+ \left(\frac{\partial u_{\text{LM}}}{\partial r_{\text{LM}}} \right) \left(\frac{\partial^2 r_{\text{LM}}}{\partial \Delta x_{\text{L}} \Delta y_{\text{M}}} \right). \tag{6}$$

To use (4)–(6) in practice, we must find explicit expressions for the first and second derivatives of interatomic distance r_{IJ} with respect to Cartesian displacements. Taking into account that

$$r_{\text{IJ}} = ((x_{\text{I}} - x_{\text{J}})^2 + (y_{\text{I}} - y_{\text{J}})^2 + (z_{\text{I}} - z_{\text{J}})^2)^{1/2}, \tag{7}$$

the first derivative of r_{IJ} with respect to the vibrational coordinate at equilibrium is given by

$$\left(\frac{\partial r_{\text{LM}}}{\partial \Delta x_{\text{L}}} \right)_{q=0} = \frac{x_{\text{L}} - x_{\text{M}}}{r_{\text{LM}}}, \quad \left(\frac{\partial r_{\text{LM}}}{\partial \Delta x_{\text{M}}} \right)_{q=0} = -\frac{x_{\text{L}} - x_{\text{M}}}{r_{\text{LM}}}. \tag{8}$$

The second derivative of the interatomic distance with respect to the coordinate $q = \Delta x_{\text{L}}$ has the form

$$\left(\frac{\partial^2 r_{\text{LM}}}{\partial \Delta x_{\text{L}}^2} \right)_{q=0} = ((y_{\text{L}} - y_{\text{M}})^2 + (z_{\text{L}} - z_{\text{M}})^2) r_{\text{LM}}^{-3}. \tag{9}$$

Calculations of the second derivatives of r_{LM} with respect to different coordinates should be performed taking into account two cases. In the first case, both coordinates refer to the same atom L. The differentiation gives

$$\left(\frac{\partial^2 r_{\text{LM}}}{\partial \Delta x_{\text{L}} \partial \Delta y_{\text{L}}} \right)_{q=0} = -(x_{\text{L}} - x_{\text{M}})(y_{\text{L}} - y_{\text{M}}) r_{\text{LM}}^{-3}. \tag{10}$$

In the second case, the two coordinates refer to different atoms L and M. If these are analogous coordinates, for instance, Δx_{L} and Δx_{M}, then

$$\left(\frac{\partial^2 r_{\text{LM}}}{\partial \Delta x_{\text{L}} \partial \Delta x_{\text{M}}} \right)_{q=0} = (-(y_{\text{L}} - y_{\text{M}})^2 - (z_{\text{L}} - z_{\text{M}})^2) r_{\text{LM}}^{-3}. \tag{11}$$

For unlike coordinates, we have

$$\left(\frac{\partial^2 r_{\text{LM}}}{\partial \Delta x_{\text{L}} \partial \Delta y_{\text{M}}} \right)_{q=0} = (x_{\text{L}} - x_{\text{M}})(y_{\text{L}} - y_{\text{M}}) r_{\text{LM}}^{-3}. \tag{12}$$

The Coulomb Component of Force Constants

The Coulomb energy of a pair of atoms L and M is $EQ_{\text{L}}Q_{\text{M}}/r_{\text{LM}}$, where the numerical constant E depends on the units that we use and Q_i are the charges of the atoms. The equations for the Coulomb component of force constants are obtained as the second derivatives of

U_{Coul} with respect to q_L and q_M at the $q = 0$ point. Using (8)–(12), we obtain

$$\left(\frac{\partial^2 U_{Coul}}{\partial \Delta x_L^2}\right)_{q=0}$$

$$= -EQ_L \sum_{\substack{I=1 \\ (I \neq L)}}^{N} Q_I r_{LI}^{-5}\{-3(x_L - x_I)^2 + r_{LI}^2\}$$

for the diagonal force constant;

$$\left(\frac{\partial^2 U_{Coul}}{\partial \Delta x_L \partial \Delta y_L}\right)_{q=0}$$

$$= EQ_L \sum_{\substack{I=1 \\ (I \neq L)}}^{N} 3Q_I r_{LI}^{-5}\{(y_L - y_I)(x_L - x_I)\}$$

for two unlike coordinates describing the displacements of one atom;

$$\left(\frac{\partial^2 U_{Coul}}{\partial \Delta x_L \partial \Delta x_M}\right)_{q=0}$$

$$= -EQ_L Q_M r_{LM}^{-5}\{3(x_L - x_M)^2 - r_{LM}^2\}$$

for two analogous coordinates describing the displacements of different atoms M and L, for instance, Δx_L and Δx_M; and

$$\left(\frac{\partial^2 U_{Coul}}{\partial \Delta y_M \partial \Delta x_L}\right)_{q=0}$$

$$= -EQ_L Q_M r_{LM}^{-5}\{3(y_L - y_M)(x_L - x_M)\}$$

for two unlike coordinates of different atoms.

The Contribution of Short-Range Forces to Force Constants

To estimate the contribution of short-range repulsive forces F_{rep} to force constants, we must introduce some particular repulsive potential. Only those empirical potentials that contain minimal numbers of parameters that are easy to determine from experimental data are of practical value. We therefore selected two-parameter potentials. A two-parameter repulsion potential function U_{rep} model was considered by Kellermann in his classic work [10]. The approach suggested by Kellermann is based on the assumption that repulsive forces in ionic crystals are central and, unlike Coulomb forces, only act between the nearest neighbors. The A and B model parameters are introduced through the derivatives of the repulsive potential u_{rep} as

$$\left[\frac{du_{rep}(r)}{dr}\right]_{r=r_0} = \frac{e^2 B}{4r_0^2}, \quad \left[\frac{d^2 u_{rep}(r)}{dr^2}\right]_{r=r_0} = \frac{e^2 A}{4r_0^3},$$

where r_0 is the equilibrium interatomic distance in the crystal and e is the elementary charge. The A and B values can be found from the conditions of crystal lattice equilibrium

$$B = -(2/3)a_M Z^2, \quad A = 12r_0^4/Ke^2 + (4/3)a_M Z^2, \quad (13)$$

where a_M is the Madelung constant, Ze is the charge of the ion, and K is the compressibility of the crystal. Equations (13) allow potential parameters to be determined from experimental data, namely, from elastic constants and equilibrium interatomic distances in the crystal. These equations determine potential derivatives rather than the potential itself, and the analytic form of the $u_{rep}(r)$ potential can therefore be selected freely; that is, any two-parameter potential can be used. We will comparatively analyze three two-parameter potentials that are used most extensively.

The Born–Landé Power Potential

This potential is given by

$$u_{rep}(r) = Cr^{-n}, \quad n = -1 - A/B,$$

$$C = \frac{e^2 B^2}{4(B+A)} r_0^{-(2B+A)/B}. \quad (14)$$

For this simplest potential, the derivative of repulsion energy U_{rep} with respect to a coordinate and the contribution of repulsive forces to a force constant are

$$\frac{\partial U_{rep}}{\partial \Delta x_L} = \sum_{I \neq L}\left(\frac{\partial u_{rep}}{\partial r_{LI}}\right)\left(\frac{\partial r_{LI}}{\partial \Delta x_L}\right)$$

$$= -nC\sum_{I \neq L}\left(\frac{\partial r_{LI}}{\partial \Delta x_L}\right) r_{LI}^{-n-1},$$

$$\left(\frac{\partial^2 U_{rep}}{\partial \Delta x_L^2}\right)_{q=0} = -nC\sum_{I \neq L}\left(\frac{\partial^2 r_{LI}}{\partial \Delta x_L^2}\right) r_{LI}^{-n-1}$$

$$+ n(n+1)C\sum_{I \neq L}\left(\frac{\partial r_{LI}}{\partial \Delta x_L}\right)^2 r_{LI}^{-n-2},$$

$$\left(\frac{\partial^2 U_{rep}}{\partial \Delta x_L \partial \Delta y_L}\right)_{q=0} = -nC\sum_{I \neq L}\left\{\left(\frac{\partial^2 r_{LI}}{\partial \Delta x_L \partial \Delta y_L}\right) r_{LI}^{-n-1}\right.$$

$$\left. - (n+1)\left(\frac{\partial r_{LI}}{\partial \Delta x_L}\right)\left(\frac{\partial r_{LI}}{\partial \Delta y_L}\right) r_{LI}^{-n-2}\right\},$$

$$\left(\frac{\partial^2 U_{rep}}{\partial \Delta x_L \partial \Delta y_M}\right)_{q=0} = -nC\left\{\left(\frac{\partial^2 r_{LM}}{\partial \Delta x_L \partial \Delta y_M}\right) r_{LM}^{-n-1}\right.$$

$$\left. - (n+1)\left(\frac{\partial r_{LM}}{\partial \Delta x_L}\right)\left(\frac{\partial r_{LM}}{\partial \Delta y_M}\right) r_{LM}^{-n-2}\right\},$$

where r_{LI} is the distance between atoms L and I, and the summation is only over the nearest neighbors.

The Born–Mayer Exponential Potential

$$u_{rep}(r) = C\exp(-|r|/\sigma), \quad \sigma = -Br_0/A,$$

$$C = \frac{e^2 B^2}{4r_0 A}\exp\left(-\frac{A}{B}\right). \tag{15}$$

For this potential, we have

$$\frac{\partial U_{rep}}{\partial \Delta x_L} = \sum_{I \ne L}\left(\frac{\partial u_{rep}}{\partial r_{LI}}\right)\left(\frac{\partial r_{LI}}{\partial \Delta x_L}\right)$$

$$= -\frac{C}{\sigma}\sum_{I \ne L}\left(\frac{\partial r_{LI}}{\partial \Delta x_L}\right)\exp\left(-\frac{r_{LI}}{\sigma}\right),$$

$$\left(\frac{\partial^2 U_{rep}}{\partial \Delta x_L \partial \Delta y_L}\right)_{q=0} = -\frac{C}{\sigma}\sum_{I \ne L}\exp\left(-\frac{r_{LI}}{\sigma}\right)$$

$$\times\left\{\left(\frac{\partial^2 r_{LI}}{\partial \Delta x_L \partial \Delta y_L}\right) - \frac{1}{\sigma}\left(\frac{\partial r_{LI}}{\partial \Delta x_L}\right)\left(\frac{\partial r_{LI}}{\partial \Delta y_L}\right)\right\},$$

$$\left(\frac{\partial^2 U_{rep}}{\partial \Delta x_L \partial \Delta y_M}\right)_{q=0} = -\frac{C}{\sigma}\exp\left(-\frac{r_{LM}}{\sigma}\right)$$

$$\times\left\{\left(\frac{\partial^2 r_{LM}}{\partial \Delta x_L \partial \Delta y_M}\right) - \frac{1}{\sigma}\left(\frac{\partial r_{LM}}{\partial \Delta x_L}\right)\left(\frac{\partial r_{LM}}{\partial \Delta y_M}\right)\right\}.$$

The Gauss Repulsion Potential

This potential has the form

$$u_{rep}(r) = C\exp(-\alpha r^2), \quad \alpha = (B-A)/2Br_0^2,$$

$$C = -\frac{e^2 B^2}{4r_0(B-A)}\exp\left(\frac{B-A}{2B}\right). \tag{16}$$

Like the Born–Mayer potential, the Gauss repulsion potential is exponential, but it decreases more rapidly as the distance increases. This potential is extensively used largely because it admits the factorization $\exp(-\alpha r^2) = \exp(-\alpha x^2)\exp(-\alpha y^2)\exp(-\alpha z^2)$ and sometimes allows the Schrödinger equation to be solved analytically.

For this potential,

$$\frac{\partial U_{rep}}{\partial \Delta x_L} = \sum_{I \ne L}\left(\frac{\partial u_{rep}}{\partial r_{LI}}\right)\left(\frac{\partial r_{LI}}{\partial \Delta x_L}\right)$$

$$= -2C\alpha\sum_{I \ne L}\left(\frac{\partial r_{LI}}{\partial \Delta x_L}\right)r_{LI}\exp(-\alpha r_{LI}^2),$$

$$\left(\frac{\partial^2 U_{rep}}{\partial \Delta x_L \partial \Delta y_L}\right)_{q=0} = -2C\alpha\sum_{I \ne L}\exp(-\alpha r_{LI}^2)$$

$$\times\left\{\left(\frac{\partial^2 r_{LI}}{\partial \Delta x_L \partial \Delta y_L}\right)r_{LI} + (1 - 2\alpha r_{LI}^2)\left(\frac{\partial r_{LI}}{\partial \Delta x_L}\right)\left(\frac{\partial r_{LI}}{\partial \Delta y_L}\right)\right\},$$

$$\left(\frac{\partial^2 U_{rep}}{\partial \Delta x_L \partial \Delta y_M}\right)_{q=0} = -2C\alpha\exp(-\alpha r_{LM}^2)$$

$$\times\left\{\left(\frac{\partial^2 r_{LM}}{\partial \Delta x_L \partial \Delta y_M}\right)r_{LM} + (1 - 2\alpha r_{LM}^2)\left(\frac{\partial r_{LM}}{\partial \Delta x_L}\right)\left(\frac{\partial r_{LM}}{\partial \Delta y_M}\right)\right\}.$$

CALCULATIONS OF $\ln\beta$ FOR VARIOUS MODELS OF FORCES IN A CRYSTAL LATTICE

Coulomb forces in ionic crystals are long-range forces and, in this respect, fundamentally differ from short-range interatomic forces. For this reason, equilibrium interatomic distances in ionic clusters of finite size differ from equilibrium distances in infinite crystals. The same is true of atoms situated close to crystal lattice defects, primarily, of atoms on surfaces. As a result, force constants in a cluster depend on its size and the positions of atoms in it. Similarly, the force constants of a surface atom differ from the force constants of an atom situated deep in the crystal lattice and, in addition, depend on where the atom is situated on the surface. We have already mentioned that, because of the long-range character of Coulomb interactions, the geometry and force field of the real crystal cannot be transferred to a cluster. This especially refers to isotope effect calculations, because isotope exchange occurs during crystal growth rather than between a crystal already formed and a solution; that is, it occurs in small ionic clusters and on the surface of a growing crystal. The atoms that are in the inner space of the crystal cannot noticeably participate in isotope exchange because of extremely low diffusion rates in ionic crystal lattices.

Before calculating cluster force constants, we must determine its equilibrium geometry. For this purpose, we created a model of a cluster in a zeroth approximation, which was a crystal lattice fragment in which atoms interacted with each other through Coulomb forces and a pair repulsion potential. The interatomic distances in the zeroth-order cluster were selected either as the distances transferred from the real crystal lattice or as values obtained by increasing or decreasing them (stretched or compressed clusters). The cluster was then allowed to relax to equilibrium interatomic distances by calculating the classical ionic motion trajectories using the Runge–Kutta method [11]. To ensure convergence to the equilibrium geometry (that is, to damp cluster oscillations caused by the deviation of the zeroth-approximation geometry from equilibrium and thereby by its excess energy), we introduced

Table 1. Calculations of vibrational frequencies and $\ln\beta$ for molecular models and LiF clusters with the use of empirical interatomic potentials and *ab initio* quantum-chemical methods

Method	ν_{max}, cm^{-1}	$\ln\beta$	r_{Li-F}, Å
	LiF		
I	946 (^{6}Li), 894 (^{7}Li)	0.07113	1.56386
II	1348, 1273	0.12350	1.56297
III	904, 854	0.06714	1.46621
IV	1134, 1071	0.09574	1.53246
V	1026, 969	0.08209	
VI	959, 906	0.07383	1.52534
VII	986, 931	0.07718	1.56035
	F–Li–F$^-$		
I	–	–	–
II	1317, 1233	0.16690	1.65798
III	878, 822	0.09380	1.60249
V	1026, 960	0.11217	
	Li$_2$F$_2$		
I	678, 641	(0.0812)	1.73700
II	973, 934	0.14080	1.73161
III	696, 668	0.08102	1.67025
VIII	666, 639	0.05434	1.62889
IX	823, 791	0.11731	1.67114
IV	797, 771	0.10887	1.68632
V	743, 719	0.09853	
IX	724, 700	0.09576	1.71561
VI	718, 694	0.09376	1.68343
VII	721, 697	0.09552	1.71335
Li$_{13}$F$_{14}^-$, a 3 × 3 × 3 cluster with Li$^+$ in the center			
I	–	–	–
II	896, 896	0.13810	1.99703
III	693, 693	0.08727	1.99720
IV	646, 636	0.08008	
Li$_{63}$F$_{62}^+$, a 5 × 5 × 5 cluster with Li$^+$ in the center			
II	757, 757	0.09314	1.98329
III	756, 756	0.09168	1.98153

Note: I, experiment; II, the Born–Landé potential; III, the Born–Mayer potential; IV, SBK RHF 4-31G*(d); V, SBK RHF 6-311G*($3d$); VI, SBK RHF 6-311++G**($3d$); VII, RHF 6-311++G**($3df$); VIII, the Gauss potential; and IX, SBK RHF 3-21G*($3d$); given in parentheses is the estimate based on known frequencies and their contribution to the $\ln\beta$ value obtained in quantum-chemical calculations (see [15]).

a dissipative force proportional to the velocity of particles into these calculations.

The vibrational frequencies and the $\ln\beta$ value for a cluster were calculated as follows. A $3N \times 3N$ GF matrix in Cartesian coordinates was constructed, where N is the number of ions in the cluster. Next, normal vibration frequencies were calculated for both the initial (unsubstituted) cluster and for the cluster in which one of the ions (the central ion) was replaced by its isotope. After frequency calculations, the $\ln\beta$ value was determined by (2).

The pair repulsion potential parameters were determined from the compressibility of the crystal and the equilibrium interatomic distance in it by (13)–(16). The compressibility was calculated as $(1/K) = (c_{11} + 2c_{12})/3$, where c_{11} and c_{12} are the elastic constants from [12]. The calculation results show that, if the central ion is involved in isotope exchange, the $\ln\beta$ value rapidly converges as the size of the cluster increases.

For comparison, $\ln\beta$ values for NaCl-type crystals were also calculated according to Kellermann [10]. In these calculations, a 6×6 dynamic matrix of the crystal lattice was constructed, whose elements were wave vector functions, and vibrational frequencies of the unsubstituted and fully substituted crystals were calculated for wave vector values uniformly distributed in the first Brillouin zone (a total of 6000 frequencies taking degeneracy into account). As previously, the $\ln\beta$ value was calculated by (2). The dynamic matrix of the crystal was constructed in the Kellermann method only based on the A and B parameters determined by (13) rather than using particular potentials.

In addition, we compared our results with the $\ln\beta$ values calculated by one more independent method based on the use of the temperature dependence of heat capacity as the initial data [6].

A COMPARISON OF THE QUALITY OF VARIOUS POTENTIALS

For performing calculations, we must estimate the quality of different potentials, that is, determine the degree of approximation that various potentials give. For this purpose, we calculated the geometry, vibrational frequencies, and $\ln\beta$ for the LiF molecule and the Li$_2$F$_2$ cluster with the use of the empirical potentials described above and *ab initio* quantum-chemical methods. The quantum-chemical calculations were performed with the PC GAMESS package [13], version 5.2, and the basis sets incorporated in it. The calculations were performed using various basis sets, which either included all electrons or the effective core potentials suggested by Stevens *et al.* [14] (the SBK potentials). The calculation results are compared in Table 1, which also contains the experimental data and the data from [15], where the LiF and Li$_2$F$_2$ molecules were calculated using an extended basis set taking into account electron correlation at the level of second-order perturbation theory (MP2). Table 1 shows that the results of quantum-chemical calculations depend on the basis set used and obtaining vibrational frequencies close to those observed experimentally requires using fairly extended basis sets. Note that this result differs from

Table 2. $\ln\beta$ values for models of ionic crystals with NaCl-type lattices

Salt	T, K	$\ln\beta_{d.m.}$	$\ln\beta_{Kell}$	$\ln\beta_{clust}$	$\ln\beta_{term}$
			$^6Li/^7Li$		
LiF	250	0.09590	0.11541	0.12625	
$K = 1.50376$	300	0.07113	0.08341	0.09140	0.08959
$r_0 = 2.013$ Å	350	0.05609	0.06291	0.06901	
LiCl	250	0.06314	0.07043	0.07583	
$K = 3.36700$	300	0.04866	0.05006	0.05395	0.04395
$r_0 = 2.57$ Å	350	0.03513	0.03733	0.04025	
LiBr	250	0.05564	0.06049	0.06485	
$K = 4.25532$	300	0.04035	0.04284	0.04596	0.03871
$r_0 = 2.751$ Å	350	0.03049	0.03186	0.03420	
LiJ	250	0.04627	0.04906	0.05244	
$K = 5.81395$	300	0.03330	0.03461	0.03702	0.03132
$r_0 = 3.006$ Å	350	0.02503	0.02568	0.02747	
			$^{39}K/^{41}K$		
KF	250	0.00358	0.00423	0.004487	
$K = 3.27869$	300	0.00255	0.00295	0.003134	
$r_0 = 2.674$ Å	350	0.00190	0.00218	0.002311	
KCl	250	0.00235	0.00288	0.003063	
$K = 5.71429$	300	0.00166	0.00201	0.002134	0.002184
$r_0 =$	350	0.00122	0.00148	0.001571	
KBr	250	0.00208	0.00256	0.002708	
$K = 6.75676$	300	0.00146	0.00178	0.001886	0.001982
$r_0 = 3.30$ Å	350	0.00108	0.00131	0.001388	
KI	250	0.00174	0.00217	0.002297	
$K = 8.54701$	300	0.00121	0.00151	0.001598	0.001708
$r_0 = 3.533$ Å	350	0.00089	0.00111	0.001176	
			$^{24}Mg/^{26}Mg$		
MgO	250	0.01977	0.04131	0.04238	
$K = 0.625$	300	0.01466	0.02949	0.03027	0.0289
$r_0 = 2.104$ Å	350	0.01125	0.02204	0.02264	
			$^{40}Ca/^{44}Ca$		
CaO	250	0.01490	0.02487	0.02535	
$K = 0.87209$	300	0.01098	0.01757	0.01792	
$r_0 = 2.401$ Å	350	0.00840	0.01305	0.01331	
			$^{35}Cl/^{37}Cl$		
LiCl	250	0.00417	0.00483	0.005219	
	300	0.00304	0.00338	0.003657	
	350	0.00231	0.00250	0.002702	
NaCl	250	0.00361	0.00434	0.004607	
	300	0.00255	0.00303	0.003216	
	350	0.00190	0.00223	0.002370	
KCl	250	0.00291	0.00355	0.003772	
	300	0.00204	0.00247	0.002629	
	350	0.00151	0.00182	0.001936	
			$^{16}O/^{18}O$		
MgO	250	0.04311	0.08765	0.08987	
	300	0.03193	0.06296	0.06461	
	350	0.02449	0.04726	0.04853	
CaO	250	0.04587	0.07351	0.07490	
	300	0.03377	0.05246	0.05348	
	350	0.02579	0.03922	0.03999	

Note: The $\ln\beta_{clust}$ values were calculated for clusters of 125 atoms ($5 \times 5 \times 5$) using the Born–Mayer potential; $\ln\beta_{Kell}$ were obtained according to Kellermann; $\ln\beta_{term}$, by the new method [6] based on experimental heat capacity data (taken from [6] for MgO); and the $\ln\beta_{d.m.}$ values were calculated for the corresponding diatomic molecules using the vibrational frequencies from [13] (given for comparison); K is the compressibility in 10^{-12} cm^2/dyn.

that reported for ion–dipole interactions [16] because, as distinguished from ion–dipole complexes, the force constant of an ionic bond is to a substantial extent determined by a correct estimate of charge transfer from the metal to the halogen atom. On the other hand, the use of effective core potentials substantially facilitates quantum-chemical calculations but has virtually no effect on the $\ln\beta$ value, as has been shown in [16].

As far as the empirical interatomic potentials are concerned, they give $\ln\beta$ estimates of a quality comparable with that of experimental estimates and the results of $\ln\beta$ calculations with extended basis sets. The reason for this is quite obvious. Indeed, the specified potentials are constructed based on experimental elastic constants and, therefore, effectively take into account the actual electronic structure of the crystal. Precisely for this reason, quantum-chemical calculations require the use of fairly extended basis sets, whereas the empirical interatomic potentials easily give correct interatomic distance values, vibrational frequencies, and $\ln\beta$ values. We studied three empirical potentials, namely, the Born–Landé power potential, the Born–Mayer exponential potential, and the Gauss exponential potential. According to Table 1, the Born–Landé potential is too stiff and overestimates the $\ln\beta$ values, whereas the Gauss potential is, conversely, too soft and gives incorrect frequency values when the harmonic approximation is used. We mentioned this property of Gauss functions in [17].

It follows that it is expedient to use the Born–Mayer exponential potential of repulsive forces for calculating $\ln\beta$ values and equilibrium isotope separation coefficients for large-sized clusters.

Table 2 contains the results of our β-factor calculations for several crystals with NaCl-type lattices by various methods (for comparison, the β-factors for the corresponding diatomic molecules are also given). For all crystals, including CaO and MgO, the effective charges of ions were set equal to ± 1. For calcium and magnesium oxides, this choice of charges was largely based on charge calculations by *ab initio* quantum-chemical methods. For comparison, Table 2 contains the results obtained not only by cluster methods but also by the methods mentioned above and oriented toward calculations of infinite crystal lattices, namely, the Kellermann method and the new method for calculating β-factors based on the literature data on the temperature dependence of heat capacity suggested by us in [6]. To illustrate the heat capacity method, the $\ln\beta_{^{24}Mg/^{26}Mg}$ value was taken from [6]. Table 2 shows that the results obtained by all methods coincide to within the attainable accuracy of crystal lattice calculations (see [9] about the attainable accuracy).

To summarize, the cluster method can be used to calculate the β-factors of ionic crystals. It should then be modified to attain convergence, namely, the $\ln\beta$ values should be calculated for ionic clusters with their actual geometries rather than for fragments mechanically cut from lattices. Increasing the cluster size then causes rapid convergence of $\ln\beta$ to its value for an infinite crystal lattice determined by the other, more complex methods.

REFERENCES

1. Bigeleisen, J. and Mayer, M.G., *J. Chem. Phys.,* 1947, vol. 15, no. 5, pp. 261–267.
2. Varshavskii, Ya.M. and Vaisberg, S.E., *Usp. Khim.,* 1957, vol. 26, pp. 1434–1468.
3. Rock, P.A., *ACS Symp. Ser.*, vol. 11: *Isotopes and Chemical Principles*, Rock, P.A., Ed., Washington: Am. Chem. Soc., 1975, pp. 131–162.
4. Polyakov, V.B. and Kharlashina, N.N., *Geochim. Cosmochim. Acta*, 1995, vol. 59, no. 12, pp. 2561–2572.
5. Polyakov, V.B., *Zh. Fiz. Khim.*, 1996, vol. 70, no. 2, pp. 346–350.
6. Knyazev, D.A. and Bochkarev, A.V., *Zh. Fiz. Khim.*, 1999, vol. 73, no. 5, pp. 875–879.
7. Knyazev, D.A., Myasoedov, N.F., Bochkarev, A.V., Gladun, L.V., and Blank, A.D., *Zh. Fiz. Khim.*, 1986, vol. 60, no. 12, pp. 2943–2947.
8. Wilson, E.B., Jr., Decius, J.C, and Cross, P.C., *Molecular Vibrations: the Theory of Infrared and Raman Vibrational Spectra,* New York: McGraw-Hill, 1955. Translated under the title *Teoriya kolebatel'nykh spektrov molekul*, Moscow: Inostrannaya Literatura, 1960.
9. Bochkarev, A.V., *Zh. Fiz. Khim.*, 1998, vol. 72, no. 8, pp. 1512–1516.
10. Kellermann, E.W., *Philos. Trans. Roy. Soc. A* (London), 1940, vol. 238, pp. 513–548.
11. Forsythe, G.E., Malcolm, M.A., and Moler, C.B., *Computer Methods for Mathematical Computations*, Englewood Cliffs, New York: Prentice-Hall, 1977. Translated under the title *Mashinnye metody matematicheskikh vychislenii*, Moscow: Mir, 1980.
12. *Landolt-Börnstein Handbook (Numerical Data and Functional Relationships in Science and Technology)*, New Series, Group 3: *Crystal and Solid State Physics*, Berlin: Springer, 1969.
13. Granovsky, A.A., http://classic.chem.msu.su/gran/gamess/index/html.
14. Stevens, W.J., Basch, H., and Krauss, M., *J. Chem. Phys.*, 1984, vol. 81, no. 12, pp. 6026–6033.
15. Solomonik, V.G. and Sliznev, V.V., *Zh. Strukt. Khim.,* 1998, vol. 39, no. 2, pp. 196–209.
16. Bochkarev, A.V., *Zh. Fiz. Khim.*, 2001, vol. 75, no. 9, pp. 1713–1716.
17. Sazonov, A.B., Magomedbekov, E.P., Bochkarev, A.V., Glotova, I.I., and Ozerov, R.P., *Zh. Fiz. Khim.,* 2000, vol. 74, no. 4, pp. 680–688.