

OTHER PROBLEMS OF PHYSICAL CHEMISTRY

Isotope Separation during Ionic Crystal Growth from Solution

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Abstract—Equilibrium (thermodynamic) separation of isotopes during the growth of ionic crystals from an aqueous solution was simulated by calculational methods (ab initio quantum-chemical and empirical potentials). It was emphasized that the thermodynamic isotope separation coefficient for monoatomic ions (Li^+ , Ca^{2+} , etc.) under these conditions is mainly determined by an equilibrium between a solvated ion in solution and the growing crystal surface (near-surface zone). An isotope separation coefficient measured for a crystal–solution system relates to the surface layer of the crystal rather than its lattice because the β -factors of near-surface and bulk ions are different; this should be taken into account when interpreting experimental data on isotope enrichment of crystals.

The crystallization of ionic crystals from solution is accompanied by isotope separation, which can be due to both kinetic (primarily diffusion) and thermodynamic factors. Under natural conditions, isotopes sometimes separate by crystallization so that the crystal is enriched with the heavier isotope (i.e., in the opposite direction to the diffusion-controlled separation). This suggests thermodynamic control of isotope separation or its decisive role in this process. Moreover, kinetic effects on isotope separation can be eliminated by slow precipitation. This makes a theoretical study of thermodynamic isotope separation by crystallization relevant. This study is devoted to the thermodynamic (equilibrium) isotope effect during crystallization.

Essentially, the problem is that isotope exchange, both in vivo and in vitro, really involves surface ions of a crystal rather than its bulk ions. The properties of surface ions—including the isotopic reduced partition function ratio (β -factors), which is the main quantity determining the tendency of a substance to be isotope enriched during isotope exchange—differ from the properties of crystal bulk ions. As a result, the separation coefficient obtained experimentally in crystal–solution systems will differ from that calculated theoretically from β -factors of a perfect crystal (also when the isotope label is distributed in the crystal bulk according to the Khlopin law, see below).

CALCULATIONAL PROCEDURE

In a study devoted to the calculation of β -factors of ionic crystals [1], we discussed possible models and methods of calculating interatomic forces. It was demonstrated that the best fit (for a given accuracy) for NaCl-type crystal lattices is provided by a combination of the precise consideration of Coulomb forces with Born–Mayer interatomic potentials. Applicability of

ab initio quantum-chemical methods was also analyzed at different theoretical levels. In this study, β -factors for the crystal models under consideration were calculated either in terms of the Born–Mayer model or by ab initio methods. All ab initio calculations were performed with the PC GAMESS program (version 6.0 for the Linux platform) [2, 3].

ISOTOPE SEPARATION DURING CRYSTAL GROWTH

Thermodynamic Isotope Separation by Nucleation-Controlled Crystallization

Nucleation is the dominant process in highly supersaturated solutions (e.g., during precipitation of low-solubility substances from solution). In this case, numerous tiny nuclei of crystallization aggregate rapidly to form an amorphous or quasicrystalline precipitate. The high-rate formation of the solid phase is implied in such a process; as a result, the precipitate “inherits” the isotope composition of the solution, and isotope separation is impossible under these conditions. Secondary processes occur in the precipitate after primary precipitation at low degrees of supersaturation (isotope exchange with the solution, growth of large crystals by absorption of small ones, etc., see below).

Isotope Separation by Crystallization Controlled by Surface Crystal Growth

Significant thermodynamic separation of isotopes of alkali and alkaline-earth metals and halogens (primarily, chlorine), including recrystallization, can be reached during steady-state crystal growth from slightly supersaturated solutions. The growth rate of a crystal itself is controlled by either diffusion, or surface nucleation, or dislocation growth [4]. In the first case,

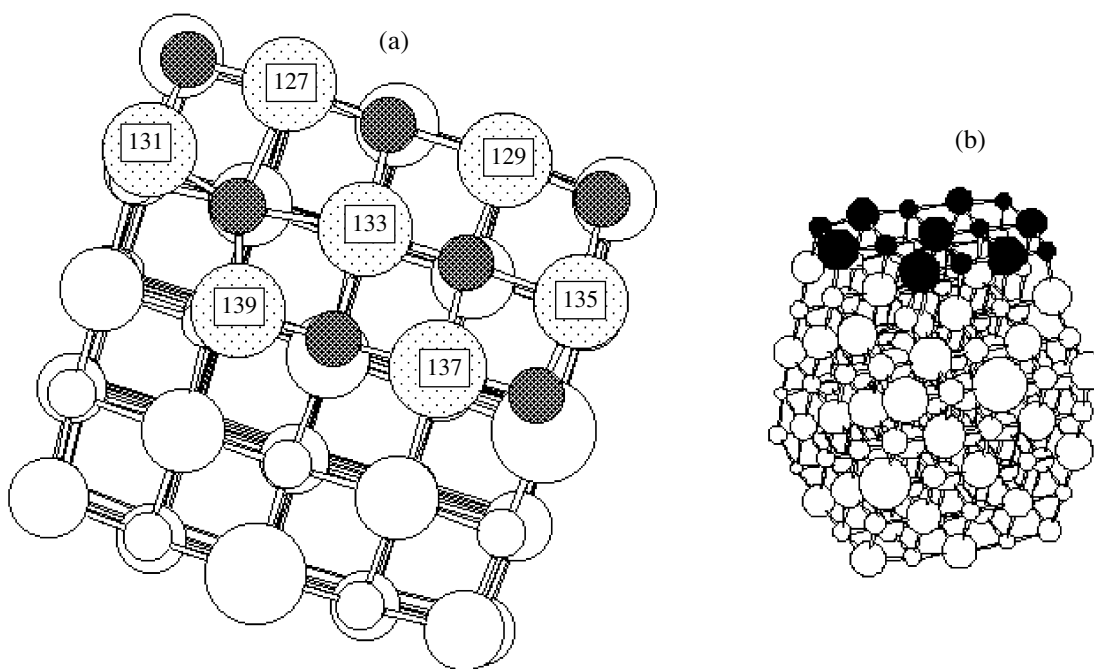
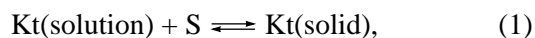


Fig. 1. Schematic representations of (a) a complete cluster and (b) a model of a growing layer at the cluster surface (full circles refer to the surface atoms). The $\ln\beta$ values of the lithium atoms at 300 K are 0.0877 (atom 139), 0.0833 (137), 0.0885 (135), 0.0884 (133), 0.0828 (131), 0.0764 (129), and 0.0783 (127). The $\ln\beta$ calculated in terms of the same model for a lithium atom in the bulk of the crystal lattice is 0.0901.

the kinetic diffusion effect is possible, while in the last two, crystallization is limited by a surface reaction: an ion passing from solution into crystal during its growth occupies a vacant adsorption center at a growth jog, which moves together with the growing crystal surface.

Thermodynamic isotope separation by crystallization (i.e., separation associated with different ion states in crystal and solution¹) is possible only when crystallization is limited by a surface reaction. In this case, the isotope separation coefficient is determined by the surface reaction:



where Kt is the cation and S is a vacant adsorption center.

It is insignificant whether a vacant adsorption center involved in this reaction is a moving vacancy in a regular growing layer (during crystal growth controlled by surface nucleation) or a jog in a helical dislocation. It is important in and of itself that a dissolved ion (Li^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , etc.) exchanges with a temporary center at the crystal surface rather than in the crystal bulk. Exchange with bulk ions is virtually impossible because of the extremely low diffusion rates of these ions in crystal at temperatures of real crystallization

from solutions.² As soon as a new layer of ions covers an ion already adhered to the surface, an isotope equilibrium between this ion and solution becomes substantially “frozen”. This was convincingly proved in a number of experiments (e.g., isotope exchange with a AgCl crystal [6]); in all cases, only surface ions are in active exchange.

To calculate the β -factor of a growing crystal, we used a model simulating a fragment of a growing layer of atoms at the surface of a cubic cluster $5 \times 5 \times 5$ ions in size (see Fig. 1; in turn, a cubic cluster composed of 125 ions simulates a crystal lattice with a growing layer at its surface). Calculation of force constants, vibrational frequencies, and $\ln\beta$ for model clusters was preceded by searching for equilibrium ion arrangement in a surface layer, as described in detail in [1] (in [1], it was shown that this cluster is sufficient for approximate calculation of the β -factor).

It follows from Fig. 1 that an ion adsorbed from solution at a vacant surface site is connected to the crystal only by three bonds (as distinct from six bonds for ions in the crystal bulk). Because of this, the β -factor of such an ion should be lower than that of a bulk ion. At the same time, the surface ion is attached to the crystal

¹ Here, “different ion states” refer to states with different coordination numbers or different ligands; i.e., differences in the nearest ion environment.

² The self-diffusion coefficient of ions in a NaCl crystal at room temperature cannot be measured; extrapolation gives $D < 10^{-20} \text{ cm}^2/\text{s}$ [5].

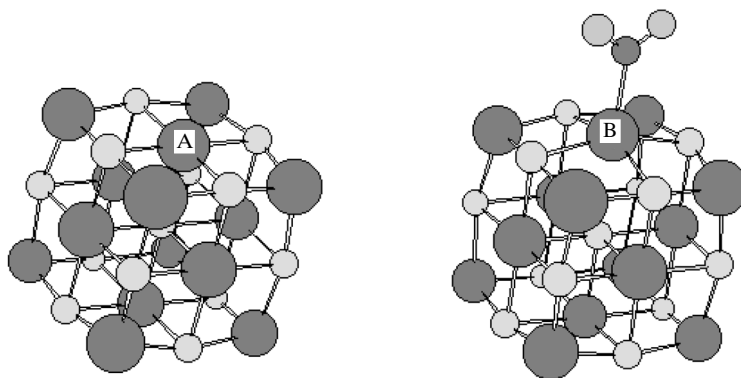


Fig. 2. Model illustrating the solvation effect on the β -factor of a surface ion; $\ln\beta = 0.0835$ for atom A and 0.0726 for atom B.

by shorter and therefore stronger bonds, which should increase its β -factor.

In solution, free valences of a surface ion become occupied by solvating water molecules. On the one hand, these additional bonds increase the β -factor; on the other hand, ion–crystal lattice bonds become weaker. To illustrate this, we calculated a model LiF cluster $3 \times 3 \times 3$ by the *ab initio* quantum-chemical method with the RHF/4-31G*(*d*) basis set with the SBK-type effective core potential (ECP) [7]. Both free and monohydrated clusters were calculated. It follows from the data obtained (Fig. 2) that hydration really does weaken bonds with a crystal lattice; the $\ln\beta$ of a surface ion is intermediate between those obtained for a bulk ion and a hydrated ion in solution. This is quite understandable since the state of a surface ion is intermediate between a hydrated ion in solution and an ion in the crystal lattice. However, strict additivity should not be expected; our study of the force constants of solvated complexes of lithium (see [8]) and calcium (see below) showed that the $\ln\beta$ values for ion–dipole interactions are not additive.

The correlation between the β -factor of a surface ion and the β -factor of an ion in the crystal lattice depends on a number of factors, primarily the ion size, polarizability, and tendency toward solvation. If the latter and, accordingly, the $\ln\beta$ of an aqua complex are low (which is true for large cations such as K^+), then the formation of an additional surface ion–solvating water bond cannot increase the β -factor noticeably.

Thus, the β -factors of surface and bulk ions in a crystal are different. For this reason, the crystal bulk is not in isotope equilibrium with solution when measuring isotope factors experimentally for an ionic crystal–solution system, even in the absence of kinetic effects on isotope separation (certainly, only monoatomic ions are meant, see below). Whenever established, such an equilibrium would indicate an isotope exchange between the crystal bulk and a solution, which is impossible for kinetic reasons. Experimentally measured separation coefficients in a crystal–solution sys-

tem are actually separation coefficients between the surface layer of a crystal and a solution, which should always be taken into account when analyzing and interpreting mass spectrometric data on isotope enrichment of crystalline rocks.

Along with isotope separation by crystallization according to reaction (1), another process is possible. This is exchange between ions in solution and ions already found in the surface layer of a growing crystal. However, this process involves only the surface layer of a crystal, as well, and therefore cannot significantly affect isotope enrichment of the whole crystal. All the above reasoning for primary crystal growth is applicable to recrystallization. Final isotope redistribution upon recrystallization can obey the Khlopin law. However, during the growth of these secondary crystals, an ion found in a mother liquor upon dissolution of a primary, smaller crystal, exchanges, at every instant, with the surface rather than bulk of a new growing crystal, and the Khlopin coefficient can be calculated from the β -factor of a surface ion.

COMPARISON WITH EXPERIMENTAL DATA

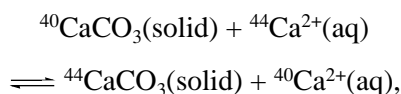
Experimental separation of lithium isotopes in crystal–solution systems was performed in [9, 10] with low accuracy (see Table 1). Nevertheless, note that the measured separation coefficients are on average half as high as they should be, judging from the β -factors of aqua complexes under the common assumption that exchange occurs between the crystal bulk and a solution. As stated in [9, 10], equilibrium was established, and such a result can be explained only by making the aforesaid, theoretically validated assumption that the β -factor of a surface ion bound to both lattice ions and water molecules is intermediate between the β -factors of an aqua complex and an ion in the crystal bulk.

The α_{calc} values given in Table 1 for lithium isotopes were calculated from the β -factors of crystals and aqua complexes calculated in [1, 8] under the assumption of an established equilibrium between the crystal bulk and

a solution, without considering the surface effects discussed here. As can be seen in Table 1, known experimental data on lithium isotope separation by crystallization confirm our model: the measured separation coefficients in crystal–solution systems are systematically two to three times lower than those calculated under the assumption of “complete” equilibrium between the crystal bulk and a solution.

In [11, 12], separation of calcium isotopes was studied in a calcite–aqueous $\text{Ca}(\text{HCO}_3)_2$ system. A calcite crystal was grown from a calcium hydrocarbonate solution by removing CO_2 very slowly. Calcium isotopes were not separated by crystallization; the measured separation coefficient was 1.000 ± 0.002 at 280 K.

To theoretically estimate the separation coefficient in the system



we calculated the vibrational frequencies of isotopic forms and the β -factors of calcium aqua complexes by the ab initio quantum-chemical method. The calculation was performed with the RHF/DZV basis set³ embedded in the PC GAMESS and supplemented with polarization and diffusion functions for hydrogen atoms.⁴ The effective core potential (ECP) of the HW type was used [13]. The geometries of complexes were optimized with the same basis set prior to calculation of vibrational frequencies.

The β -factors calculated for the complexes and crystalline CaCO_3 are given in Table 2. The β -factor for calcite was calculated in [14] from its isotopic vibrational frequencies. As can be seen in Table 2, the $\ln\alpha(^{40}\text{Ca}/^{44}\text{Ca})$ calculated for an exchange between an aqueous solution of the calcium salt and calcite from the β -factor of crystalline calcite under the assumption of established calcium isotope equilibrium between the crystal bulk and the solution is 0.004. This separation coefficient could be easily detected experimentally. However, considering the aforesaid exchange between the surface of a crystal and the solution, one should reduce this coefficient by approximately half; the resulting value (0.002) agrees with the above experimental data.

Hence, the experimental coefficient of isotope separation by crystallization from a solution provides information on the surface layer (near-surface zone) and the crystallization mechanism rather than on the crystal bulk.

³ This basis set includes 14s9p3d/11s6p3d1f/6s3p. The RHF/TZV basis set was also used, but the $\ln\beta$ values obtained with the both basis sets differ by no larger than 1%.

⁴ The use of extra-functions for H atoms is necessary because repulsion of water molecules by hydrogen atoms in the first coordination sphere of penta- and hexacoordinate complexes plays an a significant role when determining internuclear distances and force constants in these compounds.

Table 1. Separation coefficients obtained for lithium isotopes by crystallization of salts [9]

Salt	$t_{\text{cr}}, ^\circ\text{C}$	$\ln\alpha_{\text{exp}}$	$\ln\alpha_{\text{calc}}$
LiF[10]	≈ 300	0.006	0.010–0.012
LiCl	130 \rightarrow 95	–0.006	–0.017
LiCl	80 \rightarrow 20	–0.013	–0.023
LiCl	0 \rightarrow –70	–0.018	–0.039
LiBr	130 \rightarrow 100	–0.007	–0.021
LiBr	30 \rightarrow 0	–0.015	–0.036
LiNO ₃	22 \rightarrow 18	–0.012	–
Li ₂ SO ₄	0 \rightarrow 95	0.001	–

Note: The sign of $\ln\alpha$ reflects the direction of the effect; the heavier lithium isotope accumulates in the solid phase only in LiF; t_{cr} is the crystallization temperature or temperature

$$\text{range and } \alpha_{\text{exp}} = \frac{[{}^7\text{Li}]/[{}^6\text{Li}]_{\text{solid}}}{[{}^7\text{Li}]/[{}^6\text{Li}]_{\text{solution}}}.$$

Table 2. β -Factors calculated for aqua complexes of calcium $\text{Ca}(\text{H}_2\text{O})_n^{2+}$ and calcite CaCO_3 at 300 K

n	$\ln\beta$	$r(\text{Ca}-\text{O}), \text{\AA}$
1	0.00305	1.974
2	0.00598	2.009
3	0.00858	2.050
4	0.01112	2.054
5	0.01128	2.08–2.15
6	0.01124	2.154
6 [14]	0.01365	–
CaCO_3 [14]	0.00628	–

CONCLUSIONS

The results obtained have limited applicability. Note that they primarily relate to isotope separation of monoatomic alkali and alkaline-earth metal cations (e.g., Li^+ , Mg^{2+} , Ca^{2+} , or K^+) and monoatomic anions (Cl^- , Br^-). In no case, these results can be related to separation of oxygen and carbon isotopes in calcite.

The problem is that C and O atoms in both solution and a crystal are parts of polyatomic ions; moreover, these ions in solution and crystal differ in composition. Precipitation changes the chemical composition of molecules and ions: hydrated CO_2 molecules and hydrocarbonate ions pass from solution into carbonate CO_3^{2-} ions, while the excess CO_2 evolves as a gas phase. In other words, along with reaction (1), precipitation of carbonate rocks is accompanied by the chemical reaction



It is by reaction (2) that carbon and oxygen isotopes are separated. In this case, crystallization itself only leads to process (2), which changes the number and type of covalent bonds of displaced atoms, while the effect of the crystal lattice on the β -factor is secondary.

Of course, the results obtained cannot be applied to separation of hydrogen isotopes in hydrogen (gas)–transition metal hydride (solid) systems (e.g., see [15]) because hydrogen easily diffuses toward the inside of the solid phase and a true equilibrium between the crystal bulk and the gas phase is established. Neither are these conclusions applicable to crystallization from melts at high temperatures when ion diffusion in a crystal is possible.

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