

Isotopic equilibrium in a gas-crystal system near the phase-transition points

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The separation coefficient α for hydrogen isotopes in the KOH and NaOH crystal-gas systems was measured in a temperature range that included the phase-transition points. The anomalous $\alpha(T)$ dependence, which is not predicted in the harmonic approximation of the theory of isotopic effects, is due to the change of the dynamics of the librational-rotational state of the hydroxyl ion.

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Substitution of atoms in gas molecules and in structural units of a condensed phase by their isotopes produces practically no change in the particle interaction energy, but influences noticeably the dynamic characteristics of individual molecules, as well as the structural units of solutions, melts, and crystals. This manifests itself, in particular, in the thermodynamic isotope effects of saturated vapor pressure, molar volumes, thermal-expansion coefficients, heat capacity, and others.¹ The isotope effects, however, appear in the form of small corrections to the measured quantity, and this does not help determine them with sufficient reliability, or to compare them with theoretical results. The only case when an isotope effect can be measured directly is in the isotopic-exchange process.² The equilibrium isotope distribution (separation) coefficient (ISC) α reflects in fact the ratio of the thermodynamic nonequivalences (TNI) of the isotopes in two physically or chemically different states of an element; this introduces an uncertainty in the theoretical analysis of the results. To eliminate this ambiguity, one of the states is chosen to be an ideal gas, for which the isotope effects can be calculated with an accuracy exceeding the experimental capabilities.³ Thus, from the values of the ISC in a gas-crystal system it is possible to obtain experimental information on the TNI in crystals. A theoretical calculation of the thermodynamic isotope effects calls for solution of the dynamic problem for crystals with isotopic defects.^{2,4,5}

In contrast to the majority of other thermodynamic quantities, isotope effects depend selectively on the interaction parameters within the structural units of the gases, liquids, and solids, as well as between them. This makes the isotope exchange method close in effectiveness and clarity to various kinds of spectroscopic methods of studying the structure and properties of substances, including studies in the vicinity of phase-transition points. For example, it was observed in Ref. 6 that the contribution of the lattice vibrations¹⁾ in the ISC for the hydrogen-KOH crystal system decreases noticeably near the phase transition point. This effect was attributed to disintegration of the system of hydrogen bonds that govern both the stability of the low-temperature modification and a definite fraction of the TNI of hydrogen in the crystal. It was of interest to obtain the data on

the behavior of the ISC in a wider range of temperatures, including the phase-transition points, and to compare them both with the calculated values of the ISC on the basis of the harmonic approximation of the crystal-lattice theory, and with the behavior of other parameters of these crystals.

1. EXPERIMENTAL DATA ON THE TEMPERATURE DEPENDENCE OF THE ISC

In the present study, using a previously described procedure,^{6,7} we measured the ISC between hydrogen and KOH above 523 K and NaOH above 450 K. The obtained experimental results are shown in Fig. 1, where, for convenience in the analysis, the ordinate axis for the system with KOH is shifted downward by 0.4 relative to the axis for the system with NaOH. The quantities $\alpha > 1$ correspond to the deuterium concentration in the crystal. The figure shows also the data taken from Ref. 6 for KOH below 523 K and for the eutectic crystals KOH+NaOH, as well as the values of the ISC for the hypotectic hydroxyl-hydrogen gas-phase system, calculated (see Sec. 2) only with allowance for the valence vibrations of the molecular hydrogen and the hydroxyl. The frequency of the latter was assumed equal to the frequency of the OH vibrations in the crystals of the low-temperature modifications, in accordance with the data of Refs. 8 and 9.

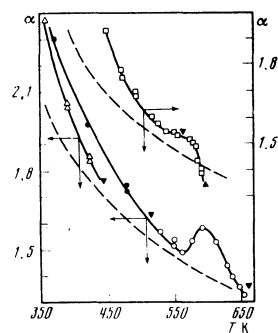


FIG. 1. Temperature dependence of the ISC in a hydrogen-crystal system: ●—KOH from Ref. 6, ○—KOH, present work, □—NaOH—present work, △—eutectic from Ref. 6. Dashed lines—theoretical calculation for OH—H₂, ▲—PT and melting points.

It is possible to conclude directly from the experimental data that the ISC differ in magnitude, and especially in their temperature dependence, both in chemically different crystals and in different forms of the same compound. We note also that at different temperatures the ISC is smaller in a system containing the eutectic than in pure KOH and NaOH, whereas considerations based on the data on the eutectic structure would lead us to expect ISC values intermediate between KOH and NaOH for the eutectic.

The most interesting experimental fact is the existence of a temperature region (530–600 K), within which the change of the ISC is nonmonotonic. For a system with KOH one observes a clearly pronounced minimum (560 K) and maximum (590 K) on the $\alpha(T)$ curve, and for the system with NaOH, with allowance for the experimental errors, an inflection is seen at 555 ± 5 K. Nonmonotonic $\alpha(T)$ curves—with extrema and inflection points—are observed experimentally or predicted theoretically for other systems.¹⁰ The cause of this phenomenon turned out to be an “accidental” ratio of the frequencies of the vibrational spectrum of the two partners of the isotope-exchange reaction, and not the singularities in the properties of one of them. A comparison of the experimental (gas–crystal) and calculated (gas–gas) curves on Fig. 1 suggests that the observed anomalies are nevertheless connected with the properties of the crystalline phase, all the more since they manifest themselves in regions close to the phase-transition points, namely, polymorphic transformations (PT) and melting (m).

For the investigated crystals the values of T_{PT} and T_m , established mainly by the thermal-analysis method, differ somewhat, but the causes of these discrepancies are not clear enough.^{11–19} Therefore the differential thermal analysis method was used to determine T_{PT} and T_m for the samples used by us. It turned out that they agree with the most frequently accepted values in the literature, and amount to $T_{PT} = 565$ K and $T_m = 585$ K for NaOH, $T_{PT} = 550$ K and $T_m = 680$ K for KOH, and $T_m = 545$ K for the eutectic. These values are shown by black triangles in Fig. 1 and in Fig. 2 below. It should be noted that the indicated values pertain to samples of natural isotopic composition with respect to hydrogen, i.e., practically pure protium samples. Yet the very character of iso-

tope-exchange experiments calls for the use of samples enriched with deuterium. One could therefore expect in principle an isotopic shift of T_{PT} and T_m but at the employed deuterium concentrations, less than 2 at.%, this phenomenon was not observed with accuracy 0.3–0.5 °C.

Thus, a qualitative examination of the experimental data reveals a certain correlation between the TNI of hydrogen in solid hydroxyls and the stability of their crystal lattice. More detailed information can be obtained by comparing the experimental data with theoretical estimates of the contribution made to the TNI by the different degrees of freedom.

2. APPROXIMATE CALCULATION OF THE TNI OF HYDROGEN IN HYDROXYL CRYSTALS

In the theory of isotope effects it is customary to consider the quantity β , which characterizes the TNI of a chemical element in a given state (e.g., crystal), so that

$$T \ln \beta = \Delta\mu - \Delta\mu_{\text{quasicl.}} \quad (1)$$

Here T is expressed in energy units, $\Delta\mu$ is the change of the chemical potential of the element following the isotope substitution (per hydrogen atom in our case); $\Delta\mu_{\text{quasicl}}$ is the same in the quasiclassical approximation, does not depend on the aggregate state,²⁰ and is introduced for convenience in normalization: $\beta \rightarrow 1$ as $T \rightarrow \infty$. The ISC between two states of an element, e.g., gas (g)–crystal (cr), is defined as $\alpha = \beta_{\text{cr}} \beta_{\text{g}}^{-1}$. In the calculation it is customary to use the harmonic approximation,¹ and in particular the dynamic theory of the crystal lattice.²

The model of the NaOH and KOH crystals, used for the calculations and based on data on their structure^{8, 16} can be represented in the following manner. We form a lattice of singly charged ions with spherically symmetrical distribution of the charge (close crystal-chemical analogs of NaF and KF, respectively)—the ion system. We place dipoles in the sites of the anion sublattice (the dipole system) in such a way that the negative pole is rigidly bound with the site, and the positive pole (proton) is located at a distance equal to the radius of the hydroxyl ion. The orientation of the dipole is determined in fact by the position of the proton on a sphere having this radius. The total energy of the crystal includes the interactions in both the ions and dipole systems, as well as between the systems, and in the ion-dipole interaction we can separate the proton-cation repulsion from the hydrogen bond of the ions. These two types of interaction, as well as the dipole-dipole interaction, exert an orienting influence on the dipoles. This leads to the appearance of libration vibrations or hindered rotation of the hydroxyl ions. The interactions in the ion system cause translational vibrations of the lattice, which depend little on the dipole orientation.

The strong O–H bond leads to valent vibrations that are practically independent of the nature of the surrounding particles and their orientation. When the different types of vibrations are independent, β_{cr} can be represented as the product of the contributions of the

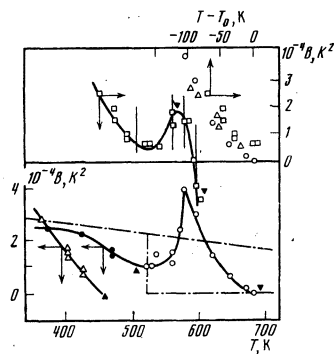


FIG. 2. Temperature dependence of $B = T^2 \ln \beta_p$. The symbols are the same as in Fig. 1. Dash-dot line—theoretical calculation of the contribution of the librations–rotations. The values of T_0 for various crystals are given in the text.

valent (v), librational (l), and translational (t) vibrations: $\beta_\alpha = \beta_v \beta_l \beta_t$. In view of the considerable localization of the valence vibrations, $\beta_v = \beta_{OH}$ is calculated, just as for gas molecules,³ using the experimental values of the O-H frequencies in the hydroxide crystals.^{8,9} The curve shown in Fig. 1 for the hydroxyl-hydrogen system represents $\alpha = \beta_{OH} \beta_\epsilon^{-1}$, where β_ϵ is for molecular hydrogen.

We shall hereafter estimate and compare with experiment the quantity

$$\beta_{lat} = \alpha_{cr} \alpha_{OH}^{-1} = \beta_l \beta_t, \quad (2)$$

which characterize the contribution made to the TNI of the hydrogen in the crystal and connected with those interactions which make the lattice stable and lead to translational vibrations of K^+ and OH^- and to librations of the hydroxyl.

β_t can be calculated in principle by the same procedure previously used in Refs. 4 and 7 for lithium hydride. In the latter case $\beta_{lat} \equiv \beta_t$ and the decisive role was played by optical translational vibrations. According to the experimental data⁷ and the theoretical estimates,⁴ β_t for LiH ranges from 1.4 to 1.1 in the temperature region 500–1000 K. The considerably smaller relative mass difference between OH and OD, as well as the lower frequencies of the translational vibrations of OH as a unit, lead to $\ln \beta_t \ll 1$ [$\omega_t(KOH) < 300 \text{ cm}^{-1} < \omega_t(LiH) \approx 800 - 1000 \text{ cm}^{-1}$]. A numerical estimate for a harmonic oscillator with $\omega = 300 \text{ cm}^{-1}$ with isotopic mass change $\epsilon = 0.06 \approx 1/17$ yields $\ln \beta_t = 5 \times 10^{-3} \omega^2 T^{-2}$, i.e., 2×10^{-3} at 500 K. This is much less than the experimental errors, and therefore we put $\beta_t = 1$ for KOH and NaOH.

The frequencies of the libration vibrations of the hydroxyl ions ($670\text{--}840 \text{ cm}^{-1}$) in the low-temperature form of KOH, according to the data of Ref. 8, change substantially (by 40%) when protium is replaced by deuterium, inasmuch as $\omega_l \sim I_{OH}^{-0.5}$, where I_{OH} is the moment of inertia. However, in dilute solutions of KOH in KOD (~5 at. % protium), the shift of the libration frequencies is only two-thirds of the shift in the case of complete isotopic substitution. A similar "non-ideality" of isotopic solutions is predicted in principle by the theory⁵ and was taken into account in the calculation of β_l . In addition, we took into account the experimentally established relation $\omega_l^2(T) = \omega_l^2(1 - 0.91 \times 10^{-3} T)$ in the interval 90–350 K for all the frequencies of the libration spectrum.⁸ In Fig. 2, the calculated values are presented in coordinates B and T , where $B = T^2 \ln \beta$. The choice of these coordinates is governed by the fact that in the harmonic approximation [$\omega \neq \omega(T)$] the quantity B tends with increasing T to a constant proportional to $\sum_i \omega_i^2$ (Ref. 1) reaching 90% of its value at $\omega T^{-1} = 1$. For comparison, Fig. 2 shows the values of B obtained from the experimental data, i.e.,

$$B_{exp} = T^2 \ln \beta_{lat} = T^2 (\ln \beta_{cr} - \ln \beta_v) = T^2 (\ln \alpha_{cr} - \ln \alpha_{OH}). \quad (3)$$

As seen from Fig. 2, in place of the calculated weak temperature dependence $B(T)$, a nonmonotonic variation is observed for NaOH and KOH near the phase-transition points, and a substantial temperature dependence is observed for all the crystals, especially when the melt-

ing point is approached.

The correlation between the stability of the lattice and the contribution of precisely the lattice vibrations in the TNI of hydrogen manifests itself in Fig. 2 quite clearly, therefore the discrepancy between the harmonic (and quasiharmonic) approximation of the theory and the experiment is not unexpected. To explain the observed correlation we take first into account the fact that in practice $\beta_t = 1$, meaning that $\beta_{lat} = \beta_l$. From the definition of β it follows that β_l (and B) reflects the changes of that particle of the chemical potential of hydrogen in KOH, which is connected with the librational-vibrational motion of the hydroxyl ions. The free rotation of the hydroxyl ion in the temperature interval above 300 K can be treated classically, i.e., $\beta_r = 1$ (r -rotation) and $B = 0$. If free rotation of the hydroxyl were to take place in KOH at $T > T_{PT}$, then the function $R(T)$ would take the form of the step shown in Fig. 2 by the dash-dot line. A steplike $B(T)$ would also be observed with changing libration frequency on going through T_{PT} . Experiment shows, however, that the evolution in the state of the OH^- ion stretches over a large temperature interval. A similar conclusion can be arrived at on the basis of the $B(T)$ curves for the NaOH in the eutectic. Such a character of the change of the properties of the crystal is observed in second-order phase transitions and is frequently satisfactorily explained by the sufficiently strong $\omega(T)$ dependence—the concept of "soft" mode. As an alternate assumption, we can consider the gradual replacement of the hydroxyl-librators by rotators. In this case the total contribution to the TNI from the rotational-librational degrees of freedom can be represented in the form

$$\ln \beta_{lat} = x_l \ln \beta_l + x_r \ln \beta_r, \quad (4)$$

where x_l and x_r are the fractions of the hydroxyls in the librational and rotational states, respectively, and $x_l + x_r = 1$. The quantity x_l plays the role of the order parameter, if the free rotation of the polyatomic structural units is assumed to be completely disordered. If $x_l(t)$ decreases as $T \rightarrow T_0$, then $B = x_l T^2 \ln \beta_l$ will also decrease, although the libration frequency will remain unchanged, so that $T^2 \ln \beta_l = \text{const}$.

From the point of view of the existence of T_0 —critical temperatures for the $B_{lat}(T)$ which are different for different crystals, it is possible to explain the differences between the ISC of NaOH and KOH, which were noted in Sec. I, on the one hand, and of their eutectic, which is a microheterogeneous equimolar mixture of components, on the other. For the eutectic, apparently, $T_0 = T_m = 445 \text{ K}$, and for pure NaOH and KOH, besides $T_0 = T_m$, we can indicate that $T_0 \approx 520 \text{ K}$ (minimum of B_{eut}). Trial of various combinations has shown that good agreement between the values of $B_{eut} = f(T - T_0)$ is obtained by choosing $T_0 = 445, 520, \text{ and } 680 \text{ K}$, respectively, for the eutectic, NaOH, and KOH (see the points in the upper right corner of Fig. 2). If this agreement is not accidental, then it means that the eutectic is a mixture of β -KOH and α -NaOH.²⁾

The foregoing explanation seems most satisfactory for a monotonic decrease of B with increasing temperature. The extremal behavior of B of KOH and NaOH

calls for a somewhat different interpretation, since the increase of B with increasing temperature, which is especially noticeable for KOH, is most probably connected with the increase of either the frequency of the libration vibrations, or the fraction of the hydroxyl-librators with high frequency. In the latter case

$$\ln \beta_{\text{lat}} = x_{11} \ln \beta_{11} + x_{12} \ln \beta_{12},$$

where 11 and 12 are different libration states of the hydroxyl ($x_{11} + x_{12} + x_r = 1$). A similar process for KOH can be represented as a transition of the hydroxyl ions from librations in hydrogen-bound chains (state 11) to librations in several equivalent positions (12), the force constant of which is governed by cation-proton repulsion. However, this transition takes place against a background of a constant increase of the fraction of freely rotating hydroxyls as the melting point is approached.

3. COMPARISON OF THE TEMPERATURE DEPENDENCE OF THE ISC AND OTHER PARAMETERS OF THE HYDROXIDE CRYSTALS

A comparison of a number of properties of halide crystals and hydroxides of alkali metals (see, e.g., Refs. 14 and 18) allows us to state that it is precisely the replacement of the halide ions by hydroxyl ions with spherically asymmetrical distribution of the charge which causes the singularities of the structure and of the dynamics of the lattice of the hydroxide and their changes in polymorphic transformations. If this is the case, then correlations should be observed in the behavior of the ISC, principally via β_{lat} , and of other thermodynamic parameters of the crystals, especially near the phase-transition points.

According to the data of Ref. 15, one can separate in the temperature dependence of the heat capacity in the case of NaOH the following regions, whose boundaries are marked in Fig. 2 by vertical strokes: up to 503 K—ordinary linear dependence, 503–568 K steep growth of the heat capacity, 568–577 K absence of reproducibility in the value of the enthalpy, 577–589 K anomalous growth of the heat capacity near the melting point. The coincidence of the corresponding temperature intervals for β_{lat} and c is hardly accidental, all the more since both parameters are governed by the dynamics of the structural units of the crystal. For KOH, the data of Ref. 19 on the character of $c(T)$ in the PT region are less detailed: the jumplike decrease of the specific heat by $0.44 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{deg}$ and the threefold increase of dc/dT on going from the monoclinic to the cubic modification. Although there is no distinct correlation between c and β_{lat} with respect to the temperature intervals, qualitatively the changes of $c(T)$ can be understood using the model of the state of OH^- (see Sec. 2): the increase of the frequency of the librators on going through T_{PT} should lead to a decrease (“jump”) of the specific heat, as well as to an increase of its temperature dependence, as is typical of a system of harmonic oscillators at $\omega T^{-1} < 1$.

The structural parameters are connected with the dynamics of the structural units of the crystal less explicitly, but the O–O and proton–cation distances, as

well as the volume per “molecule,” should correlate with the possibility of free rotation of the hydroxyl. For KOH at $T > 573 \text{ K}$ a structure of the NaCl type was registered,²¹ and the molar volume in the monoclinic–cubic transition increases by 20% ($\sim 3 \text{ cm}^3 \text{ mol}^{-1}$), and this favors the transition of the hydroxyls to a state of free rotation. For NaOH, on the contrary, the change of the molar volume at 573 K is negligible ($-0.5 \text{ cm}^3 \text{ mol}^{-1}$), both in accordance with x-ray structure data,¹⁶ and in accordance with the data of Ref. 18, where the phase diagram of NaOH was studied for 300–650 K and 0–40 kbar. According to neutronoscopic data,¹⁶ the PT produce in NaOH only reversal of the dipoles and a change in the character of their mutual orientation. One can expect, however, this process to be extended over a large temperature interval, and in some region the character of the orientation is close to complete disorder, while the OH state is close to free rotation. Such a point may be 513 K, which manifests itself in calorimetric measurements¹⁵ as the start of a steep growth of the specific heat, and in isotopic-exchange measurements (Fig. 2) as a minimum of B_{lat} , and also in x-ray structure measurements¹⁷ as a maximum of the intensity of a definite band of the spectrum.

Despite the relatively good correlation of a number of properties of the hydroxide of potassium and sodium, the character of the variation of the librational-rotational state of OH^- , from data on both isotopic exchange and from calorimetric and x-ray structure data, cannot be quite unambiguously established. The model of gradual replacement of the librators by rotators, and a model of the constant lowering of the libration frequency in all the hydroxyls, are practically equivalent when it comes to explaining $B(T)$. Various models that describe the behavior of proton-containing particles XH in the region of the order-disorder phase transition are dealt with in a number of papers. A theoretical analysis of the phase transitions in solid hydrogen halides leads to the conclusion that between the fully ordered and disordered phases there exists an intermediate phase with continuous variation of the order parameter, but the dynamics of the proton has not been considered.²² It was established by the neutron-scattering method that in the case of the trigonal–cubic transition in NaSH and the tetragonal–cubic transition in CsSH the frequency of the librations is practically preserved.²³ The free rotation of SH^- in the cubic phase is excluded by the authors of this paper, and the difference between the two modifications is attributed to an order-of-magnitude increase of the frequency of the reorientation of the anion with subsequent growth of the reorientation as melting is approached.

The results of the indicated studies^{22, 23} which attest to preservation of a definite orientation and accordingly of the librational vibrations of XH in a lattice in the cubic phase, confirm our analysis of the data on the isotopic equilibrium for KOH under the assumption that the hydroxyls are preserved, albeit only partially, in the libration state in the monoclinic–cubic transition.

¹⁾ Here and elsewhere, vibrations other than those of the in-

ternal vibrations of polyatomic structural units will be designated as lattice vibrations.

²We use here α and β as the traditional symbols for polymorphic modifications.

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Orientalional autolocalization of electrons in multivalley or anisotropic ferromagnetic semiconductors

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We consider ferromagnetic semiconductors having a multivalley or essentially anisotropic electron spectrum, in which the energy of the bottom of the band depends, owing to the spin-orbit interaction (SOI), on the direction of the magnetization. It is shown that autolocalized states (AS) of the conduction electrons, due to local changes of the magnetization orientation, can be produced in such crystals. Favorable conditions for the production of these AS obtain in crystals with low magnetic anisotropy, low Curie points, strong SOI, and small distance between the bands. The produced quasiparticles have a large radius and a large effective mass. Their formation leads to a substantial change of the electric and magnetic properties of the crystal and can be regulated by a relatively weak external field and by the temperature.

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A sufficiently strong exchange s - f (or s - d) interaction of the conduction electrons in a ferromagnetic semiconductor with the electrons of magnetic atoms should lead to autolocalization of the conduction electrons at finite temperatures. An electron that happens to be near a fluctuation change of the magnetization is then localized and stabilizes this change by its field.¹⁻⁷ The produced autolocalized states (AS) of large radius (fluctuons) are thermodynamically favored if the lowering of the average potential energy of the electron by the localization exceeds the increase of its kinetic energy and of the thermodynamic potential of the spin of the atoms. At $T=0$ the potential energy is minimal even for a band electron at the bottom of the conduction band, and no autolocalization takes place, so that fluctuations are produced in ferromagnets only at not too low temperatures: $T > T_1^*$. In this respect fluctuons differ

from polarons in ionic crystals⁸ and other AS in ordered systems (with which they have conceptually much in common).

In ferromagnetic semiconductors with anisotropic dispersion law (e.g., in multivalley or uniaxial semiconductors) and with strong spin-orbit interaction (SOI), there can be produced AS of another type, which are stable at low temperatures. When account is taken of the SOI in such semiconductors, the energy of the bottom of the conduction band $E_0(\mathbf{n})$ depends on the orientation of the magnetization vector $\mathbf{M} = M\mathbf{n}$ relative to the crystallographic axes. The equilibrium direction \mathbf{n}_0 of \mathbf{M} in the absence of electrons is determined by the magnetic anisotropy of the crystal and does not necessarily correspond to the minimum of $E_0(\mathbf{n})$. Then the average potential energy of the electron can be low-