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Thermodynamic Theory of Isotope Effects in Thermodiffusion of Silicate Melts

Semen Semenov [1],*, Martin Schimpf [2]

[1] Institute of Biochemical Physics RAS ul. Kosygina 4, 119334 Moscow, Russian Federation
[2] Boise State University, Boise, ID 83725, USA, E-Mail: Mschimpf@boisestate.edu

* Author to whom correspondence should be addressed; E-Mail: sem@triniti.ru.

Abstract: Isotope effects in the thermodiffusion of dilute atomic liquids are examined using a non-equilibrium thermodynamic model, where the thermodynamic parameters are calculated using equations rooted in statistical mechanics. In this approach, isotope effects in thermodiffusion are quantified through the variation in chemical potential and its temperature dependence with the isotope mass. The model is applied to silicate melts, in order to compare our results to recent approaches that incorporate quantum mechanics and kinematic concepts. We show that the previous theories either require unrealistic values of physical parameters or are based on invalid assumptions. The model provides an adequate description of isotope effects in thermodiffusion in silicate melts, with reasonable values of the Soret coefficient.

Keywords: thermodiffusion; isotopic effects; non-equilibrium thermodynamics

1. Background

Recent attempts to explain isotope effects in the thermodiffusion of silicate melts using quantum-mechanical models have been a topic of considerable discussion in the literature [1-6]. The quantum-mechanical model is based on the mass dependence of vibrational and librational frequencies. The view that classical approaches cannot adequately describe isotope effects [7-9] is based on the fact that "classical" differences in the isotope chemical potentials are identical in all possible phase states. In a recent paper [10], however, molecular dynamics simulations were used to argue that isotope effects in thermodiffusion can be explained through classical mechanical effects.

The quantum-mechanical model of thermodiffusion [4] relies on the standard mechanism of isotope effects employed in chemical kinetics, with translational vibrations as the primary factor. Thermodiffusion is a result of differences in the vibrational zero-point energies between isotopes, which leads to a difference in the probability of a jump from one potential well to another. The model has been criticized [5] for the unacceptably large value of the vibrational zero-point energy that resulted from fitting the model to empirical data in silicate melts. The best-fit value of that zero-point energy is comparable to the characteristic energy of a chemical bond, whereas the calculated diffusion coefficients indicate a value that is several to ten times smaller in magnitude. Thus, this model cannot describe isotope effects at room temperature or higher.

In another work [11], quantum effects in the molecular librations related to the mass difference were used to explain isotope effects in thermodiffusion. The authors communicated an acceptable agreement with experimental data, but only by ignoring much larger classical contributions related to the kinetic energy of translational and rotational motion. That oversight resulted from an approach to thermodiffusion [12-15] that expresses parameters of mass and thermodiffusion through pressure, which is proportional to the volume derivative of the partition function Z [8, 9]:

$$P = -kT \frac{\partial}{\partial V} \ln Z \tag{1}$$

According to Ref. [9], the partition function mentioned in Ref. [11] can be written as $Z = Z_{classic} \left[1 - \frac{1}{24} \left(\frac{h\omega}{kT} \right)^2 \right]$ where $Z_{classic}$ is the classical partition function, which is a function of particle mass and moment of inertia; h is Planck's constant; and ω is the frequency of the librational motion, which depends on the mass distribution within the particle. The term $\frac{1}{24} \left(\frac{h\omega}{kT} \right)^2$ is the relative quantum-mechanical contribution mentioned in Refs. [11, 12] and is about one percent of the ignored classical term $Z_{classic}$. A similar proportion exists between the other classical and quantum-mechanical components of the partition function.

The classical mass-dependent terms in the partition function are related to kinetic energy, which is a function of mass and its distribution through the particle body, not volume. Consequently, the much larger classic partition function, as defined in these works, made no contribution to thermodiffusion in the classical approximation, so that only the much smaller quantum mechanical terms yielded an expression containing both mass and volume dependence. In this approach the classical terms in the material transport parameters corresponding to kinetic energy of the translational and rotational motion are lost. As discussed in Ref. [16], the theory of material transport in non-equilibrium thermodynamics should use chemical potentials as the primary parameter rather than pressure, since the fundamental thermodynamic fluxes are expressed through the chemical potentials:

$$\mu_i = -kT \frac{\partial}{\partial N_i} \ln Z \tag{2}$$

Here N_i is the number of atoms of the i'th component. In contrast to Eq. (1), Eq. (2) keeps the mass dependence of the classical partition function.

We have expressed diffusion and thermodiffusion parameters through chemical potentials [16], allowing isotope effects in thermodiffusion to be described using both classical and quantum-

mechanical terms in the partition function, and have found the contribution of the quantum-mechanical terms to be marginal. This approach is the standard approach based on non-equilibrium thermodynamics, which was refined in Ref. [16]. The only new assumption in Ref. [16] concerns the macroscopic pressure gradient in non-homogenous and non-isothermal systems. While most of the previous theories where macroscopic pressure has assumed to be constant (see for example ref. [8]), we used the general form of the Gibbs-Duhem equation to determine the pressure gradient in the mentioned system. The validity of this our assumption will be briefly discussed below. Examples of expressing material transport parameters through the temperature and concentration dependence of the binary chemical potential can also be found in Refs. [13-15]. However, the final expressions in those works express the binary chemical potential through the (non-uniform) excess pressure using the Gibbs-Duhem equation, which causes problems with the mass dependence, as discussed above. The binary chemical potential at constant pressure, expressed through the chemical potentials μ_i of the respective components is

$$\mu_{ik}^* = \mu_i - \frac{v_i}{v_k}\mu_k \tag{3}$$

In Refs. [13-15] the binary chemical potential was expressed through the partial excess or osmotic pressure P_i^{osm} using the Gibbs-Duhem equation in the form

$$\delta\mu_2^* = \frac{v_2}{\phi_2}\left(\delta P - \frac{\delta\mu_s}{v_s}\right) \tag{4}$$

Here δ indicates the difference in the parameter between hot and cold reservoirs, μ_s and v_s are the chemical potential and specific molecular volume of the solvent, respectively, P is pressure, and ϕ_2 is the volume fraction of the solute. Parameter $\frac{\delta\mu_s}{v_s}$ was interpreted in Refs. [13-15] as the difference in the pure-solvent partial pressure between reservoirs, and Eq. (4) was rewritten as

$$\delta\mu_2^* = \frac{v_2}{\phi_2}\delta P_2^{osm} \tag{5}$$

A similar approach was used in Ref. [12], albeit in a more convoluted manner.

In Eq. (5), a microscopic equation based on Eq. (1) can be used for the osmotic pressure, and microscopic Eq. (2) can be used for the chemical potentials. Working within the framework of classical statistical physics, we can say that only the left-hand side of Eq. (5) contains the mass-dependent classical contribution. In this situation, the use of the chemical potential is preferable because the basic expression for material fluxes $\vec{J}_i$, which can be defined by the non-equilibrium thermodynamics expression for entropy production, contains only chemical potentials and not excess pressure:

$$\vec{J}_i = -n_i L_i \nabla\frac{\mu_i}{T} - n_i L_{iQ}\nabla\frac{1}{T} \tag{6}$$

Here L_i and L_{iQ} are the Onsager coefficients. This approach yields a more realistic and broader physical picture of thermodiffusion.

The theory developed in Ref. [17] uses a kinematic approach, and defines the momentum transport in an ideal binary non-isothermal system during particle collisions. All other intermolecular interactions are ignored, and the erroneous assumption of constant pressure in the system is used. The pressure in a non-homogeneous mixture cannot be constant.

Mechanical equilibrium in a binary ideal isothermal non-homogenous system is expressed by the following form of the Gibbs-Duhem equation:

$$n_1 \frac{\partial \mu_1}{\partial n_1} \nabla n_1 + n_2 \frac{\partial \mu_2}{\partial n_2} \nabla n_2 = kT \nabla (n_1 + n_2) = kT \left(1 - \frac{v_2}{v_1} \right) \nabla n_2 \qquad (7)$$

Here n_1 and n_2 are the numeric volume concentrations of the two components, μ_1 and μ_2 are their molecular chemical potentials $[\mu_i(c_i) \approx kT \ln n_i]$ and $v_1 n_1 + v_2 n_2 = 1$, where v_i are the specific molecular volumes. The right-hand side of Eq. (7) represents the non-zero pressure gradient. The equation for force balance equivalent to the Gibbs-Duhem equation [Eq. (7)] at constant pressure (that is with the zero right-hand part) is erroneously used in Ref. [17] to calculate the mean spacing parameter l, which is usually termed the free path length. This parameter is used to make the theory self-consistent. However, due to the unrealistic assumption of constant pressure, the theory yields the temperature dependence in the spacing parameter $l(T) = \frac{l(T_0)}{2} \left(1 + \frac{T}{T_0} \right)$ that is too strong. In fact, this parameter has very weak temperature dependence in liquids. It is close to the mean distance between the closest surfaces of neighboring molecules, and can vary only due to thermal expansion:

$$l(T) = l(T_0) \left[1 + \frac{\alpha_T}{3} (T - T_0) \right] \qquad (8)$$

Here $\alpha_T \approx 10^{-3} K^{-1}$ is the thermal expansion coefficient. It is easy to show that with a realistic temperature dependence of the free path length, the theory proposed in [17] cannot be made self-consistent. It yields a mean thermal force that always drives the particle along the temperature gradient toward the cold side. Consequently, the theory cannot explain observations of thermodiffusion toward the hot side. Instead, Ref. [17] uses two fitting parameters to fit the theoretical linear curve to experimental data on isotope effects. Only by extrapolation with fitting parameters is thermodiffusion to the hot side explained.

Thermodiffusion isotope effects have been the subject of computations using molecular dynamics ([10,18,19]). Using fitting parameters or simplifying assumptions, these computations yield results close to experimental data. These works also yield a reasonable dependence of the thermodiffusion isotope effect on the difference in the particle mass and in the moment of inertia. However, the computations include questionable assumptions and fittings, and contradictions exist between the results of different works. In Ref. [10], for example, the results were obtained for a model having a four-fold difference in mass. The data was then extrapolated to a more realistic mass difference of several percent, and an acceptable agreement with experimental data was obtained. The authors assumed a linear dependence of the isotope effect on relative mass difference throughout the range of the mass differences, which is difficult to accept because it is known that a linear dependence may be assumed for only very small relative mass differences. In Ref. [18], the dependence of the isotope effect on the relative mass difference is shown to be strongly non-linear, with the results yielding good

agreement with empirical data on mixtures of n-pentane/n-decane. In Ref. [19] the dependence on mass difference was also shown to be strongly non-linear.

Another problem with these works is the fitting values for the energetic parameters that were used in the computations. The authors calculated energetic parameters that were typically less than kT, while common sense and the direct comparison with molar enthalpies of organic solvents [20] indicate that these parameters should be on the order of several kT at room temperatures.

A. The thermodynamic Soret coefficient.

For calculating the concentration distribution we use standard mass transport equations of non-equilibrium thermodynamics with restrictions placed on the Onsager kinetic coefficients necessary to providing the unique solution that is independent of the specific selection of which component is labeled as the solvent [16]. These restrictions yield a relationship that expresses the heat of transport through the chemical potential of the respective component. Next, the chemical potentials are calculated using statistical mechanics. The general mass transport equation for component i in an N-component mixture is

$$\frac{\partial \phi_i}{\partial t} = \nabla \frac{\phi_i D_i}{2kT} \frac{\sum_{j=1}^{N} \phi_j v_j D_j \left(2\sum_{k>1}^{N} \frac{\partial \mu_{ij}^*}{\partial \phi_k} \nabla \phi_k + \frac{\partial \mu_{ij}^*}{\partial T} \nabla T \right)}{\sum_{k=1}^{N} \phi_k v_k D_k} \tag{9}$$

where t is time, D_i is the Stokes-Einstein diffusion coefficient, v_i the specific molecular volume, and $\phi_i = n_i v_i$ is the volume fraction of the respective component. Eq. (9) is a system of equations requiring knowledge of each component. For liquid silicates, most of the required parameters are unavailable. Therefore, we will consider only dilute isotope components in this analysis.

When the volume fraction of a component is small, we can ignore its contribution to the properties of the system, as well as interactions between isotopes. In this case, the concentration dependence of parameter μ_{ik}^* can be written as $kT \ln \phi_i$ [8, 9] and the mass transport equations take the following form:

$$\frac{\partial \phi_i}{\partial t} = D_i \left(\nabla \phi_i + \frac{\phi_i}{2kT} \frac{\partial \mu_i^*}{\partial T} \nabla T \right) \tag{10}$$

The Soret coefficient that characterizes the concentration distribution in stationary quasi-dilute non-isothermal systems can be defined as

$$S_T^i = -\frac{\nabla \phi_i}{\phi_i \nabla T} = \frac{\partial \mu_i^* / \partial T}{2kT} \tag{11}$$

where μ_i^* is the quasi-binary effective chemical potential related to the solvent medium. Detailed discussion on this thermodynamic approach can be found in [21]. Similar expressions for the Soret coefficient can be obtained using the methods used in Refs [12-15].

For a dilute component in a liquid solvent, the chemical potential at constant volume can be calculated as [22, 23]

$$\mu_{iV} = \mu_{0i} + 4\pi \int_0^1 d\lambda \int_R^\infty \frac{g_{i1}(r,\lambda)}{v_1} \Phi_{i1}(r) r^2 dr \qquad (12)$$

Here, R is the particle radius and r is the distance between a molecule of liquid and the center of the solute; $g_{i1}(r,\lambda)$ is the pair correlative function, which expresses the probability of finding a molecule of liquid at $\vec{r}_1$ ($r = |\vec{r}_1|$) if the internal molecule or atom is placed at $\vec{r} = 0$; and $\Phi_{i1}(r)$ is the respective intermolecular potential. Parameter

$$\mu_{0i} = kT \ln \phi_i v_i - \frac{3}{2} kT \ln \left[\frac{2\pi m_i kT}{h^2} \right] \qquad (13)$$

is the chemical potential or free energy of a non-interacting solute ($\Phi_{21}(|\vec{r}_2 - \vec{r}_1|) = 0$) and h is Planck's constant. Parameter λ describes the gradual "switching on" of the intermolecular interaction. A detailed description of this construct can be found in Refs. [22, 23]. Without information on moments of inertia we will, for the present, ignore the contribution of rotational motion. The chemical potential of the solvent particle is written in a similar way.

From Eqs. (12) and (13) it is clear that Eq. (11) can contain classical terms independent of the system volume but dependent on mass. This possibility means that classical isotope effects in the mass transport described by Eq. (11) are lost with the use of Eqs. (1) and (5). Only the erroneous use of partial osmotic pressure as the governing parameter in thermodiffusion allows one to ignore the classical mass-dependent terms, independent of volume.

B. Statistical-mechanical expression for the Soret coefficient.

The mass of the atom or molecule is contained in terms of the partition function and chemical potential related to translational and rotational kinetic energy. This approach has been used for a qualitative explanation of isotope effects in the thermodiffusion of deuterium-substituted hydrocarbon isotopes [24]. In that work, the role of molecular symmetry in isotopic substitution was shown to be important in the explanation of empirical data. That work and the work in Ref. [25] demonstrates the utility of using classical expressions for relevant microscopic parameters to account for isotope effects in measured Soret coefficients, without the need to invoke quantum-mechanical contributions.

In the following calculations, we will use the approximation

$$g_{21}(r,\lambda) = 1 \qquad (14)$$

This approximation assumes the local distribution of solvent molecules is not disturbed by the particle under consideration, and has been widely and effectively used in theories of liquids. In Refs [26-28], for example, the approximation was used in a kinetic approach to the thermodiffusion of colloidal particles. In Refs [29-31] it was used in a hydrodynamic approach to the thermodiffusion of polymer solutions. The approximation of constant local density is also used in theories of regular solutions [32] and leads to the following equation:

$$\mu_{iV} = \mu_{0i} + 4\pi \int_R^\infty \frac{\Phi_{i1}(r)}{v_1} r^2 dr \qquad (15)$$

The last term on the right-hand side of Eq. (15) is identical to the expression obtained in Refs. [26-28].

In Eq. (3), parameter $\dfrac{v_i}{v_1}\mu_{1V}$ can be written as $N_i\mu_{1V}$, where N_i is the number of solvent molecules displaced by the respective particle. Parameter $N_i\mu_{1V}$ can be thought of as the chemical potential of a virtual particle having the same size as the atom or molecule of the i'th isotope, while the remaining parameters are equated to those of a virtual particle of N_i solvent molecules that have been replaced by that isotope. Using the above symmetry between parameters μ_{iV} and $N_i\mu_{1V}$, we can write the effective chemical potential at constant volume as

$$\mu_{iV} - N_i\mu_{1V} = -\frac{3}{2}kT\ln\left(\frac{m_i}{N_i m_1}\right) + 4\pi\int_R^\infty \frac{\Phi_{i1}(r) - \Phi_{11}(r)}{v_1}r^2 dr \qquad (16)$$

Eq. (16) indicates that isotope effects are more pronounced for particles of a molecular size in which the chemical potentials of the non-interacting particles are comparable to the terms related to inter-particle interactions. For larger particles these effects are masked by contributions from the interaction between particles. The increasing effect of particle interactions with size is confirmed by simulations of thermodiffusion of nanoparticles in Ref. [33], where the thermodiffusion parameters are independent of particle mass.

C. Chemical potential at constant pressure.

In thermodynamic and kinetic mass transport equations, the chemical potentials are typically expressed at constant pressure. The chemical potentials at constant pressure and volume for a suspended molecular or colloidal particle can be related through the forces acting on the particle:

$$\nabla\mu_{iP} = \nabla\mu_{iV} + \int_{V_{out}^i} \nabla\Pi_i^{loc} dv \qquad (17)$$

Here Π_i^{loc} is the local distribution of the excess pressure around the particle. In deriving the local excess pressure we follow the method outlined in Ref. [34]. The local pressure distribution is widely used in hydrodynamic theories of kinetic effects in liquids [29-31] and is usually obtained from the condition of local mechanical equilibrium in the liquid. This equilibrium condition is written as $\nabla\left[\Phi_{i1}(r)/v_1 + \Pi_i^{loc}\right] = 0$ and can be obtained by formulating the condition for local equilibrium in a thin spherical layer of thickness l and area S when that layer is shifted from position r to $r+dr$. The resulting change in free energy is defined as

$$dF(r) = \nabla\left[\frac{\Phi_{i1}(r)}{v_1} + \nabla\Pi_i^{loc}\right]lSdr = 0 \qquad (18)$$

In such a closed layer, there is also a change in free energy $\dfrac{\Phi_{i1}(r)}{v_1}ldS$ associated with the change in layer area dS. For a spherical layer, the change in volume and surface area are related by $dV = 2rdS$ and we obtain the following modified form of Eq. (18) for a closed spherical surface:

$$\nabla\left[\frac{\Phi_{i1}(r)}{v_1} + \Pi_i^{loc}\right] + \frac{2\Phi_{i1}(r)}{v_1 r}\vec{r_0} = 0 \qquad (19)$$

where $\vec{r_0}$ is the unit radial vector.

The pressure gradient related to the change in surface area has the same nature as the Laplace (surface) pressure gradient obtained in Ref. [8]. Solving Eq. (19), we obtain

$$\Pi_i^{loc} = -\frac{\Phi_{i1}(r)}{v_1} - \int_\infty^r \frac{2\Phi_{i1}(r')}{v_1 r'} dr' \tag{20}$$

Substituting Eq. (20) into Eq. (17), using Eq. (16), and calculating the temperature-induced pressure gradient related to the temperature dependence of the solvent specific molecular volume v_1, we obtain the following potential gradient related to intermolecular interactions:

$$\frac{\partial \mu_{iP}}{\partial T} = \frac{2\alpha_T}{v_1} \int_{V_{out}^i} dv \nabla_\vartheta T \int_\infty^r \frac{\Phi_{i1}(r')}{r'} dr' \tag{21}$$

Here, $\nabla_\vartheta T$ is the component of the temperature gradient tangent to the surface of a spherical particle and α_T is the thermal expansion coefficient of the solvent. Applying the same procedure to the virtual particle that consists of liquid displaced by the solute, we obtain

$$S_T^i = \frac{2\pi^2 \alpha_T}{v_1 kT} \int_R^\infty r^2 dr \int_\infty^r \frac{\Phi_{i1}(r') - \Phi_{11}(r')}{r'} dr' - \frac{3}{4T} \ln\left(\frac{m_i}{N_i m_1}\right) \tag{22}$$

The molecular interaction potentials of the solute and virtual particle can be defined by the London potentials [35] as

$$\Phi_{i1} = -\varepsilon_{i1}(\sigma_{i1}/r)^6 \tag{23}$$

Here, ε_{i1} is the energy of interaction and σ_{i1} is the minimal atomic approach distance. In the integration of Eq. (21), the lower limit is $R = \sigma_{i1}$. The potential Φ_{11} is determined in a similar manner, with $\sigma_{11} = \sigma_{i1}$ and parameter ε_{11} the energy parameter for interaction between a virtual particle and the solvent molecule.

2. Theory of Isotope Effects

Using Eqs. (22) and (23), the molecular Soret coefficient can be written as

$$S_T^i = S_T^{0i} - \frac{3}{4T} \ln\left(\frac{m_i}{N_i m_1}\right) \tag{24}$$

where

$$S_T^{0i} = \frac{\pi^2 \alpha_T \sigma_{i1}^3 (\varepsilon_{11} - \varepsilon_{i1})}{9 v_1 kT} \tag{25}$$

is the contribution to the Soret coefficient associated with intermolecular interactions.

Studies of isotopic effects in thermodiffusion involve measurements of the following parameter [1-7]:

$$\delta_{ij} = \frac{\phi_i(l)/\phi_i(0)}{\phi_j(l)/\phi_j(0)} - 1 \tag{26}$$

where ϕ_i and ϕ_j are the volume fractions of the respective isotope components at points 0 and l along the temperature gradient. At small temperature intervals, parameter δ_{ij} can be expressed through the Soret coefficient S_T of the respective component [1-7]:

$$\delta_{ij} = -\left(S_T^i - S_T^j\right)\left[T(l) - T(0)\right] \tag{27}$$

The definition of parameter δ_{ij} used in Eqs. (26) and (27) allows for the elimination of factors that are identical for the two isotopes. However, determining the factors that are relevant is a non-trivial task, which we consider below.

When differences in the relevant parameters are small, Eqs (24) and (25) can be used to express the difference in Soret coefficients for isotopes:

$$S_T^i - S_T^j = \frac{m_i - m_j}{m_i}\left[\frac{\partial \ln \sigma_{j1}^3}{\partial m} - \frac{\partial \ln\left(\varepsilon_{11} - \varepsilon_{j1}\right)}{\partial m}\right]S_T^{0j} - \frac{m_i - m_j}{m_i}\left(1 - \frac{\partial \ln \sigma_{j1}^3}{\partial m}\right)\frac{3}{4T} \tag{28}$$

The terms in brackets related to inter-molecular interactions are non-zero when the molecular volumes and/or energetic parameters of the isotopes are different. The fact that such size differences are significant is demonstrated by the ability to separate isotopes in liquids by diffusion, and such differences have been explained by differing bond length [37]. The dependence of diffusion coefficients on atomic mass has been shown to fit the following equation [36]:

$$\frac{D_i}{D_j} = \left(\frac{M_j}{M_i}\right)^{\beta} \tag{29}$$

where β is an empirical dimensionless parameter. This size dependence may be another classical mechanism of isotope effect in thermodiffusion. Using Eq. (29) and the Stokes-Einstein expression for the diffusion coefficient, and assuming the hydrodynamic radius and the minimal atomic approach distance in Eq. (23) are proportional, we can write

$$\frac{\sigma_{i1}}{\sigma_{j1}} = \left(\frac{M_i}{M_j}\right)^{\beta} \tag{30}$$

Using Eq. (30), Eq. (28) can be written as

$$S_T^i - S_T^j = \frac{m_i - m_j}{m_i}\left[3\beta\left(S_T^{0j} + \frac{3}{4T}\right) - \frac{3}{4T}\right] \tag{31}$$

Eq. (31) can be used to compare predictions of the model with empirical data. In this comparison, we use the approach used in Refs [1-7], where parameter δ_{ij} in Eq. (25) is expressed as

$$\delta_{ij} = -\alpha_0 \frac{m_i - m_j}{m_i + m_j}\frac{T - T_0}{T_0} \tag{32}$$

Here α_0 is an empirical parameter that is either calculated numerically or obtained from experimental data in the literature. Comparing Eqs (32), (30), and (31), we obtain the following theoretical expression for α_0 in systems where the difference in isotope mass is small and the temperature range is narrow:

$$\alpha_0 = 6\beta\left(TS_T^{0j} + \frac{3}{4}\right) - \frac{3}{4} \qquad (33)$$

There are also the data regarding the mass dependence of the energetic parameters [38, 39]. However there is no specific information regarding the silicate melts. For this reason we assume that the mass dependence of the isotope energetic parameters is also described in the similar way as the isotope molecular size [see Eqs (29-30)]. This approach yields the modified Eq. (33):

$$\alpha_0 = 8\beta\left(TS_T^{0j} + \frac{9}{16}\right) - \frac{3}{4} \qquad (34)$$

In the comparison with the empiric results, we will use both Eq. (33) and Eq. (34) to obtain the best fitting.

3. Results

Eqs (33) and (34) can be used to calculate S_T^{0j} in the Soret coefficient related to intermolecular interactions. In turn, the calculated values of S_T^{0j} can be used to calculate the respective Soret coefficients from Eqs. (24) and (25). The resulting Soret coefficients are calculated using the assumption that $\ln\left(\frac{m_i}{N_i m_1}\right) \approx \ln\frac{\rho_i}{\rho_0}$ in Eq. (25), where ρ_i is the density of the respective element and ρ_0 is the density of the solvent medium:

$$S_T^i = S_T^{0i} - \frac{3}{4T}\ln\frac{\rho_i}{\rho_0} \qquad (35)$$

The values of parameter $E = 2\beta$ were collected from several sources, but are summarized in Ref. [36].

Eqs. (33-34) are now used to evaluate predictions of the proposed model. The most direct way to do such an evaluation is to calculate values of parameter α_0 by substituting the value of the Soret coefficient predicted from Eq. (34) into Eq. (33). However, it is difficult to find a consistent set of the parameters S_T^i, α_0, and β, as the variance in data from different sources for the same system is quite large. Consequently, we calculated values of the Soret coefficient using known experimental values δ and β, and compared the calculated values with experimental values from other experiments.

In these calculations, the values of parameter δ were taken from Ref. [1] (sample ZM98B), where the data for isotopes dissolved in basalt are collected. The values of β for basalt-rhyolite are taken from Ref. [36] and the experimental values of S_T^i for comparison are obtained from Ref. [37]. The values of the Soret coefficients are obtained by the graphical differentiation of the experimental plots in [37].

Values of the Soret coefficients calculated using Eq. (31) were obtained with the assumption that the density of the basalt is $\rho_0 = 3.0\ g/cm^3$. The densities of the isotopes are assumed to be equal to those of their melts: $\rho_{Fe} = 6.98\ g/cm^3, \rho_{Ca} = 1.55\ g/cm^3$, and $\rho_{Mg} = 1.75\ g/cm^3$. In calculating the Soret coefficient, we assumed that differences between isotope parameters are negligibly small. The comparison of the theoretically calculated Soret coefficients and the experimental values is summarized in Table 2.

Table 1. Literature values of parameters.

Isotope Pair	Separation factor δ from Ref. [1] (10^{-3})	β [27]	Calculated factor α_0 [Eq. (32)]	Density of isotopes, g/cm^3
^{56}Fe/^{54}Fe	-0.38	0.03	0.137	6.98
^{44}Ca/^{40}Ca	-2.28	0.075	0.239	1.55
^{26}Mg/^{24}Mg	-1.73	0.05	0.376	1.75

Table 2. Comparison of Theoretical Model with Empirical Data*

Isotope Pair	Calculated Soret coefficient (10^3 K^{-1})	Experimental Soret coefficient (10^3 K^{-1}) [37]
^{56}Fe/^{54}Fe	2.5 -2.6**	1.9 – 2.5
^{44}Ca/^{40}Ca	1.1 – 1.2	0.5 – 0.7
^{26}Mg/^{24}Mg	1.9 - 2.0	1.6 – 1.9

*The density of basalt is assumed to be 3.0 g/cm^3.

**Calculated using Eq. (34). The other two values are calculated taking into account the mass dependence of energetic parameter [Eq. (35)].

Considering the parameters we used were taken from different sources, that the complex composition is considered a simple quasi-binary system because the component parameters are unknown, and that very coarse approximations for the parameters of the virtual particle were used, the agreement between experiment and theory is sufficient to conclude that the model is reasonable.

4. Conclusions

In conclusion, the theory developed in Refs. [16, 24, 34] yields an adequate description of isotope effects in thermodiffusion in silicate melts, providing reasonable values of the Soret coefficients given the coarse approximations utilized. The model based on classical statistical mechanics relates isotope effects in thermodiffusion to differences in the thermal velocities of isotopes having the same thermal energy but different masses and sizes, which is not possible using methods described previously.

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