Verification of the Onsager Reciprocal Relations in a Molten Silicate Solution

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A key hypothesis in the generalized theory of nonequilibrium thermodynamics is the principle of microscopic time invariance as enunciated by Onsager in the 1930s. At the macroscopic level, Onsager's hypothesis is represented by a set of relations known as the Onsager reciprocal relations, which, when applied to isothermal, multicomponent diffusion, demand the symmetry of the phenomenological matrix that connects mass fluxes to chemical potential gradients. On the basis of experimentally determined diffusion coefficients and thermochemical data for the molten system CaO-Al_2O_3-SiO_2, the Onsager phenomenological coefficients have been computed, including an analysis of error. Within experimental uncertainty, the Onsager matrix is indeed symmetric.

Many important diffusion problems in the earth sciences and other disciplines involve multicomponent materials. Nevertheless, it is common practice to apply the binary diffusion formalism, which goes back more than 140 years (*1*), to these problems. The pseudo-binary approximation cannot explain all features of diffusion in multicomponent systems, such as nonmonotonic composition profiles in isothermal diffusion couples, and may introduce sizable errors in the prediction of mass transfer rates. The quality of the pseudo-binary approximation is difficult to evaluate because it depends on the composition of the diffusion couple and the particular component being considered. Furthermore, it is not theoretically justified. The classic studies of Onsager, beginning in the 1930s (*2*), gave multicomponent diffusion a coherent phenomenological basis, including cross terms (*3*).

The presence of cross-coupling and the symmetry of the phenomenological coefficient matrix had been anticipated earlier for a few transport processes (*4*), but it was the statistical mechanical approach of Onsager, based on the principle of microscopic reversibility, that enabled formulation of a generalized approach to the thermodynamics of irreversible phenomena (*5*). A key element of the theory of irreversible processes, or nonequilibrium thermodynamics, is the set of relations known as the Onsager reciprocal relations (ORR)—when the thermodynamic forces and fluxes are chosen appropriately, the phenomenological coefficient matrix is symmetric. Similar to the fundamental laws of equilibrium thermodynamics, the ORR can only be verified experimentally.

A large impediment to experimental tests is the prerequisite of obtaining experimental data for both diffusion coefficients and activity coefficients in the same range of composition so that the experimental D_{ik} matrix can be transformed to the Onsager phenomenological L_{ik} matrix. Because of the lack of thermodynamic data, the validity of the ORR for isothermal, multicomponent chemical diffusion has been confirmed for a relatively small number of aqueous and metallic systems (*6*). Indeed, the ORR have not been verified for molten silicate solutions, although accurate D_{ik} are known for several ternary systems (*7, 8*). In this report, we summarize the results of calculations that enable an accurate test of Onsager's reciprocity hypothesis for the molten ternary system consisting of 40% CaO, 20% Al_2O_3, and 40% SiO_2 by weight. We have performed the tedious, but otherwise straightforward, calculations utilizing available diffusion (*7*) and thermochemical (*9*) data for this system. When using numeric subscripts, the components are numbered as follows: (CaO) = 1, (Al_2O_3) = 2, and (SiO_2) = 3.

The classical irreversible thermodynamic analysis of isothermal, multicomponent diffusion is widely accepted and well known (*5*). Here, a brief sketch of the theory is provided with a focus upon those relations needed to test the Onsager hypothesis. The starting point in the analysis is the development of an expression for the volumetric entropy production rate (σ) in terms of an appropriate set of independent fluxes and thermodynamic forces. For an isotropic, n-component, nonelectrolyte mixture in the absence of external fields, pressure gradients, and chemical reactions, the entropy production rate is

$$\sigma = \sum_{i=1}^{n-1} j_i \left\{ \sum_{k=1}^{n-1} \left(\delta_{ik} + \frac{w_k}{w_n} \right) \frac{1}{T} \nabla \mu_k \right\} \tag{1}$$

where δ_{ik} is the Kronecker delta, w_k is the mass fraction of component k, T is absolute temperature, μ_k is the specific (per unit mass) chemical potential of component k, ∇ is the gradient operator, and j_i is the mass diffusion flux of component i with respect to a barycentric reference frame (*10*). In writing Eq. 1, the mass conservation relation

$$\sum_{i=1}^{n} j_i = 0 \tag{2}$$

and the isothermal, isobaric Gibbs-Duhem equation

$$\sum_{i=1}^{n} w_i (\nabla \mu_i)_{T,P} = 0 \tag{3}$$

where P is pressure, have been used to eliminate the dependent flux (j_n) and chemical potential gradient ($\nabla \mu_n$).

The phenomenological equations, written for the choice of fluxes and thermodynamic forces used in Eq. 1, define the matrix of phenomenological coefficients L_{ik}:

$$-j_i = \sum_{k=1}^{n-1} L_{ik} \left(\delta_{ik} + \frac{w_k}{w_n} \right) \frac{1}{T} \nabla \mu_k \qquad (i = 1, 2, \ldots, n-1) \tag{4}$$

The empirical diffusion matrix, D_{ik} (values given in Table 1), is defined in a barycentric reference frame according to

$$-j_i = \rho \sum_{k=1}^{n-1} D_{ik} \nabla w_k \quad (i = 1, 2, \ldots, n-1) \tag{5}$$

where ρ is the melt density. The relation between the phenomenological matrix, which is based on spatial gradients of the chemical potentials, and the empirical diffusion matrix, which is based on spatial gradients of the mass fractions, may be found by equating the expressions for the mass flux j_i. Comparison of Eqs. 4 and 5 leads to the desired relation between D_{ik} and L_{ik}:

Table 1. Diffusion coefficients at high temperature for a melt of composition 40% CaO, 20% Al_2O_3, and 40% SiO_2 by weight (*7*). Uncertainties represent 1 SD. The absolute values of the cross-coupling coefficients are not necessarily small compared with the on-diagonal values.

T (K)	D_{11} ($m^2 s^{-1}$)	D_{12} ($m^2 s^{-1}$)	D_{21} ($m^2 s^{-1}$)	D_{22} ($m^2 s^{-1}$)
1723	$(6.8 \pm 0.3) \times 10^{-11}$	$(-2.0 \pm 0.5) \times 10^{-11}$	$(-3.3 \pm 0.5) \times 10^{-11}$	$(4.1 \pm 0.7) \times 10^{-11}$
1773	$(1.0 \pm 0.1) \times 10^{-10}$	$(-2.8 \pm 0.8) \times 10^{-11}$	$(-4.2 \pm 0.8) \times 10^{-11}$	$(7.3 \pm 0.4) \times 10^{-11}$
1823	$(1.8 \pm 0.2) \times 10^{-10}$	$(-4.6 \pm 0.6) \times 10^{-11}$	$(-6.4 \pm 0.5) \times 10^{-11}$	$(1.5 \pm 0.1) \times 10^{-10}$

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$$\rho D_{i\ell} = \frac{1}{T}\sum_{j=1}^{n-1} L_{ij}\sum_{k=1}^{n-1}\left(\delta_{jk} + \frac{w_k}{w_n}\right)\mu_{k\ell}$$

$$(i,\ell = 1, 2, \ldots, n-1) \qquad (6)$$

Here $\mu_{k\ell}$ is the matrix of derivatives of the chemical potential at constant temperature and pressure with respect to mass fractions:

$$\mu_{k\ell} = \left(\frac{\partial \mu_k}{\partial w_\ell}\right)_{P,T,w_j}$$

$$(j = 1, 2, \ldots, n-1; j \neq \ell) \qquad (7)$$

In order to compute $\mu_{k\ell}$, use is made of a Margules solution formulation for the molar excess Gibbs free energy of the liquid, $\tilde{G}^E$ (*11*). The thermodynamic model is constrained by liquidus relations, the miscibility gap in the subsystem CaO-SiO$_2$, solid-solid reactions under polybaric and polythermal conditions, and calorimetrically determined standard state entropies, enthalpies, and volumes of crystalline phases in the system CaO-Al$_2$O$_3$-SiO$_2$ (9). It recovers the CaO-Al$_2$O$_3$-SiO$_2$ phase diagram quite well, including liquid compositions along cotectic curves and at invariant points. Maximum differences between calculated and experimentally determined invariant points are 17 K and 1.5% by weight in any component. Values for the Margules parameters are given in Table 2.

Derivatives of the molar chemical potential with respect to mole fraction ($\tilde{\mu}_{ik}$) may be written in terms of the excess free energy using the definition of the chemical potential.

$$\tilde{\mu}_{11} = \left(\frac{\partial \tilde{\mu}_1}{\partial x_1}\right)_{x_2} = \frac{RT}{x_1} + x_2\left[\frac{\partial}{\partial x_1}\left(\frac{\partial \tilde{G}^E}{\partial x_1}\right)_{x_3}\right]_{x_2} + x_3\left(\frac{\partial^2 \tilde{G}^E}{\partial x_1^2}\right)_{x_2} \qquad (8a)$$

$$\tilde{\mu}_{12} = \left(\frac{\partial \tilde{\mu}_1}{\partial x_2}\right)_{x_1} = x_2\left[\frac{\partial}{\partial x_2}\left(\frac{\partial \tilde{G}^E}{\partial x_1}\right)_{x_3}\right]_{x_1} + x_3\left[\frac{\partial}{\partial x_2}\left(\frac{\partial \tilde{G}^E}{\partial x_1}\right)_{x_2}\right]_{x_1} \qquad (8b)$$

$$\tilde{\mu}_{21} = \left(\frac{\partial \tilde{\mu}_2}{\partial x_1}\right)_{x_2} + x_1\left[\frac{\partial}{\partial x_1}\left(\frac{\partial \tilde{G}^E}{\partial x_2}\right)_{x_3}\right]_{x_2} + x_3\left[\frac{\partial}{\partial x_1}\left(\frac{\partial \tilde{G}^E}{\partial x_2}\right)_{x_1}\right]_{x_2} \qquad (8c)$$

$$\tilde{\mu}_{22} = \left(\frac{\partial \tilde{\mu}_2}{\partial x_2}\right)_{x_1} = \frac{RT}{x_2} + x_1\left[\frac{\partial}{\partial x_2}\left(\frac{\partial \tilde{G}^E}{\partial x_2}\right)_{x_3}\right]_{x_1} + x_3\left(\frac{\partial^2 \tilde{G}^E}{\partial x_2^2}\right)_{x_1} \qquad (8d)$$

where R is the gas constant. Finally, $\tilde{\mu}_{ik}$ is transformed to μ_{ik} by the linear transformation

$$\mu = \mathbf{M}\tilde{\mu}\mathbf{N} \qquad (9)$$

by use of the supplementary relations

$$\mathrm{M}_{ij} = \delta_{ij}\mathrm{M}_i \qquad (10)$$

$$N_{ij} = \delta_{ij}\frac{\mathrm{M}}{\mathrm{M}_i} + x_i\left(\frac{\mathrm{M}}{\mathrm{M}_n} - \frac{\mathrm{M}}{\mathrm{M}_j}\right) \qquad (11)$$

where M_i is the kilogram formula weight of the ith component and M is the kilogram formula weight of the bulk composition ($x_1 = 0.453$, $x_2 = 0.125$, $x_3 = 0.423$) computed according to

$$\mathrm{M} = \sum_{i=1}^{n} x_i \mathrm{M}_i \qquad (12)$$

At this point, the only unknowns in Eq. 6 are the Onsager phenomenological coefficients, L_{ik}. If one defines

$$\mathrm{G}_{ik} = \left(\delta_{ik} + \frac{w_k}{w_n}\right)\mu_{ik} \qquad (13)$$

then the phenomenological coefficients for a ternary system take the form

$$L_{11} = \frac{\rho T(D_{12}\mathrm{G}_{21} - D_{11}\mathrm{G}_{22})}{(\mathrm{G}_{12}\mathrm{G}_{21} - \mathrm{G}_{11}\mathrm{G}_{22})} \qquad (14a)$$

$$L_{12} = \frac{\rho T(D_{11}\mathrm{G}_{12} - D_{12}\mathrm{G}_{11})}{(\mathrm{G}_{12}\mathrm{G}_{21} - \mathrm{G}_{11}\mathrm{G}_{22})} \qquad (14b)$$

$$L_{21} = \frac{\rho T(D_{22}\mathrm{G}_{21} - D_{21}\mathrm{G}_{22})}{(\mathrm{G}_{12}\mathrm{G}_{21} - \mathrm{G}_{11}\mathrm{G}_{22})} \qquad (14c)$$

$$L_{22} = \frac{\rho T(D_{21}\mathrm{G}_{12} - D_{22}\mathrm{G}_{11})}{(\mathrm{G}_{12}\mathrm{G}_{21} - \mathrm{G}_{11}\mathrm{G}_{22})} \qquad (14d)$$

Our results are summarized in Table 3, which has all of the parameters needed in Eq. 14, except for D_{ik}, which are in Table 1. The reported errors in L_{ik} are 1 SD from the mean. We computed errors using the reported uncertainties on D_{ik} and a conservative estimate of 5% relative errors for the Margules solution parameters (9) needed to compute G_{ik}. Because the ratio of L_{12} to L_{21} is unity within the experimental uncertainty (Table 3), we conclude that the ORR are satisfied (*12*).

The fact that the ORR have proven to be valid for such a wide range of chemical systems should encourage scientists to apply the multicomponent formalism instead of the pseudo-binary approximation. In addition to providing a more accurate description of chemical diffusion, the multicomponent theory provides an elegant solution for many problems based on the fact that the diffusion matrix is diagonalizable and has real, positive eigenvalues (5). In fact, it can be shown that the pseudo-binary approxi-

Table 2. Interaction parameters for the Margules-solution model of the CaO-Al$_2$O$_3$-SiO$_2$ system (*9*). Margules parameters used in the expression for $\tilde{G}^E$ are given by $\tilde{W} = \tilde{W}_H - T\tilde{W}_S$.

Index	$\tilde{W}_H$ (J mol^{-1})	$\tilde{W}_S$ (J mol^{-1} K^{-1})
1112	−455,634.210	−2.470
1122	−725,166.290	−255.390
1222	−240,214.840	−26.700
1113	−898,692.640	−240.770
1133	−350,208.150	48.620
1333	−14,081.800	35.490
2223	63,617.160	23.740
2233	1,642,663.510	763.870
2333	−106,635.220	−28.130
1123	209,108.930	313.360
1223	−2,149,042.640	−641.840
1233	−2,847,911.220	−1,046.350

Table 3. Test of the Onsager reciprocity relations. For this ternary system, symmetry of the matrix L_{ik} requires that $L_{12} = L_{21}$. Uncertainties in L_{ik} were determined by from the reported error on D_{ik} (*7*) and from assumed 5% relative errors in the G_{ik}.

	T = 1723 K	T = 1773 K	T = 1823 K
ρ (kg m^{-3})	2693 ± 6	2684 ± 6	2674 ± 6
μ_{11} (J kg^{-1})	4.0401×10^6	4.0425×10^6	4.0448×10^6
μ_{12} (J kg^{-1})	1.7832×10^6	1.7474×10^6	1.7115×10^6
μ_{21} (J kg^{-1})	2.1099×10^5	1.3563×10^5	6.0272×10^4
μ_{22} (J kg^{-1})	1.5805×10^6	1.5024×10^6	1.4243×10^6
G_{11} (J kg^{-1})	8.1858×10^6	8.1528×10^6	8.1198×10^6
G_{12} (J kg^{-1})	4.3566×10^6	4.2459×10^6	4.1352×10^6
G_{21} (J kg^{-1})	4.3566×10^6	4.2459×10^6	4.1352×10^6
G_{22} (J kg^{-1})	4.1539×10^6	4.0009×10^6	3.8480×10^6
L_{11} (kg K m^{-1} s^{-1})	$(1.14 \pm 0.21) \times 10^{-10}$	$(1.69 \pm 0.33) \times 10^{-10}$	$(3.04 \pm 0.56) \times 10^{-10}$
L_{12} (kg K m^{-1} s^{-1})	$(-1.42 \pm 0.30) \times 10^{-10}$	$(-2.13 \pm 0.47) \times 10^{-10}$	$(-3.85 \pm 0.78) \times 10^{-10}$
L_{21} (kg K m^{-1} s^{-1})	$(-0.975 \pm 0.212) \times 10^{-10}$	$(-1.56 \pm 0.31) \times 10^{-10}$	$(-2.99 \pm 0.58) \times 10^{-10}$
L_{22} (kg K m^{-1} s^{-1})	$(1.48 \pm 0.32) \times 10^{-10}$	$(2.52 \pm 0.44) \times 10^{-10}$	$(5.11 \pm 0.86) \times 10^{-10}$
L_{12}/L_{21}	1.46 ± 0.44	1.36 ± 0.40	1.29 ± 0.36

mation is only valid when the diffusion couple lies along an eigenvalue direction. Consequently, the quality of the pseudobinary approximation cannot be reliably estimated because it is impossible to know a priori the directions of the eigenvectors. A promising alternative to experimental measurement of D_{ik} is the use of molecular dynamics simulations that generalize established methods for calculating binary interdiffusion coefficients (*13*).

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3. Diffusion studies in binary systems involve the determination of a single diffusion coefficient that may be a function of temperature, pressure, and composition. In a ternary system, there are four independent chemical diffusion coefficients; in a quaternary system, nine diffusion coefficients; and, in general, $(n - 1)^2$ diffusion coefficients in an *n*-component system. Written as a matrix (D_{ik}), the off-diagonal terms (for example, D_{12} and D_{21} in a ternary system) are referred to as the cross-coupling terms because they link the flux of one component to the concentration gradient of a different component.
4. For example, the thermoelectric effect [W. Thomson, *Proc. Roy. Soc. Edinburgh* **3**, 225 (1854)] and the heat conduction in anisotropic solids [G. Stokes, *Camb. Dublin Math J.* **6**, 215 (1851)].
5. Irreversible phenomena as diverse as thermoelectricity, heat conduction in anisotropic materials, thermogalvanomagnetism, isothermal chemical diffusion, and chemical diffusion in a thermal gradient are some notable examples [see S. R. deGroot and P. Mazur, *Non-Equilibrium Thermodynamics* (Dover, New York, 1984); D. D. Fitts, *Nonequilibrium Thermodynamics* (McGraw-Hill, New York, 1962); S. Wisniewski, B. Staniszewski, R. Szymanik, *Thermodynamics of Nonequibirum Processes* (Reidel, Dordrecht, the Netherlands, 1976)]. Experimental data supporting Onsager's approach to these phenomena is summarized in D. G. Miller, *Chem. Rev.* **60**, 15 (1960).
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8. A. K. Varshneya and A. R. Cooper, *J. Am. Ceram. Soc.* **55**, 312 (1972); H. Wakabayashi and Y. Oishi, *J. Chem. Phys.* **68**, 2046 (1978).
9. R. G. Berman and T. H. Brown, *Geochim. Cosmochim. Acta* **48**, 661 (1984). Uncertainties on the Margules parameters are not provided, but relative errors are most likely in the range 5 to 15%.
10. The definition of the diffusive mass flux is deceptively simple: $j_i = \rho w_i(v_i - v)$, where ρ is the density, v_i is the average velocity of component *i*, and *v* is the reference velocity. However, the equation of mass conservation (Eq. 2) and the relation between the fluxes and concentration gradients (Eq. 5) must be written differently, depending on the reference velocity used. A number of reference velocities are in common use, including volume, mass, mole, and solvent average velocities. In this report, *v* is the mass average (or barycentric) velocity.
11. The molar chemical potential for component 1 in a ternary system is given by

$$\tilde{\mu}_1 = \tilde{\mu}^o{}_1 + RT\ln(x_1) + \tilde{G}^E + x_2\left(\frac{\partial \tilde{G}^E}{\partial x_1}\right)_{x_3} + x_3\left(\frac{\partial \tilde{G}^E}{\partial x_1}\right)_{x_2}$$

where $\tilde{\mu}^o{}_1$ is the reference state chemical potential, *R* is the gas constant, x_i is the mole fraction of component *i*, and $\tilde{G}^E$ is the excess Gibbs free energy of the melt. The chemical potential of components 2 and 3 may be found by permutation of the subscripts. The Margules solution model for the excess Gibbs free energy is

$$\tilde{G}^E = \tilde{W}_{1112}x_1^3x_2 + \tilde{W}_{1122}x_1^2x_2^2 + \tilde{W}_{1222}x_1x_2^3 + \tilde{W}_{1113}x_1^3x_3 + \tilde{W}_{1133}x_1^2x_3^2 + \tilde{W}_{1333}x_1x_3^3 + \tilde{W}_{2223}x_2^3x_3 + \tilde{W}_{2233}x_2^2x_3^2 + \tilde{W}_{2333}x_2x_3^3 + \tilde{W}_{1123}x_1^2x_2x_3 + \tilde{W}_{1223}x_1x_2^2x_3 + \tilde{W}_{1233}x_1x_2x_3^2$$

The Margules parameters are functions of temperature and follow the relation $\tilde{W} = \tilde{W}_H - T\tilde{W}_S$, where *H* is enthalpy, *S* is entropy, and the subscripts defining specific component interactions have been dropped for convenience.
12. If the matrix G_{ik} is ill-conditioned (for example, $\det(G_{ik}) = G_{12}G_{21} - G_{11}G_{22}$ is small) the values of L_{ik} will not be accurately determined by Eq. 14. It is still possible to test the validity of the ORR, however. Equating L_{12} and L_{21} leads to the conclusion that the reciprocal relations are valid if $(D_{11}G_{12} - D_{12}G_{11} + D_{21}G_{22} - D_{22}G_{21})$ equals zero. This type of singularity occurs near critical points and is not a problem for the CaO-Al_2O_3-SiO_2 composition under consideration.
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Comparative Compressibilities of Silicate Spinels: Anomalous Behavior of $(Mg,Fe)_2SiO_4$

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Compressibilities of five silicate spinels, including γ-Mg_2SiO_4, γ-Fe_2SiO_4, Ni_2SiO_4, and two ferromagnesian compositions, were determined on crystals positioned in the same high-pressure mount. Subjection of all crystals simultaneously to the same pressure revealed differences in compressibility that resulted from compositional differences. Ferromagnesian silicate spinels showed an anomalous 13 percent increase in bulk modulus with increasing iron content, from Mg_2SiO_4 (184 gigapascals) to Fe_2SiO_4 (207 gigapascals). This result suggests that ferrous iron and magnesium, which behave similarly under crustal conditions, are chemically more distinct at high pressures characteristic of the transition zone and lower mantle.

Knowledge of the compression behavior of oxide and silicate minerals helps to reveal the structure and dynamics of the Earth's deep interior. Furthermore, data on these minerals provide an understanding of the varied effects of pressure on structure and bonding. In this report, I describe anomalous compression behavior in ferromagnesian silicate spinels, which are assumed to be major minerals in the Earth's transition zone.

Most crustal minerals, including magnesium-iron silicates, may be modeled as ionic compounds with bond strengths determined to a first approximation by Coulombic forces. In the 1920s, Bridgman first demonstrated empirical inverse correlations between bulk modulus and molar volume and rationalized his results on an electrostatic model (*1*). Relations between bulk modulus and volume have subsequently developed into useful tools to predict properties of oxides, halides, silicates, and many other compounds. Such relations for isomorphous isoelectronic series (*2*), as well as for individual cation coordination polyhedra (*3*), provide a basis for comparison of bulk moduli and individual bond compressibilities throughout a wide range of condensed materials.

The high-pressure behavior of minerals with Mg-Fe^{2+} solid solution has been studied intensively because of the importance of these minerals in models of the Earth. Polymorphs of $(Mg,Fe)SiO_3$ and $(Mg,Fe)_2SiO_4$ are of particular concern because the major element bulk composition of the mantle is believed to fall somewhere between those stoichiometries. A key issue in geophysics and mineral physics has been the nature of the seismic discontinuity at 670 km, which marks the boundary between the transition zone and lower mantle. Both $(Mg,Fe)SiO_3$ silicate perovskite and $(Mg,Fe)O$ are believed to exist below this boundary, whereas $(Mg,Fe)_2SiO_4$ silicate spinel occurs above

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