Diffusion in Metamorphic Tectonites: Lattice-Fixed Reference Frames

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Diffusion in metamorphic tectonites: lattice-fixed reference frames

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The nature of volume diffusion during metamorphism may be studied by examining compositional zoning in metamorphic minerals. Garnets with sharp optical zones and internal fabrics related to deformation are of special interest, because they provide a link between partitioning by growth and by diffusion.

Diffusion in the almandine-rich garnets of pelitic schists involves, at the very least, the migration of four ionic components (Fe^{2+}, Mn^{2+}, Mg^{2+} and Ca^{2+}). Because of the possible occurrence of uphill diffusion and other phenomena we do not intuitively associate with diffusion, the search for evidence of volume diffusion must be preceded by a careful theoretical and experimental examination of diffusion in multicomponent minerals.

The theoretical and experimental investigation of diffusion in silicates may be simplified by: (1) the choice of ions as components in the flux equations; (2) the construction of lattice-fixed reference frames to reduce the number of flux equations and diffusion coefficients.

Flux equations are developed specifically for diffusion via ionized vacancies, but they may be easily modified to treat diffusion via neutral vacancies or by one to one exchange of ions. Methods are presented for solving the flux equations under the constraint that the crystal remain electrically neutral during diffusion.

The transition-state theory of Lane & Kirkaldy (1964), which allows the calculation of the matrix of chemical diffusion coefficients from the mobility of individual ions, is adapted to the particular lattice-fixed frames developed here.

Introduction

We may divide diffusion processes during metamorphism into intergranular diffusion and volume diffusion. At very low grades of metamorphism, or during metasomatism, a continuous, interstitial fluid may be present. Except in unusual circumstances, however, the dimensions of the pores and channels occupied by the fluid may be expected to be small and surface effects at the liquid–solid contact will influence the properties of the interstitial fluid. Thus diffusion in the interstitial fluid may be very different to that in a bulk fluid of the kind in which experiments are normally conducted, and in which surface effects are carefully excluded or minimized. At higher metamorphic grades, there is no textural evidence for the existence of an interstitial fluid. At least at the stage of evolution recorded by the texture, intergranular diffusion proceeded along coherent grain boundaries.

Intergranular diffusion presents very difficult theoretical and experimental problems (Fisher & Elliot 1974), especially in aggregates composed of a number of phases sharing three or more components. There may be some advantage in attempting to treat some kinds of intergranular diffusion as volume diffusion in a particular phase with well-defined properties. For example, diffusion in an interstitial fluid might be considered as volume diffusion in a fluid whose properties are determined not only by temperature, pressure and composition, but also by geometric factors and surface effects. By examining the influence of surface effects on

the mobility of individual ions, it may be possible to approximate diffusion in the interstitial fluid by suitable modification of theories developed for diffusion in bulk fluids. Kinetic theories, one example of which is discussed in a later section of this paper, appear to be of particular significance in this connexion.

By introducing the concept of a dividing surface (Gibbs 1873), it is possible to assign thermo-dynamic functions to grain boundaries. Physically then, grain boundaries may be treated as a continuum in the same fashion as interconnected pores in sediments have been analysed by Bear (1972). But, in contrast to the previous case, where the bulk fluid might be envisaged as a reference system for the description of diffusion in the interstitial fluid, the choice of a reference system is not as evident.

Evidently, a geometric factor must appear in the diffusion equations to account for non-linear paths. Where diffusion occurs along boundaries between phases in which the diffusion components are essentially insoluble (e.g. Fe, Ca, etc. along quartz–quartz boundaries), a tor-tuosity tensor may be defined in a straight forward way (Bear 1972). In contrast, where components may cross the boundaries of the continuum, the formal definition of the tortuosity tensor becomes complicated.

With the definition of a continuum with well-defined thermodynamic properties at each point, interstitial diffusion may be broken up into: (1) volume diffusion along concentration gradients within and parallel to the boundaries of the continuum; (2) the non-equilibrium transfer of material across the boundaries of the continuum.

During metamorphism, volume diffusion acts to homogenize individual grains; interstitial and volume diffusion act to create domains of local chemical equilibrium among minerals that share mutually soluble elements. With the electron microprobe, we may hope to decipher some-thing of the magnitude and role of each process. In general, both processes will involve the diffusion of three or more species – that is multicomponent diffusion. A complete formal analysis of multicomponent diffusion, drawing on non-equilibrium thermodynamics, was initiated by Onsager in 1945. An elegant and lucid treatment, incorporating developments between 1945 and 1960, has been given by de Groot & Mazur (1962). Binary diffusion may be treated with some advantage as a special case of multicomponent diffusion.

The analysis of volume diffusion in metamorphic minerals presents three problems: (1) Adaptation of the present theory to deal specifically with silicates. There are important dif-ferences between diffusion in silicates and diffusion in metals and aqueous electrolytes where most experimental and theoretical work has been concentrated; (2) Construction of analytical or approximate theories to reduce the burden of experimental work. This problem is common to multi-component diffusion in metals, glasses, aqueous electrolytes, etc., but assumes a special importance in silicates. Direct measurement of diffusion coefficients in four component systems such as metamorphic garnets may be technically impossible. The petrologist is also faced with the additional problems of a limited supply of natural or synthetic materials and experiments of long duration; (3) Last, and perhaps most importantly, is a systematic search for the nature and magnitude of diffusion in metamorphic rocks. Without a complete theoretical and experi-mental understanding of multicomponent diffusion in silicates, we may easily overlook the effects of diffusion in rocks. The creation or maintenance of discontinuities in chemical com-position, or the transport of material from regions of low to high concentration, are not phenomena we intuitively associate with diffusion. Yet experimental work has documented these phenomena in metals and glasses. Excellent examples of 'uphill' diffusion – the diffusion

of a component up its own concentration gradient – have been given by Cooper (1974) in silicate glasses (see also Darken 1951).

The theoretical analysis of diffusion in silicates reduces to the problem of constructing a set of lattice-fixed reference frames, in which the conditions of electrical neutrality may be imposed (Anderson & Buckley 1974). It is the purpose of this paper to show that the treatment of de Groot & Mazur (1962) may be extended in a simple and natural way to solve this problem. A modified version of the transition-state theory of Lane & Kirkaldy (1964) to fit the lattice-fixed reference frames developed here is also presented.

Although the discussion below is restricted to volume diffusion, it may serve to illuminate some of the theoretical and experimental problems inherent in the analysis of intergranular diffusion in multicomponent aggregates. The model of Lane & Kirkaldy (1964) has been employed with slight modification to approximate diffusion coefficients in aqueous electrolytes with significant success (Lane & Kirkaldy 1965, 1966; Miller 1967a).

To illustrate various arguments, reference is made to diffusion in a garnet with the ideal composition $(Fe^{2+}, Ca, Mn^{2+}, Mg)_3Al_2Si_3O_{12}$. Deviations from this stoichiometric composition, associated with the presence of point defects, are considered in later sections of the paper. The arguments themselves, however, are perfectly general and applicable to diffusion in any ionic or partially ionic crystal of two or more components.

Diffusion fluxes

A diffusion flux is, by definition, the amount of material crossing unit area of a plane per unit of time. The reference plane may be attached to the local centre of volume, the local centre of mass, a particular species, etc. Thus the fluxes are described wth respect to a set of Galilean coordinate systems, each moving with a different velocity v^a relative to an arbitrary, external coordinate system (for example, the walls of a diffusion cell in an experiment with liquids constitute an external cordinate system; Kirkwood et al. 1960). For simplicity of notation, all equations are written in one-dimensional form. Thus v^a is the component of the velocity parallel to the axis of diffusion. Subscripts attached to a component of a vector quantity (e.g. v_i or v_k) refer to the chemical components of the solution.

The flux J_i of species i, moving with a mean velocity v_i is defined as (in a particular reference frame a, and for molar fluxes),

$$J_i^a = c_i(v_i - v^a) \quad (i = 1, 2, \ldots, n),$$ (1)

where c_i is the molar concentration of i. The reference velocities v^a for various reference frames are defined by

$$v^a = \sum_{i=1}^{n} a_k v_k,$$ (2)

where the weighing factors a_i are subject to the normalization condition

$$\sum_{i=1}^{n} a_i = 1.$$ (3)

Weighing factors and reference velocities for different reference frames are given in de Groot & Mazur (1962, p. 240) for mass fluxes and for molar fluxes in Haase (1969, p. 218). For mass fluxes, the partial density of i replaces the molar concentration c_i in (1).

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Throughout this paper, diffusion is considered in an isobaric, isothermal system of n components $(1, 2, \ldots, n)$ in the absence of applied fields. From the linear form of the entropy production due to diffusion, we may infer the $n-1$ independent flux equations (de Groot & Mazur 1962)

$$J_i^{\mathrm{a}} = \sum_{i=1}^{n-1} L_{ik}^{\mathrm{a}} X_k^{\mathrm{a}} \quad (i = 1, 2, \ldots, n-1), \tag{4}$$

where the independent thermodynamic forces are

$$X_k^{\mathrm{a}} = -\sum_{l=1}^{n-1} A_{kl}^{\mathrm{a}} \operatorname{grad} \mu_l \quad (k = 1, 2, \ldots, n-1). \tag{5}$$

Here μ_l is the chemical potential of component l at constant T, P and C_k $(k \neq 1)$; the $n-1$ dimensional matrix A_{kl}^{a} is

$$A_{kl}^{\mathrm{a}} = \delta_{kl} + \frac{a_i}{a_0} \frac{C_k}{C_l} \quad (k, l = 1, 2, \ldots, n-1), \tag{6}$$

($\delta_{kl} =$ Kronecker function.)

The L_{ik}^{a} in (4) are, in the terminology of non-equilibrium thermodynamics, phenomenological coefficients. They are in fact diffusion coefficients related to gradients in chemical potentials; as such they may be contrasted with *practical* diffusion coefficients (Kirkwood *et al.* 1960) which are related to concentration gradients. If, for garnet, we choose simple ionic components (Fe^{2+}, Al^{3+}, Si^{4+}, etc.), (4) expands to six flux equations containing thirty-six phenomenological coefficients. However, if the flux equations are written correctly, the Onsager reciprocal relations (Onsager 1945)

$$L_{ik}^{\mathrm{a}} = L_{ki}^{\mathrm{a}} \quad (i, k = 1, 2, \ldots, n-1) \tag{7}$$

may be used to reduce the number of independent coefficients to 21.

LATTICE-FIXED REFERENCE FRAMES

Diffusion in silicates occurs on a number of sub-lattices (in the literature on diffusion, the term *lattice* is used in a general way to denote arrays of structural sites in a crystal. Although connected, this usage differs from the more abstract notion of a lattice in crystallography). For example, in garnets, we may envisage a series of cation sub-lattices defined separately by the dodecahedral, octahedral and tetrahedral sites and an anion sub-lattice composed of the oxygen sites. In many instances it is possible, and convenient, to combine some of the cation sub-lattices and the oxygen sub-lattice to form a complex anion sub-lattice $Al_2Si_3O_{12}^{6-}$. The number of independent phenomenological coefficients may be drastically reduced by this device.

For a lattice-fixed reference frame, the velocity v^{a} may be taken as either the average velocity of lattice points, or as the average velocity of a particular species that is more or less fixed relative to the lattice (Haase 1969, p. 221). There appears to be no simple method of defining weighing factors for the first alternative. On the other hand, the choice of the velocity of a particular species as a reference velocity is a common practice in the analysis of diffusion in liquids. The species chosen is generally the solvent in liquids (solvent-fixed frame), although the formal treatment holds for any species. The weighing factors are the Kronecker function δ_{in} where n denotes the solvent species. Of the various reference frames that appear in the treatment of multicomponent diffusion, the solvent-fixed frame is perhaps the most

fundamental. Where the migration of charged species is involved, the flux equations must contain not only chemical potential gradients, but also electrical potential gradients. In the absence of applied electromagnetic fields, the electrical potential gradient must disappear at each point. The constraint of local electrical neutrality can only be rigorously applied in reference frames – such as the solvent-fixed reference frame – in which the reference velocity can be set equal to zero (de Groot & Mazur 1962, Ch. 13).

In simple compounds such as alkali halides with one cation and one anion sub-lattice, it is reasonable to assume that cations and anions are confined during diffusion to their own sub-lattices (Howard & Lidiard 1964). With this assumption, cross terms involving cations and anions (e.g. L_{ik}^{a} where i is a cation and k an anion) may be dropped from the flux equations, reducing the number of independent coefficients. A similar assumption may be applied to the various cation sub-lattices and the oxygen sub-lattice in silicates. The situation, however, is more complex with respect to interaction between a single cation sub-lattice and a complex anion sub-lattice. Indeed, there is no point in attempting to establish a complex anion sub-lattice, if diffusion proceeds by direct interaction between different cation sub-lattices. For example in garnets, an $Al_2Si_3O_{12}^{6-}$ sub-lattice is only valid if the Ca, Fe, Mn or Mg ions do not occupy during diffusion, even as an intermediate step, octahedral or tetrahedral sites. Were such direct interaction between sub-lattices to occur, diffusion on one sub-lattice may be influenced by the concentration or rate of migration of defects on the other sub-lattice. The conditions of electrical neutrality become more difficult to apply in these circumstances.

To combine sub-lattices in a useful way, we need some knowledge of actual diffusion mechanisms. Even without this specific information however, we may infer some general constraints on the interaction between different cation sub-lattices. It appears unlikely that diffusion in silicates, and in particular those with a close-packed oxygen structure, can proceed by direct interchange of cations on the same or different sub-lattices: vacancy or interstitial mechanisms of diffusion are much more probable (Anderson & Buckley 1974). Although the possibility cannot be entirely dismissed, it also seems unlikely that diffusion of a cation on one sub-lattice can proceed to any extent via vacancies on another cation sub-lattice. This would appear to be especially so, if the transfer from one sub-lattice to another violates the general rules of ionic substitution. The temporary transfer of a Ca, Fe, or Mg ion to the tetrahedral sub-lattice clearly violates these rules. On the other hand, the same ions might conceivably occupy a vacant octahedral site as an activated state in a diffusion step. Then, however, a complex ring mechanism, with a correspondingly high activation energy, is required to complete the diffusion step (Anderson & Buckley 1974, p. 46). Experience in oxides, of which silicates may be considered a special example, favours diffusion via a simple vacancy mechanism.

To establish a lattice-fixed reference frame, we set the local velocity of the anion sub-lattice to zero (i.e. $J_n^i = 0$) and measure the velocity of other species relative to this as a reference velocity. The greater the number of components that can be included in the anion sub-lattice, the simpler the flux equations. The choice of an $Al_2Si_3O_{12}^{6-}$ sub-lattice in garnets, reduces the number of flux equations to 4 and the number of phenomenological coefficients to 16, or 9 if the Onsager reciprocal relations hold. The only interaction between the dodecahedral and complex anion sub-lattices is an indirect electrical coupling that balances the space charge on each sub-lattice.

Because of changes of unit cell dimensions with composition during diffusion, elements of the anion sub-lattice would appear to move during diffusion with different velocities

to an observer located at a fixed point outside of the diffusion zone. When we measure concentration profiles in either experimental diffusion couples or natural crystals, we are imposing an arbitrary (fixed) coordinate system. That is, we are acting as a fixed observer at a single, frozen instant in the history of the system. The relationship between diffusion coefficients determined in the fixed coordinate system and volume-fixed or solvent-fixed coefficients has been investigated by Kirkwood *et al.* (1960) among others (see also Crank 1956).

It should be stressed that it is the local velocity of the *solvent* species that is set to zero. To a fixed observer, the flow of material across a fixed plane is made up of bulk (convective) flow and a diffusive flow (the carefully drawn analogy of Darken (1948) still provides the best explanation of this point). By attaching the reference plane to the solvent species at each point, the bulk motion is eliminated from (4). The bulk flow, in the absence of non-hydrostatic stresses, results from volume changes throughout the system (due to non-ideal mixing).

IONIC AND MOLECULAR FLUXES

Fick's first law for multicomponent solutions is (Onsager 1945)

$$J_i^a = - \sum_{k=1}^{n} D_{ik}^a \, \partial y_k / \partial x \quad (i = 1, 2, ..., n), \tag{8}$$

where y_k is a compositional parameter (partial mass density, partial molar concentration, mole fraction, etc.). The D_{ik} are chemical diffusions coefficients relating diffusion fluxes to concentration gradients rather than chemical potential gradients. Relationships between the phenomenological coefficients of (4) and the D_{ik}^a of (8) are developed in Kirkwood *et al.* (1960), Fitts (1962), de Groot & Mazur (1962) and Haase (1969). Restrictions on the solution of (8) related to the partial molar volumes of the components, and the nature of the diffusion coefficients found, have been thoroughly discussed by Kirkwood *et al.* (1960) and Trimble *et al.* (1965).

For solutions in which the molar volume is a linear function of concentration, (8) yields diffusion coefficients in a volume-fixed reference frame ($a = v$). Diffusion coefficients in other reference frames must be obtained by systematic transformation of the volume-fixed diffusion coefficients – except that molecular and volume-fixed diffusion coefficients are equal in binary systems (Trimble *et al.* 1965), or in systems of three or more components if the partial molar volumes of all components are equal.

Concentration gradients, and not chemical potential gradients, are directly measurable. Thus Fick's law appears in the solution of practical problems, either in the calculation of diffusion coefficients from concentration against distance curves, or the calculation of concentration curves from known diffusion coefficients. The phenomenological coefficients are only important in the theoretical analysis of diffusion.

It is always possible to remove one flux equation from (8) (Onsager 1945), reducing the number of independent diffusion coefficients. The matrix D_{ik}^a is not symmetric.

The n components in (8) may be taken as elements, oxides or molecular components. Clearly n is minimized by the selection of molecular components, for example, the end-members almandine, grossular, spessartine and pyrope, for the ideal garnet proposed in the introduction. As noted below, with the presence of ferric ion, point defects and impurities, the actual number of components will normally be more than four.

There are $(n-1)^2$ independent diffusion coefficients in (8) for a system of n components. If, as is generally true, the chemical diffusion coefficients are dependent on concentrations, then $(n-1)$ chemical diffusion experiments are needed to determine all of the independent coefficients (Duda & Vrentas 1956) at one particular composition (for a fixed temperature and pressure and, in systems containing transition-state metals, a fixed oxygen fugacity). Thus in a quaternary system, we need three diffusion couples with six different terminal compositions. Furthermore, the diffusion paths in the three couples must intersect at a single point in a three dimensional (compositional) space: the $(n-1)^2$ independent diffusion coefficients are uniquely determined only at this single point. Because diffusion paths are not predictable *ab initium*, and may be strongly curved, chemical diffusion experiments in quaternary systems are, to all intents and purposes, impossible. Even in ternary systems, where couples of any composition may be readily synthesized, the experimenter is faced with a prolonged task. Consequently, a great deal of attention has been devoted to connecting chemical diffusion coefficients to the diffusion coefficients of individual ions measured with radioactive isotopes. Whether we are interested in solving (8) for elements, oxides or molecules as components, the problem is to calculate the compositionally dependent D_{ik}^a from tracer diffusion coefficients of ions measured at one or more particular compositions of the crystalline solutions. With the appearance of ions in the flux equations, account must be taken of diffusion potentials.

In the absence of externally imposed electrical gradients, the diffusion potential (Haase 1969, p. 291) may be thought of as a virtual electrical field that acts to keep the crystal electrically neutral. Where diffusion occurs by a one to one interchange of ions of the same valence (sign and magnitude), the preservation of electrical neutrality is automatic. Where, however, diffusion proceeds by a vacancy or interstitial mechanism (Shewmon 1963; Swalin 1972), or involves ions of different valences, the motions of individual ions must be constrained: any tendency for ions to migrate in a manner such as to create a local electrical field is immediately countered by the same electric field (the diffusion potential). Therefore, although the intrinsic rate of migration of individual ions may be very different, their motions are coupled to prevent the creation of electrical gradients in the crystal.

The condition of electrical neutrality is imposed by adding an additional term to (4) (de Groot & Mazur 1962, Ch. 13),

$$J_i^a = -\sum_{k=1}^{n-1} l_{ik}^a (\partial \mu_k / \partial x + 3_k F \, \partial \phi / \partial x) \quad (i = 1, 2, ..., n-1), \tag{9}$$

where ϕ is the diffusion potential in volts (3_k is the signed valence of the k the ion and F the Faraday). The set of $n-1$ equations (9) are then solved simultaneously so that $\partial \phi / \partial x$ is always zero. A solution of this problem has been given by Miller (1967*a, b*) for aqueous electrolytes with a common anion in a neutral solvent. A similar derivation for solutions composed entirely of ionic components is proposed below.

There is a further important problem. As written, (9) contains the chemical potentials of ionic species. Although the chemical potential of an ion may be assigned a physical meaning, it is not in principle, a measurable quantity (Denbigh 1966, p. 303). Attempts have been made to write (9) in terms of ionic concentrations rather than chemical potentials (Sundheim 1957). Concentrations, however, are not intensive thermodynamic quantities; because both (4) and (9) are inferred from non-equilibrium thermodynamics, chemical potentials – which are thermodynamic quantities – must appear in the initial equations. The relation between chemical

potentials and concentrations always assumes an equation of state: no analytical relation is prescribed by thermodynamics.

In contrast, the chemical potential of a neutral component is indirectly measurable or may be calculated from standard thermodynamic data. During the solution of (9), the chemical potentials of ions must therefore be replaced by the chemical potentials of neutral components.

Ions may not be the only components that must appear in (9). Experience with simple metal oxides has revealed that vacancies may play a fundamental role in diffusion; vacancy diffusion must be reckoned a strong possibility in silicates. Whether the vacancies are neutral or ionized, they must appear in the solution of (9). For completeness, solutions of (9) and modification of the Lane & Kirkaldy model are developed for a vacancy mechanism of diffusion. All of the derivations outlined are easily simplified to treat exchange or interstitial diffusion.

Point defects

For a vacancy mechanism of diffusion, the flow of ions in one direction is balanced by a flow of vacancies in the opposite direction. The vacancies appear as a separate component in the diffusion equations and in the kinetic equations of Lane & Kirkaly (1964). The original derivation of Lane & Kirkaldy makes use of the fact that, at thermal equilibrium the chemical potential of vacancies in metals is zero. This condition is rarely true in partially ionic or strongly ionic compounds where vacancies are normally ionized (Howard & Lidiard 1964).

The nature and concentration of point defects in a compound depend on equilibrium with external phases. By considering defects as dilute chemical components in solution, we may write chemical equations and compute equilibrium constants as we would for major components (Swalin 1962; van Gool 1966). Other texts which discuss defects and their role in diffusion include: Flynn 1972; Girifalco 1964, 1973; Manning 1968b; Shewmon 1963. The list of defects that might occur in any compound is almost endless, but, in practice, few defects exert a significant influence on diffusion. Moreover, for a given set of external conditions, we may expect one defect to dominate with respect to diffusion.

In ideally stoichiometric compounds, vacancies on a cation sub-lattice must be accompanied by vacancies on the anion sub-lattice or interstitial cations to preserve electrical neutrality (Swalin 1962). In non-stoichiometric compounds – that is all real materials – cation vacancies may also be associated with aliovalent impurities or excess anions in the crystal. The latter has proven to be especially important in transition metal oxides (Swalin 1962), where equilibrium takes place with an oxygen-bearing gas. Buening & Buseck (1973) have demonstrated that chemical diffusion coefficients in natural olivine are a function of oxygen fugacity. Their results can be explained by the same model that has been invoked, and verified by conductance experiments, in many transition-metal oxides. Although experimental evidence is lacking, there must be a strong suspicion that a similar mechanism may operate in many iron-rich silicates (the almandine-rich garnets of pelitic schists, for example, may contain as much as 40 % FeO and 1–10 % MnO). This model will be used to illustrate the discussion below, as it also emphasizes the possible importance of external phases on volume diffusion. With suitable changes, the argument could be applied to any defect that influences diffusion.

An excess of anions in a crystal may be formed by the reaction

$$\tfrac{1}{2}O_2 \text{ (gas)} = O \text{ (crystal)} + V,$$

where V is a neutral cation vacancy (alternatively, excess anions may be formed by placing oxygen atoms in interstitial positions. This mechanism may be safely ignored in at least those silicates with a close-packed oxygen structure). The neutral vacancies, by acting as acceptors, may ionize once

$$V = V^- + e^+$$

or twice

$$V^- + V^{2-} + 2e^+,$$

where e^+ is an electron hole in the valence band of the ion donating the electrons. In iron oxides and olivine, the formation of doubly charged vacancies is associated with the oxidation of ferrous to ferric ion.

The chemical potential of the doubly ionized vacancy (or any ionized vacancy) is not zero. The equilibrium condition at constant temperature and pressure and composition of other components is

$$\mu_V = 0 = \mu_{V^{2-}} + 2\mu_{e^+} \tag{10}$$

from the dissociation reaction

$$V = V^{2-} + 2e^+.$$

Ionic fluxes in a lattice-fixed reference frame

To complete the definition of lattice-fixed reference frame, we now introduce new concentration and distance units. The distance x in $\partial c_i/\partial x$ or $\partial \phi/\partial x$ in (9) cannot in general be measured on a linear scale. To define x on a linear scale is to impose an external coordinate system that only corresponds to a lattice-fixed reference frame if – as is rarely true in crystalline solutions – unit cell dimensions are not a function of composition. To continue, it is assumed that lattice parameters are indeed dependent on composition.

Fluxes measured relative to an external coordinate system (linear x) combine the diffusion flux J_i^L with a mass flow of i. Similar problems appear in a rigorous definition of the term $\partial \phi/\partial x$. A non-uniform space charge is associated with each sub-lattice in a crystal of variable composition. Identical gradients, however, appear in each sub-lattice, so that at each point, there is no net electrical charge. But (9) is applied to one sub-lattice at a time – for example the dodecahedral sub-lattice in garnet – without reference to other sub-lattices. The diffusion potential is a virtual electrical field that is superimposed on the non-uniform space charge associated with that particular sub-lattice. Thus, in the solution of (9), it is necessary to eliminate the gradient of any electrical field that results solely from changes in unit cell dimensions. This may be accomplished by a suitable choice of a nonlinear scale for x.

The most obvious choices of units are related to the unit cell (Birchenall *et al.* 1948; Kirkaldy 1957; Anderson & Buckley 1974) with concentration units defined as the number of atoms or moles of i per unit cell and the distance defined as the number of unit-cell edges parallel to x.

Away from dislocations, internal and external surfaces, the number of structural sites in each sub-lattice is conserved. Thus in the dodecahedral sub-lattice of garnets, the fluxes are restricted by the condition

$$\sum_{i=1}^{n-1} J_i^L + J_V^0 = 0. \tag{11}$$

With (11), we may rewrite (9) as

$$J_i^L = -\sum_{k=1}^{n-1} l_{ik}^L [(\partial \mu_k/\partial x - \partial \mu_v/\partial x) + 3_k F\, \partial \phi/\partial x] \quad (i = 1, 2, ..., n-1). \tag{12}$$

The total electrical current on the dodecahedral sub-lattice due to diffusion is

$$I = \sum_{i=1}^{n-1} 3_i F J_i^L + 3_v F J_v^L = 0, \tag{13}$$

where 3_v is the signed valence of a cation vacancy ($3_v = 0$ for a neutral vacancy).

The vacancy flux may be eliminated between (11) and (13), to give

$$F \sum_{i=1}^{n-1} J_i^L (3_i - 3_v) = 0. \tag{14}$$

By substituting in (14) from (12) for J_i^L, solving for $\partial\phi/\partial x$ and resubstituting in (12), we obtain (Miller 1967a, equations 23, 24, 25), for $n = 4$ for garnet,

$$J_i^L = -\frac{\sum\limits_{j=1}^{4}\sum\limits_{k=1}^{4}\sum\limits_{l=1}^{4}(3_k - 3_v)\, l_{ij} l_{kl} \left[3_l \dfrac{\partial(\mu_j - \mu_v)}{\partial x} - 3_j \dfrac{\partial(\mu_l - \mu_v)}{\partial x} \right]}{\sum\limits_{k=1}^{4}\sum\limits_{l=1}^{4}(3_k - 3_v) l_{kl} 3_l} \quad (i = 1, 2, 3, 4), \tag{15}$$

where the summations run over the four ionic components (Fe, Mg, Mn and Ca).
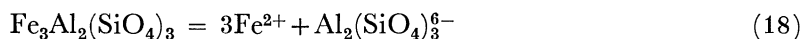
The chemical potentials of ionic and molecular species (μ_{in}) are connected by (Miller 1967a, b),

$$\mu_{in} = r_{ic}\mu_i + r_{in}\mu_n \quad (i = 1, 2, ..., n-1), \tag{16}$$

where the r_{ic} and r_{in} are stoichiometric coefficients in the dissociation equation

$$C_{r_{ic}} A_{r_{in}} = r_{ic} C^{3i} + r_{in} A^{3n}. \tag{17}$$

For garnets (17) has the form

$$Fe_3 Al_2 (SiO_4)_3 = 3Fe^{2+} + Al_2(SiO_4)_3^{6-} \tag{18}$$

with $3n = -6$.

Many exchange processes in silicates involve only ions of the same valence, for example the mutual exchange of Fe^{2+}, Mg^{2+} and Mn^{2+}, or K^+ and Na^+, etc. Under these conditions (15), may be considerably simplified for

$$3_1 = 3_2 = ... = 3_n - 1 \tag{19}$$

and

$$r_{ic} = r_{2c} = ... = r_{(n-1)c}. \tag{20}$$

Therefore,

$$-3_l(\partial\mu_v/\partial x) + 3_j(\partial\mu_v/\partial x) = 0 \tag{21}$$

in (15), and

$$3_l(\partial\mu_j/\partial x) - 3_j(\partial\mu_l/\partial x) = 3_l(\partial\mu_j/\partial x - \partial\mu_l/\partial x) \tag{22}$$

which is zero for $j = 1$. By (16), the term in parenthesis on the right hand side of (22) becomes, $j \neq 1$,

$$\partial\mu_j/\partial x - \partial\mu_l/\partial x = (\partial\mu_{jn}/\partial x - \partial\mu_{ln}/\partial x)/r_{ic} \tag{23}$$

for all combinations of j and l. Thus with (21), (22) and (23), (15) may be rearranged to give

$$J_i^L = -\frac{\sum\limits_{j=1}^{4}\sum\limits_{k=1}^{4}\sum\limits_{l=1}^{4} l_{ij} l_{kl} (3_k - 3_v)\, 3_l[\partial\mu_{jn}/\partial x - \partial\mu_{ln}/\partial x]}{r_{ic} \sum\limits_{k=1}^{4}\sum\limits_{l=1}^{4}(3_k - 3_v)\, l_{kl} 3_l} \quad (i = 1, 2, 3, 4). \tag{24}$$

Equation (24) relates the fluxes of ionic components, measured relative to anion sub-lattice, to the chemical potentials of neutral components.

Equation (24) has the form

$$J_i^L = -\sum_{k=1}^{4} L_{ik}^L (\partial\mu_k/\partial x) \quad (i = 1, 2, 3, 4).$$

Here, the coefficient L_{12}^L, say, gathers together all combinations of l^L coefficients that modify $(\mu \partial_2/\partial x)$ in the expansion of (24) for $i = 1$. Even though (24) seems complex, expansion for numerical calculation is rendered simple by the ordered pattern of l^L coefficients that immediately appears.

The presence of vacancies adds an extra component to the ideal composition of a garnet suggested in the introductory section. Analysis of diffusion in a garnet through (4) or (8) then involves, with the choice of molecular components, four independent fluxes – the same number of independent fluxes as in (24). Thus the choice of a lattice-fixed frame for ionic fluxes does not lead to a reduction in the number of components, flux equations or diffusion coefficients. It does, however, allow us to connect diffusion to the mobility of individual ions without adding further components (in this case, Al, Si and O).

For low concentrations of vacancies on the dodecahedral sub-lattice, it may be sufficient to solve (24) for three of the four ion fluxes. The distribution of the fourth ionic component may then be reduced from stoichiometry with acceptable accuracy. All summations on the right hand side of (24), however, still run from one to four. Impurities that are not located on the dodecahedral sub-lattice need not be inserted as separate components; only impurities or defects that affect the stoichiometry of the dodecahedral sub-lattice needed be counted as components. Similar remarks apply to the solution of (4) or (8) for molecular components, although impurities and defects must be handled in a slightly different way.

Approximate calculation of ionic fluxes

Lane & Kirkaldy (1964) applied transition state theory (Darken & Gurry 1953) to the interchange of pairs of atoms on adjacent atomic planes to calculate diffusion fluxes. The activated complex for diffusion in metals may be visualized as an atom in transit between its original site and a vacant site. The diffusion step in silicates may include several intermediate steps and a series of activated complexes. There is, however, in the form the theory is finally applied, no loss of detail if the sequence of step is analysed in terms of a single activated complex (Anderson & Buckley 1974).

Lane & Kirkaldy (1964) derive the kinetic equation for one dimensional diffusion (in a molecular reference frame; $a = m$)

$$J_i^m = -\sum_{j \neq i}^{n} k_{ij} a_i a_j (\partial \mu_i/\partial x - \partial \mu/\partial x) \quad (i = 1, 2, ..., n) \tag{25}$$

with

$$k_{ij} = \frac{\lambda^2}{N^1 RT}\left[\frac{\nu_{ij}}{\gamma_{ij}} \exp\left(-\Delta G_{ij}^*/RT\right)\right] \tag{26}$$

and where: λ and N^1 are the lattice spacing and number of moles per cubic centimetre of lattice planes parallel to the x direction; ν_{ij} is the frequency of transitions forward through the activated state (see Darken & Gurry 1953, footnote p. 470); ΔG_{ij}^* and γ_{ij}^* are respectively the Gibbs energy of formation and the activity coefficient of the activated complex; and a_i are activities.

The factor 10^{-6} is required to convert molar concentrations to mol/cm³ to keep units consistent in (25) (assuming 1 l = 1000 cm³).

Equation (25) describes diffusion by interchange of i and j atoms; by replacing species j with a vacancy, and assuming only interchanges of atoms with vacancies contribute to diffusion, we obtain

$$J_i^m = -k_{iv} a_i a_v (\partial \mu_i/\partial x - \partial \mu_v/\partial x) \quad (i = 1, 2, ..., n). \tag{27}$$

The terms in square brackets in (26) represent the probability P_i that an ion will jump into an adjacent vacancy. Hence, (26) may be written in the condensed form

$$k_{iv} = \lambda^2 P_i / N^l RT \quad (i = 1, 2, \ldots, n). \tag{28}$$

The fluxes J_i^m may be transferred to a lattice-fixed frame by (Kirkwood et al. 1960)

$$J_i^L = J_i^m + C_i u, \tag{29}$$

where u is the velocity of the molecular frame relative to the lattice-fixed frame by definition

$$J_n^L = 0 = J_n^m + C_n u$$

and

$$u = -J_n^m / C_n. \tag{30}$$

Substitution for u in (29) and rearrangement gives

$$J_i^L = \sum_{k=1}^{n-1} J_k^m \left(\delta_{ik} + \frac{C_i}{C_n} \right) \quad (i = 1, 2, \ldots, n-1), \tag{31}$$

where the definition of a molecular reference frame

$$J_n^m + \sum_{k=1}^{n-1} J_k^m = 0 \tag{32}$$

(Haase 1969) for molar fluxes has been used.

Substitution for the J_k^m in (31) from (27) yields

$$J_i^L = -\sum_{k=1}^{n=1} k_{kv} a_k a_v \left(\delta_{ik} + \frac{C_i}{C_n} \right) (\partial \mu_k / \partial x - \partial \mu_v / \partial x) \quad (i = 1, 2, \ldots, n{-}1). \tag{33}$$

The last equation has the general form

$$J_i^L = -\sum_{k=1}^{n-1} l_{ik}^L (\partial \mu_k / \partial x - \partial \mu_v / \partial x) \quad (i = 1, 2, \ldots, n-1) \tag{34}$$

with

$$l_{ik}^L = k_{kv} a_k a_v \left(\delta_{ik} + \frac{C_i}{C_n} \right) \quad (i = 1, 2, \ldots, n-1). \tag{35}$$

Thus if the k_{kv} and the activities are known, the phenomenological coefficients needed in (24) may be calculated.

Approximate values for k_{iv} may be obtained from isotope tracer diffusion data (Lane & Kirkaldy 1964). Tracer diffusion experiments are usually performed such that the isotope is a very dilute, component in an otherwise homogeneous material. At infinite dilution, all reference frames become identical as volume changes of mixing go to zero. The flux of a isotope of i is (Lane & Kirkaly 1964)

$$J_i^{*m} = -l_{ii}^{*m} (\partial \mu_i^* / \partial x) = -D_i^{*m} (\partial x_i^{*m} / \partial x). \tag{36}$$

The tracer diffusion coefficient D_i^{*m} is found experimentally from a plot of the concentration of the isotope against depth after annealing.

For ideally dilute solutions

$$\partial \mu_i^* / \partial x = (RT / x_i^*) (\partial x_i^* / \partial x) \tag{37}$$

and with (36)

$$l_{ii}^{*m} = D_i^{*m} x_i^* / RT. \tag{38}$$

For isotope diffusion, (27) and (28) combine to give

$$J_i^{*m} = -\frac{\lambda^2}{N^l RT} (a_i^* a_v P_i^*) (\partial \mu_i^* / \partial x) \tag{39}$$

($\partial \mu_v / \partial x = 0$ in a homogeneous material; even though $\mu_v \neq 0$). From (36), (38), and (39),

$$P_i^* = D_i^* N^l / \lambda^2 \gamma_i^* a_v. \tag{40}$$

With the approximation $P_i = P_i^*$, the k_{iv} may be calculated. Note that it is not necessary to know N^1, λ, ∂_i^* or a_v to calculate the l_{ik}^L; all of these terms are eliminated between (28) and (35). The difference between P_i and P_i^* reflects changes in $\nu_{iv8} \gamma_{iv}^*$ and ΔG_{iv}^* with concentration. All of these terms may be expected to depend on concentration; the proportion of different ions around a vacancy influences the properties of the vacancy and the jump probabilities of ions into the vacancy. The approximation is increasingly poor as the concentration of the solution differ from that in which P_i^* is determined. This trend has been confirmed in tests of the model in aqueous electrolytes (Lane & Kirkaldy 1966). Even there, however, where the model might be expected to perform more poorly than in crystals, reasonably accurate diffusion coefficients are obtained over a moderate range of compositions (Lane & Kirkaldy 1966, 1967).

The approximation of P_i does not remove the concentration dependence of the $l_i^L k$. The presence of a_i, c_i and c_n in (35) provides the major portion of this dependency.

The approximations that replace P_i with P_i^* rob the model of all of its kinetic information. However, the model is extremely useful for keeping track of relationships, and it gives an intuitive feel for diffusion processes that is absent from purely macroscopic models.

The derivation of (24) is consistent with the principles of non-equilibrium thermodynamics and the L_{ik}^L should be symmetric. Trial calculations with estimated tracer diffusion coefficients (Anderson & Buckley 1974) prove that the matrix L_{ik}^L is indeed symmetric.

It appears that vacancy-wind and correlation effects (Manning 1968a, b, 1974) may not be adequately accounted for in the model of Lane & Kirkaldy (1964); see, however, comments by Lane & Kirkaldy (1967).

These two effects have proven to be especially important in iron oxides and may prove to be important in iron-bearing silicates. It may, perhaps, be argued that with the substitution of P_i for P_i^*, these effects have been included through the measurement of the tracer diffusion coefficient. It remains to evaluate how rapidly the approximation of P_i by P_i^* deteriorates because of these effects.

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