11-1975

Chemical Components and Diffusion

John B. Brady
Smith College, jbrady@smith.edu

Recommended Citation

Brady, John B., "Chemical Components and Diffusion" (1975). Geosciences: Faculty Publications, Smith College, Northampton, MA.
https://scholarworks.smith.edu/geo_facpubs/206

[AMERICAN JOURNAL OF SCIENCE, VOL. 275, NOVEMBER, 1975, P. 1073-1088]

CHEMICAL COMPONENTS AND DIFFUSION

JOHN B. BRADY*

Department of Geological Sciences, Harvard University,
Cambridge, MA 02138

ABSTRACT. Chemical components for use in the description of a system involved in a diffusion process may be selected according to the same criteria followed in the selection of components for an equilibrium system. The various possible sets of components are not independent and may be interrelated through a component transformation. Actual components are preferred over nonvariable components, since they simplify descriptions and avoid theoretically nonmeasureable quantities. Two systems involved in an interdiffusion process may always be described using components that are actual components of both systems. For example, ternary reciprocal exchange of alkalis between alkali feldspars and dioctahedral alkali micas may be described using binary equations in terms of the exchange component, KNa_{-1}, which is an actual component of both minerals. Small quantities of additional components in approximately binary systems may have significant effects on measured diffusion coefficients, if neglected. Nevertheless, binary solutions to the continuity equation may be used, if the system is constrained in any of several ways to some binary or to a single set of boundary conditions.

INTRODUCTION

A phenomenological description of a diffusion process details the macroscopic changes of a thermodynamic system that result from mass transfer by diffusion. For any specific diffusion process, the form of the phenomenological description given will depend on a number of arbitrary decisions concerning the manner of presentation. For example, any of a large number of sets of chemical components may be used to specify composition changes, fluxes, et cetera, as in describing an equilibrium system. Because mass transfer is involved, a large number of possible reference frames are available, as in describing motion in any physical system. Also, one of many possible empirical diffusion constants must be selected, each of which may vary in magnitude with the choice of reference frame, components, and units. Of course the diffusion process is independent of any decision on matters of presentation. Thus, at least in principle, the various possible descriptions may all be interrelated.

One of the decisions concerning the form of a phenomenological description of a diffusion process, namely the selection of chemical components, is discussed in this paper. The other decisions, selection of reference frame and diffusion coefficient, are considered only briefly here, for an extensive treatment of these topics may be found elsewhere (Brady, 1975). The discussion begins with a brief statement of the equations commonly used to describe diffusion. This will serve both to emphasize the arbitrary choices involved in using these equations and to clarify the notation used in the rest of the paper.

MULTICOMPONENT DIFFUSION EQUATIONS

One-dimensional, steady-state, isothermal, isobaric diffusion in a homogeneous thermodynamic system of n components may be described by the equations

---

* Present address: Department of Geology, Smith College, Northampton, MA 01060

$$J_i^R = -\sum_{j=1}^{n} D_{ij}^{R,C}\left(\frac{\partial C_j}{\partial x}\right)_{P,T,t} \qquad (i=1,2,\ldots,n) \qquad (1)$$

(Onsager, 1945). J_i^R is the flux of component i with respect to reference frame R. C_j is an arbitrary intensive variable, such as density or mole fraction, giving the system composition in terms of component j. x is distance, t time, P pressure, T temperature. $D_{ij}^{R,C}$ is an empirical constant, defined by equation (1), which relates the flux of component i with respect to reference frame R to the gradient of composition variable C_j. The units of $D_{ij}^{R,C}$ depend on the choice of units for J_i^R and the units of the composition variable C_j.

In order to avoid the necessity of comparing the multitude of possible diffusion coefficients it is convenient to express all flux equations in terms of "standard" diffusion coefficients, D°_{ij} (cm²/sec), defined by

$$J_i^V = -\sum_{j=1}^{n-1} D^\circ_{ij}\left(\frac{\partial \rho_j}{\partial x}\right)_{P,T,t} \qquad (i=1,2,\ldots,n-1) \qquad (2)$$

(see Hooyman, and others, 1953; Brady, 1975). J_i^V is the flux of component i with respect to the mean volume reference frame in units of (moles of i/cm²-sec). The mean volume reference frame is defined by the relation

$$\sum_{i=1}^{n} V_i J_i^V = 0 \qquad (3)$$

where V_i is the partial molar volume of component i (see Hooyman, 1956; Kirkwood and others, 1960; Brady, 1975). ρ_j is the molar density of component j in units of (moles of j/cm³). Since the fluxes J_i^V are connected by (3) and the molar densities ρ_j by the thermodynamic relation

$$\sum_{j=1}^{n} V_j d\rho_j = 0 \qquad \text{(constant P,T)} \qquad (4)$$

only (n—1) fluxes and composition gradients are considered in (2) for an n-component system. Flux equations with respect to other reference frames R (mean molar frame, mean mass frame, et cetera) or using other compositional variables C_j (mole fractions, mass fractions, et cetera) may all be given in terms of the standard diffusion coefficients, D°_{ij}, if the appropriate thermodynamic relations and relative velocities are known (de Groot and Mazur, 1962; Brady, 1975).

Diffusion is generally a non-steady-state process and must be described by a form of the continuity equation. Assuming that there is *no volume change* and that the diffusion process is conservative, the continuity equation is given by

$$\left(\frac{\partial \rho_i}{\partial t}\right)_{P,T,x} = -\left(\frac{\partial J_i{}^V}{\partial x}\right)_{P,T,t} \tag{5}$$

(Landau and Lifshitz, 1959) or using (2)

$$\left(\frac{\partial \rho_i}{\partial t}\right)_{P,T,x} = \left(\frac{\partial}{\partial x}\left[\sum_{j=1}^{n-1} D^\circ{}_{ij}\left(\frac{\partial \rho_j}{\partial x}\right)_{P,T,t}\right]\right)_{P,T,t} \qquad (i=1,2,\ldots,n-1) \tag{6}$$

Equations (6) present the major barrier to a generalized analysis of diffusion in real systems. No analytical solutions to (6) are known for systems with n greater than two. Only if the diffusion coefficients $D^\circ{}_{ij}$ are independent of composition are analytical solutions available for multicomponent systems (Fujita and Gosting, 1956; Kirkaldy, 1959; Oishi, 1965). Equations (6) may then be written in the more tractable form

$$\left(\frac{\partial \rho_i}{\partial t}\right)_{P,T,x} = \sum_{j=1}^{n-1} D^\circ{}_{ij}\left(\frac{\partial^2 \rho_j}{\partial x^2}\right)_{P,T,t} \qquad (i=1,2,\ldots,n-1) \tag{7}$$

Since most natural processes are non-steady-state and involve composition dependent diffusion coefficients, the bulk of diffusion literature is confined to considerations of binary systems. The following discussion, therefore, will be concerned primarily with examples from two-component systems, although many of the principles examined may be applied to multicomponent systems.

ACTUAL COMPONENTS

We may now proceed to evaluate the sets of chemical components available for use in the diffusion equations presented above. Let us begin with some definitions. A chemical component is a specific chemical composition that may or may not correspond to the composition of any physically realizable substance (Gibbs, 1928, p. 63). The components used to describe a phase (physically homogeneous substance) may be classified into three types: actual components, possible components, and nonvariable components (Gibbs, 1928, p. 64; Thompson, 1959). By definition *actual components* may be either added to or subtracted from a phase without destroying the homogeneity of that phase. *Possible components* may be either added or subtracted, but not both. *Nonvariable components* may not be added or subtracted, independently of other components. Possible components are a special case of actual components at some compositional limit of the phase. Therefore, I shall refer only to actual components and nonvariable components in the following discussion.

Of the two types of components, actual components are clearly superior for the description of diffusion processes, for several reasons. First, note that diffusion involves the addition or subtraction of quantities of components to or from a phase or system. If the components used in the description may not be independently added to or subtracted from the phase of interest (that is, if they are nonvariable components), then "extra" equations of constraint must be carried in the description (for example, to ensure charge neutrality, stoichiometry, et cetera). While these additional equations do not invalidate the description, they may unnecessarily complicate it. A minimum number of equations of constraint are required if actual components are used.

A mineral is an **n**-component phase if all possible compositions of that mineral may be expressed by a linear combination of *not less than* **n** components (Thompson, 1959). Any set of **n** components sufficient to give all possible compositions of an **n**-component phase may be called an *ultimate* set of components for that phase (Gibbs, 1928, p. 79; Thompson, 1959). Any ultimate set of components for an **n**-component phase will consist of **n** independent actual components. Any set of components that includes even one nonvariable component must contain more than **n** components, if the set is to be sufficient to give all possible compositions of an **n**-component phase. Therefore, the minimum number of components need to be considered if an ultimate set of (actual) components is used.

The use of actual components also allows the empirical description considered here to be related to a more fundamental description in terms of chemical potential gradients, to which Onsager's reciprocal relations may be applied (Onsager, 1931a,b). Chemical potentials of actual components of a phase, ϕ, may be determined from the chemical composition of ϕ, if an equation of state for ϕ is known. However, the chemical potentials of nonvariable components of a phase, ϕ, may *not* be obtained from the composition of ϕ and an equation of state. They are specified only if ϕ is in equilibrium with other phases such that the total assemblage has as actual components the nonvariable components of ϕ. Other partial molar quantities of nonvariable components of ϕ, such as the partial molar volume V_i, are neither measureable nor specified by the presence of any assemblage in equilibrium with ϕ. This fact generally decreases the usefulness of any description in terms of nonvariable components and makes it difficult to utilize several mean velocity reference frames (Brady, 1975). All these considerations lead to the conclusion that a description in terms of an ultimate set of components is preferable to any other.

TRANSFORMATION OF COMPONENTS

While the description of a diffusion process in terms of one ultimate set of components is equivalent to a description in terms of another ultimate set, different sets of components may be convenient for different processes. It will be advantageous, therefore, to be able to interrelate two descriptions given in terms of different sets of components. This may be accomplished by following the procedures established for a transformation of the components used to describe an equilibrium system (for example, calculating a norm from a chemical analysis). For a recent discussion of component transformations see Greenwood (1975). See also Korzhinskii (1959, chap. II).

To investigate the effect of a transformation of components on the description of a diffusion process, let us consider as an example the binary system iron-sulfur. For "old" components we shall choose the physically realizable compositional limits of the system, Fe and S. For "new" components let us choose the compositions of troilite, FeS, and pyrite, FeS_2. Either of these two sets of components might be used to describe diffusion in pyrrhotite ($Fe_{1-x}S$); both are ultimate sets of components for pyrrhotite. This particular example may be of geological interest, for diffusion in pyrrhotite probably limits the rate of response of the pyrite-pyrrhotite geothermometer to a change in temperature.

The "new" components FeS and FeS_2 are related to the "old" components Fe and S by the stoichiometric relations

$$\begin{aligned} FeS &= Fe + S \\ FeS_2 &= Fe + 2\,S \end{aligned} \tag{8}$$

Equations (8) express the fact that one mole of FeS may be made from one mole of Fe combined with one mole of S, and similarly for FeS_2. What we need to know, however, is the *total* number of moles of FeS for a system given the *total* numbers of moles of Fe and S. The best procedure is generally to start with the inverse relations giving the total number of moles of iron (n_{Fe}) and sulfur (n_S) in terms of the numbers of moles of troilite (n_{FeS}) and pyrite (n_{FeS_2}). We have by inspection, then,

$$\begin{aligned} n_{Fe} &= n_{FeS} + n_{FeS_2} \\ n_S &= n_{FeS} + 2\,n_{FeS_2} \end{aligned} \tag{9}$$

Solving equations (9) for n_{FeS} and n_{FeS_2} yields

$$\begin{aligned} n_{FeS} &= 2\,n_{Fe} - n_S \\ n_{FeS_2} &= -\,n_{Fe} + n_S \end{aligned} \tag{10}$$

which is clearly not of the same form as (8).

Equations (9) and (10) may be used to obtain relations among the mole fractions N_{Fe}, N_{FeS}, et cetera to give the composition of the system in terms of the different sets of components:

$$\begin{aligned} N_{Fe} &\equiv \frac{n_{Fe}}{n_{Fe} + n_S} = \frac{1}{2 + N_{FeS_2}} \\ N_{FeS} &\equiv \frac{n_{FeS}}{n_{FeS} + n_{FeS_2}} = \frac{3\,N_{Fe} - 1}{N_{Fe}} \end{aligned} \tag{11}$$

Equations (10) may also be used to obtain the fluxes of the "new" components, $J_{FeS}{}^R$ and $J_{FeS_2}{}^R$, from measurements of fluxes of the "old" components:

$$\begin{aligned} J_{FeS}{}^R &= 2\,J_{Fe}{}^R - J_S{}^R \\ J_{FeS_2}{}^R &= -\,J_{Fe}{}^R + J_S{}^R \end{aligned} \tag{12}$$

where J_{FeS}^R is the total number of moles of FeS passing a unit cross section of reference frame R in unit time. Notice that all fluxes are given with respect to the *same* reference frame R. If a different reference frame is of interest, the above procedure must be combined with the procedures outlined in Brady (1975) for relating various reference frames.

Particular care should be exercised with regard to the reference frame used, for some reference frames depend on the choice of components. For example, the mean molar frame, N, for our "old" components is not identical with the mean molar frame, N′, for our "new" components. Indeed, at any time during a diffusion process, the two mean molar frames will have a relative velocity such that

$$J_i^N = J_i^{N'} + \rho_i \bar{v}^{N'N} \tag{13}$$

where ρ_i is the molar density of component i and $\bar{v}^{N'N}$ is the local velocity of frame N′ with respect to frame N. The mean molar frame N (for the components Fe and S) is defined by

$$J_{Fe}^N + J_S^N = 0 \tag{14}$$

and the mean molar frame N′ (for the components FeS and FeS_2) by

$$J_{FeS}^{N'} + J_{FeS_2}^{N'} = 0 \tag{15}$$

(de Groot and Mazur, 1962). Adding (13) written for i = FeS to (13) written for i = FeS_2 and using (9), (12), and (15) we have

$$\bar{v}^{N'N} = \left(\frac{1}{\rho_{FeS} + \rho_{FeS_2}}\right)\left(J_{FeS}^N + J_{FeS_2}^N \right) = \frac{J_{Fe}^N}{\rho_{Fe}} \tag{16}$$

Substituting (16) into (13) written for component S yields

$$J_S^N = J_S^{N'} + \frac{\rho_S}{\rho_{Fe}} J_{Fe}^N \tag{17}$$

or using (14)

$$J_S^{N'} = J_S^N \left(1 + \frac{\rho_S}{\rho_{Fe}} \right) = \frac{J_S^N}{N_{Fe}} \tag{18}$$

It follows from (12), (14), and (18) that

$$\begin{aligned} J_{FeS}^{N'} &= \frac{J_{Fe}^N}{N_{Fe}} \\ J_{FeS_2}^{N'} &= \frac{J_S^N}{N_{Fe}} \end{aligned} \tag{19}$$

A comparison of equations (19) and (12) will serve to demonstrate the importance of properly identifying the reference frames in use. Note also that $J_{Fe}^{N'} = 0$.

In contrast, the standard diffusion coefficient for a two component system, D°, does *not* depend on the choice of components.[1] This may be

---

[1] The subscripts have been omitted from D°_{ij} since there is only one independent D°_{ij} for a binary system.

demonstrated by expressing the fluxes of (19) in terms of the binary diffusion coefficients D° and $D^{\circ\prime}$ for the "old" and "new" components, respectively. The flux of component i with respect to the mean molar reference frame N is given by (de Groot and Mazur, 1962, p. 252)

$$J_i^N = -\frac{D^\circ}{\bar{V}}\left(\frac{\partial N_i}{\partial x}\right)_{P,T,t} \tag{20}$$

where $\bar{V}$ is the volume of the phase of interest per mole of "old" components. Using (20) along with the first equation of (19) we have

$$J_{FeS}^{N'} = -\frac{D^{\circ\prime}}{\bar{V}'}\left(\frac{\partial N_{FeS}}{\partial x}\right)_{P,T,t} = \frac{-D^\circ}{N_{Fe}\bar{V}}\left(\frac{\partial N_{Fe}}{\partial x}\right)_{P,T,t} = \frac{J_{Fe}^N}{N_{Fe}} \tag{21}$$

where $\bar{V}'$ is the volume of the phase of interest per mole of "new" components. And noting that

$$\bar{V}' \equiv \frac{V}{n_{FeS} + n_{FeS_2}} = \frac{V}{n_{Fe}} = \frac{1}{\rho_{Fe}} = \frac{\bar{V}}{N_{Fe}} \tag{22}$$

(21) becomes

$$D^{\circ\prime} = \frac{D^\circ}{N_{Fe}^2}\left(\frac{d\,N_{Fe}}{d\,N_{FeS}}\right) \tag{23}$$

Finally, evaluating the derivative in (23) using (11) we obtain

$$D^{\circ\prime} = D^\circ \tag{24}$$

Thus, a description of diffusion in pyrrhotite in terms of the components Fe and S may be readily related to one in terms of FeS and FeS_2. The same binary diffusion coefficient D° will be obtained using either of these two ultimate sets of components.

This result appears to be quite general. For any binary system there is only one standard diffusion coefficient D°, regardless of which ultimate set of components is used. Unfortunately, this simple result may not be extended to multicomponent systems where each diffusion coefficient must be carefully labeled according to the components used for the composition gradient and related flux. However, the methods discussed above may be used to interrelate fluxes for different choices of components, and the diffusion coefficients obtained for one set of components can be related to those obtained for other sets of components. For discussions of similar problems concerning multicomponent systems see Gupta and Cooper (1971), Cooper (1974), and Schönert (1960).

EXCHANGE COMPONENTS

Buckley (ms) and Anderson and Buckley (1973, 1974) have argued that the use of actual components as "diffusing" components in some instances may be inconvenient, misleading, or inaccurate. Buckley (ms) cites as an example the exchange of Mg^{+2} and Fe^{+2} between garnet and orthopyroxene. He points out that while diffusion of $FeSiO_3$ in pyroxene (where it is an actual component) is meaningful, diffusion of $FeSiO_3$ in garnet (where it is not an actual component) is not meaningful and conversely that the diffusion of $Fe_3Al_2Si_3O_{12}$ is meaningful in a garnet but not in a pyroxene. Buckley concludes from this that the total number of components needed to describe diffusion in a polyphase system is increased, if one is constrained to use actual components of the phases involved. Therefore, Buckley (ms) and Anderson and Buckley (1973, 1974) recommend the use of oxides of the elements for "diffusing" components. But the use of FeO as a "diffusing" component in garnet is little improvement over the use of $FeSiO_3$. Neither is an actual component of garnet so that both have all the disadvantages of nonvariable components discussed above.

The difficulties in using actual components presented by Buckley (ms) are not encountered, if one begins with an appropriate selection of actual components for the phases or systems of interest. In the garnet-orthopyroxene example mentioned above, this would mean choosing the "negative" component $FeMg_{-1}$ as one of the actual components for both minerals (see below). Indeed, there must always exist a set of actual components that contains the minimum number of components necessary to describe any diffusion process. To verify this, consider a generalized exchange of mass between two thermodynamic systems. Each of these two systems may be either a phase or a collection of phases. Any mass involved in the exchange must be subtracted from one of these systems and added to the other. There is no mass diffusing that is subtracted from one system and not added to the other. Therefore, it must be possible to describe the mass involved in the exchange using components that are actual components of *both* systems.[2]

For many mineral pairs (or assemblages) that might be involved in a diffusional exchange, the only actual components common to both minerals (or assemblages) are components that do not represent physically realizable compositions of the minerals (or assemblages) considered. This is perhaps best explained in terms of a simple example involving two phases in the same ternary system. Consider the exchange of Na and K between an alkali feldspar and a dioctahedral alkali mica. These two binary phases have only one actual component in common. Although not apparent on some commonly used compositional diagrams (fig. 1A), the intersection of the line of actual components for the alkali feldspars and the line of actual components for the muscovite-paragonite series gives the composition of the shared actual component, KNa_{-1} (fig. 1B). That KNa_{-1} is an actual component of both the alkali feldspars and the

---

[2] An actual component of an *assemblage of phases* is a component that may be both added to or subtracted from the assemblage without the addition of an extra phase (Thompson, 1959). An ultimate set of components for an n-component assemblage of phases is a set of n components sufficient to give all variations in the bulk composition of that assemblage. If one chooses ultimate sets of components for two systems such that the intersection of the two ultimate sets is as large as possible, then this intersection will be a set of actual components *of both systems* sufficient to describe all diffusional exchange between the two systems.

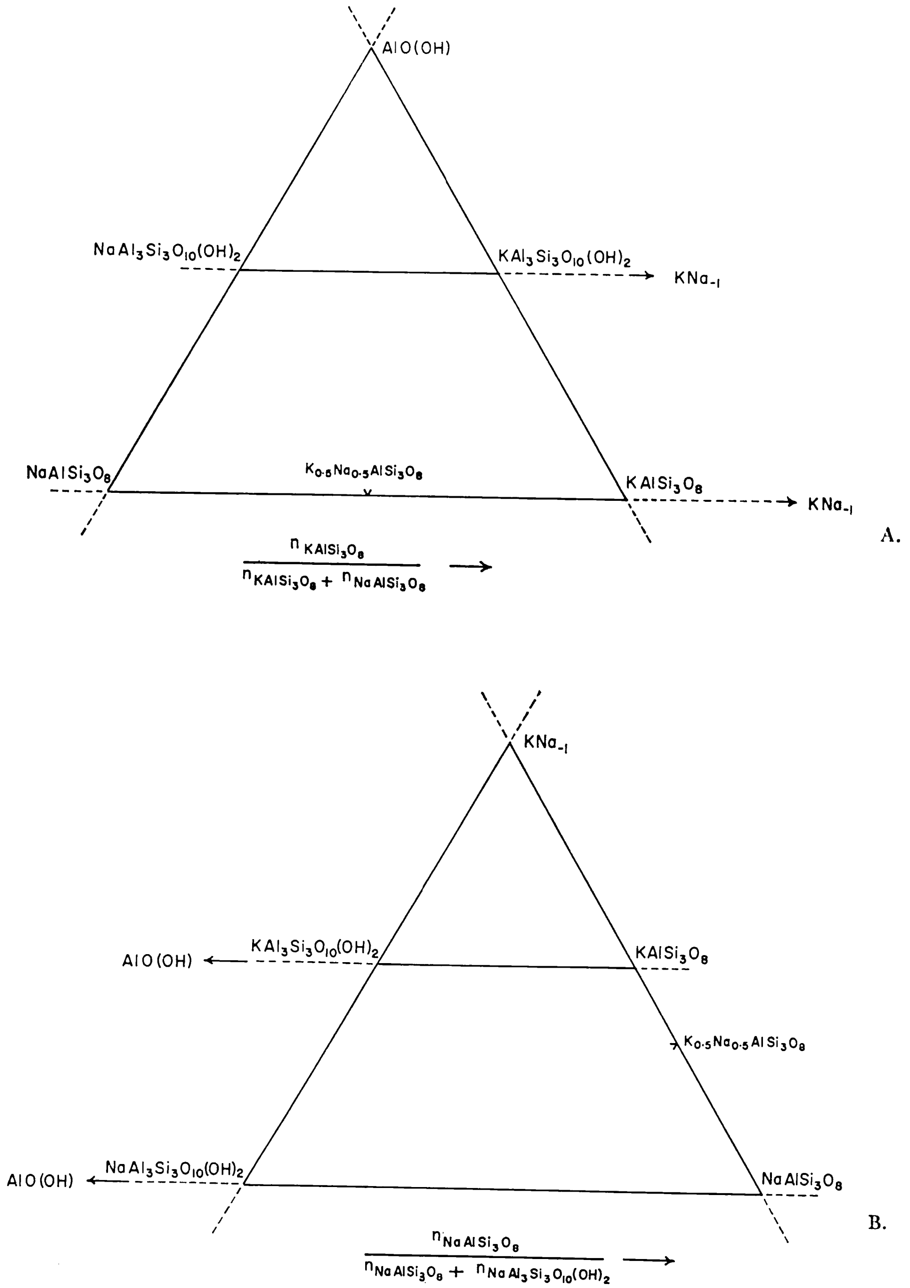

Fig. 1. Compositions of the alkali feldspars and dioctahedral alkali micas shown on two different ternary composition diagrams based on the components $NaAlSi_3O_8$, $KAlSi_3O_8$, and $AlO(OH)$ (A) and the components $NaAl_3Si_3O_{10}(OH)_2$, $NaAlSi_3O_8$, and KNa_{-1} (B).

dioctahedral alkali micas is evident from figure 1B and the stoichiometric relations

$$
\begin{aligned}
KNa_{-1} &= KAlSi_3O_8 - NaAlSi_3O_8 \\
KNa_{-1} &= KAl_3Si_3O_{10}(OH)_2 - NaAl_3Si_3O_{10}(OH)_2
\end{aligned}
\qquad (25)
$$

KNa_{-1} is an example of what I shall call an *exchange component.*[3] It does not happen to correspond to the composition of any feldspar or mica but is just as valid as any other actual component. For example, the composition of any alkali feldspar may be expressed as a linear combination of KNa_{-1} and $NaAlSi_3O_8$. In fact, using KNa_{-1} as a component for alkali feldspars is analogous to using S as a component for pyrrhotite. S is given by the stoichiometric relation

$$S = FeS_2 - FeS \qquad (26)$$

and does not correspond to the composition of any pyrrhotite.

In many respects, the exchange component KNa_{-1} is an ideal "diffusing" component for the description of alkali exchange between feldspar and mica, or any other two alkali-bearing minerals. To begin with, the use of KNa_{-1} enables one to describe a ternary reciprocal exchange in terms of *one* diffusing component. Since KNa_{-1} is an actual component of both phases, constraints of stoichiometry and electrical neutrality are automatically satisfied. In addition, the driving force for alkali exchange is a gradient in the chemical potential of the exchange component, given by

$$
\begin{aligned}
\mu_{KNA_{-1}} &= \mu_{KAlS_3O_8} - \mu_{NaAlSi_3O_8} && \text{(in feldspar)} \\
\mu_{KNA_{-1}} &= \mu_{KAl_3Si_3O_{10}(OH)_2} - \mu_{NaAl_3Si_3O_{10}(OH)_2} && \text{(in mica)}
\end{aligned}
\qquad (27)
$$

(see A. B. Thompson, 1974). Isothermal alkali exchange will cease only when the chemical potential of the exchange component is the same throughout the phases involved.

When described in terms of the flux of the exchange component, KNa_{-1}, alkali exchange between two binary phases in the same ternary system becomes mathematically equivalent to the case of interdiffusion in a binary system, when more than one phase is involved. The continuity equation has been solved for this latter case using the Boltzmann substitution (Jost, 1950, 1952, p. 75; Appel, 1968). The solution allows for a discontinuity in the concentration-distance profile but requires that the

---

[3] To my knowledge the use of exchange components like KNa_{-1} for the description of thermodynamic systems originates with J. B. Thompson, Jr. who demonstrates their convenient features in his lectures on phase equilibria (compare Thompson and Waldbaum, 1968, p. 1995; Waldbaum and Thompson, 1969, p. 1282). D. M. Burt (1972, 1974a, 1974b) has used exchange components extensively, calling them "exchange operators". For other examples of the use of "negative" components see Thompson (1972) or Korzhinskii (1959, chap. II).

magnitude of the discontinuity not change with time, for all time greater than $t = 0$ (compare Carslaw and Jaeger, 1947, p. 70).[4]

For a one-dimensional, isothermal, isobaric, isochoric exchange of alkalis between an alkali feldspar and a dioctahedral alkali mica, equation (6) may be written as

$$\left(\frac{\partial \rho_{\mathrm{KNa}_{-1}}}{\partial t}\right)_{P,T,x} = \left(\frac{\partial}{\partial x}\left[D^{\circ}\left(\frac{\partial \rho_{\mathrm{KNa}_{-1}}}{\partial x}\right)_{P,T,t}\right]\right)_{P,T,t} \quad (28)$$

If both the feldspar and mica are initially uniform in composition and juxtaposed across a planar boundary, appropriately oriented to ensure one-dimensional diffusion, then the solution to (28) modified after Jost (1950) and Appel (1968) is

$$D^{\circ} = \frac{-1}{2t}\left(\frac{dx}{d\rho_{\mathrm{KNa}_{-1}}}\right)\int_{\rho_{\mathrm{KNa}_{-1}}(-\infty)}^{\rho_{\mathrm{KNa}_{-1}}} x \, d\rho_{\mathrm{KNa}_{-1}} \quad (29)$$

$$D^{\circ} = \frac{1}{2t}\left(\frac{dx}{d\rho_{\mathrm{KNa}_{-1}}}\right)\int_{\rho_{\mathrm{KNa}_{-1}}}^{\rho_{\mathrm{KNa}_{-1}}(+\infty)} x \, d\rho_{\mathrm{KNa}_{-1}} \quad (30)$$

where $\rho_{\mathrm{KNa}_{-1}}(+\infty)$ and $\rho_{\mathrm{KNa}_{-1}}(-\infty)$ are the molar densities of KNa_{-1} far removed from the site of the diffusion. Equation (29) provides the solution for one side of the initial interface, and (30) for the other.

Exchange components may be readily applied to a great many other mineral pairs and assemblages. For example, the exchange of Fe^{+2} and Mg^{+2} between garnet and orthopyroxene discussed by Buckley (ms) may be conveniently described in terms of the exchange component FeMg_{-1} as may similar exchanges between olivine and orthopyroxene or garnet and cordierite. Similarly, oxygen isotopic exchange may be described in terms of the diffusion of $\mathrm{O}^{18}\mathrm{O}^{16}{}_{-1}$. For diffusion in multicomponent, multiphase systems several exchange components may be used. In all these cases, the use of exchange components provides the simplest description complete with all the advantages of actual components.

APPROXIMATELY BINARY SYSTEMS

Few natural or experimental systems are strictly binary; nearly all contain small quantities of impurities (additional components). To deal rigorously with all these additional components would mean having to solve equations (6) for a multicomponent system, which is difficult at best. Yet if we neglect even very small quantities of impurities and treat *nearly* binary systems as *exactly* binary systems, we run the risk of encountering nonreproducible results. Indeed, there is abundant experimental evidence

---

[4] Jost uses the correct approach but gives an incorrect result. His equations [4] (1950) and [1.337] (1952) should be modified to the mathematical form of (29) and (30) of this paper, which agree with Appel's result.

that very small quantities of impurities may have a significant effect on the magnitude of measured diffusion coefficients (Shewmon, 1963). This is due to the fact that many impurities have associated defects such as vacancies which may greatly facilitate diffusion. Fortunately, however, there are several circumstances for which a binary approach will be useful even when the system examined is not constrained by stoichiometry to be binary. These will be considered in the following paragraphs assuming for simplicity that there is only one extra component (3) in addition to the two major components (1 and 2).

A case to which the binary equations may be correctly applied occurs when the quantity of component 3 (mole fraction of 3) in the phases involved does not vary during the diffusion process. If the mole fraction of 3, N_3, does not change, then a binary description is quite correct, even if there is no stoichiometric constraint on 3. The diffusion coefficient determined, however, is valid only for the given constant N_3 and must be redetermined for other constant N_3's. A constant mole fraction of component 3 during the diffusion process means either that the chemical potential of component 3, μ_3, does not vary with N_2 at constant N_3 or that the diffusion of component 3 is very slow compared to the diffusion of components 1 and 2. The case of diffusion at constant N_3, when the diffusion coefficients are all independent of composition, is a special case of ternary diffusion that was emphasized by Gupta and Cooper (1971). These authors pointed out that there will always be two directions in composition space (that is, two choices of component 3) for which diffusion will occur at constant N_3. See also Cooper and Varshneya (1968) and Varshneya and Cooper (1972a,b,c).

If N_3 is not constant and the diffusion coefficients depend on composition, a binary solution may still be used if one is interested in only a *single* set of boundary conditions. Cooper (1968) has shown that for a semi-infinite diffusion couple with given boundary conditions, N_2 $(+\infty)$ and N_2 $(-\infty)$, the diffusion path (in composition space) will be unique. In other words, for each value of N_2 there will be a unique value of N_1, N_3, and D° (for the given boundary conditions). Therefore, a single experiment will suffice for a single set of specific boundary conditions, but other measurements will be necessary for other values of N_2 $(+\infty)$ and N_2 $(-\infty)$.

An alternative approach which may be used for some systems is to constrain an otherwise ternary system to behave as if it were binary by externally buffering the value of one or more chemical potentials. As an example let us consider diffusion in the common olivines. Although the compositions of many common olivines may be largely represented by a linear combination of the components $Mg_6(SiO_4)_3$ and $Fe^{+2}{}_6(SiO_4)_3$, most olivines contain some ferric iron as well. Assuming that charge balance is maintained by the introduction of vacancies, open square $\square$, on metal sites along with the ferric iron, we may represent the presence of ferric iron in olivine in terms of the component $\square_2Fe^{+3}{}_4\ (SiO_4)_3$. The

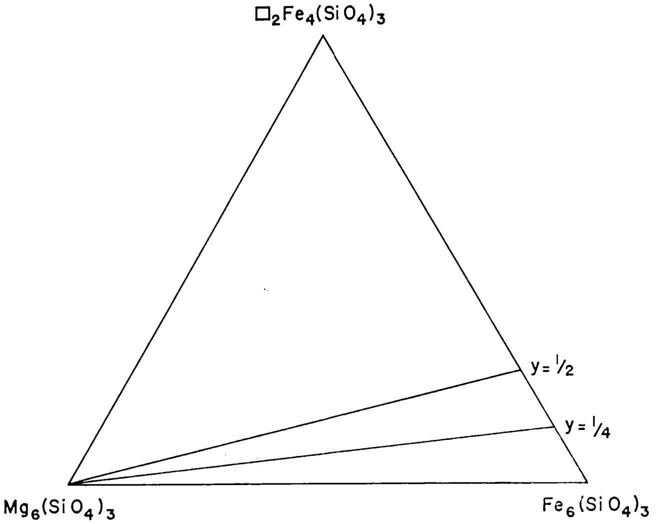

Fig. 2. A ternary composition diagram for the compositions of common olivines containing ferric iron, assuming that local charge balance is maintained by the presence of vacancies. The lines through the points labeled $y = \frac{1}{2}$ and $y = \frac{1}{4}$ each represent a series of compositions with the same ferric-ferrous ratio. The points labeled $y = \frac{1}{2}$ and $y = \frac{1}{4}$ have compositions given by the formula $Fe^{+2}_{6-3y}\ (\square\ Fe^{+3}_2)_y\ (SiO_4)_3$.

ferric component along with the ferrous and magnesian components define a ternary system (fig. 2).

A potentially interesting set of binary subsystems contained within this ternary olivine system would correspond to the lines in figure 2 which radiate from the $Mg_6\ (SiO_4)_3$ corner (that is, those drawn to points labeled $y = \frac{1}{4}$ and $y = \frac{1}{2}$). Each of these lines is the locus of compositions with a constant ferric-ferrous ratio. All compositions along any one such line may be represented by a linear combination of the components $Mg_6(SiO_4)_3$ and $Fe^{+2}_{6-3y}\ (\square\ Fe^{+3}_2)_y\ (SiO_4)_3$, where the y will be different for different lines (that is, for different ferric-ferrous ratios).

Assuming that the ternary olivines of figure 2 form an ideal solution, a constant ferric-ferrous ratio means that the chemical potential of Fe is constant (for constant pressure and temperature). To see that this is true note the equilibrium condition

$$\mu_{Fe} = \frac{1}{2}\left[\mu_{Fe_6\ (SiO_4)_3} - \mu_{\square\ _2Fe_4\ (SiO_4)_3}\right] \tag{31}$$

Substituting expressions for the chemical potentials in terms of mole fractions into (31), assuming ideality (Thompson, 1967, eq 4), yields

$$\mu_{Fe} = \frac{1}{2}\left[\ \mu^{\circ}_{Fe_6\ (SiO_4)_3} - \mu^{\circ}_{\square\ _2Fe_4\ (SiO_4)_3} + aRT\ln\left(\frac{N_{Fe_6\ (SiO_4)_3}}{N_{\square\ _2Fe_4\ (SiO_4)_3}}\right)\right] \tag{32}$$

If μ_{Fe} is constant, then $(N_{Fe_6(SiO_4)_3} / N_{\square_2 Fe_4(SiO_4)_3})$ must also be constant and conversely, since the other terms in (32) have definite values at a given pressure and temperature (the μ°_{i} terms give the chemical potentials of the pure end members and a is a constant depending on the number of exchangeable sites per mole of the chosen components). Therefore, if we could externally constrain μ_{Fe}, possible olivine compositions would lie along one of the lines y in figure 2, and the diffusion is constrained to be binary.

An experiment corresponding to the desired conditions would entail controlling μ_{O_2} in addition to having an iron oxide present. If the olivines in the experiment were initially equilibrated separately at the μ_{O_2} of the diffusion run, and if the $Fe^{+2}{}_{3} \longleftrightarrow \square Fe^{+3}{}_{2}$ exchange is as rapid as the $Fe^{+2} \longleftrightarrow Mg^{+2}$ exchange, then the diffusion may be treated as binary (to the extent that the olivines are ideal). Buening and Buseck (1973) have measured Fe–Mg diffusion in olivines under conditions similar to those suggested here. They found a significant μ_{O_2} dependence of their measured binary diffusion coefficients. I suggest that what they have determined are binary diffusion coefficients for interdiffusion between forsterite and various fayalites with different ferric-ferrous ratios (that is, for different values of y (fig. 2)). A similar approach might be utilized to measure interdiffusion in other Fe–Mg solid solutions.

CONCLUSIONS

Of the many possible sets of components available for use in describing diffusion in an n-component system, an ultimate set of (actual) components is preferred because (1) a minimum number of equations of constraint are necessary, (2) a minimum number of components need be considered, and (3) inherently nonmeasureable quantities are avoided. Descriptions of diffusion in terms of one ultimate set of components may be easily transformed into descriptions in terms of another ultimate set of components. Special care must be exercised, however, when the reference frames used depend on the choice of components. The description of many diffusion problems may be simplified if one is willing to use actual components, which may contain negative amounts of atoms. Particularly convenient are "exchange components" like KNa_{-1}, as demonstrated above for the case of ternary reciprocal exchange between alkali feldspars and dioctahedral alkali micas. Small quantities of additional components in approximately binary systems may significantly affect diffusion processes and should not be neglected. However, solutions to the continuity equation for a two component system may be used if (1) the system is constrained by stoichiometry to be binary, (2) the system is constrained by kinetics to be binary, (3) the system is constrained to be binary by externally buffering certain chemical potentials, or (4) only one set of boundary conditions is of interest.

ACKNOWLEDGMENTS

Special thanks belong to Professor James B. Thompson, Jr. whose lectures and comments have provided the background for this paper. Early drafts were improved by the suggestions of Alan Bruce Thompson, John M. Ferry, George W. Fisher, D. M. Burt, and many other patient friends. This work is published under the auspices of the Committee on Experimental Geology and Geophysics at Harvard University.

REFERENCES

Anderson, D. E., and Buckley, G. R., 1973, Zoning in garnets—diffusion models: Contr. Mineralogy and Petrology, v. 40, p. 87-104.

———— 1974, Modeling of diffusion controlled properties of silicates, *in* Hofmann, A. W., Giletti, B. J., Yoder, H. S., Jr., and Yund, R. A., eds., Geochemical transport and kinetics: Washington, D.C., Carnegie Inst. Washington, p. 31-52.

Appel, M., 1968, Solution for Fick's 2nd law with variable diffusivity in a multi-phase system: Scripta Metallurgica, v. 2, p. 217-222.

Brady, J. B., 1975, Reference frames and diffusion coefficients: Am. Jour. Sci., v. 275, p. 954-983.

Buckley, G. R., ms, 1973, The effect of diffusion on garnet zoning: Ph.D. thesis, Univ. Illinois at Urbana-Champaign, 112 p.

Buening, D. K., and Buseck, P. R., 1973, Fe-Mg lattice diffusion in olivine: Jour. Geophys. Research, v. 78, p. 6852-6862.

Burt, D. M., 1972, The influence of fluorine on the facies of Ca–Fe–Si skarns: Carnegie Inst. Washington Year Book 71, p. 443-450.

———— 1974a, Alternative choices of components for modeling geochemical systems [abs.]: Am. Geophys. Union Trans., v. 55, p. 452.

———— 1974b, Concepts of acidity and basicity in petrology—The exchange operator approach: Geol. Soc. America Abs., v. 6, p. 674-676.

Carslaw, H. S., and Jaeger, J. C., 1947, Conduction of heat in solids: Oxford, Oxford Univ. Press, 386 p.

Cooper, A. R., 1968, The use and limitations of the concept of an effective binary diffusion coefficient for multicomponent diffusion, *in* Wachtman, J. B., Jr., and Franklin, A. D., eds., Mass transport in oxides: Washington, D.C., U.S. Govt. Printing Office, Natl. Bur. Standards Spec. Pub. 296, p. 79-84.

———— 1974, Vector space treatment of multicomponent diffusion, *in* Hofmann, A. W., Giletti, B. J., Yoder, H. S., Jr., and Yund, R. A., eds., Geochemical transport and kinetics: Washington, D.C., Carnegie Inst. Washington, p. 15-30.

Cooper, A. R., and Varshneya, A. K., 1968, Diffusion in the system K_2O–SrO–SiO_2: I, effective binary diffusion coefficients: Am. Ceramic Soc. Jour., v. 51, p. 103-106.

Fujita, H., and Gosting, L. J., 1956, An exact solution of the equations for free diffusion in three-component systems with interacting flows, and its use in evaluation of the diffusion coefficients: Am. Chem. Soc. Jour., v. 78, p. 1099-1106.

Gibbs, J. W., 1928, The collected works of J. Willard Gibbs, v. 1: New Haven, Conn., Yale Univ. Press, 434 p.

Greenwood, H. J., 1975, Thermodynamically valid projections of extensive phase relationships: Am. Mineralogist, v. 60, p. 1-8.

de Groot, S. R., and Mazur, P., 1962, Nonequilibrium thermodynamics: Amsterdam, North Holland Publishing Co., 510 p.

Gupta, P. K., and Cooper, A. R., Jr., 1971, The [D] matrix for multicomponent diffusion: Physica, v. 54, p. 39-59.

Hooyman, G. J., 1956, Thermodynamics of diffusion in multicomponent systems: Physica, v. 22, p. 751-759.

Hooyman, G. J., Holtan, H., Jr., Mazur, P., and de Groot, S. R., 1953, Thermodynamics of irreversible processes in rotating systems: Physica, v. 19, p. 1095-1108.

Jost, W., 1950, Bemerkung zur mathematischen Behandlung komplizierter Diffusionsprobleme: Zeitschr. Physik, v. 127, p. 163-167.

———— 1952, Diffusion in solids, liquids, gases: New York, Academic Press, Inc., 558 p.

Kirkaldy, J. S., 1959, Diffusion in multicomponent metallic systems IV. A general theorem for construction of multicomponent solutions from solutions of the binary diffusion equation: Canadian Jour. Physics, v. 37, p. 30-34.

Kirkwood, J. G., Baldwin, R. L., Dunlop, P. J., Gosting, L. J., and Kegeles, G., 1960, Flow equations and frames of reference for isothermal diffusion in liquids: Jour. Chem. Physics, v. 33, p. 1505-1513.

Korzhinskii, D. S., 1959, Physio-chemical basis of the analysis of the paragenesis of minerals: New York, Consultants Bur., 142 p.

Landau, L. D., and Lifshitz, E. M., 1959, Fluid mechanics, Course on theoretical physics, v. 6: Reading, Mass., Addison Wesley, 536 p.

Oishi, I., 1965, Analysis of ternary diffusion: solutions of diffusion equations and calculated concentration distribution: Jour Chem. Physics, v. 43, p. 1611-1620.

Onsager, L., 1931a, Reciprocal relations in irreversible processes, I: Phys. Rev., v. 37, p. 405-426.

——— 1931b, Reciprocal relations in irreversible processes, II: Phys. Rev., v. 38, p. 2265-2279.

——— 1945, Theories and problems of liquid diffusion: New York Acad. Sci. Anal., v. 46, p. 241-265.

Schönert, H., 1960, Diffusion and sedimentation of electrolytes and non-electrolytes in multicomponent systems: Jour. Phys. Chemistry, v. 64, p. 733-737.

Shewmon, P. G., 1963, Diffusion in solids: New York, McGraw-Hill Book Co., 203 p.

Thompson, A. B., 1974, Calculations of muscovite–paragonite–alkali feldspar phase relations: Contr. Mineralogy Petrology, v. 44, p. 173-194.

Thompson, J. B., Jr., 1959, Local equilibrium in metasomatic processes, *in* Abelson, P. H., ed., Researches in geochemistry: New York, John Wiley & Sons, p. 427-457.

——— 1967, Thermodynamic properties of simple solutions: *in* P. H. Abelson, ed., Researches in geochemistry II: New York, John Wiley & Sons, p. 340-361.

——— 1972, Oxides and sulfides in regional metamorphism of pelitic schists: Internat. Geol. Cong., 24th, Montreal 1972, Sec. 10, p. 27-35.

Thompson, J. B., Jr., and Waldbaum, D. R., 1968, Mixing properties of sanidine crystalline solutions: I. calculations based on ion-exchange data: Am. Mineralogist, v. 53, p. 1965-1999.

Varshneya, A. K., and Cooper, A. R., 1972a, Diffusion in the system K_2O–SrO–SiO_2: II, cation self-diffusion coefficients: Am. Ceramic Soc. Jour., v. 55, p. 220-223.

——— 1972b, Diffusion in the system K_2O–SrO–SiO_2: III, interdiffusion coefficients: Am. Ceramic Soc. Jour., v. 55, p. 312-317.

——— 1972c, Diffusion in the system K_2O–SrO–SiO_2: IV, mobility model, electrostatic effects, and multicomponent diffusion: Am. Ceramic Soc. Jour., v. 55, p. 418-421.

Waldbaum, D. R., and Thompson, J. B., Jr., 1969, Mixing properties of sanidine crystalline solutions: IV. phase diagrams from equations of state: Am. Mineralogist, v. 54, p. 1274-1298.