

## REVIEW AND COMPARISON OF SIMPLE TRANSFER AND EXCHANGE EQUILIBRIA

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### ABSTRACT

Equations of equilibrium of plagioclase crystals and a melt of plagioclase composition (a transfer system), and between associated calcic clinopyroxene and orthopyroxene (an exchange system) are reproduced and compared. Thermodynamic theory has been remarkably successful in dealing with these two fundamentally different kinds of phase-equilibrium relations.

*Keywords:* transfer equilibrium, plagioclase, exchange equilibrium, clinopyroxene, orthopyroxene.

### SOMMAIRE

Les équations servant à décrire l'équilibre entre cristaux de plagioclase et un bain fondu de la composition d'un plagioclase (un système de transfert), et entre un clinopyroxène calcique et un orthopyroxène associé (un système d'échange) sont reproduites et comparées. L'approche théorique thermodynamique a réussi remarquablement bien à traduire ces deux sortes de relations fondamentalement différentes entre phases à l'équilibre.

(Traduit par la Rédaction)

*Mots-clés:* équilibre de transfert, plagioclase, équilibre d'échange, clinopyroxène, orthopyroxène.

### INTRODUCTION

Several kinds of equilibria involving phases of variable composition are of interest to geologists. The well-known equilibrium of plagioclase crystals and a melt of plagioclase composition is an example. As near-equilibrium crystallization occurs in this system, atoms belonging to both solution components, NaAlSi<sub>3</sub>O<sub>8</sub> and CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, are displaced from melt to crystals (resulting in an increase in the volume of crystals), as diffusion occurs to eliminate concentration gradients. The resulting change in composition is an increase in the Na/(Na + Ca) ratio in *both* phases in this system. Prigogine & Defay (1954, p. 276) referred to the "transfer of two components from one phase to another", and the term *transfer equilibrium* is here adopted for the kind of equilibrium that occurs in the plagioclase system. In another kind of transformation involving binary mixtures, one of the two phases, calcic clinopyroxene, yields atoms of Mg to the second phase, orthopyroxene, in exchange for Fe, or *vice versa* (with virtually no change in volume), until a new condition of equilibrium is obtained. The result is that the ratio Mg/(Mg + Fe) increases in one phase and decreases

in the other. These are here referred to as *exchange equilibria*. In the present review, equations of transfer and of exchange equilibrium are reproduced and compared, leading to the conclusion that the two kinds of equilibria differ fundamentally, and must be carefully distinguished from each other.

### TRANSFER EQUILIBRIUM

A thermodynamic analysis of transfer equilibrium in binary systems was carried out by van Laar (1908) (Reisman 1970, Chapters 27 and 28), and the resulting equations were applied by Bowen (1913). Retaining the plagioclase crystal (c) – melt (m) system as an example, the mass-balance and energy-balance equations are,

$$\text{mass: } (\text{NaAlSi}_3\text{O}_8)^c \rightleftharpoons (\text{NaAlSi}_3\text{O}_8)^m \quad (1a)$$

$$(\text{CaAl}_2\text{Si}_2\text{O}_8)^c \rightleftharpoons (\text{CaAl}_2\text{Si}_2\text{O}_8)^m \quad (1b)$$

$$\text{energy: } \mu_{ab}^c = \mu_{ab}^m \quad (2a)$$

$$\mu_{an}^c = \mu_{an}^m \quad (2b)$$

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where  $\mu$  denotes chemical potential (*i.e.*, partial molar Gibbs energy), and the albite (ab) and anorthite (an) components are  $\text{NaAlSi}_3\text{O}_8$  and  $\text{CaAl}_2\text{Si}_2\text{O}_8$ . By substitution of four equations of the kind

$$\mu = G + RT \ln X \quad (3)$$

where  $G$  stands for molar Gibbs energy,  $R$  for the gas constant,  $T$  for absolute temperature, and  $X$  for molar fraction,

$$G^{\text{Ab(c)}} + RT \ln X_{\text{ab}}^{\text{c}} = G^{\text{Ab(m)}} + RT \ln X_{\text{ab}}^{\text{m}} \quad (4a)$$

$$G^{\text{An(c)}} + RT \ln X_{\text{an}}^{\text{c}} = G^{\text{An(m)}} + RT \ln X_{\text{an}}^{\text{m}} \quad (4b)$$

Here, Ab and An (with a capital A) refer to pure  $\text{NaAlSi}_3\text{O}_8$  and  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , and both melt and crystal are assumed to behave as ideal mixtures. By rearrangement of terms,

$$X_{\text{ab}}^{\text{m}} / X_{\text{ab}}^{\text{c}} = \exp [-(G^{\text{Ab(m)}} - G^{\text{Ab(c)}}) / RT] \quad (5a)$$

$$X_{\text{an}}^{\text{m}} / X_{\text{an}}^{\text{c}} = \exp [-(G^{\text{An(m)}} - G^{\text{An(c)}}) / RT] \quad (5b)$$

Note that at equilibrium, both (5a) and (5b) must be satisfied simultaneously, and because  $X_{\text{ab}}^{\text{c}} + X_{\text{an}}^{\text{c}} = 1.0$ , only two concentration variables appear in these equations. At constant pressure, the expressions on the right of each equal sign in (5a) and (5b) are functions only of temperature. Thus, at a specified temperature, we have two equations and two variables, and these two variables must become *fixed*, *i.e.*, at constant temperature and pressure, the plagioclase system is *invariant*. This is apparent from the phase diagram (Fig. 1).

Equations (5a) and (5b) are now used to derive equations for the liquidus and solidus (upper and lower) curves in the phase diagram for plagioclase (Fig. 1). Differentiating these two equations with respect to temperature, recalling that

$$\frac{\delta(\Delta G / T)}{\delta T} = \frac{-\Delta H}{T^2} \quad (6),$$

followed by an integration from the melting temperature of albite,  $T^{\text{Ab}}$ , and the melting temperature of anorthite,  $T^{\text{An}}$ , we obtain

$$\frac{X_{\text{ab}}^{\text{m}}}{X_{\text{ab}}^{\text{c}}} = \exp \left[ \frac{-\Delta H^{\text{Ab(m-c)}}}{R} \left( \frac{1}{T} - \frac{1}{T^{\text{Ab}}} \right) \right] = \lambda^{\text{Ab}} \quad (7a)$$

$$\frac{X_{\text{an}}^{\text{m}}}{X_{\text{an}}^{\text{c}}} = \exp \left[ \frac{-\Delta H^{\text{An(m-c)}}}{R} \left( \frac{1}{T} - \frac{1}{T^{\text{An}}} \right) \right] = \lambda^{\text{An}} \quad (7b)$$

Solving explicitly for  $X_{\text{ab}}^{\text{m}}$  and  $X_{\text{an}}^{\text{m}}$  as functions of temperature yields the van Laar equations,

$$\text{liquidus: } X_{\text{an}}^{\text{m}} = \frac{\lambda^{\text{An}} (\lambda^{\text{Ab}} - 1)}{(\lambda^{\text{Ab}} - \lambda^{\text{An}})} \quad (8a)$$

$$\text{solidus: } X_{\text{an}}^{\text{c}} = \frac{(\lambda^{\text{Ab}} - 1)}{(\lambda^{\text{Ab}} - \lambda^{\text{An}})} \quad (8b)$$

where  $\lambda^{\text{Ab}}$  and  $\lambda^{\text{An}}$  are defined by equations (7a) and (7b), and  $\Delta H$  stands for the molar heat of melting [Reisman (1970), p. 286-288, equations (17) and (19), and chapter 28]. By use of the following data,

$$T^{\text{An}} = 1550^\circ\text{C} = 1823 \text{ K (P = 1 bar)}$$

$$T^{\text{Ab}} = 1100^\circ\text{C} = 1373 \text{ K (P = 1 bar)}$$

$$\Delta H^{\text{An(m-c)}} = 121\,350 \text{ J mol}^{-1}$$

$$\Delta H^{\text{Ab(m-c)}} = 53\,238 \text{ J mol}^{-1}$$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1},$$

Bowen (1913) plotted equations (8a) and (8b), as shown in Figure 1, to obtain near-perfect agreement with his experimental results. Subsequent estimates of thermodynamic properties for this system have changed slightly, but the procedure followed by N.L. Bowen was entirely appropriate.

Equations (3) to (8) apply where both mixtures in the transfer system are ideal. This assumption can be relaxed by replacing mole fraction terms ( $X$ ) by activity terms ( $a$ ); the two are related by  $a = \gamma X$ , where  $\gamma$  is the activity coefficient. Some possibilities for liquidus and solidus curves in systems where one or both binary phases are not ideal mixtures were explored by Onk (1981).

The crystallization of plagioclase from natural melts also is a transfer process, but different composition – temperature equations are needed. This problem was considered, for example, by Ghiorso *et al.* (1983).

#### EXCHANGE EQUILIBRIUM

The exchange of cations between associated rock-forming minerals is analogous to ion exchange in soils, which in 1850 was studied by H.S. Thompson and J.T. Way, and a few years later by J. Lemberg, who attributed the process to clay and zeolite minerals (Helfferich 1962). One of the first studies of exchange between two crystalline phases was by Tubandt & Reinhold (1929), who found that the equilibrium distribution of Ag and Cu between  $(\text{Ag,Cu})\text{I}$  and  $(\text{Ag,Cu})_2\text{S}$  is a function of temperature. The theory of exchange equilibrium was introduced to Geology by Ramberg & DeVore (1951).

As an example of exchange equilibrium, consider a system composed of crystals of orthopyroxene (a mixture of components  $\text{MgSiO}_3$ , denoted en, and  $\text{FeSiO}_3$ , denoted fs), together with crystals of Ca

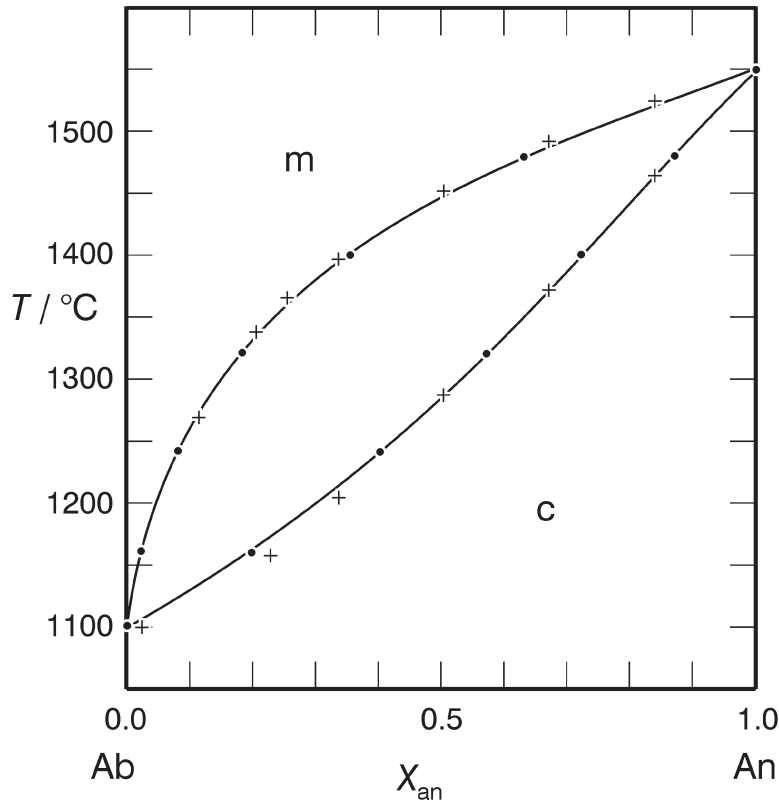
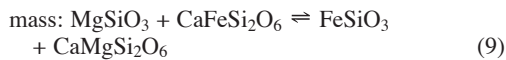


FIG. 1. Transfer equilibrium in the plagioclase crystal – melt system at 1.0 bar pressure, showing experimental data (+) of Bowen (1913) and the writer's solutions to equations (8a) and (8b) in text (dots and curves).

pyroxene (a mixture of components  $\text{CaMgSi}_2\text{O}_6$ , denoted di, and  $\text{CaFeSi}_2\text{O}_6$ , denoted hd). Simplified formulas are used. A condition of equilibrium with regard to the distribution of Mg and  $\text{Fe}^{2+}$  atoms between crystals of orthopyroxene (Opx) and Ca pyroxene (Cpx) in this system is described by the following single mass-balance equation and single energy-balance equation:



$$\text{energy: } \mu_{\text{en}}^{\text{Opx}} + \mu_{\text{hd}}^{\text{Cpx}} = \mu_{\text{fs}}^{\text{Opx}} + \mu_{\text{di}}^{\text{Cpx}} \quad (10)$$

By substitution of four equations of type (3), *i.e.*, assuming ideal mixing in both phases,

$$\frac{X_{\text{fs}}^{\text{Opx}} / X_{\text{en}}^{\text{Opx}}}{X_{\text{hd}}^{\text{Cpx}} / X_{\text{di}}^{\text{Cpx}}} = \exp - \left[ \frac{G^{\text{Fs}} + G^{\text{Di}} - G^{\text{En}} - G^{\text{Hd}}}{RT} \right] = \exp - \left( \frac{\Delta G^{(9)}}{RT} \right) \quad (11)$$

The quotient on the far left of this equation is commonly written

$$\frac{X_{\text{fs}} (1 - X_{\text{hd}})}{(1 - X_{\text{fs}}) X_{\text{hd}}} = K_{\text{D}} \quad (12).$$

Notice that at low concentrations of Fe (*i.e.*, where Fe forms a minor or trace element), quotient (12) becomes very nearly equal to the ratio  $X_{\text{fs}} / X_{\text{hd}}$ , which forms one expression of the Nernst distribution law (Nernst 1904).

The orthopyroxene – Ca pyroxene exchange equilibrium can be represented by a distribution diagram in which  $X_{\text{fs}}$  is plotted against  $X_{\text{hd}}$ , to produce an isothermal distribution curve (Fig. 2). At constant temperature and pressure, the system is obviously univariant (not invariant), and because  $\Delta G$  in equation (11) is a function of temperature,  $K_{\text{D}}$  is expected to vary with temperature:

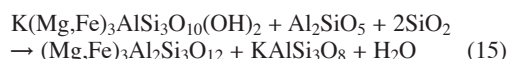
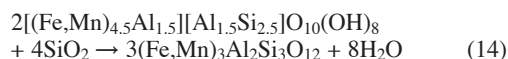
$$\frac{\delta \ln K_D}{\delta(1/T)} = - \left( \frac{1}{R} \right) \frac{\delta(\Delta G^{(9)} / T)}{\delta(1/T)} = - \frac{\Delta H^{(9)}}{R} \quad (13)$$

where  $\Delta H^{(9)}$  is the enthalpy change for reaction (9), with components as pure phases. For several exchange-type systems, the anticipated dependence of  $K_D$  on  $T$  has indeed been demonstrated experimentally. Here, as in the transfer system (above), departure from ideal mixing can be accommodated if necessary. In the orthopyroxene – Ca pyroxene system at granulite-facies conditions, the distribution coefficient remains nearly constant at 1.80 (the plotted curve in Fig. 2), and departures from ideal mixing seem small.

Fifty years ago, various terms and symbols were used in Chemistry for the quotient (12), and of these the writer (1959, 1961) chose distribution coefficient and  $K_D$ . Since then, other terms and symbols have appeared in the geological literature, especially for the distribution of trace elements (Beattie *et al.* 1993).

## DISCUSSION

Although the best-known examples of transfer systems in Geology are the plagioclase and the (Mg, Fe) olivine crystal–melt systems, Ramberg (1952) pointed out that analogous equilibria occur in solid-state (metamorphic) systems as well, for example,



Where a third solution component is added to a transfer system, *e.g.*,  $\text{Mn}_2\text{SiO}_4$  to the (Mg, Fe) olivine crystal – melt system, the liquidus and solidus lines become curved *planes*, equations for which were derived by Seltz (1935). In transfer systems (14) and (15), above, the chemical potential of  $\text{H}_2\text{O}$  in the crystal-boundary phase becomes an additional variable.

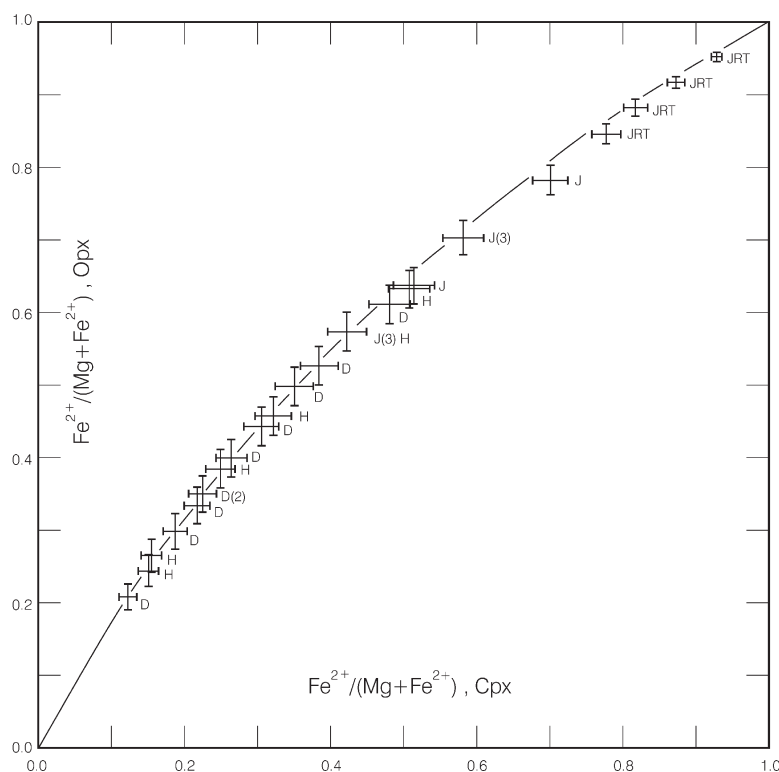
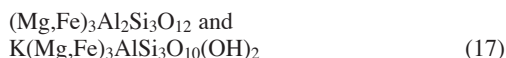


FIG. 2. Distribution of Mg and  $\text{Fe}^{2+}$  between orthopyroxene (Opx) and Ca pyroxene (Cpx) in three widespread granulite-grade terranes ( $T \approx 800^\circ\text{C}$ ,  $P \approx 8$  kbar), as a demonstration of exchange equilibrium. Data are from India (H: R.A. Howie), Australia (D: L.R. Davidson) and the Adirondacks in North America (J: L.-S. Jen; JRT: H.W. Jaffe, P. Robinson, R.J. Tracy). Numbers, *e.g.*, J(3), indicate number of near-identical samples. The curve is for  $K_D = 1.80$  [(11) and (12) in text]. From Kretz (1994, p. 230).

Many exchange systems have been studied, principally ones in which Mg and Fe<sup>2+</sup> are shared by two phases, for example,



In exchange systems, the distribution coefficient can be displaced by the presence of another component, for example the addition of Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> to garnet in (17) (Kretz 1994, p. 225).

In the above derivations, pressure was assumed to remain constant. The effect of pressure on the equilibria can be readily evaluated by use of standard equations.

Comparing the simple transfer and exchange systems described above, recall that the variance of the plagioclase transfer system (at constant pressure) is *one*, and that of the pyroxene exchange system is *two*. Thus at constant pressure and temperature, the composition of both plagioclase crystal and melt is fixed (Fig. 1), whereas in the exchange system, the composition of both orthopyroxene and Ca pyroxene can vary (Fig. 2), the only restriction being that the composition of one is a function of the composition of the other.

Now it would be possible to divide one of the transfer equations (5b) by the other (5a), to produce an equation that resembles the exchange equation (11), with a quotient,

$$\frac{X_{\text{an}}^{\text{m}} (1 - X_{\text{an}}^{\text{c}})}{(1 - X_{\text{an}}^{\text{m}}) X_{\text{an}}^{\text{c}}} \quad (18),$$

which resembles the distribution coefficient (12). But the equation cannot describe the liquidus and solidus curves, nor their dependence on the heat of melting, nor equivalent curves in solid–solid systems. Moreover, the equation does not fix the composition of the two phases (at constant T and P) as required. Although this equation could at times be useful, it has no place in the theory of transfer equilibrium, and quotient (18) should not be referred to as a distribution coefficient. Also, one could attempt to define a transfer system by combining *one* of the transfer equations, analogous to (5a) or (5b), with an exchange quotient such as (12). But this procedure also is theoretically incorrect.

As an example of a system in which a transfer reaction could dominate during heating, followed by minor exchange during cooling, consider the mineral assemblage in equation (15). In high-grade metamorphic terranes, biotite evidently reacts with sillimanite and quartz to produce garnet, K-feldspar and H<sub>2</sub>O, as both biotite and garnet increase in Mg relative to Fe (Ramberg 1952, p. 158, Schmid & Wood 1976, Kretz 1990). During cooling, the reaction could reverse, but

where only a slight increase in Fe is found in the rim of garnet crystals, where in contact with biotite, it seems more likely that a local Fe–Mg (garnet–biotite) exchange reaction has occurred instead (Hess 1971, Tracy *et al.* 1976, Spear 1993).

## CONCLUSION

Although thermodynamic theory cannot provide information on the properties of minerals and melts (*e.g.*, melting temperatures of crystals, and the heat of melting), the theory is remarkably successful in providing a definition of chemical equilibrium, and in describing different kinds of composition – temperature relations to be expected in different kinds of mineral or mineral–melt systems.

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