

CORRELATION OF SOME PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION OF SOLID SOLUTION

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ABSTRACT

The tacit assumption for the linear correlation of the density and the chemical composition of a solid solution is twofold: one is an ideal solid solution and the other identical or nearly identical molar volumes of the components. In an ideal solid solution, the difference in densities obtained by the non-linear and linear treatments are discussed. These are applied to the spessartite-almandite, almandite-pyrope, forsterite-fayalite and wurtzite-greenockite systems. The garnet systems can be treated practically by the linear correlation, but the olivine and the wurtzite systems must be treated with caution. Coefficients of thermal expansion and compressibilities of the ideal solid solution can be discussed in the same manner. But when the solid solution is ideal, the linear correlation of molar heat capacities and chemical composition is possible. The linear correlation of refractive index and chemical composition of an isotropic solid solution can be derived from the Gladstone-Dale equation, but it is required that the system must be ideal and the molar volumes of the components are equal or nearly equal. If the concept of the volume fraction is introduced, density, coefficient of thermal expansion, compressibility and refractive index can be correlated linearly with the volume fraction in an ideal system.

I. DENSITY

Density has been correlated linearly for the determination of the chemical composition of a solid solution. Bloss (1952), however, found out that this is not actually true in an ideal binary solid solution. This can be proved more rigorously in a multicomponent system by a simple thermodynamical discussion. The difference between the densities obtained by the non-linear and linear treatments in the ideal system is of considerable interest to us. Since we usually use the linear correlation for the determination of the composition, we want to know the maximum density difference from non-linear correlation, so the accuracy of the density measurements for the linear correlation can be stated. See Fig. 1

Zen (1956a) discussed the validity of Vegard's law in an ideal cubic solid solution and concluded that unless molar volumes of the components are equal or nearly equal, the law does not hold. A similar situation arises in the correlation of density and chemical composition of a solid solution. The importance of the molar volumes of the components in the correlation has been pointed out by Bloss. He suggested that the negative and positive deviations of the non-linear treatment from that of the linear depend entirely upon the ratio of the molar volumes of the components in an ideal binary solid solution.

In the m component solid solution, the mass, M , is given by

$$M = \sum_i^m n_i \rho_i \bar{V}_i \quad (1)$$

where n_i , ρ_i and \bar{V}_i are the number of moles, the density and the molar volumes of the i th component of the solid solution, respectively. The volume of the solid solution, V , is

$$V = \sum_i^m n_i \left(\frac{\partial V}{\partial n_i} \right)_{nk} = \sum_i^m n_i \bar{V}_i \tag{2}$$

where \bar{V}_i is the partial molar volume of the i th component, and k denotes all the components except the i th. The volume can be also expressed by

$$V = \bar{V} \sum_i^m n_i \tag{3}$$

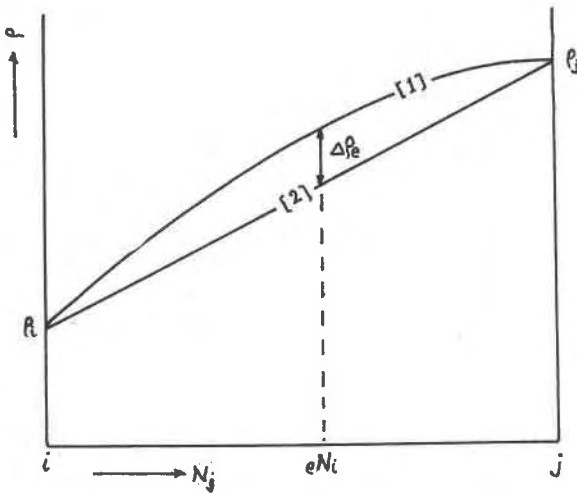


FIG. 1. Correlation of density and chemical composition of an ideal binary solid solution. The curve [1] is the non-linear correlation and [2] linear approximation. For other symbols, see the text. The example is given for the case of $\Delta\rho_e > 0$, which is termed the positive deviation from linearity. When the error of the density measurement is larger than $\Delta\rho_e$, the [2] correlation can be used approximately instead of [1]. If the density measurement is designed to be more accurate and the error is smaller than $\Delta\rho_e$, the correlation should be more properly made by the non-linear curve [1]. It is noticed that $eN_i \approx 0.5$.

where \bar{V} is the molar volume of the solid solution. The division of (1) by (2) gives the density of the solid solution, that is,

$$\rho = \frac{1}{V} \sum_i^m N_i \rho_i \bar{V}_i \tag{4}$$

Also

$$\rho = \frac{1}{\sum N_i \bar{V}_i} \sum N_i \rho_i \bar{V}_i \tag{4'}$$

since

$$\frac{n_i}{\sum_i^m n_i} = N_i$$

where N_i is the mole fraction of the i th component. This procedure of deriving (4) is essentially the same as that of Bloss. But (4) can be applied for both cases, ideal or non-ideal solid solution systems.

In an ideal solid solution we can set

$$\bar{V}_i = \bar{V}_i. \quad (5)$$

Therefore, we have

$$\rho = \frac{1}{\sum N_i \bar{V}_i} \sum N_i \rho_i \bar{V}_i. \quad (6)$$

If the densities of all the components happen to be same, from (6)

$$\rho = \rho_i.$$

Of course, in this case, the density measurements fail to determine the chemical composition of the solid solution. Instead, if the molar volumes of the components are identical, from (6)

$$\rho = \sum_i^m N_i \rho_i \quad (7)$$

since

$$\sum_i^m N_i = 1.$$

Equation (7) indicates the linear relation between the density and chemical composition. Thus the tacit assumptions for the linear correlation are: an ideal solid solution and identical molar volumes of the components. However, this is not new and only confirms Bloss' finding.

We now consider the ideal system in which the densities of the components are not identical, nor the molar volumes. In an ideal solid solution, the difference between the densities given by the non-linear and linear treatments is as follows.

$$\Delta\rho = \frac{\sum N_i \rho_i \bar{V}_i}{\sum N_i \bar{V}_i} - \sum N_i \rho_i. \quad (8)$$

The function, $\Delta\rho$, has at least one extremum (maximum or minimum). Though no detailed mathematical proof is given here, this is quite clear since $\Delta\rho=0$ at the pure end members. The N_i at which $\Delta\rho$ has the extremum can be solved by transformation of mole fraction in (8) into

number of moles, differentiating both sides of the equation with respect to n_i and setting

$$\left(\frac{\partial(\Delta\rho)}{\partial n_i}\right)_{nk} = 0.$$

The reason for this transformation is obvious from the independent property of number of moles. Arranging the results with the reverse transformation of n_i into N_i , we have

$$\bar{V}_i \frac{\rho_i \sum N_i \bar{V}_i - \sum N_i \rho_i \bar{V}_i}{\rho_i - \sum N_i \rho_i} = (\sum N_i \bar{V}_i)^2. \tag{9}$$

However, it must be noted that in the binary system only one equation is necessary, but two for the ternary system and so forth. This can be easily understood by the property of the mole fraction.

For simplicity, only the solution for the binary system is given here. Suppose the two components are i and j , respectively, and the required mole fraction is eN_i . Then, from (9)

$$(eN_i)^2(\bar{V}_i - \bar{V}_j) + 2eN_i\bar{V}_j - \bar{V}_j = 0 \tag{10}$$

The solution of the above quadratic equation is given by

$$eN_i = \frac{\sqrt{\bar{V}_i\bar{V}_j} - \bar{V}_j}{\bar{V}_i - \bar{V}_j} \tag{11}$$

It is quite surprising to see the eN_i at which $\Delta\rho$ has the extremum is not a function of densities, but of the molar volumes of the components. The negative sign in front of the square root of (11) has been dropped, since $0 \leq N_i \leq 1$.

We know

$$\frac{\bar{V}_i + \bar{V}_j}{2} > \sqrt{\bar{V}_i\bar{V}_j}$$

in (11). Thus if

$$\frac{\bar{V}_i + \bar{V}_j}{2}$$

is substituted into (11) in the place of $\sqrt{\bar{V}_i\bar{V}_j}$, $eN_i = \frac{1}{2}$ is obtained. Therefore, eN_i approaches $\frac{1}{2}$, as \bar{V}_i approaches \bar{V}_j , or vice versa, because

$$\frac{\bar{V}_i + \bar{V}_j}{2} \approx \sqrt{\bar{V}_i\bar{V}_j},$$

when $\bar{V}_i \approx \bar{V}_j$. This is why Bloss found in some of his studies that the mole fraction at which the deviation is extremum is about 0.5. (Fig. 1)

If eN_i determined by (11) is substituted into (8), this will give us the extremum deviation of the non-linear treatment from the linear $\Delta\rho_e$, that is,

$$\Delta\rho_e = \frac{\sqrt{\bar{V}_i} - \sqrt{\bar{V}_j}}{\sqrt{\bar{V}_i} + \sqrt{\bar{V}_j}} (\rho_i - \rho_j) \quad (12)$$

According to (12), the function, $\Delta\rho_e$, may be positive or negative depending on the sign of $(\sqrt{\bar{V}_i} - \sqrt{\bar{V}_j})$ and $(\rho_i - \rho_j)$.

The following examples are given under the assumption of ideality except in the case of the forsterite-fayalite system. This is somewhat arbitrary, since we do not have experimental data to support this. However, this is the simplest way for the purpose of the present discussion.

Example 1. Spessartite-Almandite System

According to Skinner (1956), the densities are 4.190 and 4.318 for spessartite and almandite, respectively. Also the molar volumes are 118.15 cc./mole for spessartite and 115.28 for almandite. From equation (11), the mole fraction of spessartite, eN_i , is found to be 0.49₈ which is quite close to 0.5. The deviation of density $\Delta\rho_e$ is -0.000_6 . Thus the deviation is almost insignificant compared to the accuracy of the present density measurements and the linear correlation can be justified.

Example 2. Almandite-Pyrope System

Skinner gives, for pyrope, the density, 5.582 and the molar volume, 113.29 cc./mole. The desired mole fraction of almandite eN_i is found to be 0.49₇ and the extremum deviation $\Delta\rho_e$ is -0.003_2 . By the same reason as the former example, the linear correlation is possible, if the error in the density measurements is greater than 0.003₂g/cc.

Example 3. Forsterite-Fayalite System

Yoder and Sahama (1957) concluded from the heat of solution and additivity of the molar volumes that this system belongs to an ideal system within the accuracy of the measurements. They give the densities, 3.222 for synthetic forsterite and 4.392 for synthetic fayalite. The molar volumes are also given, 43.7cc./mole for forsterite and 46.4 for fayalite. The desired mole fraction for fayalite eN_i is 0.49₂ and the deviation $\Delta\rho_e$ is $+0.017_6$. The deviation is rather high. This can be explained if we look at the equation (12). That is, when the molar volumes of the components are small and the density difference is large, the deviation becomes larger. As shown already, the maximum deviation of the density is about 0.5%. Thus caution will be necessary in using the linear correlation.

Example 4. Wurtzite-Greenockite System

Hurlbut (1957) noticed that the density data of the intermediate compositions in this system fall below the straight line in the linear correlation, though the difference is not much. The data for the present calculation are taken from Hurlbut. Wurtzite has the density, 4.1, $a_0 = 3.811 \text{ \AA}$ and $c_0 = 6.234 \text{ \AA}$, and greenockite, the density, 4.9, $a_0 = 4.142 \text{ \AA}$ and $c_0 = 6.724 \text{ \AA}$.

The number of formula weights in a unit cell is two. Using Avogadro number $N = 6.023 \times 10^{23}$, the molar volumes calculated are 23.6 cc./mole for wurtzite and 30.1 for greenockite. The desired mole fraction of wurtzite eN_i is 0.477 and the maximum difference between the non-linear and the linear treatment, $\Delta\rho_e$ is $+0.0487$ in density, which is about 1.1% deviation from linearity. The conclusion starting from the ideality of the solid solution gives the positive deviation but the experimental data contradict this, that is, the data by Hurlbut give the negative deviation. If the negative deviation is true, the $\sum N_i \bar{V}_i < \sum N_i \bar{V}_i$ from (8). Thus the volume increase can be expected by the mixing according to (4). However, the calculation of the molar volumes of the intermediate and end members of the synthetic wurtzite-greenockite system from his data indicates a volume decrease by mixing. If the density of greenockite is chosen to be 4.8, which is calculated from his x-ray data for synthetic greenockite, instead of the measured value of 4.9, his density data show the positive deviation as the present theory predicts. However, a further study is necessary in this respect.

II. COEFFICIENT OF THERMAL EXPANSION, COMPRESSIBILITY AND HEAT CAPACITY

In an ideal m component solid solution, we have

$$\bar{V} = \sum_i^m N_i \bar{V}_i \quad (13)$$

Differentiating the molar volumes with respect to temperature at constant pressure or with respect to pressure at constant temperature, the following equations can be obtained.

$$\begin{aligned} \left(\frac{\partial \bar{V}}{\partial T} \right)_p &= \sum N_i \left(\frac{\partial \bar{V}_i}{\partial T} \right)_p \\ \left(\frac{\partial \bar{V}}{\partial p} \right)_T &= \sum N_i \left(\frac{\partial \bar{V}_i}{\partial p} \right)_T \end{aligned} \quad (14)$$

However,

$$\begin{aligned} \alpha &= \frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial T} \right)_p, & \alpha_i &= \frac{1}{\bar{V}_i} \left(\frac{\partial \bar{V}_i}{\partial T} \right)_p \\ \beta &= \frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial p} \right)_T, & \beta_i &= -\frac{1}{\bar{V}_i} \left(\frac{\partial \bar{V}_i}{\partial p} \right)_T \end{aligned} \quad (15)$$

Then the suitable substitution of (15) into (14) gives

$$\alpha = \frac{1}{\sum N_i \bar{V}_z} \sum N_i \alpha_i \bar{V}_i \quad (16)$$

$$\beta = \frac{1}{\sum N_i \bar{V}_i} \sum N_i \beta_i \bar{V}_i \quad (17)$$

where α and α_i are the coefficients of thermal expansion of the solid solution and the i th component, and β and β_i are the compressibilities. Here again, if the molar volumes of the components are equal or nearly equal, (16) and (17) can be reduced into

$$\alpha = \sum_i^m N_i \alpha_i \quad (18)$$

$$\beta = \sum_i^m N_i \beta_i \quad (19)$$

Therefore, the analogous equations such as (8) to (12) can be constructed in the correlation of coefficients of thermal expansion and compressibilities with chemical composition. Equation (11) shows that the mole fraction of the i th component at which the deviation of density from the linear is maximum, is a function of molar volumes of the components only, thus the mole fraction is common in the cases of correlation of density, coefficient of thermal expansion and compressibility with the chemical composition of the solid solution.

The molar heat content, H , of a solid solution can be expressed by

$$H = \sum N_i \left(\frac{\partial H}{\partial n_i} \right)_{n_k} = \sum N_i \bar{H}_i \quad (20)$$

where \bar{H}_i is the partial molar heat content of the i th component. Differentiating both sides of (20) with respect to temperature at constant pressure, we have

$$\left(\frac{\partial H}{\partial T} \right)_p = \sum N_i \left(\frac{\partial^2 H}{\partial T \partial n_i} \right)_{n_k}$$

Exchanging the order of differentiation in the right hand side of the above equation and from

$$\left(\frac{\partial H}{\partial T} \right)_p = C_p,$$

which is the molar heat capacity.

$$C_p = \sum N_i \left(\frac{\partial}{\partial n_i} C_p \right) = \sum N_i \bar{C}_{pi} \quad (21)$$

where \bar{C}_{pi} is the partial molar heat capacity of the i th component. In an ideal system

$$C_{pi} = \bar{C}_{pi} \quad (22)$$

Thus we can have

$$C_p = \sum N_i C_{pi} \quad (23)$$

Therefore, the correlation of the molar heat capacity with the chemical composition of a solid solution is linear as far as the solid solution is ideal. Apparently few experimental data exist for the discussion of Part II.

III. REFRACTIVE INDEX

In general practice, the index of refraction of an isotropic solid solution is linearly represented as follows.

$$\gamma = \sum_i^m N_i \gamma_i \quad (24)$$

where γ and γ_i are the refractive indices of m component solid solution and its i th component, and N_i is the mole fraction of the i th. Equation (24) has been also generalized for anisotropic solid solutions. According to Barth (1930), the equation is analogous to the second theoretical equation by Mallard which is the same as that obtained by Duffet empirically. The tacit assumption in his practice will be studied from the property of refractivity. The total refractivity, R , is expressed by

$$R = \frac{\gamma^2 - 1}{\gamma^2 + 2} V \quad (\text{Lorentz-Lorenz}) \quad (25)$$

or

$$R = (\gamma - 1)V \quad (\text{Gladstone-Dale}) \quad (26)$$

The calculation of the index of refraction from the density data has been attempted by several authors (e.g., Larsen (1921), Jaffe (1956) and Allen (1956)), though Barth stated that the relation between the two is not simple. However, the empirical equation by Gladstone-Dale rather than the theoretical one by Lorentz-Lorenz generally appears to be in the best agreement with the observed facts (Eitel (1954)).

We define the partial molar refractivity of the i th component of the solid solution as follows.

$$\bar{R}_i = \left(\frac{\partial R}{\partial n_i} \right)_{n_k} \quad (27)$$

And generalization of the equation by Guggenheim (1957) gives

$$R = \sum_i^m n_i \bar{R}_i \quad (28)$$

The differentiation of both sides of Lorentz-Lorenz equation (25) with respect to n_i gives

$$\bar{R}_i = \frac{\gamma^2 - 1}{\gamma^2 + 2} \bar{V}_i \quad (29)$$

From (25), (28) and (2), with transformation of n_i into N_i ,

$$\sum N_i \bar{R}_i = \frac{\gamma^2 - 1}{\gamma^2 + 2} \sum N_i \bar{V}_i \quad (30)$$

Call R_i the molar refractivity of the i th component and then the following equation is valid.

$$\sum N_i R_i = \sum N_i \frac{\gamma_i^2 - 1}{\gamma_i^2 + 2} \bar{V}_i \quad (31)$$

The division of (30) by (31) gives

$$\frac{\sum N_i \bar{R}_i}{\sum N_i R_i} = \frac{\frac{\gamma^2 - 1}{\gamma^2 + 2} \sum N_i \bar{V}_i}{\sum N_i \frac{\gamma_i^2 - 1}{\gamma_i^2 + 2} \bar{V}_i} \quad (32)$$

If the deviation of ideality is not great in a solid solution, then

$$\frac{\sum N_i \bar{R}_i}{\sum N_i R_i} \approx 1 \quad (33)$$

Thus

$$\frac{\gamma^2 - 1}{\gamma^2 + 2} \approx \frac{1}{\sum N_i \bar{V}_i} \sum N_i \frac{\gamma_i^2 - 1}{\gamma_i^2 + 2} \bar{V}_i \quad (34)$$

Equation (34) may be expanded as follows.

$$\begin{aligned} \left(1 - \frac{2}{\gamma^2} + \frac{4}{\gamma^4} - \frac{8}{\gamma^6} + \frac{16}{\gamma^8} \cdots\right) &\approx \frac{1}{\sum N_i \bar{V}_i} \\ &= \sum N_i \left(1 - \frac{2}{\gamma_i^2} + \frac{4}{\gamma_i^4} - \frac{8}{\gamma_i^6} + \frac{16}{\gamma_i^8} \cdots\right) \bar{V}_i \end{aligned} \quad (35)$$

Then we can have

$$\left. \begin{aligned} \frac{1}{\gamma^2} &\approx \frac{1}{\sum N_i \bar{V}_i} \sum N_i \frac{1}{\gamma_i^2} \bar{V}_i \\ \frac{1}{\gamma^4} &\approx \frac{1}{\sum N_i \bar{V}_i} \sum N_i \frac{1}{\gamma_i^4} \bar{V}_i \\ &\vdots \end{aligned} \right\} \quad (36)$$

These are obtained by equating the terms of both sides of (36), which have the same power of r and r_i . This method indicates also $\sum N_i \bar{V}_i \approx \sum N_i \bar{V}_i$ from the first term. This can be understood from (33). If this is an ideal solid solution and the molar volumes of the components are equal or nearly equal, equation (36) becomes

$$\frac{1}{\gamma^l} = \sum N_i \frac{1}{\gamma_i^l}, \quad l = 2q, \quad q = 1, 2, 3, \cdots \quad (37)$$

However, when $q=1$ in the equation above, we have

$$\frac{1}{\gamma^2} = \sum N_i \frac{1}{\gamma_i^2} \quad (38)$$

which is analogous to the first equation given by Mallard theoretically in 1884 for the binary cubic mixed crystals. Barth (1930) believes that Mallard's theory depends on the analogy of the phenomena produced by the superposition of thin crystalline plates. It is proved that Mallard's equation can be derived from Lorentz-Lorenz equation. And the equations for $q>1$ should be tested by experiments.

From Gladstone-Dale equation,

$$\bar{R}_i = (\gamma - 1)\bar{V}_i \quad (39)$$

Under the same assumption and with the same procedures as before, we have

$$\gamma \approx \frac{\sum N_i \gamma_i \bar{V}_i}{\sum N_i \bar{V}_i} \quad (40)$$

When the solid solution is ideal, (40) becomes

$$\gamma = \frac{\sum N_i \gamma_i \bar{V}_i}{\sum N_i \bar{V}_i} \quad (41)$$

In addition, if the molar volumes of the components are equal or nearly equal, (41) can be reduced into (24). The linear correlation can be derived from Gladstone-Dale equation under the condition of the ideal solid solution and identical or nearly identical molar volumes of the components. The similarity of equation (41) to those of density, coefficient of thermal expansion, and compressibility equations is obvious. Therefore, it is suggested that the analogous equation such as (8) to (12) may be constructed in the correlation of the refractive index and the chemical composition of the solid solution. But equation (41) should be tested by experiments. The simplest test may be the measurements of the refractive indices of an ideal binary solution.

SUMMARY AND CONCLUSION

The simple linear correlation of the density and the refractive index with the chemical composition of a solid solution which is found in standard textbooks in mineralogy was analyzed in Part I and Part III. In Part I, the conservation of mass and additivity of partial molar volumes are the basis of the discussion. In Part II, additivity of molar volumes (in an ideal system) and that of partial molar heat content are utilized. In Part III, the discussion was conducted from additivity of partial

molar refractivity, which is not a thermodynamical quantity and also from that of partial molar volumes.

In an ideal system, equations (6), (16), (17) and (41) indicate that these physical properties of the components are weighted to their proportion of volumes and then give the average properties of the solid solution. As already shown, these equations can be summarized as follows.

$$\frac{\sum N_i \rho_i \bar{V}_i}{\rho} = \frac{\sum N_i \alpha_i \bar{V}_i}{\alpha} = \frac{\sum N_i \beta_i \bar{V}_i}{\beta} = \frac{\sum N_i \gamma_i \bar{V}_i}{\gamma} = \sum N_i \bar{V}_i \quad (42)$$

We define the volume fraction, v_i , in the following manner.

$$v_i = \frac{N_i \bar{V}_i}{\sum N_i \bar{V}_i} \quad (43)$$

Thus

$$\sum_i^m v_i = 1 \quad (44)$$

In terms of the volume fraction, (42) can be expressed by

$$\begin{aligned} \rho &= \sum \rho_i v_i \\ \alpha &= \sum \alpha_i v_i \\ \beta &= \sum \beta_i v_i \\ \gamma &= \sum \gamma_i v_i \end{aligned} \quad (45)$$

In other words, these physical properties can be correlated linearly with the volume fraction of the components. When the molar volumes of the components happen to be identical, the volume fraction is identical with the mole fraction. This can be shown from (43). As shown by (44) and (45), measurements of one physical property is sufficient to determine the volume fraction in an ideal binary solid solution, two for an ideal ternary system and so on. One might prefer the use of "degree of freedom" in this kind of discussion. But, according to the present discussion, the determination of the lattice constant is only involved in equation (44). Thus this does not introduce a new physical property to determine the volume fraction, that is to say, the determination of the lattice constant does not reduce the degree of freedom of the system to determine the volume fraction. On the contrary, the lattice constant determination can be used for the conversion of the volume fraction into the mole fraction. For simplicity, suppose a cubic ideal solid solution, then

$$\bar{V} = \frac{Na^3}{Z}, \quad \bar{V}_i = \frac{Na_i^3}{Z} \quad (46)$$

where a and a_i are the lattice constants of the solid solution and its i th

component, N is Avogadro number and Z is number of the formula in a unit cell. No structure change is assumed in this solid solution. Equation (46) is substituted into (13), thus we have

$$a^3 = \sum N_i a_i^3 \quad (47)$$

Therefore, the volume fraction can be expressed by

$$v_i = N_i \left(\frac{a_i}{a} \right)^3 \quad (48)$$

And the conversion of volume fraction into mole fraction can be done by the following equation.

$$N_i = \left(\frac{a}{a_i} \right)^3 v_i \quad (48')$$

Regression equations relating chemical compositions and physical properties have been prepared for dolomite by Zen (1956b) and for anthophyllite by Hey (1956). Hey emphasized certain inherent limitations for their use, that is, a regression equation can only be utilized for one particular purpose. An equation or set of equations derived to predict the physical properties at the given chemical composition, can not properly be used to predict the chemical compositions at the given physical properties. This restriction in regression equations is lucidly illustrated by Moroney (1956). If it is desired to predict the chemical composition, given an adequate number of physical data, a set of regression equations must be calculated for this purpose (e.g., Zen (1957)), as Hey asserts.

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