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Multi-site order-disorder kinetics in crystalline solids: A generalized formulation

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ABSTRACT

Many crystalline solids have multiple nonequivalent sites among which different atoms show substitutional long-range order-disorder phenomena. The order-disorder kinetics of an atom among any n nonequivalent sites in a crystal can be described by the equation

$$x_i = c_{i1} + \sum_{j=2}^{n} c_{ij}(t)e^{\lambda_j t}$$

where x_i is the site occupancy of the atom at site s_i, n is the number of nonequivalent sites, λ_j ($\lambda_1 = 0$) is constant at a given temperature, pressure, and total composition of the crystal, and $c_{ij}(t)$ is constant or polynomial in t. Four theorems governing a multi-site order-disorder process have been proved, requiring that λ_j must be either zero (only $\lambda_1 = 0$), a negative real number, or a complex-valued quantity with the real part being a nonpositive number. The kinetic model becomes constrained and naturally complies with crystal-chemical conditions when the mole number per formula unit is chosen as the unit of all site-occupancy variables, or site multiplicities are explicitly incorporated into the model. When the mole fraction is directly used as the unit, the model becomes unconstrained, but it is a valid treatment that is as equally applicable to the multi-site order-disorder kinetics as the constrained model.

INTRODUCTION

Substitutional long-range ordering-disordering of different atoms or ions among two or more crystallographically nonequivalent sites (multi-site) is a common phenomenon in many crystalline solids. Typical examples include the ordering-disordering of Fe^{2+}, Mg^{2+}, Mn^{2+}, and Ca^{2+} among the four octahedral sites M1, M2, M3, and M4 in amphibole, and Al^{3+}, B^{3+}, Ga^{3+}, Si^{4+}, and Ge^{4+} among the four tetrahedral sites T1, T2, T3, and T4 in natural and synthetic feldspar (Hafner and Ghose 1971; Seifert and Virgo 1975; Dal Negro et al. 1978; Ungaretti et al. 1981; Ghose and Ganguly 1982; Hawthorne 1983a; Skogby 1987; Makino and Tomita 1989; Phillips et al. 1989; Burns and Fleet 1990; Fleet 1991, 1992; Kroll et al. 1991; Hirschmann et al. 1994). Some order-disorder processes involve even more than ten nonequivalent sites (Takéuchi et al. 1984a, 1984b; Yao and Franzen 1990, 1991; Yao et al. 1992). For instance, Nb and Ta atoms can undergo ordering-disordering among twelve distinct sites in the synthetic crystal $Ta_{6.74}Nb_{5.26}S_4$ (Yao and Franzen 1991), and Bi^{3+}, Pb^{2+}, and Sb^{3+} show strong order-disorder phenomena among twenty-four nonequivalent sites in izoklakeite (Makovicky and Mumme 1986; Armbruster and Hummel 1987). Investigations into such order-disorder phenomena are important to understand the thermodynamic properties and intracrystalline mixing behavior of solid solutions as well as the thermal history of geological processes (Saxena and Ghose 1970; Navrotsky 1971; Seifert and Virgo 1975; Ganguly 1982; Cohen 1986; Anovitz et al. 1988; Sack and Ghiorso 1991; Ganguly et al. 1994; Ghiorso et al. 1995; Ganguly and Domeneghetti 1996). Furthermore, differing site occupancies and their resulting entropy of mixing can significantly affect the formation and stability of some crystalline solids, particularly differential site-occupancy stabilized materials (Franzen and Köckerling 1995).

Several researchers made contributions to the kinetic theories of order-disorder processes. Following the pioneering work of Dienes (1955), Mueller (1967) proposed a model for order-disorder kinetics in quasibinary crystals based on an exchange reaction of two different atoms or ions between two nonequivalent sites. Ganguly (1982) reexamined this model and made a rather comprehensive review on the crystal chemistry, thermodynamics, and kinetics of order-disorder in ferromagnesian minerals. The Mueller model has been widely used to fit experimental data and estimate the kinetic coefficients (Besancon 1981; Ganguly 1982; Saxena et al. 1987, 1989; Anovitz et al. 1988; Skogby 1992; Sykes-Nord and Molin 1993). Despite its success, Sha and Chappell (1996a) pointed out that if a two-site order-disorder process involves three or more atoms or ions, Mueller's method gives no explicit solution to the kinetic differential equations. Furthermore, if two atoms or ions undergo ordering-disordering among three or more nonequivalent sites, there is no explicit solution to his model (Mueller 1969). Therefore, the Muel-

ler model is applicable only to pure or nearly pure binary ordering-disordering between two nonequivalent sites.

To solve the above problems, Sha and Chappell (1996a) proposed an alternative kinetic model for two-site multi-cation ordering-disordering, which can be used to calculate the forward and reverse kinetic coefficients of each individual cation. Sha and Chappell (1996b) also presented an explicit solution for three-site ordering-disordering. However, there is no kinetic model available for the ordering-disordering of atoms or ions among any n nonequivalent sites. In this paper, we present such a general model and prove some basic theorems that govern a multi-site order-disorder process.

Formulation of a multi-site order-disorder kinetic model

The formula of a crystalline phase can be written as

$$(s_1)_{\omega_1}\,(s_2)_{\omega_2}\ldots(s_i)_{\omega_i}\ldots(s_n)_{\omega_n}\,Z$$

and

$$s_i = (e_1, e_2, \ldots, e_l, \ldots, e_q, W_i)$$

where $s_1, s_2, \ldots, s_i, \ldots, s_n$ are n nonequivalent sites, and $e_1, e_2, \ldots, e_l, \ldots, e_q$ are the constituent atoms (cations, anions, or neutral atoms) showing order-disorder; W_i (i = 1, 2, ..., n) refers to all other atoms that only occur at site s_i; ω_i is the multiplicity of the s_i site; Z represents the rest of the chemical formula. Because an order-disorder process can occur not only in ionic crystals but also in metallic, covalent, and molecular crystals, in this paper, whenever necessary we simply use the term atom instead of cation or anion.

The kinetic reactions involved in an n-site order-disorder process can be written as

$$e_l(s_i) \underset{k_{ji}}{\overset{k_{ij}}{\rightleftarrows}} e_l(s_j) \qquad (i, j = 1, 2, 3, \cdots, n;\ i \neq j;\ l = 1, 2, 3, \cdots, q) \tag{1}$$

where k_{ij} and k_{ji} are the kinetic coefficients for the forward and backward reactions respectively. The kinetic equation governing the order-disorder process is

$$\frac{dx_i}{dt} = \sum_{\substack{j=1\\ j\neq i}}^{n} (k_{ji}x_j - k_{ij}x_i) \tag{2}$$

where x_i and x_j are the site occupancies of an atom e_l (l = 1, 2, 3, ..., q) at sites s_i and s_j, respectively.

Expanding Equation 2 gives a group of equations

$$\frac{dx_1}{dt} = -\left(\sum_{j=2}^{n} k_{1j}\right)x_1 + k_{21}x_2 + k_{31}x_3 + \cdots + k_{n1}x_n \tag{3.1}$$

$$\frac{dx_2}{dt} = k_{12}x_1 - \left(\sum_{\substack{j=1\\ j\neq 2}}^{n} k_{2j}\right)x_2 + k_{32}x_3 + \cdots + k_{n2}x_n \tag{3.2}$$

$$\frac{dx_3}{dt} = k_{13}x_1 + k_{23}x_2 - \left(\sum_{\substack{j=1\\ j\neq 3}}^{n} k_{3j}\right)x_3 + \cdots + k_{n3}x_n \tag{3.3}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$\frac{dx_n}{dt} = k_{1n}x_1 + k_{2n}x_2 + k_{3n}x_3 + \cdots - \left(\sum_{j=1}^{n-1} k_{nj}\right)x_n. \tag{3.n}$$

Writing $\boldsymbol{A} = \{a_{ij}\}$ where $a_{ij} = k_{ji} (i \neq j)$,

$$a_{11} = -\sum_{j=2}^{n} k_{1j},$$

$$a_{ii} = -\sum_{\substack{j=1\\ j\neq i}}^{n} k_{ij} \qquad (i = 2, 3, \cdots, n-1)$$

$$a_{nn} = -\sum_{j=1}^{n-1} k_{nj} \quad \text{and} \quad \boldsymbol{X} = \{x_i\} = [x_1\ x_2\ x_3 \cdots x_n]^{\mathrm{T}}$$

where T represents a transpose operation of the vector, it follows that

$$\frac{d\boldsymbol{X}}{dt} = \boldsymbol{AX} \tag{4}$$

with the initial site-occupancy vector being $\boldsymbol{X}(t = t_0) = \boldsymbol{X}_0 = [x_1^0\ x_2^0\ x_3^0 \ldots x_n^0]^{\mathrm{T}}$.

Summing the above equations from 3.1 to 3.n gives

$$\frac{dx_1}{dt} + \frac{dx_2}{dt} + \cdots + \frac{dx_i}{dt} + \cdots + \frac{dx_n}{dt} = \frac{d\sum_{i=1}^{n} x_i}{dt} = 0 \tag{5}$$

which is equivalent to the condition

$$\sum_{i=1}^{n} x_i = \sum_{i=1}^{n} x_i^0 = \gamma_0 \tag{6}$$

where x_i^0 is the initial site occupancy of an atom at the s_i site and γ_0 is a constant equal to the sum of the site occupancies of the atom at all n nonequivalent sites.

Integrating Equation 4 from $\boldsymbol{X}_0$ to $\boldsymbol{X}$ for the site-occupancy vector and from t_0 to t for the time gives

$$\boldsymbol{X} = \{x_i\} = e^{\boldsymbol{A}t}e^{-\boldsymbol{A}t_0}\boldsymbol{X}(t = t_0) = e^{\boldsymbol{A}(t-t_0)}\boldsymbol{X}_0 \tag{7}$$

where the function $e^{\boldsymbol{A}t} = \boldsymbol{E} + \boldsymbol{A}t + \boldsymbol{A}^2t^2/2! + \cdots + \boldsymbol{A}^kt^k/k! + \ldots$ is an $n \times n$ fundamental matrix whose components are functions of time, eigenvalues and their corresponding eigenvectors; $\boldsymbol{E}$ is an $n \times n$ identity matrix.

The eigenvalues of the matrix $\boldsymbol{A}$ are the roots of the following nth-degree algebraic equation

$$\begin{aligned} G(\lambda) &= \mathrm{Det}(\boldsymbol{A} - \lambda \boldsymbol{E}) \\ &= b_n\lambda^n + b_{n-1}\lambda^{n-1} + \cdots + b_1\lambda + b_0 \\ &= (\lambda - \lambda_1)^{f_1}(\lambda - \lambda_2)^{f_2} \cdots (\lambda - \lambda_r)^{f_r} \cdots (\lambda - \lambda_h)^{f_h} \\ &= 0 \end{aligned} \tag{8}$$

where $\lambda_1, \lambda_2, \ldots, \lambda_r, \ldots, \lambda_h$ $(1 \le h \le n)$ are the h distinct eigenvalues with corresponding multiplicities $f_1, f_2, \ldots, f_r, \ldots, f_h$.

The explicit form of the matrix Solution 7 differs in the following two cases:

(1) When all n eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_r, \ldots, \lambda_n$ are distinct [i.e., $f_r = 1$ $(r = 1, 2, \ldots, n)$], there exist n linearly independent constant eigenvectors $\boldsymbol{u}_1, \boldsymbol{u}_2, \ldots, \boldsymbol{u}_r, \ldots, \boldsymbol{u}_n$, which are the nontrivial solutions of the equation

$$(\boldsymbol{A} - \lambda_i \boldsymbol{E})\boldsymbol{u}_i = 0. \tag{9}$$

In this case, the matrix exponential function becomes

$$e^{\boldsymbol{A}t} = [\boldsymbol{u}_1 e^{\lambda_1 t}\ \boldsymbol{u}_2 e^{\lambda_2 t}\ \boldsymbol{u}_3 e^{\lambda_3 t} \ldots \boldsymbol{u}_n e^{\lambda_n t}] \tag{10}$$

and $e^{-\boldsymbol{A}t_0} = [\boldsymbol{u}_1 e^{-\lambda_1 t_0}\ \boldsymbol{u}_2 e^{-\lambda_2 t_0}\ \boldsymbol{u}_3 e^{-\lambda_3 t_0} \ldots \boldsymbol{u}_n e^{-\lambda_n t_0}]$. Equation 7 has the explicit form

$$X = \{x_i\} = \left\{\sum_{j=1}^{n} c_{ij} e^{\lambda_j t}\right\} \tag{11}$$

where $c_{ij}(i, j = 1, 2, \ldots, n)$ are constants that are determined by the eigenvalues, eigenvectors, and initial site occupancies.

(2) When the kinetic coefficient matrix $\boldsymbol{A}$ has eigenvalues with their multiplicities greater than one, two subcases may occur:

(a) There are still n linearly independent eigenvectors in spite of the presence of repeated eigenvalues, and the explicit solution remains in the same form as Equation 11.

(b) The matrix $\boldsymbol{A}$ has less than n linearly independent eigenvectors. In this case, if an eigenvalue λ_r with a multiplicity f_r has g_r linearly independent eigenvectors and $g_r < f_r$, then these g_r linearly independent solutions will be

$$\boldsymbol{u}_{r_1} e^{\lambda_r t}, \boldsymbol{u}_{r_2} e^{\lambda_r t}, \ldots, \boldsymbol{u}_{r_{g_r}} e^{\lambda_r t}.$$

The remaining $f_r - g_r$ linearly independent solutions will be of the form

$$\boldsymbol{u}_{r_{g_r+1}} e^{\lambda_r t}, \boldsymbol{u}_{r_{g_r+2}} e^{\lambda_r t}, \ldots, \boldsymbol{u}_{f_r} e^{\lambda_r t}$$

where

$$\boldsymbol{u}_{r_{g_r+f}} = \sum_{d=1}^{f} \boldsymbol{v}_d \frac{t^{(f-d)}}{(f-d)!} \qquad (f = 1, 2, \cdots, \theta;\ \theta = f_r - g_r),$$

and $\boldsymbol{v}_1, \boldsymbol{v}_2, \ldots, \boldsymbol{v}_d, \ldots, \boldsymbol{v}_\theta$ are a group of generalised eigenvectors corresponding to the eigenvector λ_r and are defined by

$$\boldsymbol{v}_d = (\boldsymbol{A} - \lambda_r \boldsymbol{E})^{\theta - d}\boldsymbol{v} \ (d = 1, 2, \ldots, \theta)$$

where the vector $\boldsymbol{v}$ is called the generalised eigenvector of rank θ associated with the eigenvalue λ_r if

$$(\boldsymbol{A} - \lambda_r \boldsymbol{E})^{\theta}\boldsymbol{v} = 0 \text{ and } (\boldsymbol{A} - \lambda_r \boldsymbol{E})^{\theta - 1}\boldsymbol{v} \neq 0.$$

From the above relations, we know that, in the second subcase, Equation 7 will be of the form

$$X = \{x_i\} = \left\{\sum_{j=1}^{n} c_{ij}(t) e^{\lambda_j t}\right\} \tag{12}$$

where $c_{ij}(t)$ is the following polynomial in t

$$c_{ij}(t) = \sum_{\epsilon=0}^{\delta_{ij}} p_{ij\epsilon} t^{\epsilon} \quad (0 \le \delta_{ij} \le n - 1) \tag{13}$$

in which δ_{ij} is an integer for a given distinct eigenvalue λ_j and their values depend on the multiplicity of the eigenvalue and the number of eigenvectors corresponding to this eigenvalue. The coefficients $p_{ij\epsilon}$ are constants. Substituting Equation 13 into Equation 12 gives

$$X = \{x_i\} = \left\{\sum_{j=1}^{n} \left(\sum_{\epsilon=0}^{\delta_{ij}} p_{ij\epsilon} t^{\epsilon}\right) e^{\lambda_j t}\right\}. \tag{14}$$

When all $\delta_{ij} = 0$, then $c_{ij}(t) = c_{ij} = p_{ij0} =$ constant, which implies that Equations 11 and 14 have the same form. Therefore, Equation 12 or 14 is the general kinetic model of a multi-site order-disorder process. For order-disorder processes involving multiple nonequivalent sites, it is possible that some of the pre-exponential terms $c_{ij}(t)$ are polynomials in t.

Some basic theorems governing a multi-site order-disorder process

The kinetic coefficient matrix $\boldsymbol{A}$ completely controls the characteristics of an order-disorder process for a given initial site-occupancy vector. Here, we will prove some basic theorems concerning the kinetic coefficient matrix $\boldsymbol{A}$, which is given by (see below)

$$A = \begin{bmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2n} \\ a_{31} & a_{32} & a_{33} & \cdots & a_{3n} \\ \vdots & \vdots & \vdots & & \vdots \\ a_{n1} & a_{n2} & a_{n3} & \cdots & a_{nn} \end{bmatrix} = \begin{bmatrix} -\sum_{j=2}^{n} k_{1j} & k_{21} & k_{31} & \cdots & k_{n1} \\ k_{12} & -\sum_{\substack{j=1 \\ j\neq 2}}^{n} k_{2j} & k_{32} & \cdots & k_{n2} \\ k_{13} & k_{23} & -\sum_{\substack{j=1 \\ j\neq 3}}^{n} k_{3j} & \cdots & k_{n3} \\ \vdots & \vdots & \vdots & & \vdots \\ k_{1n} & k_{2n} & k_{3n} & \cdots & -\sum_{j=1}^{n-1} k_{nj} \end{bmatrix}. \tag{15}$$

Each of the $n(n-1)$ kinetic coefficients is a function of temperature, and can be expressed by the Arrhenius equation

$$k_{ij} = Q_{ij}e^{-E_{ij}/RT}$$

where Q_{ij} and E_{ij} are the pre-exponential factor and activation energy, respectively. The kinetic coefficient matrix $\boldsymbol{A}$ has some very important characteristics, which are stated in the following lemma and theorems.

Lemma 1

For an $n \times n$ kinetic coefficient matrix $\boldsymbol{A}$, represented by Matrix 15 of an n-site order-disorder process, each off-diagonal entry is positive; each diagonal entry is negative, and its absolute value is equal to the sum of all other off-diagonal entries in the same column as the diagonal entry.

This lemma implies that $\mathrm{Det}(\boldsymbol{A}) = 0$ and indicates that there are only $n-1$ independent variables in the site-occupancy vector $\boldsymbol{X} = \{x_i\} = [x_1\ x_2\ x_3\ \cdots\ x_n]^{\mathrm{T}}$; this is consistent with Equation 6.

Theorem 1

Let $\boldsymbol{A}_{r1}, \boldsymbol{A}_{r2}, \boldsymbol{A}_{r3}, \ldots, \boldsymbol{A}_{ru}$ $(r = 1, 2, 3, \ldots, n-1)$ be the principal submatrices of order r of the $n \times n$ kinetic coefficient matrix $\boldsymbol{A}$, where

$$u = \binom{n}{r} = \frac{n!}{r!(n-r)!};$$

all the determinants $\mathrm{Det}(\boldsymbol{A}_{ri})$ $(i = 1, 2, 3, \ldots, u)$ or the principal minors of order r of $\boldsymbol{A}$ have the same sign $(-1)^r$, and are nonzero real numbers.

Proof: to illustrate the general characteristics of the principal minors, let us first examine the case $n = 4$. Consider the matrix (see below)

$$\boldsymbol{A} = \begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{bmatrix}$$

$$= \begin{bmatrix} -(k_{12}+k_{13}+k_{14}) & k_{21} & k_{31} & k_{41} \\ k_{12} & -(k_{21}+k_{23}+k_{24}) & k_{32} & k_{42} \\ k_{13} & k_{23} & -(k_{31}+k_{32}+k_{34}) & k_{43} \\ k_{14} & k_{24} & k_{34} & -(k_{41}+k_{42}+k_{43}) \end{bmatrix}.$$

For $r = 1$, there are four principal submatrices of order one, and their determinants are

$$\mathrm{Det}(\boldsymbol{A}_{11}) = a_{11} = (-1)^1(k_{12}+k_{13}+k_{14}), \qquad \mathrm{Det}(\boldsymbol{A}_{12}) = a_{22} = (-1)^1(k_{21}+k_{23}+k_{24}),$$

$$\mathrm{Det}(\boldsymbol{A}_{13}) = a_{33} = (-1)^1(k_{31}+k_{32}+k_{34}), \qquad \mathrm{Det}(\boldsymbol{A}_{14}) = a_{44} = (-1)^1(k_{41}+k_{42}+k_{43}),$$

For $r = 2$, there are six principal submatrices of order two, and their determinants are

$$\mathrm{Det}(\boldsymbol{A}_{2p}) = \begin{vmatrix} a_{ii} & a_{ij} \\ a_{ji} & a_{jj} \end{vmatrix} = (-1)^2\left[\left(\sum_{\substack{l=1 \\ l\neq i}}^{4} k_{il}\right)\left(\sum_{\substack{l=1 \\ l\neq j}}^{4} k_{jl}\right) - k_{ij}k_{ji}\right] = (-1)^2\left[(k_{if}+k_{ig})\left(\sum_{\substack{l=1 \\ l\neq j}}^{4} k_{jl}\right) + k_{ij}(k_{jf}+k_{jg})\right]$$

where $f, g = \{1, 2, 3, 4\} - \{i, j\}$, and $i, j = 1, 2, 3, 4$ and $p = 1, 2, 3, 4, 5, 6$. For example,

$$\mathrm{Det}(\boldsymbol{A}_{21}) = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = (-1)^2[(k_{13}+k_{14})(k_{21}+k_{23}+k_{24}) + k_{12}(k_{23}+k_{24})]$$

$$\mathrm{Det}(\boldsymbol{A}_{22}) = \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} = (-1)^2[(k_{21}+k_{24})(k_{31}+k_{32}+k_{34}) + k_{23}(k_{31}+k_{34})].$$

For $r = 3$, there are four principal submatrices, and their determinants are

$$\mathrm{Det}(\boldsymbol{A}_{31}) = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = (-1)^3[k_{14}(k_{21}k_{31} + k_{23}k_{31} + k_{24}k_{31} + k_{21}k_{32} + k_{24}k_{32} + k_{21}k_{34} + k_{23}k_{34} + k_{24}k_{34})$$

$$+ k_{12}(k_{24}k_{31} + k_{24}k_{32} + k_{23}k_{34} + k_{24}k_{34}) + k_{13}(k_{21}k_{34} + k_{24}k_{32} + k_{23}k_{34} + k_{24}k_{34})]$$

$$\mathrm{Det}(A_{32}) = \begin{vmatrix} a_{11} & a_{12} & a_{14} \\ a_{21} & a_{22} & a_{24} \\ a_{41} & a_{42} & a_{44} \end{vmatrix} = (-1)^3[k_{13}(k_{21}k_{41} + k_{23}k_{41} + k_{24}k_{41} + k_{21}k_{42} + k_{23}k_{42} + k_{21}k_{43} + k_{23}k_{43} + k_{24}k_{43})$$
$$+ k_{12}(k_{23}k_{41} + k_{23}k_{42} + k_{23}k_{43} + k_{24}k_{43}) + k_{14}(k_{23}k_{42} + k_{21}k_{43} + k_{23}k_{43} + k_{24}k_{43})]$$

$$\mathrm{Det}(A_{33}) = \begin{vmatrix} a_{11} & a_{13} & a_{14} \\ a_{31} & a_{33} & a_{34} \\ a_{41} & a_{43} & a_{44} \end{vmatrix} = (-1)^3[k_{12}(k_{31}k_{41} + k_{32}k_{41} + k_{34}k_{41} + k_{31}k_{42} + k_{32}k_{42} + k_{34}k_{42} + k_{31}k_{43} + k_{32}k_{43})$$
$$+ k_{13}(k_{32}k_{41} + k_{32}k_{42} + k_{34}k_{42} + k_{32}k_{43}) + k_{14}(k_{31}k_{42} + k_{32}k_{42} + k_{34}k_{42} + k_{32}k_{43})]$$

$$\mathrm{Det}(A_{34}) = \begin{vmatrix} a_{22} & a_{23} & a_{24} \\ a_{32} & a_{33} & a_{34} \\ a_{42} & a_{43} & a_{44} \end{vmatrix} = (-1)^3[k_{21}(k_{31}k_{41} + k_{32}k_{41} + k_{34}k_{41} + k_{31}k_{42} + k_{32}k_{42} + k_{34}k_{42} + k_{31}k_{43} + k_{32}k_{43})$$
$$+ k_{23}(k_{31}k_{41} + k_{34}k_{41} + k_{31}k_{42} + k_{31}k_{43}) + k_{24}(k_{31}k_{41} + k_{32}k_{41} + k_{34}k_{41} + k_{31}k_{43})].$$

From the above example, it can be seen that (1) except matrix A itself [$\mathrm{Det}(A) = 0$], all the determinants of the principal submatrices of a given order r ($r = 1, 2, 3, \ldots, n - 1$) have the same sign $(-1)^r$ and (2) apart from this sign, each term within the expansion of each determinant is a positive product of r kinetic coefficients that are positive real numbers in terms of their physical meaning. These features are general to any principal submatrix, as is proved below.

For any principal submatrix of order r of matrix A

$$A_{ri} = \begin{bmatrix} a_{\phi(1)\phi(1)} & a_{\phi(1)\phi(2)} & a_{\phi(1)\phi(3)} & \cdots & a_{\phi(1)\phi(r)} \\ a_{\phi(2)\phi(1)} & a_{\phi(2)\phi(2)} & a_{\phi(2)\phi(3)} & \cdots & a_{\phi(2)\phi(r)} \\ a_{\phi(3)\phi(1)} & a_{\phi(3)\phi(2)} & a_{\phi(3)\phi(3)} & \cdots & a_{\phi(3)\phi(r)} \\ \vdots & \vdots & \vdots & & \vdots \\ a_{\phi(r)\phi(1)} & a_{\phi(r)\phi(2)} & a_{\phi(r)\phi(3)} & \cdots & a_{\phi(r)\phi(r)} \end{bmatrix}$$

where $\phi(1), \phi(2), \phi(3), \ldots, \phi(r)$ is a permutation without inversion over $\{1, 2, 3, \cdots, n\}$, that is, $\phi(1) < \phi(2) < \phi(3) < \ldots < \phi(r)$. The determinant of this principal submatrix is given by

$$\mathrm{Det}(A_{ri}) = \sum \{(\mathrm{sign}P)a_{\phi(1)P[\phi(1)]}a_{\phi(2)P[\phi(2)]}a_{\phi(3)P[\phi(3)]} \cdots a_{\phi(r)P[\phi(r)]} : P \in \Phi(r)\} = Q + R$$

with $Q = (\mathrm{sign}P)a_{\phi(1)\phi(1)}a_{\phi(2)\phi(2)}a_{\phi(3)\phi(3)} \cdots a_{\phi(r)\phi(r)}$, and

$$R = \sum \{(\mathrm{sign}P)a_{\phi(1)P[\phi(1)]}a_{\phi(2)P[\phi(2)]}a_{\phi(3)P[\phi(3)]} \cdots a_{\phi(r)P[\phi(r)]} : P \in S(r)\} \tag{16}$$

where P is a permutation over $\Phi(r) = \{\phi(1), \phi(2), \phi(3), \ldots, \phi(r)\}$, $S(r)$ is the rest of $\Phi(r)$ which excludes only the permutation $\phi(1)\ \phi(2)\ \phi(3) \ldots \phi(r)$, that is $S(r) = \Phi(r) - \phi(1)\ \phi(2)\ \phi(3) \ldots \phi(r)$; $\mathrm{sign}P = (-1)^h$ is the sign of a given permutation and h is the number of inversions in the permutation. Note that the sign function in the term Q is $\mathrm{sign}P = (-1)^h = (-1)^0 = +1$ because there is no inversion in the permutation $\phi(1)\ \phi(2)\ \phi(3) \ldots \phi(r)$.

Since

$$a_{\phi(i)\phi(i)} = (-1) \sum_{\substack{j=1 \\ j \neq \phi(i)}}^{n} k_{\phi(i)j},$$

it follows that

$$\begin{aligned} Q &= (\mathrm{sign}P)a_{\phi(1)\phi(1)}a_{\phi(2)\phi(2)}a_{\phi(3)\phi(3)} \cdots a_{\phi(r)\phi(r)} \\ &= a_{\phi(1)\phi(1)}a_{\phi(2)\phi(2)}a_{\phi(3)\phi(3)} \cdots a_{\phi(r)\phi(r)} \\ &= \left\{(-1) \sum_{\substack{j=1 \\ j \neq \phi(1)}}^{n} k_{\phi(1)j}\right\} \cdot \left\{(-1) \sum_{\substack{j=1 \\ j \neq \phi(2)}}^{n} k_{\phi(2)j}\right\} \cdot \left\{(-1) \sum_{\substack{j=1 \\ j \neq \phi(3)}}^{n} k_{\phi(3)j}\right\} \\ &\quad \cdots \left\{(-1) \sum_{\substack{j=1 \\ j \neq \phi(r)}}^{n} k_{\phi(r)j}\right\} \\ &= (-1)^r \left(\sum_{\substack{j=1 \\ j \neq \phi(1)}}^{n} k_{\phi(1)j}\right)\left(\sum_{\substack{j=1 \\ j \neq \phi(2)}}^{n} k_{\phi(2)j}\right)\left(\sum_{\substack{j=1 \\ j \neq \phi(3)}}^{n} k_{\phi(3)j}\right) \\ &\quad \cdots \left(\sum_{\substack{j=1 \\ j \neq \phi(r)}}^{n} k_{\phi(r)j}\right). \end{aligned}$$

As the diagonal entry $a_{\phi(i)\phi(i)}$ is the sum of all other off-diagonal entries in the column $\phi(i)$ of A, the expansion of Q will include all the product terms that the kinetic coefficients could possibly have for a given principal submatrix of order r. As a result, in the expansion of R, each term that has an opposite sign to $(-1)^r$ will have a corresponding term in the expansion of Q, and these terms with opposite signs will cancel out in the sum $\mathrm{Det}(A_{ri}) = Q + R$, leaving the determinant $\mathrm{Det}(A_{ri})$ with terms of the same sign $(-1)^r$. Because the selection of the principal submatrix A_{ri} is arbitrary and its sign depends only on its order r, all submatrices with the same order have the same sign. Hence, the determinant can be expressed as

$$\mathrm{Det}(A_{ri}) = Q + R = (-1)^r|\mathrm{Det}(A_{ri})| \neq 0 \quad (i = 1, 2, 3, \cdots, u). \tag{17}$$

Theorem 2

All coefficients b_i ($i = 1, 2, 3, \cdots, n$) except b_0 in the characteristic Polynomial 8 of the kinetic coefficient matrix $\boldsymbol{A}$ have the same sign; that is, they must be either all positive when n is an even integer or all negative when n is an odd integer; b_0 is always zero. Proof: for the characteristic polynomial of any $n \times n$ matrix, $\boldsymbol{A} = \{a_{ij}\}$,

$$\begin{aligned} G(\lambda) &= \mathrm{Det}(\boldsymbol{A} - \lambda \boldsymbol{E}) \\ &= b_n\lambda^n + b_{n-1}\lambda^{n-1} + \ldots + b_s\lambda^s \\ &\quad + \ldots + b_2\lambda^2 + b_1\lambda + b_0 \end{aligned} \tag{18}$$

it can be proved that, for any coefficient b_i ($i = 0, 1, 2, 3, \ldots, n$) of $G(\lambda)$ (Schneider and Barker 1968),

$$b_0 = \mathrm{Det}(\boldsymbol{A}) \tag{19}$$

$$b_n = (-1)^n \tag{20}$$

and for $0 < s < n$, the coefficient b_s in λ^s is given by

$$\begin{aligned} b_s &= (-1)^s \sum_{i=1}^{u} \mathrm{Det}(\boldsymbol{A}_{(n-s)i}) \\ &= (-1)^s \sum_{i=1}^{u} (\text{all principal minors of } \boldsymbol{A} \\ &\qquad \text{of order } n - s) \end{aligned}$$

$$\left(s = 1, 2, \cdots, n-1; i = 1, 2, \cdots, u; u = \binom{n}{n-s}\right) \tag{21}$$

where $\boldsymbol{A}_{(n-s)i}$ is the principal submatrix of order $(n - s)$, and the sum includes all the determinants of principal submatrices of order $(n - s)$ of $\boldsymbol{A}$. According to Theorem 1 and Equation 17, all principal minors of order r have the same sign $(-1)^r$, and it follows that

$$\begin{aligned} b_s &= (-1)^s \sum_{i=1}^{u} (-1)^{n-s} |\mathrm{Det}(\boldsymbol{A}_{(n-s)i})| \\ &= (-1)^n \sum_{i=1}^{u} |\mathrm{Det}(\boldsymbol{A}_{(n-s)i})| \neq 0. \end{aligned} \tag{22}$$

This indicates that all $b_s (s = 1, 2, \cdots, n)$ have the same sign: $(-1)^n$.

By Lemma 1, $\mathrm{Det}(\boldsymbol{A}) = 0$; therefore, from Equation 19, it follows that $b_0 = 0$. From Equations 20 and 22, we know that, except $b_0 = 0$, all coefficients of Polynomial 8 or 18 of the kinetic matrix $\boldsymbol{A}$ have the same sign $(-1)^n$, and are nonzero real numbers. Therefore, Polynomial 8 or 18 can be expressed as

$$\begin{aligned} G(\lambda) &= \mathrm{Det}(\boldsymbol{A} - \lambda \boldsymbol{E}) \\ &= (-1)^n[\lambda^n + d_{n-1}\lambda^{n-1} + \cdots + d_s\lambda^s + \cdots + d_2\lambda^2 + d_1\lambda] \end{aligned} \tag{23}$$

where

$$d_s = |b_s| = \sum_{i=1}^{u} |\mathrm{Det}(\boldsymbol{A}_{(n-s)i})| > 0 \ (s = 1, 2, 3, \cdots, n-1).$$

Theorem 3

For the characteristic Polynomial 8 of the $n \times n$ kinetic coefficient matrix $\boldsymbol{A}$, among the n eigenvalues, there is one and only one zero eigenvalue, and all other $n - 1$ eigenvalues are either negative or complex; for complex-valued roots, the real part of each conjugate pair $\eta \pm \mu i$ must be either negative or zero.

Proof: according to Theorems 1 and 2, all the coefficients of the characteristic Polynomial 23 (or its equivalent Polynomial 8 or 18) have the same sign $(-1)^n$. Because there is no change in signs, according to the Descartes' rule of signs, the number of positive roots is zero. Therefore, all the n roots must be either negative, zero, or complex-valued. On the other hand, if λ is substituted with $-\lambda$ in Polynomial 23, there are $n - 1$ variations in the signs of the coefficients of the polynomial $G(-\lambda)$. According to the Descartes' rule of signs, the number of negative real roots is either $n - 1$ or less than $n - 1$ by an even integer. Such an even integer is just the number of conjugate (complex-value) roots.

Existence and uniqueness of the zero root: according to Polynomial 23, let $G(\lambda) = (-1)^n\lambda[\lambda^{n-1} + d_{n-1}\lambda^{n-2} + \ldots + d_s\lambda^{s-1} + \ldots + d_2\lambda + d_1] = 0$.

It follows that

$$\lambda_1 = 0 \tag{24}$$

and

$$\lambda^{n-1} + d_{n-1}\lambda^{n-2} + \ldots + d_s\lambda^{s-1} + \ldots + d_2\lambda + d_1 = 0. \tag{25}$$

Equation 24 indicates that there is at least one zero root. If there is another zero root $\lambda_2 = 0$, it must be a root of Equation 25. Substituting λ_2 into Equation 25, we get $d_1 = 0$, which contradicts Theorems 1 and 2 and Equation 22 that $d_i = |b_i| > 0$ ($i = 1, 2, 3, \ldots, n$). Therefore, λ_2 cannot be zero; in other words, there is one and only one zero root.

According to the fundamental theorem of algebra, the characteristic Polynomial 8 or 18 can be expressed as

$$\begin{aligned} G(\lambda) &= b_n\lambda^n + b_{n-1}\lambda^{n-1} + \cdots + b_2\lambda^2 + b_1\lambda + b_0 \\ &= b_n(\lambda - \lambda_n)(\lambda - \lambda_{n-1}) \cdots (\lambda - \lambda_2)(\lambda - \lambda_1) \\ &= b_n\{\lambda^n + (-1)^1\lambda^{n-1} \sum \lambda_i + (-1)^2\lambda^{n-2} \sum \lambda_i\lambda_j \\ &\quad + (-1)^3\lambda^{n-3} \sum \lambda_i\lambda_j\lambda_k + \cdots + (-1)^l\lambda^{n-l} \\ &\quad \sum \lambda_i\lambda_j\lambda_k \cdots \lambda_l + \cdots + (-1)^n\lambda_1\lambda_2\lambda_3 \ldots \lambda_n\}. \end{aligned} \tag{26}$$

Expanding the right-hand side of Equation 26 and equating the coefficient of the term λ^{n-1} on both sides of the equation give

$$b_{n-1} = (-1)b_n \sum \lambda_i = (-1)^{n+1} \sum \lambda_i. \tag{27}$$

On the other hand, considering

$$\mathrm{Det}(\boldsymbol{A}_{1i}) = a_{ii} = -\sum_{\substack{j=1 \\ j \neq i}}^{n} k_{ij}$$

and Equation 21, it follows that

$$b_{n-1} = (-1)^n \sum_{i=1}^{n} |\mathrm{Det}\{A_{[n-(n-1)]i}\}| = (-1)^n \sum_{i=1}^{n} |\mathrm{Det}(A_{1i})|$$

$$= (-1)^n \sum_{i=1}^{n} \sum_{\substack{j=1 \\ j\neq i}}^{n} k_{ij}. \tag{28}$$

From Equations 27 and 28, it follows that

$$\sum_{i=1}^{n} \lambda_i = -\sum_{i=1}^{n} \sum_{\substack{j=1 \\ j\neq i}}^{n} k_{ij}. \tag{29}$$

This indicates that the sum $\Sigma\lambda_i$ should always be negative. Because nonreal roots occur in conjugate pairs, each conjugate pair must therefore appear in the sum of all the n roots. The sum of each conjugate pair is $(\eta + \mu i) + (\eta - \mu i) = 2\eta$. Therefore, the imaginary parts cancel in the sum. As all the real roots are either negative or zero, if the real part η were positive, then sometimes a positive sum $\Sigma\lambda_i$ would occur, contradicting Theorem 2 and Relation 29. Hence, the real part of each pair of complex-valued roots must be either negative or zero.

By Theorem 3, Equation 12 can be rewritten as:

$$x_i = c_{i1} + \sum_{j=2}^{n} c_{ij}(t)e^{\lambda_j t} \tag{30}$$

where $\lambda_1 = 0$ (the zero root). This indicates that the kinetic equation of an n-site order-disorder process consists of one constant term and $n - 1$ exponential terms. Such a constant term is the equilibrium site occupancy at the s_i site.

Inverse calculation of kinetic coefficients

Once the initial site occupancies are known, the order-disorder behaviour of atoms in a given crystal is completely determined by the $n(n - 1)$ kinetic coefficients. Hence, estimating these kinetic coefficients from experimental data is an essential step in theoretical studies of multi-site ordering-disordering.

Nonlinear parameter estimation

Equations 11, 12, and 14 contain some unknown parameters that can be determined only through experiment: c_{ij} and λ_j in Equation 11, and $p_{ij\epsilon}$, δ_{ij} and λ_j ($i, j = 1, 2, \ldots, n$) in Equation 14. To calculate them, it is essential to determine the kinetic site occupancies of an atom or ion, that is, the site occupancies at different times in isothermal or isobaric conditions, at each of the n nonequivalent sites.

Inversion of kinetic coefficients

Suppose that all the above parameters have been estimated; the problem now is to calculate the $n(n - 1)$ kinetic coefficients in matrix A. Expanding Equation 30 gives

$$x_1 = c_{11} + c_{12}(t)e^{\lambda_2 t} + c_{13}(t)e^{\lambda_3 t} + \cdots + c_{1n}(t)e^{\lambda_n t} \tag{31.1}$$

$$x_2 = c_{21} + c_{22}(t)e^{\lambda_2 t} + c_{23}(t)e^{\lambda_3 t} + \cdots + c_{2n}(t)e^{\lambda_n t} \tag{31.2}$$

$$x_3 = c_{31} + c_{32}(t)e^{\lambda_2 t} + c_{33}(t)e^{\lambda_3 t} + \cdots + c_{3n}(t)e^{\lambda_n t} \tag{31.3}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$x_n = c_{n1} + c_{n2}(t)e^{\lambda_2 t} + c_{n3}(t)e^{\lambda_3 t} + \cdots + c_{nn}(t)e^{\lambda_n t} \tag{31.n}$$

$$\text{Let } X_1 = \begin{bmatrix} c_{11} \\ c_{21} \\ c_{31} \\ \vdots \\ c_{n1} \end{bmatrix}, X_2 = \begin{bmatrix} c_{12}(t)e^{\lambda_2 t} \\ c_{22}(t)e^{\lambda_2 t} \\ c_{32}(t)e^{\lambda_2 t} \\ \vdots \\ c_{n2}(t)e^{\lambda_2 t} \end{bmatrix}, X_3 = \begin{bmatrix} c_{13}(t)e^{\lambda_3 t} \\ c_{23}(t)e^{\lambda_3 t} \\ c_{33}(t)e^{\lambda_3 t} \\ \vdots \\ c_{n3}(t)e^{\lambda_3 t} \end{bmatrix}, \ldots,$$

$$X_n = \begin{bmatrix} c_{1n}(t)e^{\lambda_n t} \\ c_{2n}(t)e^{\lambda_n t} \\ c_{3n}(t)e^{\lambda_n t} \\ \vdots \\ c_{nn}(t)e^{\lambda_n t} \end{bmatrix}.$$

Note that X_1 is a constant vector because of the uniqueness and existence of the zero root $\lambda_1 = 0$ by Theorem 3. It can be shown that $X_1, X_2, X_3, \ldots, X_n$ are n linearly independent solutions of Equation 4, and it follows that

$$\frac{dX_1}{dt} = X_1' = AX_1, \frac{dX_2}{dt} = X_2' = AX_2, \frac{dX_3}{dt} = X_3'$$

$$= AX_3, \cdots, \frac{dX_n}{dt} = X_n' = AX_n$$

which is equivalent to

$$[X_1' \; X_2' \; X_3' \ldots X_n'] = A[X_1 \; X_2 \; X_3 \ldots X_n]. \tag{32}$$

Let $\Phi(t) = [X_1 \; X_2 \; X_3 \ldots X_n]$, which is the fundamental solution matrix of Equation 4; then Equation 32 becomes

$$\Phi(t)' = A\Phi(t) \tag{33}$$

and the kinetic coefficient matrix is

$$A = \Phi(t)' \, \Phi(t)^{-1}. \tag{34}$$

Because all the parameters in Equations 31.1 to 31.n have been completely determined through nonlinear parameter estimations from the experimental kinetic site-occupancy data, Equation 34 can be calculated. By equating each component of the right-hand side of the matrix Equation 34 to the corresponding component of the kinetic coefficient Matrix 15, we obtain the $n(n - 1)$ kinetic coefficients. It should be noted that, although each component of $\Phi(t)$, $c_{ij}(t)e^{\lambda_j t}$, is a function of time, the final product $\Phi(t)'\Phi(t)^{-1}$ is a constant matrix.

Units of site-occupancy variables

There are actually two options in choosing the units of the site-occupancy variables: mole number per formula unit (or atoms per formula unit) and mole fraction (or atomic fraction), both of which are valid.

Mole number per formula unit

Let m_i be the mole number of an atom at site s_i per formula unit (pfu) of a crystal, y_i the mole fraction of the atom at site s_i, ω_i the multiplicity of site s_i (pfu), and N the sum of the multiplicities or the total number of all nonequivalent sites (pfu). Then we have

$$N = \sum_{i=1}^{n} \omega_i \tag{35}$$

$$m_i = \omega_i y_i. \tag{36}$$

If we let $M = \{m_i\} = [m_1\ m_2\ m_3 \ldots m_n]^{\mathrm{T}} = [\omega_1 y_1\ \omega_2 y_2\ \omega_3 y_3 \ldots \omega_n y_n]^{\mathrm{T}}$ and $X = M$, and replace $x_1, x_2, \ldots, x_i, \ldots, x_n$ with the corresponding $m_1, m_2, \ldots, m_i, \ldots, m_n$, all results concerning X and $x_1, x_2, \ldots, x_n$ are valid for M and $m_1, m_2, \ldots, m_i, \ldots, m_n$. After such a substitution, we have

$$\frac{dm_1}{dt} = -\left(\sum_{j=2}^{n} k_{1j}\right)m_1 + k_{21}m_2 + k_{31}m_3 + \cdots + k_{n1}m_n \tag{37.1}$$

$$\frac{dm_2}{dt} = k_{12}m_1 - \left(\sum_{\substack{j=1\\ j\neq 2}}^{n} k_{2j}\right)m_2 + k_{32}m_3 + \cdots + k_{n2}m_n \tag{37.2}$$

$$\frac{dm_3}{dt} = k_{13}m_1 + k_{23}m_2 - \left(\sum_{\substack{j=1\\ j\neq 3}}^{n} k_{3j}\right)m_3 + \cdots + k_{n3}m_n \tag{37.3}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$\frac{dm_n}{dt} = k_{1n}m_1 + k_{2n}m_2 + k_{3n}m_3 + \cdots - \left(\sum_{j=1}^{n-1} k_{nj}\right)m_n. \tag{37.n}$$

After summing Equations 37.1 to 37.n, we get an expression similar to Equation 6:

$$\sum_{i=1}^{n} m_i = \sum_{i=1}^{n} m_i^0 = \text{constant} = \left(\sum_{i=1}^{n} \omega_i\right)w_l^0 = Nw_l^0 \tag{38}$$

where m_i^0 is the initial site occupancy (in mole number per formula unit) and w_l^0 is the bulk or total mole fraction of atom or ion e_l ($l = 1, 2, 3, \ldots, q$) in the crystal. In the matrix form, Equations 37.1 to 37.n can be rewritten as

$$\frac{dM}{dt} = AM. \tag{39}$$

The solution to Equation 39 is

$$M = \{m_i\} = e^{At}e^{-At_0}M(t = t_0) = e^{A(t-t_0)}M_0. \tag{40}$$

According to Equations 11 and 12, in an explicit form, Equation 40 becomes

$$M = \{m_i\} = \left\{\sum_{j=1}^{n} d_{ij}(t)e^{\lambda_j t}\right\} \tag{41}$$

where $d_{ij}(t)$ is a constant or polynomial in t.

Mole fraction

Substituting Equation 36 into Equations 37.1 to 37.n gives

$$\frac{d(\omega_1 y_1)}{dt} = -\left(\sum_{j=2}^{n} k_{1j}\right)(\omega_1 y_1) + k_{21}(\omega_2 y_2) + k_{31}(\omega_3 y_3) + \cdots + k_{n1}(\omega_n y_n) \tag{42.1}$$

$$\frac{d(\omega_2 y_2)}{dt} = k_{12}(\omega_1 y_1) - \left(\sum_{\substack{j=1\\ j\neq 2}}^{n} k_{2j}\right)(\omega_2 y_2) + k_{32}(\omega_3 y_3) + \cdots + k_{n2}(\omega_n y_n) \tag{42.2}$$

$$\frac{d(\omega_3 y_3)}{dt} = k_{13}(\omega_1 y_1) + k_{23}(\omega_2 y_2) - \left(\sum_{\substack{j=1\\ j\neq 3}}^{n} k_{3j}\right)(\omega_3 y_3) + \cdots + k_{n3}(\omega_n y_n) \tag{42.3}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$\frac{d(\omega_n y_n)}{dt} = k_{1n}(\omega_1 y_1) + k_{2n}(\omega_2 y_2) + k_{3n}(\omega_3 y_3) + \cdots - \left(\sum_{j=1}^{n-1} k_{nj}\right)(\omega_n y_n). \tag{42.n}$$

Summing Equations 42.1 to 42.n gives

$$\frac{d\left(\sum_{i=1}^{n} \omega_i y_i\right)}{dt} = 0 \tag{43}$$

which is equivalent to

$$\sum_{i=1}^{n} \omega_i y_{il} = \sum_{i=1}^{n} \omega_i y_{il}^0 = \text{constant} = \left(\sum_{i=1}^{n} \omega_i\right)w_l^0 = Nw_l^0$$
$$(i = 1, 2, 3, \cdots, n;\ l = 1, 2, 3, \cdots, q) \tag{44}$$

or

$$\sum_{i=1}^{n} p_i y_{il} = w_l^0 \tag{45}$$

where

$$p_i = \frac{\omega_i}{\sum_{i=1}^{n} \omega_i} = \frac{\omega_i}{N}$$

is defined as the fractional site multiplicity of site i in the crystal, and $y_{il}^0 = y_i^0$ is the initial site occupancy of atom or ion e_l($l = 1, 2, 3, \ldots, q$). In the above notation, the subscript l in the site-occupancy variable $y_i = y_{il}$ for atom or ion e_l is used here for clarity, but was previously omitted (above) for simplicity.

Let us define the site-multiplicity matrix Ω as

$$\Omega = \begin{bmatrix} \omega_1 & 0 & 0 & \cdots & 0 \\ 0 & \omega_2 & 0 & \cdots & 0 \\ 0 & 0 & \omega_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \cdots & \vdots \\ 0 & 0 & 0 & \cdots & \omega_n \end{bmatrix}. \tag{46}$$

Then in the matrix form, Equation 36 becomes

$$M = \Omega Y \tag{47}$$

and Equations 42.1 to 42.n has the form

$$\frac{d(\Omega Y)}{dt} = A(\Omega Y). \tag{48}$$

As the site-multiplicity matrix Ω is an $n \times n$ nonsingular constant diagonal matrix, its inverse matrix Ω^{-1} exists. By differentiating the matrices at the left-hand side of Equation 48 and rearranging it, we have

$$\frac{dY}{dt} = BY \tag{49}$$

where the matrix B is defined as

$$B = \Omega^{-1}A\Omega \tag{50}$$

which indicates that matrix B is similar to matrix A. The characteristic polynomial of B is

$$\begin{aligned} F(\lambda) &= \mathrm{Det}(B - \lambda E) = \mathrm{Det}(\Omega^{-1}A\Omega - \lambda E) \\ &= \mathrm{Det}[\Omega^{-1}A\Omega - \Omega^{-1}(\lambda E)\Omega] = \mathrm{Det}(\Omega^{-1}(A - \lambda E)\Omega) \\ &= \mathrm{Det}(\Omega^{-1})\mathrm{Det}(A - \lambda E)\mathrm{Det}(\Omega) \\ &= \mathrm{Det}(A - \lambda E) = G(\lambda). \end{aligned} \tag{51}$$

Equation 51 proves that both matrices A and B have the same eigenvalues, which is important enough to be stated as the following theorem.

Theorem 4.

For a multi-site order-disorder process, the eigenvalues of matrices A and B of the governing matrix Equations 39 and 49 are the same and independent of the multiplicities of all nonequivalent sites in a crystal, no matter what units are chosen for the site-occupancy variables.

By Theorem 4, the matrix solution to Equation 49 is

$$\begin{aligned} Y = \{y_i\} &= \Omega^{-1}e^{At}e^{-At_0}\Omega Y(t = t_0) = \Omega^{-1}e^{A(t-t_0)}\Omega Y_0 \\ &= e^{B(t-t_0)}Y_0 \end{aligned} \tag{52}$$

where the inverse form of the site-multiplicity matrix Ω^{-1} and the initial conditions are

$$\Omega^{-1} = \begin{bmatrix} \frac{1}{\omega_1} & 0 & 0 & \cdots & 0 \\ 0 & \frac{1}{\omega_2} & 0 & \cdots & 0 \\ 0 & 0 & \frac{1}{\omega_3} & \cdots & 0 \\ \vdots & \vdots & \vdots & \cdots & \vdots \\ 0 & 0 & 0 & \cdots & \frac{1}{\omega_n} \end{bmatrix}, \quad M_0 = \begin{bmatrix} m_1^0 \\ m_2^0 \\ m_3^0 \\ \vdots \\ m_n^0 \end{bmatrix}, \quad Y_0 = \begin{bmatrix} y_1^0 \\ y_2^0 \\ y_3^0 \\ \vdots \\ y_n^0 \end{bmatrix}.$$

Equation 52 has the following explicit form

$$Y = \{y_i\} = \left\{\frac{1}{\omega_i}\sum_{j=1}^{n} d_{ij}(t)e^{\lambda_j t}\right\}. \tag{53}$$

Let $\Gamma = \{d_{ij}(t)e^{\lambda_j t}\}$ and $\Psi = \{1/\omega_i\, d_{ij}(t)e^{\lambda_j t}\}$ be $n \times n$ matrices whose column vectors form fundamental-solution sets to Equations 39 and 49, respectively; then it follows that

$$\Gamma(t) = \Omega\Psi(t). \tag{54}$$

The kinetic coefficient matrices B and A can be similarly inverted to give

$$\begin{aligned} B &= \Psi(t)'\Psi(t)^{-1} = [\Omega^{-1}\Gamma(t)]'[\Omega^{-1}\Gamma(t)]^{-1} \\ &= \Omega^{-1}\Gamma(t)'\Gamma(t)^{-1}\Omega \end{aligned} \tag{55}$$

$$A = \Omega B\Omega^{-1} = \Gamma(t)'\Gamma(t)^{-1}. \tag{56}$$

Constrained versus unconstrained treatments

There exist virtually two different approaches to the treatment of order-disorder kinetic Equations 3.1 to 3.n: constrained and unconstrained

Constrained treatment and crystal-chemical conditions

In the constrained approach, two external crystal-chemical conditions are often exerted on site occupancies during the experimental derivation of these variables (Finger 1969a, 1969b; Hawthorne 1983b; Skogby and Annersten 1985; Hirschmann et al. 1994):

(1) For each site s_i, we have

$$\sum_{l=1}^{q} y_{il} = \rho_i^0 \le 1 \qquad (i = 1,2,3,\cdots,n;\ l = 1,2,3,\cdots,q) \tag{57}$$

where ρ_i^0 is a constant for site s_i, and is equal to unity when only atoms $e_1, e_2, \ldots, e_l, e_q$ occupy the s_i site ($W_i = 0$). This condition can be always satisfied in both constrained and unconstrained treatments.

(2) For each atom or ion e_l, we get

$$\sum_{i=1}^{n} m_i = \sum_{i=1}^{n} \omega_i y_{il} = \left(\sum_{i=1}^{n} \omega_i\right) w_l^0 = N w_l^0$$
$$(i = 1, 2, 3, \cdots, n;\ l = 1, 2, 3, \cdots, q) \tag{58}$$

where w_l^0 is the bulk or total mole fraction of atom or ion e_l in the crystal.

From Equations 38 and 44, it is clear that the governing Equations 37.1 to 37.n or Equations 42.1 to 42.n naturally comply with the crystal-chemical Constraint 58 when either the mole number per formula unit or mole fraction (associated with the site multiplicities) is used as the unit of the site-occupancy variables.

Unconstrained treatment

In the unconstrained method, no additional external conditions are constrained on the site-occupancy variables. This approach can be rationalized by the following reasons:

(1) In view of the theory of chemical kinetics, the validity of the governing Equations 3.1 to 3.n for a multi-

site order-disorder process does not necessarily require any other external constraints.

(2) The site occupancies of atoms at nonequivalent sites can be experimentally determined, independently of the crystal chemistry, such as Constraint 58 (e.g., Ungaretti et al. 1981; Rossi et al. 1983; Molin 1989; Molin et al. 1991; Skogby et al. 1992). This is because the diffraction data or the quantities derived from them, such as unit cell parameters, atomic positions, bond lengths and angles as well as mean atomic numbers, also contain information on the bulk chemistry of the crystal (Hawthorne 1983b; Domeneghetti et al. 1995). Therefore, when deriving the experimental site occupancies there are two schools of researchers: one uses crystal-chemical Constraint 58 (e.g., Finger 1969a, 1969b; Ghose and Weidner 1972; Skogby and Annersten 1985; Ganguly et al. 1994; Hirschmann et al. 1994), whereas the other ignores it (e.g., Ungaretti et al. 1981; Rossi et al. 1983; Molin 1989; Molin et al. 1991; Skogby et al. 1992). However, these two different approaches give quite consistent results within experimental errors (Ganguly et al. 1994; Domeneghetti et al. 1995).

(3) When site multiplicities do not appear explicitly in the governing Equations 3.1 to 3.n, a group of symmetrically equivalent sites are merged and treated as a single site. In such a case, the kinetic coefficients implicitly contain the contribution of site multiplicities to the order-disorder kinetics.

(4) Constraint 58 is actually a mass conservation equation, whereas Equation 6 is an equivalent form of mass conservation in which a group of equivalent sites are treated as a single site.

In this treatment, we choose directly the mole fraction as the unit of all site-occupancy variables and explicitly exclude the site multiplicities from the governing Equations 3.1 to 3.n. Let the site-occupancy vector be

$$\boldsymbol{Z} = \{z_i\} = [z_1\ z_2\ z_3\ \ldots\ z_n]^{\mathrm{T}}$$

with the initial condition being

$$\boldsymbol{Z}(t = t_0) = \boldsymbol{Z}_0 = [z_1^0\ z_2^0\ z_3^0\ \ldots\ z_n^0]^{\mathrm{T}}.$$

If we let $\boldsymbol{X} = \boldsymbol{Z}$ and replace $x_1, x_2, \ldots, x_i, \ldots, x_n$ with corresponding $z_1, z_2, \ldots, z_i, \ldots, z_n$ in all the relevant equations, all the conclusions regarding $\boldsymbol{X}$ and $x_1, x_2, \ldots, x_i, \ldots, x_n$ will be applicable to $\boldsymbol{Z}$ and $z_1, z_2, \ldots, z_i, \ldots, z_n$.

It can be noted that the unconstrained kinetic model can be easily switched to the constrained ones (Equations 41 and 52), only by changing the choice of the unit of the site-occupancy variables from the mole number per formula unit or mole fraction associated with the site multiplicities to the mole fraction dissociated with the site multiplicities, or vice versa.

Discussion

Equations 11 and 12 or Equations 41 and 53 can be used to predict the general form of the kinetic equations of a multi-site order-disorder process in a crystal. For instance, for two-site and three-site ordering-disordering, $n = 2$ and $n = 3$, then the kinetic equations should be of the form

$$x_i = c_{i1} + c_{i2}e^{\lambda_2 t} \tag{59}$$

and

$$x_i = c_{i1} + c_{i2}e^{\lambda_2 t} + c_{i3}e^{\lambda_3 t}. \tag{60}$$

Equations 59 and 60 are consistent with the explicit solutions for two-site and three-site ordering-disordering discussed by Sha and Chappell (1996a, 1996b). In the case of two-site order-disorder kinetics, if the mole number per formula unit is chosen as the unit of the site-occupancy variables, one only needs to substitute $x_i (i = 1, 2)$ in Equations 7 and 8 of Sha and Chappell (1996a) with m_i to get the following expressions

$$m_1 = \frac{k_{21}(m_1^0 + m_2^0)}{k_{12} + k_{21}} - \frac{(k_{21}m_2^0 - k_{12}m_1^0)}{k_{12} + k_{21}} \cdot \exp[-(k_{12} + k_{21})(t - t_0)] \tag{61}$$

$$m_2 = \frac{k_{12}(m_1^0 + m_2^0)}{k_{12} + k_{21}} + \frac{(k_{21}m_2^0 - k_{12}m_1^0)}{k_{12} + k_{21}} \cdot \exp[-(k_{12} + k_{21})(t - t_0)] \tag{62}$$

where m_1 and m_2 are the site occupancies (in mole number per formula unit) of sites s_1 and s_2 respectively, m_1^0 and m_2^0 are the corresponding initial site occupancies, and k_{12} and k_{21} are the kinetic coefficients.

Furthermore, if we want the site multiplicities to appear explicitly in Equations 61 and 62, simply substitute $m_i (i = 1, 2)$ with $\omega_i y_i$, then we have

$$\begin{aligned} y_1 &= \frac{k_{21}(\omega_1 y_1^0 + \omega_2 y_2^0)}{\omega_1(k_{12} + k_{21})} - \frac{(k_{21}\omega_2 y_2^0 - k_{12}\omega_1 y_1^0)}{\omega_1(k_{12} + k_{21})} \cdot \exp[-(k_{12} + k_{21})(t - t_0)] \\ &= \frac{k_{21}w_l^0}{p_1(k_{12} + k_{21})} + \frac{[k_{21}w_l^0 - p_1 y_1^0(k_{12} + k_{21})]}{p_1(k_{12} + k_{21})} \cdot \exp[-(k_{12} + k_{21})(t - t_0)] \end{aligned} \tag{63}$$

and

$$\begin{aligned} y_2 &= \frac{k_{12}(\omega_1 y_1^0 + \omega_2 y_2^0)}{\omega_2(k_{12} + k_{21})} + \frac{[k_{21}\omega_2 y_2^0 - k_{12}\omega_1 y_1^0]}{\omega_2(k_{12} + k_{21})} \cdot \exp[-(k_{12} + k_{21})(t - t_0)] \\ &= \frac{k_{12}w_l^0}{p_2(k_{12} + k_{21})} + \frac{[k_{21}w_l^0 - p_1 y_1^0(k_{12} + k_{21})]}{p_2(k_{12} + k_{21})} \cdot \exp[-(k_{12} + k_{21})(t - t_0)] \end{aligned} \tag{64}$$

where y_1 and y_2 are the site occupancies in mole fraction, y_1^0 and y_2^0 are the initial site occupancies, ω_1 and ω_2 are the site multiplicities, $p_1 = \omega_1/(\omega_1 + \omega_2)$ and $p_2 = \omega_2/(\omega_1 + \omega_2)$ are the fractional site multiplicities, and w_l^0 is the bulk concentration of an atom or ion e_l and has the following relation:

$$w_l^0 = (\omega_1 y_1^0 + \omega_2 y_2^0)/(\omega_1 + \omega_2) = (p_1 y_1^0 + p_2 y_2^0).$$

Sha and Chappell (1996a, 1996b) discussed the applicability of two-site and three-site order-disorder kinetic models. Using orthopyroxene and tremolite as examples of two-site and four-site order-disorder processes, they demonstrated that theoretical predictions from the kinetic models (Sha and Chappell 1996a, 1996b) are in good agreement with available experimental results (Besancon 1981; Saxena et al. 1987, 1989; Skogby 1987, 1992; Sykes-Nord and Molin 1993).

Finally, it is important to point out that the occurrence of maxima or minima of the site-occupancy functions is characteristic of multi-site ordering-disordering in contrast to two-site ordering-disordering in which the site occupancies are monotonically increasing or decreasing functions.

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