Complexities of Real Oxide Solid Solution Systems

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The complexity and richness of natural minerals and multicomponent ceramics (like UO$_2$ spent nuclear fuel) arises not only from the large number of phases and crystal structures, but also from the variety of solid solutions, complex elemental substitutions, order-disorder relations, and exsolution phenomena one encounters. Indeed, a pure mineral or ceramic of end-member composition is the exception rather than the rule. Elemental substitutions in minerals may be classified in terms of the crystallographic sites on which they occur and the formal charges of the chemical elements (ions) which participate.

For a correct description, the thermodynamic punishment must fit the structural crime. Yet the formalism must be tractable, transparent, and useful. Herein lies the challenge.
# Charge Coupled Substitutions in Minerals

<table>
<thead>
<tr>
<th>Substitution</th>
<th>Examples</th>
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</thead>
<tbody>
<tr>
<td><strong>Same charge</strong></td>
<td></td>
</tr>
<tr>
<td>(\text{Mg}^{2+}<em>{M} = \text{Fe}^{2+}</em>{M})</td>
<td>Pyroxene, olivine</td>
</tr>
<tr>
<td>(\text{Al}^{3+}<em>{T} = \text{Fe}^{2+}</em>{T})</td>
<td>Mica, clay, epidote, feldspar, tourmaline</td>
</tr>
<tr>
<td>(\text{Al}^{3+}<em>{M} = \text{Fe}^{3+}</em>{M})</td>
<td>Mica, clay, amphibole, garnet, spinel, pyroxene</td>
</tr>
<tr>
<td>(\text{Al}^{3+}<em>{T} = \text{B}^{3+}</em>{T})</td>
<td>Feldspar, tourmaline, borosilicate glass</td>
</tr>
<tr>
<td>(\text{Si}^{4+}<em>{T} = \text{Ge}^{4+}</em>{T})</td>
<td>Olivine, garnet, spinel, pyroxene, feldspar</td>
</tr>
<tr>
<td>(\text{Na}^{+} = \text{K}^{+}) or other alkali</td>
<td>Feldspar, mica, clay, zeolite</td>
</tr>
<tr>
<td><strong>Different charges</strong></td>
<td></td>
</tr>
<tr>
<td>(\text{Si}^{4+}<em>{T} + \text{Na}^{+}</em>{A} = \text{Al}^{3+}<em>{T} + \text{Ca}^{2+}</em>{A})</td>
<td>Plagioclase substitution: feldspar, pyroxene, amphibole, mica, clay, zeolite</td>
</tr>
<tr>
<td>(\text{Si}^{4+}<em>{T} = \text{Na}^{+}</em>{A}) (or other alkali) + (\text{Al}^{3+}_{T})</td>
<td>Silica stuffing substitution: amphibole, mica, clay, silica minerals, zeolite, glass</td>
</tr>
<tr>
<td>(\text{Ca}^{2+}<em>{M} + \text{Si}^{4+}</em>{T} = \text{Al}^{3+}<em>{M} + \text{Al}^{3+}</em>{T})</td>
<td>Pyroxene, amphibole, mica, clay</td>
</tr>
<tr>
<td>(\text{Mg}^{2+}<em>{M} + \text{Si}^{4+}</em>{T} = \text{Al}^{3+}<em>{M} + \text{Al}^{3+}</em>{T})</td>
<td>Pyroxene, amphibole, mica, clay</td>
</tr>
<tr>
<td>(3\text{Fe}^{2+}<em>{M} = \text{vacancy}</em>{M} + 2\text{Fe}^{3+}_{M})</td>
<td>Defects in olivine, spinel, amphibole, mica, clay</td>
</tr>
<tr>
<td>(\text{Si}^{4+}<em>{T} = 4\text{H}^{+}</em>{T})</td>
<td>Hydrogarnet</td>
</tr>
</tbody>
</table>
Examples of charge-coupled substitutions

- $\text{Mg}_2\text{SiO}_4-\text{Fe}_2\text{SiO}_4$, $\text{Mg}_2\text{SiO}_4-\text{Mg}_2\text{GeO}_4$
- $\text{NaAlSi}_3\text{O}_8-\text{CaAl}_2\text{Si}_2\text{O}_8$
- $\text{ZrO}_2-\text{YO}_{1.5}$
- $\text{CoO}-\text{Li}_{0.5}\text{Co}_{0.5}\text{O}$
- $\text{LaGaO}_3-\text{SrGaO}_{2.5}$
Any expression one writes for a free energy of mixing, an activity, or an activity coefficient has buried in it some assumptions about the mixing process on an atomic scale. Therefore one must make sure those assumptions are reasonable. **There is no escaping this.**

Equations, whose form is constrained by theoretical considerations and whose parameters are physically reasonable, are more reliably extrapolated than arbitrary polynomials fit to data in a small $P, T, X$ range.

Models which simultaneously include constraints imposed by phase equilibria, calorimetry, and crystal chemistry are more reliable than those based on any one source alone.
General Reaction

\[ x_A A + x_B B = A(x_A)B(x_B) \]

\[ \Delta G^o_{\text{mix}} = \Delta H^o_{\text{mix}} - T\Delta S^o_{\text{mix}}. \]

\( \Delta H > 0 \), clustering and phase separation
\( \Delta H < 0 \), ordering and compound formation

Partial molar quantities and activities

\[ G^o_T(\text{solid solution}) = x_A \mu^o_T(A) + x_B \mu^o_T(B) + x_A \Delta \mu^o(A) + x_B \Delta \mu^o(B) \]

Integral free energy of mixing

\[ \Delta G^o_{\text{mix}} = x_A \Delta \mu^o_T(A) + x_B \Delta \mu^o_T(B) \]
The thermodynamic activity is defined as

\[ \Delta \mu^o(A) = RT \ln a(A) \quad \text{and} \quad \Delta \mu^o(B) = RT \ln a(B) \]

The changes in chemical potential on mixing can be related to partial molar enthalpies and entropies of mixing:

\[ \Delta \mu^o_T(A) = \Delta h^o_T(A) - T \Delta s^o_T(A) \quad , \quad \Delta \mu^o_T(B) = \Delta h^o_T(B) - T \Delta s^o_T(B) \]
FeAl$_2$O$_4$-FeCr$_2$O$_4$: 

One mole of ions mixed

\[ a(\text{Fe}_{0.5}\text{AlO}_2) = x_A, \text{ where } A = \text{Fe}_{0.5}\text{AlO}_2. \text{ and } a(\text{Fe}_{0.5}\text{CrO}_2) = x_B, \text{ where } B = \text{Fe}_{0.5}\text{CrO}_2. \]

Two moles of ions mixed, entropy an extensive parameter

\[ \Delta S_{\text{mix}} = -2R[x_A \ln x_A + x_B \ln x_B] \]

\[ \Delta \mu(\text{FeCr}_2\text{O}_4) = -2RT \ln x_A, \Delta \mu(\text{FeAl}_2\text{O}_4) = -2RT \ln x_B \]

\[ a(\text{FeCr}_2\text{O}_4) = x_A^2, a(\text{FeAl}_2\text{O}_4) = x_B^2 \]
Multicomponent solid solutions: no unique choice of components

Spinel \((\text{Fe}^{2+},\text{Ni})(\text{Cr} \text{ Fe}^{3+})_2\text{O}_4\) a ss between \(\text{Fe}_3\text{O}_4\) and \(\text{NiCr}_2\text{O}_4\) or \(\text{FeCr}_2\text{O}_4\) and \(\text{NiFe}_2\text{O}_4\).

\[
\text{Fe}_3\text{O}_4 + \text{NiCr}_2\text{O}_4 = \text{Nife}_2\text{O}_4 + \text{FeCr}_2\text{O}_4 \quad \Delta G \text{ not zero}
\]

“reciprocal term” must be incorporated.

Clinoptilolite zeolites, occurring in the tuffs at Yucca Mountain: \((\text{Na,K})_6\text{Al}_6\text{Si}_{30}\text{O}_{72} \cdot 20\text{H}_2\text{O}\)

\[
a(\text{Nax}_6\text{Al}_6\text{Si}_{30}\text{O}_{72} \cdot 20\text{H}_2\text{O}) = [x(\text{Nax}_6\text{Al}_6\text{Si}_{30}\text{O}_{72} \cdot 20\text{H}_2\text{O})]^6
\]

\[
a(\text{NaAlSi}_5\text{O}_{12} \cdot 3.67\text{H}_2\text{O}) = x \ (\text{NaAlSi}_5\text{O}_{12} \cdot 3.67\text{H}_2\text{O})
\]
Starting point: useful but inherently contradictory assumption that, though the heats of mixing are not zero, the configurational entropies of mixing are those of random solid solution.

\[ \Delta G^o_{\text{mix, ex}} = \Delta H^o_{\text{mix}} - T\Delta S^o_{\text{mix, ex}} \]

For a two-component system, the simplest formulation is:

\[ \Delta G_{\text{excess}} = \Delta H_{\text{mix}} = \alpha x_A x_B = W_H x_A x_B \]
Generalization

- For a binary system, the Guggenheim or Redlich-Kister based on a power-series expression for the excess molar Gibbs energy $G_m^E$ mixing which reduces to zero when either $x_1$ or $x_2$ approach unity:

$$G_m^E = RT \left( x_1 \ln f_1 + x_2 \ln f_2 \right) = R T x_1 x_2 \sum_r \alpha_r (x_1 - x_2)^r$$

where the coefficients $\alpha_r$ are called interaction parameters. Activity coefficients can be obtained by the partial differentiation of over the mole fraction $x_1$ or $x_2$:

$$\ln f_1 = x_2^2 (\alpha_0 + \alpha_1 (3x_1 - x_2) + \alpha_2 (x_1 - x_2)(5x_1 - x_2) + ...)$$

$$\ln f_2 = x_1^2 (\alpha_0 - \alpha_1 (3x_2 - x_1) + \alpha_2 (x_2 - x_1)(5x_2 - x_1) + ...)$$
Generalization

• The subregular model is equivalent to the asymmetric Margules model in the Thompson-Waldbaum notation

\[ G^E = RT(x_1 \ln f_1 + x_2 \ln f_2) = x_1 x_2 (W_{12} x_2 + W_{21} x_1) \]

where the parameters are related to those used in the Redlich-Kister model as

\[ W_{12} = RT(\alpha_0 - \alpha_1); W_{21} = RT(\alpha_0 + \alpha_1) \]

and, in general, depend on temperature and pressure. In the Thompson-Waldbaum model, the activity coefficients of end-members are expressed as

\[ RT \ln f_2 = (2W_{12} - W_{21})x_1^2 + 2(W_{21} - W_{12})x_1^3 \]

\[ RT \ln f_1 = (2W_{21} - W_{12})x_2^2 + 2(W_{12} - W_{21})x_2^3 \]
Some more details on configurational entropy, grounded in statistical mechanics.
Application 2: Statistical Entropy, Third Law of Thermodynamics, and Zero Point Entropy

\[ S = k \ln W \]

as \( T \to 0 \), if ground state not degenerate

\( W \to 1 \) (\( q \to 1 \))

\( S \to 0 \)

If ground state is degenerate, \( n \) states of same energy

\( S \to k \ln n \) per molecule, \( R \ln n \) per mole

Example: CO, \( S^0 = R \ln 2 \)

\[ \text{has same energy in crystal as} \]

In general, calculate as a configurational entropy of mixing:

\[ S = -R \sum x_i \ln x_i \] mole fraction of different species or configurations
A) NaAlSi$_3$O$_8$ - KAlSi$_3$O$_8$ Feldspar

assume no Al, Si disorder

Na, K mix at random

for Na$_x$K$_{1-x}$AlSi$_3$O$_8$ have one mol of sites for Na,K missing

Total number of sites is N (Avogadro's Number)

number of Na atoms is xN

number of K atoms is yN = (1-x)N

W = number of ways of arranging atoms over N sites, where occupancy (whether K or Na) is distinguishable but can not tell which atom (of all the Na or of all the K) is on which site

Number of ways of arranging atoms is

W= N! / (xN)! (yN)!

k ln W = k [ ln N! - ln( xN! ) - ln( yN! ) ]

for large N, ln N! = N ln N - N

k ln W = k [ N ln N - N - Nx ln(Nx) + Nx - Ny ln(Ny) + Ny ]

= k [ N ln N - N - Nx ln N - Nx ln x + Nx - N(1-x) ln N - N(1-x) ln(1-x) + N (1-y) ]

= k ln W = k [ N ln N - N(x+(1-x)) ln N - N + N (x+(1-x)) - Nx ln N - N(1-x) ln(1-x)]

= -Nk [ x ln x + (1-x) ln (1-x) ]

$S_{conf} = -R [ x ln x + (1-x) ln (1-x) ]$
B) $\text{Mg}_2\text{SiO}_4 - \text{Fe}_2\text{SiO}_4$ olivines
two sites over which Mg and Fe can mix

$W = (2N)! / (2Nx)! (2Ny)!$

then

$S_{\text{conf}} = -2R \left[ x \ln x + (1-x) \ln (1-x) \right]$
suppose had written formula as

$\text{Mg}_x\text{Fe}_{1-x}\text{Si}_{0.5}\text{O}_2$

Then $S_{\text{conf}} = -R \left[ x \ln x + (1-x) \ln (1-x) \right]$

So configurational entropy is an extensive parameter


C) $x \text{CaAl}_2\text{Si}_2\text{O}_8 - (1-x) \text{NaAlSi}_3\text{O}_8$ totally disordered feldspar or melts

assume no Al-avoidance. This is so-called "two lattice" model

On tetrahedral sites Al and Si mix on a total of 4 sites

On large sites, Ca and Na mix on total of one site
\[ S_{\text{conf}} = S_{\text{conf}}(\text{Na, Ca}) + S_{\text{conf}}(\text{Si, Al}) \]

\[ S_{\text{conf}}(\text{Na, Ca}) = -R \left[ x \ln x + (1-x) \ln(1-x) \right] \]

\[ S_{\text{conf}}(\text{Si, Al}) = -4R \left[ X_{\text{Si}} \ln X_{\text{Si}} + X_{\text{Al}} \ln X_{\text{Al}} \right] \]

\[ X_{\text{Si}} = \frac{(2x + 3(1-x))}{4} = \frac{(3-x)}{4} \]

\[ X_{\text{Al}} = \frac{(2x + 1(1-x))}{4} = \frac{(1+x)}{4} \]

\[ S_{\text{conf}}(\text{Si, Al}) = -R \left[ (3-x) \ln((3-x)/4) + (1+x) \ln((1+x)/4) \right] \]

= \(-R\left[ (3-x) \ln(3-x) + (1+x) \ln(1+x) - (3-x) \ln 4 - (1+x) \ln 4 \right]\)

= \(-R\left[ (3-x) \ln(3-x) + (1+x) \ln(1+x) - 4 \ln 4 \right]\)

\[ \boxed{S_{\text{conf}} = -R \left[ x \ln x + (1-x) \ln(1-x) + (3-x) \ln(3-x) + (1+x) \ln(1+x) - 4 \ln 4 \right]} \]

Entropy of mixing:

\[ \Delta S_{\text{mix}} = S_{\text{conf, solution}} - (1-x) S_{\text{conf, Ab}} - x S_{\text{conf, An}} \]

\[ S_{\text{conf, Ab}} = -4R \left[ \frac{1}{4} \ln 1/4 + \frac{3}{4} \ln 3/4 \right] \]

= \(-R \left[ -\ln 4 + 3 \ln 3 - 3 \ln 4 \right]\)

= \(R \left[ 4 \ln 4 - 3 \ln 3 \right]\)

\[ S_{\text{conf, An}} = -4R \left[ \frac{1}{2} \ln 1/2 + \frac{1}{2} \ln 1/2 \right] = 4R \ln 2 \]
\[ \Delta S_{\text{mix}} = -R \left[ x \ln x + (1-x) \ln(1-x) + (3-x) \ln(3-x) + (1+x) \ln(1+x) - 8 \ln 2 + (1-x)( 8 \ln 2 - 3 \ln 3) + x 4 \ln 2 \right] \]

\[ = -R \left[ x \ln x + (1-x) \ln(1-x) + (3-x) \ln(3-x) + (1+x) \ln(1+x) - 8 \ln 2 + 8 \ln 2 - 8x \ln 2 - 3 \ln 3 + 3x \ln 3 + 4x \ln 2 \right] \]

\[ \Delta S_{\text{mix}} = -R \left[ x \ln x + (1-x) \ln(1-x) + (3-x) \ln(3-x) + (1+x) \ln(1+x) - 4x \ln 2 - 3 \ln 3 + 3x \ln 3 \right] \]

The entropy of mixing should be zero for the end-members. Check:

x=0, \[ \Delta S_{\text{mix}} = -R \left[ 0 + 0 + 3 \ln 3 + 0 - 0 - 3 \ln 3 + 0 \right] = 0 \]

x=1, \[ \Delta S_{\text{mix}} = -R \left[ 0 + 0 + 2 \ln 2 + 2 \ln 2 - 4 \ln 2 - 3 \ln 3 + 3 \ln 3 \right] = 0 \]
Fig. 11.10 Activities in the system iron-nickel at 1600 °C (From G. R. Hiday, S. I. Payne, J. P. Morris, and F. I. Kapp. The Activities of Iron and Nickel in Liquid Fe-M Alloys. Trans. AIME, 215, 181 (1959).

Fig. 11.11 Activity coefficients in the system iron-nickel at 1600 °C.
Order- Disorder Phenomena

If ordering slow, several series of solid solutions, each having a differing degree of order, can exist.

Thermodynamics of mixing one set of species (e.g. Na, K or Na, Ca in feldspars) may depend on the degree of order of another (Al, Si).

Extent of ordering depends on temperature in a complex fashion. Risky extrapolation.

Enthalpy and entropy of mixing depend strongly on $T$.

$\Delta S$ and $\Delta G$ of mixing can be asymmetric because the configurational entropy term itself departs from symmetrical behavior. A solvus may develop.
Observed degree of order is often kinetically controlled. Low $T$, can not order. High $T$, can not quench

Metastable disordered solid solutions may form.

Strong tendency to ordering is manifested in significant negative heats of mixing and sometimes leads to compound formation, (e.g. dolomite. $\Delta H$, $\Delta S$ and $\Delta G$ of mixing depend strongly on the degree of order.)
Destabilizing energetics of mixing in the disordered state may be present at the same time as stabilizing effect of ordering, leading to complex interplay between ordering and exsolution (conditional spinodal).

**Change in symmetry:** First or higher order phase transitions lead to unconventional phase diagram topologies. Lattice parameters can vary nonlinearly with composition (depart from Vegard’s rule)
ORDER PARAMETERS, PHASE TRANSITIONS, AND LANDAU THEORY

Many transitions occur such that the high temperature phase is related to the low temperature phase by a disordering of one or more physical parameters. The low temperature phase has a lower symmetry because of ordering; this goes to higher symmetry in a first, second, or mixed-order phase transition. In general, one can define a long range order parameter $s$, to have a value of 1 for the fully ordered state and a value of zero for the random state. Some examples follow

<table>
<thead>
<tr>
<th>Phenomenon</th>
<th>Physical entities</th>
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<tbody>
<tr>
<td>Magnetic transition</td>
<td>electron spins</td>
</tr>
<tr>
<td>Distortional transition</td>
<td>tilt angle of octahedra, difference in lattice parameters (deviation from cubic) piezoelectric coefficient, non linear optical coefficient</td>
</tr>
<tr>
<td>Positional disorder</td>
<td>site occupancy- cations in spinel, Si -Al in feldspar, metals in alloy</td>
</tr>
<tr>
<td>Orientational disorder</td>
<td>alignment of species (carbonate groups, organic molecules)</td>
</tr>
</tbody>
</table>

If $p$ is the physical parameter, and $s$ the order parameter

$$s = \frac{p \text{ (observed)} - p \text{ (completely disordered)}}{p \text{ (completely ordered)} - p \text{ (completely disordered)}}$$
Structural Aspects of Solid Solutions in Relation to their Stability and Miscibility

- Fluorite-based structures
- Spinels
- Carbonates
Order- Disorder Phenomena

Extent of ordering depends on T. Observed degree of order is often kinetically controlled. Low T, can not order. High T, can not quench. Metastable disordered solid solutions may form.

Strong tendency to ordering is manifested in significant negative heats of mixing and sometimes leads to compound formation, (e.g. dolomite. $\Delta H$, $\Delta S$ and $\Delta G$ of mixing depend strongly on the degree of order. They can be asymmetric because the configurational entropy term itself departs from symmetrical behavior. A solvus may develop.

Order-disorder reactions often involve a change in the symmetry of the structure. First-order or higher order phase transitions leading to unconventional phase diagram topologies. Lattice parameters can vary nonlinearly with composition (depart from Vegard’s rule)
Fluorite Structure
Fluorite Derivatives

- Parent cubic structure: CeO$_2$, UO$_2$, PuO$_2$, high T ZrO$_2$ and HfO$_2$
- Tetragonal and monoclinic distortions: ZrO$_2$ and HfO$_2$
- Oxygen excess phases UO$_{2+x}$, PuO$_{2+x}$ (?)
- Oxygen vacancy phases, M$^{3+}$ and M$^{2+}$ doping, e.g. YSZ, Y$_x$Zr$_{1-x}$O$_{2-0.5x}$
- Pyrochlore
Crystal structure of defect-fluorite \((Fm3m)\)
Cubic stabilized $\text{MO}_2$

- $M^{4+} = Ln^{3+} + 0.5$ oxygen vacancy
- High oxide ion conductivity which goes through a maximum with increasing doping
- Structural evidence for short range order in cubic solid solutions
- Low T long range ordered phases sluggish to form
Local ordering of vacancies in C-type rare earth structure (bixbyite) $Y_2O_3$
Enthalpy of formation from m-ZrO$_2$ and C-YO$_{1.5}$ of c-Y$_x$Zr$_{1-x}$O$_{2-0.5x}$ (YSZ)
X-ray diffraction patterns of (a) Disordered \( \text{Zr}_{0.43} \text{Y}_{0.57} \text{O}_{1.96} \) c-YSZ phase
(b) Ordered \( \text{Y}_4 \text{Zr}_3 \text{O}_{12} \) \( \delta \)-phase,
\( \Delta H \) (ordered – disordered) is \( 0.4 \pm 1.4 \) kJ/mol =
0 short range order rules!!!
Interaction Parameter for Mixing in Fluorite Phase

![Graph showing interaction parameter vs ionic potential](image)
Generalizations

• Strong ionic size control on properties
• Negative heats of mixing related to siting of vacancies
• Prediction $\text{UO}_2\cdot\text{LnO}_{1.5}$ should have little stabilization unless U is oxidized
Enthalpies of formation from oxides (UO$_2$, UO$_3$ and CaO or YO$_{1.5}$) of samples with as-synthesized oxygen contents. (b) Enthalpies of formation of modeled fully reduced (all uranium tetravalent) UO$_2$-CaO and UO$_2$-YO$_{1.5}$ solid solutions relative to UO$_2$ and CaO or YO$_{1.5}$. The correction for the effect of oxidation was made assuming that oxidation of U$^{4+}$ to U$^{6+}$ in the solid solution matrix has the same enthalpy as oxidation of UO$_2$ to UO$_3$. 

![Diagram](image-url)
Conclusions: Fluorite

- Short range order dominates the thermodynamics
- Strongly negative heats of mixing are compensated by much less than random entropies of mixing
- The m-c transition has a much higher enthalpy for HfO$_2$ than ZrO$_2$
- The ceria system is different because of different short range order
- Ionic size determines the ordering and energetics
Spinel Structure
What is unique about spinel?

- Tetrahedral and octahedral sites accept cations of roughly equal size
- Order-disorder prevalent
- Variable valence, transition metals, magnetic and electronic properties
- High pressure silicate spinels in the mantle
SPINELS

• \( AB_2O_4 \), two octahedral and one tetrahedral site per formula unit
• Normal \( A[B_2]O_4 \), inverse \( B[AB]O_4 \), random \( A_{1/3}B_{2/3}[A_{2/3}B_{4/3}]O_4 \)
• Cation distribution varies with \( T \)
• Effect on enthalpy and entropy of mixing and thermodynamic properties
SPINEL DISORDERING

O'NEILL AND NAVROTSKY MODEL

\[ \Delta G_D = \alpha x^2 + \beta x^2 - T \Delta S_{\text{non}} + RT[x \ln x + (1-x) \ln (1-x) + x \ln (x/2) + (2-x) \ln (1-x/2)] \]  

(59)

At equilibrium, \((d\Delta G_D/dx) = 0\), and (neglecting the nonconfigurational entropy)

\[ -RT \ln \left( \frac{x^2}{(1-x)(2-x)} \right) = \alpha + 2\beta x \]  

(60)

\(\alpha\) and \(\beta\) roughly equal in magnitude, opposite in sign

If \(\beta\) is a function of charge type only, \(\alpha\) retains the meaning of an interchange energy or difference of site preference energies.
Spinel structure

Three Parameters

Lattice parameter, a
Oxygen parameter, u
Cation distribution parameter, x

\[
\begin{align*}
  x &= 0 & \text{A[B}_2\text{]X}_4 & \text{normal} \\
  x &= 1 & \text{B[AB]X}_4 & \text{inverse} \\
  x &= x & \text{A}_{x\text{,B}}\text{[A}_x\text{B}_{2-x}]\text{X}_4 & \text{intermediate} \\
  x &= 0.667 & \text{A}_{1/3}\text{B}_{2/3}\text{[A}_{1/3}\text{B}_{2/3}]_2\text{X}_4 & \text{random}
\end{align*}
\]

Relations among distances

\[
\begin{align*}
  r_{AX} &= \sqrt{3} \ a(u -0.25) \\
  &= 0.217a \text{ for } u = 0.375 \\
  r_{BX} &= a(0.625 - u ) \\
  &= 0.25a \text{ for } u = 0.375 \\
  r_{AA} &= \frac{\sqrt{3}}{4} \ a = 0.433a \\
  r_{BB} &= \frac{\sqrt{2}}{4} \ a = 0.354a
\end{align*}
\]
### Some representative spinels $\text{AB}_2\text{X}_4$

<table>
<thead>
<tr>
<th>Formula</th>
<th>Lattice parameter (Å)</th>
<th>Cation Distribution, $x =$ fraction of tetrahedral sites occupied by B ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{MgAl}_2\text{O}_4$</td>
<td>8.086</td>
<td>0 to $\sim$ 0.3</td>
</tr>
<tr>
<td>$\text{MnAl}_2\text{O}_4$</td>
<td>8.241</td>
<td>0.3</td>
</tr>
<tr>
<td>$\text{FeAl}_2\text{O}_4$</td>
<td>8.10</td>
<td>0 to 0.1</td>
</tr>
<tr>
<td>$\text{CoAl}_2\text{O}_4$</td>
<td>8.105</td>
<td>0 to 0.1</td>
</tr>
<tr>
<td>$\text{NiAl}_2\text{O}_4$</td>
<td>8.046</td>
<td>0.7 to 0.9</td>
</tr>
<tr>
<td>$\text{CuAl}_2\text{O}_4$</td>
<td>8.086</td>
<td>0.4</td>
</tr>
<tr>
<td>$\text{ZnAl}_2\text{O}_4$</td>
<td>8.086</td>
<td>0 to 0.05</td>
</tr>
<tr>
<td>$\text{MgFe}_2\text{O}_4$</td>
<td>8.360</td>
<td>0.7 to 0.9</td>
</tr>
<tr>
<td>$\text{MgCr}_2\text{O}_4$</td>
<td>8.333</td>
<td>0</td>
</tr>
<tr>
<td>$\text{MgGa}_2\text{O}_4$</td>
<td>8.282</td>
<td>0.7 to 0.9</td>
</tr>
<tr>
<td>$\text{MgV}_2\text{O}_4$</td>
<td>8.413</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Fe}_3\text{O}_4$</td>
<td>8.394</td>
<td>0.67 to 1.0</td>
</tr>
<tr>
<td>$\text{FeCr}_2\text{O}_4$</td>
<td>8.377</td>
<td>0</td>
</tr>
<tr>
<td>$\text{FeCrS}_4$</td>
<td>9.998</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Mg}_2\text{SiO}_4$</td>
<td>8.082</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{SiO}_4$</td>
<td>8.234</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Co}_2\text{SiO}_4$</td>
<td>8.140</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Ni}_2\text{SiO}_4$</td>
<td>8.044</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Mg}_2\text{GeO}_4$</td>
<td>8.255</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Mg}_2\text{TiO}_4$</td>
<td>8.440</td>
<td>1</td>
</tr>
<tr>
<td>$\text{Mg}_2\text{SnO}_4$</td>
<td>8.601</td>
<td>1</td>
</tr>
<tr>
<td>$\gamma\text{-Al}_2\text{O}_3$</td>
<td>7.905</td>
<td>Octahedral vacancies</td>
</tr>
<tr>
<td>$\text{Li}_2\text{NiF}_4$</td>
<td>8.310</td>
<td>1</td>
</tr>
</tbody>
</table>
Configurational entropy depends on number of sites and site occupancies

Example: FeAl$_2$O$_4$-FeCr$_2$O$_4$ :

One mole of ions mixed

\[ a(\text{Fe}_{0.5}\text{Al}_2\text{O}_2) = x_A, \text{ where } A = \text{Fe}_{0.5}\text{Al}_2\text{O}_2. \text{ and } a(\text{Fe}_{0.5}\text{Cr}_2\text{O}_2) = x_B, \text{ where } B = \text{Fe}_{0.5}\text{CrO}_2 \]

Two moles of ions mixed, entropy an extensive parameter

\[ \Delta S_{\text{mix}} = -2R[x_A \ln x_A + x_B \ln x_B] \]

\[ \Delta \mu(\text{FeCr}_2\text{O}_4) = -2RT \ln x_A, \Delta \mu(\text{FeAl}_2\text{O}_4) = -2RT \ln x_B \]

\[ a(\text{FeCr}_2\text{O}_4) = x_A^2, a(\text{FeAl}_2\text{O}_4) = x_B^2 \]
Octahedral Site Preference Energies

Experimental thermodynamic basis of site preference energies and enthalpies of formation of spinels. Crystal field effects are but a small contribution.
Figure 7.13. Thermodynamics of cation distribution in Fe$_3$O$_4$-FeCr$_2$O$_4$ (from O'Neill and Navrotsky 1984). (a) Lattice parameters: (1) experimental data, (2) calculated using O'Neill and Navrotsky model for 298 K, (3) calculated for 1000 K. (b) Calculated solvus.
Calorimetric studies of heats of formation of iron manganese spinels confirm the ideas of oxidation-reduction energetics presented in 1968 and quantify effects of tetragonal distortions.
Calcite and Dolomite Structure
Calcite

\[ \text{CaCO}_3 \]

Dolomite

\[ \text{CaMg(CO}_2\text{)}_3 \]
Note - schematic and not according to phase rule

CaCO₃ (calcite)

Ca₀.₅Mg₀.₅CO₃ (dolomite)

Ca(Fe, Mg)(CO₃)₂ (ankerite)

MgCO₃ (magnesite)

(Fe, Mg)(CO₃) Solid solution

FeCO₃ (siderite)
Ca_{1+x}Mg_{1-x}CO_3 Dolomite

Fig. 2. Enthalpies of formation of Ca-rich dolomite. The solid line is the best fit of the data.
Energetics in CaMg(CO$_3$)$_2$-CaFe(CO$_3$)$_2$

Figure 4. Enthalpy of formation from the binary carbonates of phases projected along the MgCa(CO$_3$)$_2$-FeCa(CO$_3$)$_2$ join, as discussed in text. Solid circles represent ordered dolomite and largely ordered natural samples. Squares represent the largely disordered synthetic MgCa(CO$_3$)$_2$, described in this work and the synthetic samples showing no superstructure reflections measured by Chai and Navrotsky (1996). Triangles represent partly ordered samples, the quenched heat-treated Eugui dolomite of Navrotsky and Capobianco (1987) and the synthetic samples with weak superstructure reflections measured by Chai and Navrotsky (1996). The lines, though least-squares fits, are presented as aids to the eye in emphasizing the three distinct trends. The exact degree of order of each sample differs and this may account for the scatter about these trends.
Energetics of Dolomite Disordering

• A second order transition, gradual disordering
• Described by Bragg-Williams, pair or tetrahedral approximation cluster variation methods, but hard to quantify
• Complicated by decomposition so CdCO$_3$-MgCO$_3$ studied as an analogue system with lower disordering T
Conclusions - Carbonates

- Several series of solid solutions ranging from ordered dolomite type to disordered calcite type, each having its own enthalpy trend and complex entropy of mixing.
- Disordering process needs complex models for proper description.
CONCLUSIONS

• Must consider structural details to formulate thermodynamics properly

• Many unanswered questions, lots of work for you, the students and future generation of investigators.

• Lots of fun !!