Critical Evaluation and Thermodynamic Optimization of Calcium–Magnesium–Manganese–Oxygen System

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#### Abstract

The prediction of thermodynamic properties and phase equilibria of an oxide system can plays an important role in the development and understanding of metallurgical, ceramic and geological processes. The thermodynamic databases, developed by a critical evaluation and optimization of all existing thermodynamic properties and phase diagram, can help in understanding the reaction mechanism in various industrial processes more clearly and in developing new technology for various industries.

As part of a large thermodynamic database development for steelmaking applications, all solid and liquid phases of Ca-Mg-Mn-O system were critically evaluated and optimized in the present study. The optimization of all systems in this study is self-consistent with thermodynamic principles. All the binary and ternary system have been critically evaluated and optimized based upon available phase-equilibrium and thermodynamic data. All thermodynamic models for each solutions used in this study were developed on the basis of their structure. In this way, the configurational entropy of solution can be taken into account properly in the Gibbs energy of solution. The molten oxide was modeled by the Modified Quasichemical Model, which takes into account short-range ordering of second-nearest-neighbor cations in the ionic melt. Extensive solid solutions such as spinel were modeled within the framework of the Compound Energy Formalism with consideration of their complex sublattice crystal structures. Other solid solutions such as monoxide were modeled using random mixing of ions on cation sites using a polynomial expansion of the excess Gibbs energy. All the thermodynamic calculations in the present study were carried out using FactSage<sup>TM</sup> thermodynamic software.

## RÉSUMÉ

La prédiction des propriétés thermodynamiques et des équilibres de phases d'un système d'oxydes peut jouer un rôle important dans le développement et la compréhension de processus metallurgiques, céramiques et géologiques. Les bases de données thermodynamiques, mises au point par une évaluation critique et l'optimisation de toutes les propriétés thermodynamiques et diagrammes de phase existants, peut aider à comprendre plus clairement les mécanismes de réaction impliqués dans plusieurs procédés industriels et aider à développer de nouvelles technologies pour diverses industries.

Dans le cadre du développement d'une grande base de données thermodynamiques pour des applications sidérurgiques, toutes les phases solides et liquides du système Ca-Mg-Mn-O ont été évaluées de façon critique et optimisées dans la présente étude. L'optimisation de tous les systèmes est en accord avec les principes thermodynamiques. Tous les systèmes binaires et ternaires ont été évalués de façon critique et optimisés en utilisant toutes les données thermodynamiques et d'équilibre de phase disponibles. Tous les modèles thermodynamiques employés pour chacune des solutions utilisées dans cette étude ont été élaborées sur la base de leur structure. De cette façon, l'entropie de configuration de la solution peut être correctement prise en compte dans l'énergie de Gibbs. La phase liquide fut modélisée avec le Modèle Quasichimique Modifié qui tient en compte dans le liquide de la mise en ordre locale des cations qui sont les deuxièmes voisins les plus proches. Des solutions solides, telles que le spinelle, ont été modélisés avec le Formalisme de l'Énergie des Composés en tenant compte de la structure cristalline complexe de leur sous-réseau. D'autres solutions solides telles que le monoxyde ont été modélisés en utilisant un mélange aléatoire des ions sur les sites cationiques et un polynôme pour l'énergie de Gibbs. Tous les calculs thermodynamiques de la présente étude ont été réalisés en utilisant le logiciel thermodynamique FactSage<sup>TM</sup>.

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# List of Symbols

C <sub>p</sub>	Molar Heat Capacity (J/mol.K)
$G^{o}{}_{i}$	Standard Gibbs energy of i
$G^m$	Gibbs energy of solution
$G^E$	Exess Gibbs energy in solution
$g^{\scriptscriptstyle E}$	Molar excess Gibbs energy in Solution
$g^{o}{}_{i}$	Molar Gibbs energy of i
$\Delta g_{ij}$	Gibbs energy change for the formation of two moles of i-j pairs
$H^{o}{}_{i}$	Standard enthalpy of i
$\Delta H$	Molar enthalpy of mixing
$\Delta H_T$	Enthalpy of formation of the compound from the elements
n <sub>ij</sub>	Number of moles of i-j bonds in one mole of the solution
$q^{ij}_{AB}$	Excess interaction parameter between A and B
$S^{o}{}_{i}$	Standard entropy of component i
$\Delta S_T$	Entropy of formation of the compound from the elements
$\Delta S^{conf}$	Molar configurational entropy of solution
S <sup>non-conf</sup>	Molar non-configurational entropy of solution
n <sub>i</sub>	Number of moles of component i
Т	Absolute temperature (K)
wt.%	Weight percent
<i>Y</i> <sub>i</sub>	Site fraction of component i
$Y_i$	Coordination-equivalent fractions
Xi	Mole fraction of component i in solution
X <sub>ij</sub>	Pair fraction of i-j pairs
$Z_i$	Coordination number of i
$Z^{i}{}_{ii}$	The value of $Z_i$ when all the nearest neighbors of an <i>i</i> are <i>i</i> 's
$Z^{i}{}_{ij}$	The value of $Z_i$ when all the nearest neighbors of an <i>i</i> are <i>j</i> 's

#### **1. Introduction**

#### 1.1. Motivation of research

The Ca-Mg-Mn-O system is important in the ceramics and metallurgical industries, particularly for its role in many refractories. Despite its importance, the phase equilibria in this system have not been well studied. Experimental study of the system is complicated by the strong dependence of the equilibria on the oxygen pressure and by the high melting temperature of the spinel phase. Therefore, critical assessment of the data is required in order to understand and model this system more accurately.

#### **1.2 Research objective**

The main goal of the present study is to perform a critical assessment and optimization of the thermodynamic properties and phase equilibria of MgO-MnO-Mn<sub>2</sub>O<sub>3</sub> (Mg-Mn-O) system and CaO-MnO-Mn<sub>2</sub>O<sub>3</sub> (Ca-Mn-O) system. In the thermodynamic 'optimization' of a chemical system, all available thermodynamic and phase equilibrium data are evaluated simultaneously in order to obtain one set of model equation for the Gibbs energies of all phases as functions of temperature and composition. From these equations, all of the thermodynamic properties and phase diagram can be back calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagram and phase diagram measurements can be used to deduce thermodynamic properties. Discrepancies in the available data can be often being resolved, and interpolations and extrapolations can be made in a thermodynamically correct manner.

The following are the objective of my thesis:

#### 1.2.1. Thermodynamic Optimization of Mg-Mn-O phase diagram

In the present study, the thermodynamic properties of the Mg-Mn-O system were optimized on the basis of the previously optimized Mn-O and MgO-MnO system. The present optimization covers the range from reduce oxygen pressure to air pressure and temperature from 25°C to liquidus.

#### 1.2.2. Thermodynamic Optimization of Ca-Mn-O phase diagram

The thermodynamic properties of the Ca-Mn-O system were also optimized on the basis of the previously optimized Mn-O and CaO-MnO system. The present optimization covers the range of oxygen partial pressures from equilibrations with pure oxygen to air pressure and temperature from 25°C to liquidus.

#### 2. Thermodynamic modeling

### 2.1. CALPHAD

CALPHAD is a acronym for CALculations of PHAse Diagrams. It is better described as: "The Computer Coupling of Phase Diagrams and Thermochemistry."

Kattner in 1997 described phase diagram as "visual representation of the state of a material as a function of temperature, pressure and concentration of the constituent components." It is a basic tool which helps us in understanding phase equilibria for higher order systems. Pelton and Schmalzried(Pelton and Schmalzried, 1973) defined a phase diagram as "the geometric representation of the loci of the thermodynamic parameters when equilibrium among phases under a specified set of conditions is established." However, not much experimental work has been done for predicting the phase diagram for multicomponent system. So, in order understand the phase equilibria and thermodynamic properties of the multicomponent systems, construction of multicomponent thermodynamic database started in late 1960's.

In this technique, all types of thermodynamic data such as phase diagrams, phase equilibria and activity *etc.* are critically evaluated and optimized simultaneously, using proper thermodynamic models, in order to construct a database for multicomponent system.

At present, there are numerous research groups which are using CALPHAD technique for preparation of multicomponent database. Some of the well-established groups are Thermo-Calc group (Thermo-Calc, 2002) at KTH in Sweden, the THERMODATA group (THERMODATA, 2002) in France, Thermotech Inc. (Thermotech, 2002) in the UK, and the thermochemical group at NIST (NIST, 2002) in the USA, the FACT group (FactSage, 2002) at Ecole Polytechnique in Canada, the MTDATA group (MTDATA, 2002) at NPL in the UK and the IRSID GROUP in France. Moreover, Scientific Group Thermodata Europe (SGTE, 2002) is a consortium of research groups formed to accelerate the development of alloy database. The thermochemical

software's and multicomponent database developed by these groups are of immense help in understanding and interpreting the phase equilibria in high order systems which can be applied in academics and industries.

#### 2.2. Thermodynamic models

Thermodynamic models are essential to appropriately represent the thermodynamic properties of any materials. For proper representation of the thermochemical properties of a complex solution, we require a sophisticated and refined model. For this, all the models which are used are based on the structure of the solution to adequately represent the configurational entropy of the solution. Also these models have high predictive capability in higher-order systems. A good model should be able to represent the thermodynamic properties with just a small numbers of adjustable parameters. Hence, models have been developed which can describe the configurational entropy of the solutions without the addition of large arbitrary model parameters. *Basic Equations* 

#### Pure compounds

The standard Gibbs energy of a pure substance 'i' is written as:

$$G_i^o = H_i^o - TS_i^o$$

$$(2.1)$$

where  $G_i^o$ ,  $H_i^o$  and  $S_i^o$  are respectively the standard Gibbs energy, enthalpy and entropy of substance i, and T is the absolute temperature.

#### For solutions

#### **Bragg-Williams random mixing solution:**

When two components A and B are mixed then the Gibbs energy of the solution depends upon the interaction between the A and B atoms or molecules. The Gibbs energy of a solution in which there is no interaction between A and B is an ideal solution for which:

$$g^{m} = g_{A}^{o} n_{A} + g_{B}^{o} n_{B} - T\Delta S^{cont}$$

$$(2.2)$$

where  $G^m$  is the molar Gibbs energy of the solution,  $g_i^o$  is the molar Gibbs energy of component i, and  $\Delta S^{conf}$  is configurational entropy obtained by randomly mixing  $n_A$  moles of A and  $n_B$  moles of B on the same sublattice. It can be written as:

$$\Delta S^{\text{conf}} = -RT \left( n_A \ln X_A + n_B \ln X_B \right)$$
(2.3)

However all solutions do have interactions among the atoms mixing to form a solution. Such interactions can be called  $g^E$ , the molar excess Gibbs energy of the solution. In that case the energy of the solution is given by:

$$g^{m} = g_{A}^{o} n_{A} + g_{B}^{o} n_{B} - T\Delta S^{conf} + g^{E}$$

$$(2.4)$$

 $g^E$  can expanded as a polynomial in the mole fractions as:

$$g^{E} = \sum q^{ij}{}_{AB} X^{i}{}_{A} X^{j}{}_{B}$$

$$(2.5)$$

where  $X_{A}^{i}$  and  $X_{B}^{j}$  are the more fractions of 'i' and 'j' and the excess interaction parameters  $q_{AB}^{ij}(=a + bT + cT^{2} + ...)$  are the model parameters. If only  $q_{AB}^{11}(=a + bT + cT^{2} + ...)$  are the model parameters. If only  $q_{AB}^{11}(=a + bT + cT^{2} + ...)$  are the model parameters. If only  $q_{AB}^{11}(=a + bT + cT^{2} + ...)$  are the model parameters. If only  $q_{AB}^{11}(=a + bT + cT^{2} + ...)$  are the model parameters. If only  $q_{AB}^{11}(=a + bT + cT^{2} + ...)$  are the model parameters. If only  $q_{AB}^{11}(=a + bT + cT^{2} + ...)$  are the model parameters. If only  $q_{AB}^{11}(=a + bT + cT^{2} + ...)$  are the model parameters. If only  $q_{AB}^{11}(=a + bT + cT^{2} + ...)$  are the model parameters. If only  $q_{AB}^{11}(=a + bT + cT^{2} + ...)$  are the model parameters. If only  $q_{AB}^{11}(=a + bT + cT^{2} + ...)$  are the model parameters. If only  $q_{AB}^{11}(=a + bT + cT^{2} + ...)$  are the model parameters. If only  $q_{AB}^{11}(=a + bT + cT^{2} + ...)$  are the model parameters. If only  $q_{AB}^{11}(=a + bT + cT^{2} + ...)$  are the model parameters.

#### Development of a model

In many cases, the thermodynamic properties of a binary solution can be described using the above expression. Problem arises, when such an expression is used to predict the thermodynamic properties of higher order system from the model parameters of the low-order sub-systems. Sometimes a large number of temperature- and composition-dependent excess model parameters are needed in order to represent all the thermodynamic properties of a binary system as well as higher order system. This results in non-configurational entropy terms of the model to be large and decreases predictive ability of the model for higher order system.

Therefore, during development of a model, one of the most important factors is how well the configurational entropy of the solution is described without the addition of large arbitrary model parameters. That is, during modeling the real structure of the solution must be taken into account in the model. In the present study, solution phases such as liquid slag, spinel and monoxide are described using different thermodynamic models which are based on real solution structures.

#### 2.2.1. Liquid solutions (slag)

The liquid phase is technologically one of the most important phases appearing in every system. The adequate representation of its Gibbs energy plays an important role in database preparation for multicomponent alloys. Therefore, to adequately represent the thermodynamic properties of the liquid phase, Pelton and Blander [1] and more recently by Pelton *et al.* [2] developed the Modified Quasichemical Model (MQM). In this, they modified the classical quasichemical model by expressing the energy of pair formation as a polynomial in the pair formation rather than the component functions.

#### 2.2.1.1. Structure

One of the very examples of a liquid solution is a sodium silicate glass [3]. In this, the silicon atoms are surrounded by 4 oxygen atoms which hare arranged in the form of tetrahedron. The Si and O atoms form SiO<sub>4</sub> tetrahedra which are joined together in chains or rings by bridging atoms (BO). Cations such as Na<sup>+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Ca<sup>2+</sup>, etc. tend to break these BO and form non-bridging oxygen's, O<sup>-</sup>, or free oxygen ions, O<sup>2-</sup>. These silicate melt contains various 3 dimensional interconnected anion units such as SiO<sub>2</sub>, Si<sub>2</sub>O<sub>5</sub><sup>2-</sup>, Si<sub>2</sub>O<sub>6</sub><sup>4-</sup>, Si<sub>2</sub>O<sub>7</sub><sup>2-</sup> and SiO<sub>4</sub><sup>2-</sup>. The degree of depolymerisation of a silicate melt is often expressed by the ratio (NBO/T), where T is the number of tetrahedrally coordinated atoms such as Si. This ratio (NBO/T) affects the physical properties of the silicate melts such as thermal conductivity, viscosity etc. Figure 2.1 shows the schematic structure of silicate melts.



Figure 2.1: Schematic representation of the structure of sodium silicate glass by Warren and Biscoe [3]

#### 2.2.1.2. Modified Quasichemical Model

The modified quasichemical model [1-2], which takes into account short-range ordering of second-nearest-neighbor cations in the ionic melt, is used for modeling the slag (molten oxide). For example, for the MgO-MnO-MnO<sub>1.5</sub> slag these reactions are:

$$(A - A) + (B - B) = 2(A - B); \qquad \Delta g_{AB}$$
 (2.6)

Where (i - j) represents a first nearest-neighbour pair.  $\Delta g_{AB} = (\omega - \eta T)$  is the nonconfigurational Gibbs energy change for the formation of two moles of (A-B) pairs.

Let  $n_A$  and  $n_B$  be the number of moles of A and B,  $n_{ij}$  be the number of moles of (i - j) pairs, and  $Z_A$  and  $Z_B$  be the coordination numbers of A and B. The pair fractions, mole fractions, and "coordination-equivalent" fractions are defined respectively as:

$$X_{AB} = \frac{n_{AB}}{(n_{AA} + n_{BB} + n_{AB})}$$
(2.7)

$$X_{A} = \frac{n_{A}}{(n_{A} + n_{B})} = 1 - X_{B}$$
(2.8)

$$Y_{A} = \frac{Z_{A}n_{A}}{(Z_{A}n_{A} + Z_{B}n_{B})} = \frac{Z_{A}X_{A}}{(Z_{A}X_{A} + Z_{B}X_{B})} = 1 - Y_{B}$$
(2.9)

The following equations may also be written as follows by mass balance:

$$Z_A X_A = 2n_{AA} + n_{AB} \tag{2.10}$$

$$Z_{B}X_{B} = 2n_{BB} + n_{AB}$$
(2.11)

where Z<sub>i</sub>X<sub>i</sub> represents total number of bonds emanating from an i atom, ions or molecules.

In "coordination equivalent fractions" defined in equation (2.11),  $(Z_A X_A + Z_B X_B)/2$  is the total number of pairs in one mole of a solution. If  $X_{ij}$  be the fraction of 'i-j' pairs in solution, equation (2.10) and (2.11) can be written as

$$2Y_{A} = 2X_{AA} + X_{AB} \tag{2.12}$$

$$2Y_{\rm B} = 2X_{\rm BB} + X_{\rm AB} \tag{2.13}$$

The molar enthalpy and excess entropy of mixing are assumed to be directly related to the number of A-B pairs:

$$\Delta H - TS^{non-config} = (Z_A X_A + Z_B X_B) X_{AB} (\omega - \eta T)/4$$
(2.14)

The gibbs energy of the solution can be written as:

$$G^{m} = (n_{A}g_{A}^{o} + n_{B}g_{B}^{o}) - T\Delta S^{config} + \left(\frac{n_{AB}}{2}\right)\Delta g_{AB}$$
(2.15)

$$= (n_A g_A^{o} + n_B g_B^{o}) - T\Delta S^{\text{config}} + g^E$$
(2.16)

where  $g_A^{o}$  and  $g_B^{o}$  are the molar Gibbs energies of the pure component and  $\Delta S^{config}$  is the configurational entropy of mixing of random distribution of the (A – A), (B – B) and (A – B) pairs in the one dimensional Ising approximation:

$$\Delta S^{\text{config}} = -R(n_A \ln X_A + n_B \ln X_B) - R\left[n_{AA} \ln\left(\frac{X_{AA}}{Y_A^2}\right) + n_{BB} \ln\left(\frac{X_{BB}}{Y_B^2}\right) + n_{AB} \ln\left(\frac{X_{AB}}{2Y_A Y_B}\right)\right]$$
(2.17)

 $\Delta g_{AB}$  is expanded in terms of the pair fractions:

$$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{i \ge 1} g^{i0}_{AB} X^{i}_{AA} + \sum_{j \ge 1} g^{0j}_{AB} X^{j}_{BB}$$
(2.18)

where  $\Delta g^{o}_{AB}$ ,  $g^{i0}_{AB}$  and  $g^{0j}_{AB}$  are the parameters of the model which may be functions of temperature.

The equilibrium pair distribution is calculated by minimizing  $G^m$  with respect to  $n_{AB}$  at constant composition.

$$\left(\frac{\partial G}{\partial n_{AB}}\right)_{n_A, n_B} = 0 \tag{2.19}$$

This gives the "equilibrium constant" for the "quasichemical reaction" of (Eq.1):

$$\frac{X_{AB}^2}{X_{AA}X_{BB}} = 4\exp\left(-\frac{\Delta g_{AB}}{RT}\right) = 4\exp\left(-\frac{(\omega - \eta T)}{RT}\right)$$
(2.20)

When  $\Delta g_{AB} (= \omega - \eta T) = 0$ , the solution of the equation (2.9), (2.12) and (2.13) gives a random distribution with  $X_{AA} = Y_A^2$ ,  $X_{BB} = Y_B^2$  and  $X_{AB} = 2Y_AY_B$ , and equation (2.17) reduces to ideal Roultian entropy of mixing. When  $\Delta g_{AB} (= \omega - \eta T)$  becomes progressively more negative, the reaction (Eq. 1) is shifted progressively to the right, resulting in the plot of  $\Delta H - T\Delta S^{non-config}$  versus composition to become V-shaped and that of  $\Delta S^{config}$  versus composition to become W-shaped and that of  $\Delta S^{config}$  versus composition to become m-shaped with minima at  $Y_A = Y_B = \frac{1}{2}$ . When  $\Delta g_{AB} (= \omega - \eta T)$  becomes postive, (A-A) and (B-B) pairs dominate. Therefore, the Quasichemical model can also treat such clustering which accompanies positive deviation from ideality. Usually, the  $(\omega - \eta T)$  parameter is expanded as a polynomial term of equivalent fractions.

At maximum SRO, the composition is determined by the ratio of the coordination numbers  $Z_B / Z_A$  as given by the following equations:

$$\frac{1}{Z_A} = \frac{1}{Z_{AA}^A} \left( \frac{2n_{AA}}{2n_{AA} + n_{AB}} \right) + \frac{1}{Z_{AB}^A} \left( \frac{n_{AB}}{2n_{AA} + n_{AB}} \right)$$
(2.21)

$$\frac{1}{Z_{B}} = \frac{1}{Z_{BB}^{B}} \left( \frac{2n_{BB}}{2n_{BB} + n_{AB}} \right) + \frac{1}{Z_{BA}^{B}} \left( \frac{n_{AB}}{2n_{BB} + n_{AB}} \right)$$
(2.22)

where  $Z_{AA}^{A}$  and  $Z_{AB}^{A}$  are the values of  $Z_{A}$  respectively when all the nearest neighbors of an A are A's, and when all nearest neighbors of an A are B's, and where  $Z_{BB}^{B}$  and  $Z_{BA}^{B}$  defined similarly. (Note:  $Z_{AB}^{A}$  and  $Z_{BA}^{B}$  represent the same quantity and can be used interchangeably.)

This model is sensitive to the ratio of the coordination numbers and less sensitive to their absolute values. The use of the one-dimensional Ising model in equation (2.17) introduces a mathematical approximation into the model which can be partially compensated by selecting values of  $Z_B$  and  $Z_A$  which are smaller than the actual values.

#### 2.2.1.3. Extension to a ternary system from binary system

Several "geometric" models have been proposed to estimate the excess Gibbs energy of a ternary system from optimized binary model parameters. Pelton [4] model presented a detail description of these models which are illustrated in Figure 3. The selection geometric models depends upon the nature of each binary system whose model parameters are interpolated to the ternary system.

In all these models the excess Gibbs energy ( $g^E$  in Equation 2.16) of a solution at any composition p can be estimated from the binary interaction parameter or the excess Gibbs energies of the binary sub-system at points a, b and c.

The excess Gibbs energy when the solution is modeled using the MQM is:

$$g^{E} = \frac{X_{12}\Delta g_{12}}{2} + \frac{X_{13}\Delta g_{13}}{2} + \frac{X_{23}\Delta g_{23}}{2} + (\text{ternary terms})$$
(2.23)

where  $\Delta g_{ij}$  is the Gibbs energy change for the reaction:

$$i - i + j - j = 2 (i - j)$$
 (2.24)

If ternary data is available, 'ternary terms' can be used to estimate the ternary interactions. However, precautions are taken to keep these terms as small as possible, otherwise doubts is cast upon the predictive ability of the model. These ternary polynomial terms are identically zero in the three binary sub-systems.

The Kohler and Muggianu models [4] in Figure 2.2 are "symmetric" models, whereas the Kohler/Toop and Muggianu/Toop models in Figure 2.2 are "asymmetric" models as one component is singled out. If component 2 and 3 are chemically similar while component 1 is chemically different, then asymmetric model is more physically reasonable than symmetric model. A symmetric model and an asymmetric model will give very different results, when  $g^E$  is large and  $\Delta g_{ij}$  depends strongly upon composition. Pelton [4] showed that if the models are used improperly then it can lead to thermodynamically inconsistent and unjustifiable results.



Figure 2.2: Some geometric models used for estimating ternary thermodynamic properties from the optimized binary data (reproduced from Pelton [4]).

Chartrand and Pelton [5] gave a detailed description of the estimation of the excess Gibbs energies in a ternary solution from binary model parameters when liquid phase is modeled by MQM. If the three binary subsystems of a ternary system have been optimized and the parameters are in the form of Equation 2.18 and symmetric Kohler-type approximation is chosen for the 1-2 subsystem, then  $\Delta g_{12}$  can be written:

$$\Delta g_{12} = \Delta g^{o}_{12} + \sum_{l \le (i+j)} g^{ij}_{12} \left( \frac{X_{11}}{X_{11} + X_{12} + X_{22}} \right)^{i} \left( \frac{X_{22}}{X_{11} + X_{12} + X_{22}} \right)^{j}$$
(2.25)

If Toop-type approximation is chosen, then  $\Delta g_{12}$  can be written as:

$$\Delta g_{12} = \Delta g_{12}^{o} + \sum_{l \le (i+j)} g_{12}^{ij} X_{11}^{i} (X_{22} + X_{23} + X_{33})^{j}$$
(2.26)

To estimate the Gibbs energy of ternary or multicomponent solutions from the optimized lowerorder parameters, FactSage<sup>TM</sup> thermodynamic software [6] allows users to use any of these "geometric models" which increase the flexibility and the ability to find out the Gibbs energy.

#### 2.2.2. Solid Solutions

Thermodynamic modeling of solids includes stoichiometric compounds, terminal solid solution or stoichiometric compounds with wide range of homogeneity. Sometimes some compounds have such a large homogeneity range that they are called with specific names such as spinel solid solution.

For any stoichiometric phase  $A_x B_y$  per mole of atoms is represented as:

$$g^{A_{x}B_{y}}(T) = \frac{x}{x+y} g^{0}_{A} + \frac{y}{x+y} g^{0}_{B} + \Delta H_{T} - T\Delta S_{T}$$
(2.27)

where  $\Delta H_T$  and  $\Delta S_T$  are the enthalpy of formation of the compound from the states i and j of elements A and B respectively.

#### 2.2.2.1. Monoxide solutions

Monoxide solid solution has a space group Fd3m which are MO based oxides where  $M^{2+}$  is a divalent cation such as Mg, Ca, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, etc. Almost all monoxide shows complete solid solution except CaO-MgO system, which exhibits limited mutual solubility's. Some of the N2O3 type solid oxides get dissolved in the monoxide solution where N is a trivalent cation such as Al<sup>3+</sup>, Cr<sup>3+</sup> and Fe<sup>3+</sup>. Monoxide solution has a structure similar to that of NaCl (halite), therefore known as "halite (rock salt)" solution (Figure 2.3). In a monoxide solid solution, when two MO oxides mix, the mixing usually occurs between the cations in the cation sites. Based on this, the following model is being used to model the monoxide solutions.



Figure 2.3: Schematic representation of a NaCl crystal structure

## 2.2.2.1.1. Regular solution model

Regular solution model is used to model terminal solid solutions or monoxide solutions which appeared in binary systems. In this, the model assumes random mixing of the atoms on one sub lattice while the other lattice is fixed, one randomly replacing the other by substitution on lattice sites. The Gibbs energy of such a solution in which atoms A and B replace each other on one lattice sites is given as:

$$G^{m} = (x_{A} g_{A}^{o} + x_{B} g_{B}^{o}) + RT[x_{A} \ln x_{A} + x_{B} \ln x_{B}] + g^{E}$$
(2.28)

The phases which exhibit homogeneity in two or more sublattices are modeled using sublattice models. The sublattice model with random mixing on each sublattice in its most general form is called as Compound Energy Formalism.

#### 2.2.2.2. Spinel solution

#### 2.2.2.2.1. Structure

Most of the spinel compounds belong to the space group Fd3m. Figure 2.4 shows the schematic structure of spinel. It has a general formula AB<sub>2</sub>O<sub>4</sub>. In one unit cell of AB<sub>2</sub>O<sub>4</sub> shown in Figure 1, A atoms are located in the 8 tetrahedral positions (represented by green circles), B atoms are in the 16 octahedral positions (represented by red circles) and oxygen atoms in the 32 positions (represented by blue circle). One unit cell contains 32 oxygen atoms, so, there are eight AB<sub>2</sub>O<sub>4</sub> formula units. The lattice parameter in oxide spinel is approximately 0.8-0.9 nm.

A simple spinel contains two different cations in the ratio of 2:1. Theoretically, all spinels may be classified into three classes, normal, inverse and mixed. A normal spinel is one in which all the (A) cations reside in the tetrahedral site all the (B) cations reside in the octahedral sites. A fully inverse spinel is a one in which the (B) cations are evenly split between tetrahedral and octahedral site and all the (A) cations are reside in the octahedral sites. All real spinels generally fall in the category of "mixed spinels", i.e. both the cations (A) and (B) are present in both tetrahedral and octahedral sites.

All the well-known oxide spinels are thermodynamically very stable at 1 bar total pressure. For example: MgAl<sub>2</sub>O<sub>4</sub> (spinel), Fe<sub>3</sub>O<sub>4</sub> (magnetite), FeAl<sub>2</sub>O<sub>4</sub> (hercynite), MgFe<sub>2</sub>O<sub>4</sub> (magnesium ferrite), MgCr<sub>2</sub>O<sub>4</sub> (magnesium chromite), FeCr<sub>2</sub>O<sub>4</sub> ( iron chromite), MnAl<sub>2</sub>O<sub>4</sub> (galaxite), CoAl<sub>2</sub>O<sub>4</sub>, NiAl<sub>2</sub>O<sub>4</sub> *etc.* However, some silicate spinels, Mg<sub>2</sub>SiO<sub>4</sub>, Fe<sub>2</sub>SiO<sub>4</sub>, Co<sub>2</sub>SiO<sub>4</sub> and Ni<sub>2</sub>SiO<sub>4</sub> are stable under high pressure because the olivine structure (A<sub>2</sub>SiO<sub>4</sub>) transforms to the spinel structure at high pressure. Oxide spinels can dissolves  $\gamma$ -A<sub>2</sub>O<sub>3</sub> type oxides e.g.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Cr<sub>2</sub>O<sub>3</sub>, etc. This results in introduction of vacancies on octahedral sites which eventually leads to wide ranges of solid solution.



Figure 2.4: Structure of a unit cell of spinel AB<sub>2</sub>O<sub>4</sub>

The spinel structure has unique characteristics of cation distributions (order/disorder). The cation distribution of a spinel varies with temperature. The usual way of determining cation distribution is to quench the sample at one particular temperature and do crystallography measurements. But, the distribution of cation within tetrahedral and octahedral sites is unquenchable above a certain temperature because after that temperature the ordering-disordering process is too fast to be quenched. That temperature is known as unquenchable temperature,  $T_{unquen}$ . In this case, in-situ measurements are the only solution. On the other hand, the spinel does not reach an equilibrium distribution of cations within two sites below a certain temperature because below that temperature the ordering-disordering process is too slow and does not reach equilibrium. That temperature is known as frozen temperature,  $T_{froz}$ . In case of MgAl<sub>2</sub>O<sub>4</sub>, Jung *et al.* [7] did

thermodynamic optimization of  $MgAl_2O_4$  cubic spinel and found out the frozen and unquenchable temperature to be approximately 700°C and 923°C, respectively (Figure 2.5).



Figure 2.5: The variation of cation distribution of  $MgAl_2O_4$ . The inversion parameter is defined as the mole fraction of  $Al^{3+}$  on tetrahedral sites. [7]

#### 2.2.2.2. Compound Energy Formalism

For modelling a spinel, a two-sublattice model by Degterov *et al.* [8] in the framework of the Compound Energy Formalism (CEF) by Hillert *et al.* [9] is used for describing the Gibbs energy of spinel solutions.

The Gibbs energy of the spinel solution is expressed, in the CEF, as

$$G^{m} = \sum_{i} \sum_{j} Y_{i}^{T} Y_{j}^{O} G_{ij} - TS^{config} + G^{excess}$$
(2.29)

where  $Y_i^T$  and  $Y_j^O$  represent the site fractions of constituents 'i' and 'j' on the tetrahedral and the octahedral sublattices, respectively;  $G_{ij}$  is the Gibbs energy of n "end member  $[i]^T[j]_2^OO_4$ " in which T (tetrahedral site) and O (octahedral site) sites are occupied only by *i* and *j* cations, respectively;  $S^{config}$  is the configurational entropy which takes into account random mixing on each sublattice:

$$S^{\text{config}} = -R\left(\sum_{i} Y_{i}^{T} \ln Y_{i}^{T} + 2\sum_{j} Y_{j}^{T} \ln Y_{j}^{T}\right)$$
(2.30)

and G<sup>excess</sup> is the excess Gibbs energy:

$$G^{excess} = \sum_{i} \sum_{j} \sum_{k} Y_{i}^{T} Y_{j}^{T} Y_{k}^{O} L_{ij:k} + \sum_{i} \sum_{j} \sum_{k} Y_{k}^{T} Y_{i}^{O} Y_{j}^{O} L_{k:ij}$$
(2.31)

where  $L_{ij:k}$  parameters is the interaction energies between cations 'i' and 'j' on the first sublattice when the second sublattice is occupied only by 'k' cations and similarly the  $L_{k:ij}$  parameters is the interaction energies between cations 'i' and 'j' on second sublattice when the first sublattice is occupied only by 'k' cations . The interaction energies,  $L_{ij:k}$  and  $L_{k:ij}$  are internally set in the model as follows:

$$L_{ij:k} = L_{ij:s} = \dots$$
 (2.32)

$$L_{k:ij} = L_{s:ij} = \dots$$
 (2.33)

The interaction between 'i' and 'j' on a sublattice is assumed to be the same, independent of which cation resides on the other sublattice.

The interaction energies can be expressed by Redlich-Kister a power series expansion (Redlich and Kister [10] and Pelton and Bale [11]) which depends upon the composition:

$$L_{ij:k} = \sum_{m} L_{ij:k} (y_j^{T} - y_i^{T})^{m}$$
(2.34)

$$L_{k:ij} = \sum_{m} L_{k:ij} (y_j^{O} - y_i^{O})^m$$
(2.35)

Gibbs energies  $G_{ij}$  of end-members of the model are formed by taking 'i' from tetrahedral sublattice and 'j' from octahedral sublattice. These are the primary model parameters. However, it is not possible to determine from the experimental data alone the Gibbs energies of all end-members. For fixing the values of these Gibbs energies properly, certain logical and physically

meaningful assumptions should be made. In the present model, physically meaningful linear combinations of the end-members Gibbs energies  $G_{ij}$  pertaining to certain site exchange reactions occurring between cations are used as the models parameters. For a fully normal spinel, for example,  $G_{AB} = G_0(AB_2O_4)$ , is the (measurable) Gibbs energy of pure normal  $AB_2O_4$  which can be used directly as an optimized parameter.

The Gibbs energy of site exchange reactions between cations in the tetrahedral and octahedral sites are the model parameters and are denoted by  $\Delta$  and *I* parameter.

Gibbs energies  $\Delta_{AB}$  of following site exchange reaction is given by

$$AB + BA = AA + BB \tag{2.36}$$

$$\varDelta_{AB} = G_{AA} + G_{BB} - G_{AB} - G_{BA} \tag{2.37}$$

which is used as model parameters. O'Neill and Navrotsky [12] found out that the  $\Delta_{AB}$  should have the value of about 40kJ/mol.

Gibbs energies  $I_{AB}$  of following site exchange reaction is given by

$$2AB = AB + BA \tag{2.38}$$

$$I_{\rm AB} = G_{\rm AB} + G_{\rm BA} - 2G_{\rm AB} \tag{2.39}$$

which are indicators of tendency of spinel towards the formation of an inverse spinel structure and this model parameter helps in optimizing the cation distribution data.

The present system is a concern as the spinel contains Mn. Mn has three valence states in spinel,  $Mn^{2+}$ ,  $Mn^{3+}$  and  $Mn^{4+}$ . Therefore, the structure of the spinel solution and their Gibbs energy formula is more complex. This will be explaining in detail in Chapter 4.

#### 2.3. References

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### **3. Method of Operation**

The objective of the present work was to prepare a critically evaluated thermodynamic database for Ca-Mg-Mn-O system. All the calculations and optimizations in the present work were performed with the FactSage<sup>TM</sup> thermochemical software. The various steps followed in the present work which collectively come under the CALPHAD approach were:

(i) Identification of the binary system to be optimized.

(ii) Collection of data in the literature for the system:

- Thermodynamic data: includes phase equilibria (phase diagrams, two- or three-phase equilibria among solids/liquid/gas), calorimetric data (heat capacity, enthalpy of formation and enthalpy of mixing), enthalpy of formation for compounds, vapour pressures (Knudsen cell, Langmuir method), chemical potentials (emf), activities of constituents in a solution, etc.
- Structural data: includes cation distributions between sublattices, lattice parameters, etc.
- Physical properties such as magnetism, electrical conductivity, etc. may sometimes help in the evaluation of the system.
- If very few experimental data are available which are not sufficient to define the thermodynamic properties of the system, useful data from a higher-order system of which the system of interest is a sub-system can be used.

(iii) Selection of the appropriate thermodynamic model:

An appropriate thermodynamic model representing the Gibbs energy functions for a phase is required. For that, a good physical model based on the structure of the phase is selected which increases the accuracy of predictions of solution properties of multicomponent systems from lower order (binary + ternary) model parameters.

(iv) Critical evaluation of collected experimental data:

The literature data which includes all experimental data must be evaluated before doing the optimization. The experimental data by different authors were often found to differ from each other by more than the stated experimental error limits. Sometimes experimental data for a

particular system were not thermodynamically consistent with each other. Therefore, all the available experimental data were evaluated on the basis of experimental techniques, sample preparation and thermodynamic consistency. Sometimes, the accuracy of the experimental data was difficult to evaluate from the description of the experimental technique, then their consistency or inconsistency was judged during the optimization of the entire system. Moreover, the accuracy of the experimental data in lower-order systems can be evaluated from the data in higher-order systems by extrapolation. All possible experimental errors should be considered during the evaluation and optimization of a system.

(v) Optimization of model parameters for a system:

After evaluation of the experimental data, the next step is optimization which was performed on the basis of selected reliable data to obtain the values of the model parameters.

(vi) Back calculation of all thermodynamic data and phase diagrams:

Once satisfactory model parameters were obtained, all the thermodynamic data and experimental data were back-calculated from the thermodynamic models for comparing with the optimized values. The FactSage<sup>TM</sup> (FactSage 6.3) thermochemical software was used to perform all calculations for a particular system.

(vii) Evaluation of ternary systems:

To estimate the Gibbs energies of solutions in the ternary systems, the obtained model parameters for the binary sub-systems were combined with previously optimized binary parameters of the other binary sub-systems. By doing this, evaluations and predictions were made for the ternary systems.

#### 4. Critical evaluation and thermodynamic modelling of the Mg-Mn-O system

#### 4.1. Introduction

The magnesium-manganese oxide is of great interest in metallurgical fields (iron and steel making, high manganese steel production) since the manganese plays an important role as a major alloying element in steel. Therefore, the knowledge for the manganese oxide containing system is valuable to the industries. In this regard, a research on the thermodynamic properties and phase equilibria in the Mg-Mn-O is necessary. In this system Mg-Mn-O, spinel phases (cubic and tetragonal) is of interest in the view of thermodynamic modeling because there are couples of things to be considered (ex., valencies of Mn, cation distribution on tetrahedral and octahedral sites). Despite its importance, the phase equilibria in this system have not been well studied. Experimental study of the system is complicated by the strong dependence of the equilibria on the oxygen pressure and by the high melting temperature of the spinel phase. Therefore, critical assessment of the data is required in order to understand and model this system more accurately. The present study is a part of a complete database development of the CaO-Fe<sub>1</sub>O-SiO<sub>2</sub>-MgO-MnO-Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-CaF<sub>2</sub> system for application in the steel industries. All the thermodynamic calculations in the present study were performed with the FactSage [1] software.

#### 4.2. Phases and thermodynamic models

The calculated phase diagram of the Mg-Mn-O system at  $1000^{\circ}$  C and 1 bar total pressure is presented in Figure 4.1. The following solution phases are found in the MgO-MnO-Mn<sub>2</sub>O<sub>3</sub> system:

- (i) Slag (molten oxide phase): MgO-MnO-MnO<sub>1.5</sub>
- (ii) Monoxide (periclase): MgO-MnO-MnO<sub>1.5</sub>

(iii) Cubic spinel (encompassing cubic-MgMn<sub>2</sub>O<sub>4</sub>, cubic-Mn<sub>3</sub>O<sub>4</sub>):  $(Mg^{2+},Mn^{2+})^{T}[Mg^{2+},Mn^{2+},Mn^{2+}]$ 

 $Mn^{3+}, Mn^{4+}, Va]_{2}^{O}O_{4}$ 

(iv) Tetragonal spinel (encompassing tetragonal  $Mn_3O_4$ ):  $(Mg^{2+},Mn^{2+},Mn^{3+})^T [Mg^{2+},Mn^{2+},Mn^{2+},Mn^{3+}, Va]_2^OO_4$ 

(v) Mg<sub>6</sub>MnO<sub>8</sub>: built from the existing MgO and MnO<sub>2</sub> from FToxide database.

Cations shown within a set of brackets for spinel occupy the same sublattice. T and O represent the tetrahedral and octahedral cationic sites in spinel, respectively.

#### 4.2.1. Molten oxide (slag)

The modified quasichemical model [2-5], which takes into account short-range ordering of second-nearest-neighbor cations in the ionic melt, is used for modeling the slag. For example, for the MgO-MnO-MnO<sub>1.5</sub> slag these reactions are:

$$(A - A) + (B - B) = 2(A - B)$$
  $\Delta g_{AB}$  (4.1)

where A and B are  $Mg^{2+}$ ,  $Mn^{2+}$  and  $Mn^{3+}$ , and (A - B) represents a second-nearest-neighbour A-B pair. Gibbs energies of these above reaction  $\Delta g_{AB}$  are the parameters of the model which may be expanded as empirical functions of composition. The Gibbs energy of the solution is given in Eq. 2.15.

The component of the slag is taken as MgO-MnO-MnO<sub>1.5</sub>. Although Mn can have higher oxidation states, only the divalent and trivalent oxidation states, which predominate at oxygen partial pressures less than 1.0 bar, are considered in the present study. The components are written as  $MnO_{1.5}$  rather than  $Mn_2O_3$  simply to indicate that  $Mn^{3+}$  ions are distributed as independent particles between oxygen in the liquid solution and not as ion pairs.

The binary sub-systems  $MnO-MnO_{1.5}$  [6] and MgO-MnO [7] has already been critically evaluated and optimized and the optimized model parameters are used as the basis of the present study. All second-nearest-neighbor "coordination numbers" used in the present model for the slag are the same as in previous studies. The binary sub-system MgO-MnO<sub>1.5</sub> has been optimized in the present studies which are listed in Table 4.1.

The properties of the ternary MgO-MnO-MnO<sub>1.5</sub> slag solution were calculated from the binary parameters using a symmetric "Kohler-like" approximation [8] which assumes that the energy  $\Delta g_{AB}$  of reaction (4.1) remains constant as MnO<sub>1.5</sub> is added to an MgO-MnO solution at constant MgO/MnO ratio, and similarly for addition of MnO to MgO-MnO<sub>1.5</sub> solutions and of MgO to MnO-MnO<sub>1.5</sub> solutions. No ternary interaction parameters are needed.

#### 4.2.2. Monoxide solution

Monoxide solution has rock-salt structure. It was modeled as a simple random mixture of all cations,  $Mg^{2+}$ ,  $Mn^{2+}$ , and  $Mn^{3+}$  ions on cation sites using a simple polynomial excess Gibbs energy terms [8]. It is assumed that cation vacancies remain associated with  $Mn^{3+}$  to maintain electrical neutrality and so do not contribute to the configurational entropy. The Gibbs energy per mole of the solution is expressed as follow:

$$G_{m} = \sum_{i} X_{i}G_{i}^{0} + RT \sum_{i} X_{i}\ln X_{i} + \sum_{i} \sum_{j} X_{i}X_{j}(\frac{X_{i}}{X_{i}+X_{j}})^{m}(\frac{X_{j}}{X_{i}+X_{j}})^{n}q_{ij}^{mn} + g_{ternary}^{ex}$$
(4.6)

where  $G_i^o$  is the Gibbs energy of component like MgO, MnO and MnO<sub>1.5</sub> and X<sub>i</sub> is mole fraction of component. The binary parameter  $q_{ij}^{mn}$  of MgO-MnO and MgO-MnO<sub>1.5</sub> system was optimized in the present study as described in the following section. These are listed in Table 4.1.  $q_{ij}^{mn}$  of MnO-MnO<sub>1.5</sub> was optimized previously [6]. The properties of ternary monoxide MgO-MnO-MnO<sub>1.5</sub> were calculated from the binary parameters with asymmetric 'Kohler-like' approximation [8]. No ternary excess parameter  $g_{ternary}^{ex}$  was used in the present study.

#### 4.2.3. Spinel: cubic and tetragonal

Tetrahedral and octahedral sites are the two distinct cationic sites of spinel. Thus, cationic distribution between these two sublattices is important for determining the physical and thermodynamic properties of spinel. There are two types of spinel phases in the Mg-Mn-O system: cubic and tetragonal spinels. Grundy *et al.* [9] observed that pure  $Mn_3O_4$  has tetragonal spinel structure and it transforms to cubic spinel over 1172 °C in air. The ionic configuration of both tetragonal and cubic  $Mn_3O_4$  spinel was found out by Dorris and Mason [10] from their electrochemical seebeck experimental technique. This structural information was properly implemented in the development of the present thermodynamic models for the cubic and tetragonal spinel phases in the Mg-Mn-O system.

For both the spinel solution, a two sublattice spinel model [11] has been developed within the framework of the compound energy formalism (CEF) [12]. It has earlier been explained in Section 2.2.2.2.2.

Certain linear combinations of the  $G_{ij}$  parameters ( $\Delta$ ) having physical significance is used as the optimized model parameters as shown in Table 4.1. The physical significance of these linear combinations ( $\Delta$ ) is already been discussed [13] which are related to the energies of classical site exchange reactions. By doing this, the model parameters could have certain physical meaning which helps in completing the thermodynamic modeling than individually giving a value to the  $G_{ij}$  parameters without any particular reason. Moreover, it helps in increasing the predictive ability of the model. Details of the linear combinations of  $G_{ij}$  parameters for both cubic and tetragonal spinels are given in Table 4.1. Here, B, J, K, L and V stands for  $Mg^{2+},Mn^{2+},Mn^{3+},Mn^{4+}$  and Vacancy, respectively.

#### 4.2.3.1. Cubic spinel

Cubic spinel has  $(Mg^{2+},Mn^{2+})^{T}[Mg^{2+},Mn^{2+},Mn^{3+},Mn^{4+},Va]_{2}^{O}O_{4}$  structure including vacancy (Va) on octahedral site. 10 end-member Gibbs energies are required for the model. Among them, four end members Gibbs energies (G<sub>JJ</sub>, G<sub>JK</sub>, G<sub>JL</sub> and G<sub>JV</sub>) were already fixed from the Mn-O system (Mn<sub>3</sub>O<sub>4</sub>) [6] and two more (G<sub>BB</sub> and G<sub>BV</sub>) were fixed in the optimization of the Mg-Al-O spinel solution [14]. Optimized values of the four remaining parameters (G<sub>BK</sub>, G<sub>BJ</sub>, G<sub>BL</sub> and G<sub>JB</sub>) were obtained in the present study as described in the following sections. Physically meaningful combinations of G<sub>ij</sub> for the cubic spinel are listed in Table 4.1. These are the model parameters which are optimized in the present study.

There are 4 model parameters which consist of 3  $\Delta$  parameters along with the Gibbs energy of stoichiometric spinel MgMn<sub>2</sub>O<sub>4</sub> as one parameter. As, two of the  $\Delta$  parameter ( $\Delta_{BJ:JK}$ ,  $\Delta_{BJ:LK}$ ) has same effect on the Mn rich side, therefore, one  $\Delta$  parameter ( $\Delta_{BJ:JK}$ ) is set to zero and another  $\Delta$  parameters ( $\Delta_{BJ:LK}$ ) along with the Gibbs energy of stoichiometric spinel MgMn<sub>2</sub>O<sub>4</sub> parameter is used to optimize the available experimental data. The fourth parameter ( $\Delta_{JB:BK}$ ) was optimized to determine the cation distribution of MgMn<sub>2</sub>O<sub>4</sub>. The values of all the model parameters are given in Table 4.1.

Due to Jahn-Teller distortion [15], the cubic  $MgMn_2O_4$  show the slightly distorted tetragonal structure. However, it is different from standard tetragonal spinel structure like tetragonal  $Mn_3O_4$  spinel. From the thermodynamic viewpoint, Jahn-Teller distortion is not the first order transition

as there is no sudden change in lattice parameters with temperature [16]. Thus, in the present study, the distorted tetragonal structured spinel was treated as extension of cubic spinel.

#### 4.2.3.2. Tetragonal spinel

Tetragonal spinel has  $(Mg^{2+},Mn^{2+},Mn^{3+})^{T}[Mg^{2+},Mn^{2+},Mn^{3+},Va]_{2}^{O}O_{4}$  structure including vacancy (Va) on octahedral sites. Like cubic spinel, 12 end-member Gibbs energies are required for the model. Among them, 8 end member Gibbs energies were already determined from the Mn-O [6] and Mg-Al-O [14]. 4 other Gibbs energies were determined in the present study. The model parameters are presented in Table 4.1.

#### 4.2.4. Stoichiometric compound

Mg<sub>6</sub>MnO<sub>8</sub>, Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> were treated as stoichiometric compound.

#### 4.2.5. Metallic phases

All metallic phases (CBCC, CUB, FCC, BCC and Liquid) were treated as simple substitutional solutions and their Gibbs energy of mixing were taken from FSstel database [17].

#### Table 4.1: Optimized model parameters of solutions in the MgO-MnO-Mn<sub>2</sub>O<sub>3</sub> system

Cubic Spinel:  $(Mg^{2+},Mn^{2+})^{T}[Mg^{2+},Mn^{2+},Mn^{3+},Mn^{4+},Va]_{2}^{O}O_{4}$ 

 $G_{BK} = G^{o}(cubic-MgMn_{2}O_{4}) = G^{o}(MgO) + G^{o}(Mn_{2}O_{3}) + \Delta H_{f} - T\Delta S_{f} (\Delta H_{f} = -16317.60 \text{ J/mol and} \Delta S_{f} = 1.2552 \text{ J/mol-K})$ 

 $\Delta H_{298}^{o} = -1552818.54736 \text{ J/mol}$ 

 $S_{298}^o = 145.703 \text{ J/mol K}$ 

$$\begin{split} C_p &= 5142.109 - 31.111T + 0.048T^2 - 296.199T^{-0.5} - 621154.004T^{-2} + 5844612.027T^{-3}(298K < T < 320K); \\ 194.610 + 0.012T - 296.199T^{-0.5} - 10000T^{-1} - 907458.766T^{-2} + 5844612.027T^{-3}(320K < T < 1161K); \\ 199.716 - 296.199T^{-0.5} - 621154.004T^{-2} + 5844612.027T^{-3}(1161K < T < 3097.910K); \\ 205.550 (3097.910K < T < 3050K) \end{split}$$

 $\Delta_{BJ:JK}=G_{BJ}+G_{JK}-G_{JJ}-G_{BK}=0$
$\Delta_{BJ:LK} = G_{BL} + G_{JK} - G_{JL} - G_{BK} = -158992 \text{ J/mol}$ 

 $\Delta_{JB:BK} = G_{JB} + G_{BK} - G_{BB} - G_{JK} = -133888 + 54.392T \text{ J/mol}$ 

Notations B, J, K, L and V are used for Mg<sup>2+</sup>, Mn<sup>2+</sup>, Mn<sup>3+</sup>, Mn<sup>4+</sup> and Va, respectively.

# Tetragonal Spinel: $(Mg^{2+},Mn^{2+},Mn^{3+})^{T}[Mg^{2+},Mn^{2+},Mn^{3+},Va]_{2}^{O}O_{4}$

$$\label{eq:GBK} \begin{split} G_{BK} &= G^o \mbox{ (tetragonal-MgMn_2O_4)} = G^o \mbox{ (MgO)} + G^o \mbox{ (Mn_2O_3)} + \Delta H_f \mbox{ - } T\Delta S_f \mbox{ (} \Delta H_f \mbox{ = -} 25522.4 \mbox{ J/mol} \mbox{ and } \Delta S_f \mbox{ = 8.368 J/mol} \mbox{ K)} \end{split}$$

 $\Delta_{KB}=G_{KK}+G_{BB}-G_{BK}-G_{KB}=0$ 

 $\Delta_{BJK} = G_{BK} + G_{JJ} - G_{JK} - G_{BJ} = -167360 \text{ J/mol}$ 

 $\Delta_{JBK} = G_{JK} + G_{BB} - G_{BK} - G_{JB} = 0$ 

Notations B, J, K and V are used for  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Mn^{3+}$  and Va, respectively.

### Monoxide Phase: MgO-MnO-MnO<sub>1.5</sub>

 $q_{MnO,MnO_{1.5}}^{31} = 20,920^{a}$   $q_{MgO,MnO}^{11} = 11,344.257$   $q_{MgO,MnO}^{41} = 2976.457$   $q_{MgO,MnO_{1.5}}^{11} = 41003.2 - 12.552T$   $q_{MgO,MnO_{1.5}}^{21} = 7531.2$ 

### Liquid Phase: MgO-MnO-MnO<sub>1.5</sub>

 $\Delta g_{MgO-MnO}^{00} = 4184$ 

 $\Delta g_{MgO-Mn_2O_3} = 0$ 

## Compound: Mg<sub>6</sub>MnO<sub>8</sub>

 $\Delta H_{298} = -4163500$ 

 $S_{298} = 225.5$ 

$$\begin{split} C_p &= 492.938 - 3211.809 T^{-0.5} + 3246.056 T^{-1} - 3726924.024 T^{-2} + 35067672.163 T^{-3} \ (298.15 K < T < 2500 K); \ 465.544 - 1777.194 T^{-0.5} - 3726924.024 T^{-2} - 35067672.163 T^{-3} \ (2500 K < T < 3097.910 K); \ 500.550 \ (3097.910 K < T < 3500 K) \end{split}$$

<sup>a</sup> The model parameters for the Mn-O system was optimized previously by Kang and Jung [6].

#### 4.3. Critical evaluation/optimization of experimental data

The experimental data of the Mg-Mn-O system are mainly classified into three groups: (i) thermodynamic and structural data for the spinel phase (ii) thermodynamic data and phase equilibrium data for the monoxide phase and (iii) the phase equilibria data containing monoxide, spinel,  $Mg_6MnO_8$ ,  $Mn_2O_3$  and  $MnO_2$ . During the optimization, the Gibbs energy of monoxide phase was first optimized in order to reproduce the phase equilibrium data and activity data of the MgO-MnO system. Then, the Gibbs energy of spinel phase was evaluated to reproduce structural data, thermodynamic data and phase equilibrium data in air. Finally, overall optimization including the slag was carried out with further slight adjustments of the model parameters for all the phases including stoichiometric compound  $Mg_6MnO_8$  in order to reproduce all the reliable experimental data within experimental error limits.

#### 4.3.1. MgO-MnO system

The critical evaluation and thermodynamic modeling of the MgO-MnO system has been done previously by Wu *et al.* [7]. But due to recent experimental activity data [18] for the MgO-MnO system and to reproduce phase diagram data in air more accurately, the parameters for monoxide solution was slightly modified. The details are described below.

Figure 4.2 shows the activities of MgO and MnO in monoxide solution under reduced oxygen condition. The activity of MnO in this system was first reported by Woermann and Muan [19] in which they estimated the relationship from the activity composition relation in the CaO-MnO [20,21] system and the conjugation lines between the CaO-rich and MgO-rich monoxide solution in the CaO-MgO-MnO system[19]. Hahn and Muan [22] in the same year reported the MnO

activity of the MgO-MnO system at 1100°C and 1300°C estimated from the activity-composition relationship determined experimentally for ternary monoxide solution of the MgO-MnO-NiO in equilibration with Ni at controlled oxygen pressures.

Tsai and Muan [23] determined the activity of MnO by equilibrating the MnO-MgO solution with Pt-Mn alloys at 1500 and 1600°C. After the experiment, the MnO activity was calculated from the known activity of Mn and controlled oxygen partial pressure in the experiment. Recently, Wood et al. [16] performed the same experiment at 1300°C. In their experiment, they intentionally add lower or higher amount of Mn than the equilibrium Mn in Pt-Mn alloy in order to make sure the equilibration. Raghavan *et al.* [24] measured the activities of MgO in MgO-MnO solid solution using galvanic cells with MgF<sub>2</sub> solid electrolytes in the temperature range of 890°C to 1045°C. They found the activity of MgO(s) positively deviated from ideal solutions.

Gripenberg *et al.* [25] determined the enthalpies of mixing of MgO-MnO monoxide solution using HCl aqueous solution calorimeter at 40°C. The heat of mixing was measured to be positive with a maximum value of 5.4 kJ/mol at  $X_{MnO} = 0.45$  as shown in Figure 4.3. Raghavan *et al.* [24] derived mixing enthalpy from their activity measured using emf technique. The derived enthalpy was (3841 ± 0.84) kJ/mol at  $X_{MnO} = 0.5$ . The calculated heat of mixing along with the experimental data is shown in Figure 4.3.

The solidus of MgO-MnO was measured by Schenck *et al.* [26] using a hot stage microscope at reduced oxygen conditions. That is, the solidus was determined by visual observation of the beginning of the melting. The applied the same techniques for finding out the solidus for the system like CaO-MnO and FeO-MgO, which showed reasonable results. The experimental data are plotted in Figure 4.4.

#### 4.3.2. MgO-MnO-Mn<sub>2</sub>O<sub>3</sub> system

The phase equilibria of Mg-Mn-O system under oxidation condition become complex because of the formation of spinel phase. There are reasonable amount of experimental data which constraints the model parameters of spinel and other phases. Because the spinel phase is appearing at all sub solidus temperatures, the thermodynamic data and structural data of spinel phase was truly optimized and rest of phase diagram were optimized.

#### 4.3.2.1. MgMn<sub>2</sub>O<sub>4</sub> Cubic Spinel

 $MgMn_2O_4$  is known as a normal spinel at room temperature. Many investigations have been carried out to measure the cation distribution between tetrahedral and octahedral sites as function of temperature [27-34]. The measured cation distributions in terms of inversion degree (percentage of Mn cations in tetrahedral sites) are shown in Figure 4.5.

The crystallographic properties of MgMn<sub>2</sub>O<sub>4</sub> were first studied by Sinha *et al.* [27] and Sanjana *et al.* [28] which showed that the crystals were found to possess tetragonally distorted spinel structure and has normal cationic arrangements when quenched from higher temperatures. High temperature X-ray diffraction measurement by Irani *et al.* [16] found out that MgMn<sub>2</sub>O<sub>4</sub> having tetragonally distorted structure at room temperature remained normal up to 800°C. Then it converted to cubic spinel structure and inversion degree at that temperature was calculated to be approximately 0.45  $\pm$  0.05. But, during the calculation of ratio of XRD intensities did not take into account thermal vibrations of the ions in the crystal lattice due to unavailability of the proper Debye thermal parameters. Therefore, the data is not reliable as the calculation of cation distribution is done without any thermal corrections.

Manaila and Paussescu [29] by XRD measurements determined that the MgMn<sub>2</sub>O<sub>4</sub> sample quenched from 1250°C has an inversion degree of 0.489. Rosenberg and Nicolau [30] also investigated the cation distribution at 1250 C by performing structural X-ray analysis of quenched sample. The reported cation distribution at 1250°C was  $(Mg_{0.48}^{2+})^{T}$   $[Mg_{0.48}^{2+}Mn_{1.02}^{3+}Mn_{0.48}^{4+}]^{O}O_{4}$ . Radhakrishnan and Biswas [31] also measured the inversion degree of three quenched samples by neutron diffraction method at 550°C, 750°C and 950°C, and reported 0.371, 0.28 and 0.22, respectively. Barkhatov *et al.* [32] performed XRD for samples on quenched at 1000°C and found the inversion degree to be 0.453. Malavasi *et al.* [33, 34] reported the inversion degree of tetragonally distorted spinel MgMn<sub>2</sub>O<sub>4</sub> at 25°C, 400°C, 600°C, 800°C and 1000°C using XRD technique which comes out to be 0.218, 0.258, 0.263, 0.296 and 0.4. It is well known [33, 34] that the cation distribution can be frozen at low temperature due to the slow kinetic of cation exchange reaction at low temperature. Therefore, the experimental data by Malavasi [33, 34] at 25°C and 400°C (potentially up to 600°C) would be in un-equilibrium state.

The thermodynamic properties of stoichiometric  $MgMn_2O_4$  spinel have been rarely studied. There has been no experimental heat capacity measurement for  $MgMn_2O_4$  spinel neither at low temperature nor at high temperature, therefore, the entropy of  $MgMn_2O_4$  spinel at 298 K ( $S_{298.15}^o$ ) is not known. Molar enthalpy of formation of  $MgMn_2O_4$  at 700°C was determined by Navrotsky and Kleppa [35] using high temperature heat capacity measurement. The measured enthalpy of formation of  $MgMn_2O_4$  from MgO and  $Mn_2O_3$  at 700°C is  $-11.38 \pm 3$  kJ/mol.

In the present study, the end member Gibbs energy of MgMn<sub>2</sub>O<sub>4</sub> (G<sub>BK</sub>) was first estimated to be the sum of  $G^{o}_{MgO}$  and  $G^{o}_{Mn_2O_3}$ . Then,  $\Delta H^{o}_{298}$  and  $S^{o}_{298}$  were adjusted to reproduce the phase diagram in air (Figure 4.6). It should be noted that  $S^{o}_{298}$  was changed only slightly (1.26 J/mol-K). As the MgMn<sub>2</sub>O<sub>4</sub> spinel is normal spinel, the  $\Delta H^{o}_{298}$  of  $(Mg^{2+})^{T}[Mn^{3+}]^{O}_{2}O_{4}$  end member is mainly related to enthalpy of formation of real MgMn<sub>2</sub>O<sub>4</sub> spinel. The calculated enthalpy of formation of MgMn<sub>2</sub>O<sub>4</sub> spinel (considering the cation distribution in Figure 4.5) from MgO and Mn<sub>2</sub>O<sub>3</sub> is -8.651 kJ/mol which is in good agreement with experimental values, - 11.38 ± 3 kJ/mol. In order to reproduce the cation distribution data in Figure 4.5,  $\Delta_{JB:BK}$  parameter was adjusted. As can be seen in Figure 4.5, the calculated cation distributions are in good agreement with experimental data above 600°C. As mentioned above, 25° C and 400° C were not considered due to un-equilibrium state of the cation distribution of these samples.

#### 4.3.2.2. Phase diagram

Phase diagram of the Mg-Mn-O system under air was investigated by several authors. All the experimental data are shown in Figure 4.6 to 4.8 along with the calculated phase diagrams.

The MgO-Mn<sub>2</sub>O<sub>3</sub> phase diagram at air was first determined by Riboud and Muan [36] using the classical quenching method followed by XRD and microscopic phase determination. The samples of various compositions were prepared and heated between 1300 and 1700°C in air for equilibration. Under this temperature range, compound Mg<sub>6</sub>MnO<sub>8</sub> was not formed. Kasper and Prener [37] have reported the formation of Mg<sub>6</sub>MnO<sub>8</sub> at 1100°C at an oxygen pressure of 1 atm. Ghozza [38] conducted solid-solid sintering of the mixture of manganese oxide and magnesium oxide in air between 600 and 1000°C. The crystalline phases formed at the sintered temperature were analyzed by XRD technique. Many experimental samples however, were not fully equilibrated during the sintering.

Barkhatov *et al.* [39] determined the phase equilibria of Mg-Mn-O system in air ( $P_{O_2} = 0.21$  atm) between 800 and 1200°C using a high temperature XRD technique. According to the author, about 250 samples were prepared from the mixture of MgO and Mn<sub>2</sub>O<sub>3</sub> mixture and then equilibrated for 120-340 hours which is then quenched in water. On the basis of change in crystallographic parameters with composition, they drew the phase boundaries. However no real experimental data determined are presented in the reference. Recently, Silva [40] conduct the phase equilibria with In-situ XRD technique to accurately determine the cubic and tetragonal spinel area of the Mg-Mn-O system in air. In order to accelerate the equilibration, the samples of the system in air were pre-sintered at the temperature higher than the target temperature. Wartenberg and Prophet [41] with the help of heated microscope found out the solidus line between MgO and Mn<sub>3</sub>O<sub>4</sub> by equilibrating the samples in air upto 2500°C.

Oliviera and Brett [42] prepared the mixture of MgO and Mn<sub>2</sub>O<sub>3</sub> and held in TGA (Thermo Gravimetric Analysis) equipment under air atmosphere. The variations of the weight of the samples were recorded with changing of temperature from 1300 to 1600°C. Then the recorded data were converted to the isothermal ternary phase diagram of MgO-MnO-Mn<sub>2</sub>O<sub>3</sub> in air and can be seen in Figure 4.7. Their data shows the phase boundary between monoxide and cubic spinel phase, which can also be compared with other experimental data shown in Figure 4.6(b). Golikov *et al.* [43] determined the composition-oxygen partial pressure diagram of Mg-Mn-O system at 800°C, 900°C and 1000°C. Their samples equilibrated at given oxygen partial pressure were quenched and the stable phases were analyzed by XRD. Unfortunately, the details of experimental condition and composition were not given in the reference. The experimental phase diagrams are plotted in Figure 4.8.

All experimental data in Figure 4.6 to 4.8 are simultaneously considered in the optimization of the model parameters of spinel solution and monoxide solution. In the optimization, the most recent in-situ experimental data of Silva [40] are considered the most accurate data for the homogeneity range of cubic and tetragonal spinel solutions. Wattenberg and Prophet [41] experimental data were not considered in this study because their samples was getting evaporated at higher temperature and their experimental data for similar system Fe<sub>2</sub>O<sub>3</sub>-MgO were not consistent with well optimized thermodynamic modeling of Fe-Mg-O system by Jung *et al.* [44], who have reproduced other reliable experimental data quite well. The phase diagram

in Figure 4.6 is well reproduced by the present thermodynamic modeling. However, the isothermal phase diagram in Figure 4.7 is not well reproduced. The tie lines between cubic spinel and monoxide solution are well reproduced, but the boundaries of monoxide phase are not well reproduced. In fact, considering the solubility limit of  $Mn_2O_3$  in MnO in the Mn-O system, the isothermal  $-p_{O_2}$  in monoxide line shown in Figure 4.7 may be wrong.  $Mg_6MnO_8$  were adjusted to reproduce the peritectoid. The experimental data in general are well reproduced in Figure 4.6 to 4.8.

#### 4.4 Conclusions

Complete thermodynamic evaluation/optimization of experimental data for MgO-MnO-Mn<sub>2</sub>O<sub>3</sub> system was performed in this study. The optimized model can reproduce all reliable thermodynamic and structural data as well as the phase diagrams of the MgO-MnO-Mn<sub>2</sub>O<sub>3</sub> within experimental error limits. In particular, the spinel system in this system was described for the first time considering the site exchange reactions. For the spinel phase, no model parameters for interactions energies between cation on the same sublattice were needed. Proper use of thermodynamic model for each phase minimizes the number of model parameters required in the optimization and improves the extrapolation of binary and ternary parameters into multicomponent system.

The optimized model parameters can be readily used with general thermodynamic software, such as FactSage [1], to calculate phase equilibria and thermodynamic properties at any given set of conditions and to model various industrial and natural processes.

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## 4.6. Figures



Figure 4.1: Calculated phase diagram of the Mg-Mn-O at 1000 °C and 1 bar total pressure. Solid lines are the phase boundaries.





Figure 4.2: Activity of MgO and MnO in the MgO-MnO monoxide solution



Figure 4.3: Enthalpy of mixing of MgO-MnO monoxide solution



Figure 4.4: Optimized phase diagram for MgO-MnO system



Figure 4.5: Calculated cation distribution in MgMn<sub>2</sub>O<sub>4</sub> spinel



Figure 4.6: Calculated phase diagram of Mg-Mn-O at air with experimental data. (a) comparison with experimental data of Riboud et al. [36] and Ghozza et al. [38], and (b) comparison with experimental data of Barkhatov et al. [39], Silva [40], Wartenberg and Prophet [41] and Oliviera and Brett [42]. Here, C-Sp and T-Sp denotes cubic spinel and tetragonal spinel respectively.



Figure 4.7: Calculated MgO-MnO-Mn<sub>2</sub>O<sub>3</sub> ternary phase diagram in air with experimental data of Oliviera and Brett [42]. Here, C-Sp and Mono denotes cubic spinel and monoxide, respectively.





Figure 4.8: Calculated partial pressure  $(P_{O_2})$  - composition diagram for Mg-Mn-O system along with experimental data by Golikov et al. [43]: (a) 800°C (b) 900°C (c) 1000°C. Here, C-Sp and T-Sp denotes cubic spinel and tetragonal spinel respectively.

#### 5. Critical thermodynamic evaluation and optimization of the Ca-Mg-Mn-O system

#### **5.1 Introduction**

The CaO-MgO-MnO-Mn<sub>2</sub>O<sub>3</sub> is of great importance in metallurgy and geochemistry. Despite its importance, the phase equilibria in this system have not been well studied. Experimental study of the system is complicated by the strong dependence of the equilibria on the oxygen pressure and by the high melting temperature of the spinel phase. Therefore, critical assessment of the data is required in order to understand and model this system more accurately. The present study is a part of a complete database development of the CaO-Fe<sub>t</sub>O-SiO<sub>2</sub>-MgO-MnO-Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-CaF<sub>2</sub> system for application in the steel industries.

The main goal of the present study is to perform a complete review, critical assessment and optimization of thermodynamic properties of oxide phases in the Ca-Mg-Mn-O (CaO-MgO-MnO-Mn<sub>2</sub>O<sub>3</sub>) system. In the thermodynamic 'optimization' of a chemical system, all available thermodynamic and phase equilibrium data are simultaneously evaluated in order to obtain one set of model equations for the Gibbs energies of all phases as a functions of temperature and compositions. From these equations, all the phase diagrams and thermodynamic properties can be back calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagram, and phase diagram measurements can be used to deduce thermodynamic properties. Discrepancies in the available data can often be resolved, and interpolation and extrapolations can be made in a thermodynamically correct manner.

In the present study, the thermodynamic properties of the Ca-Mg-Mn-O system were optimized on the basis of the previously optimization of the CaO-MgO [1], CaO-MnO [1] and MgO-MnO [2] system whose optimized binary model parameters are used without any change. They are listed in Table 5.1. Phase diagrams calculated from the optimized parameters are shown in Figure 5.1-5.3. Overall system optimized in this study has been divided into two sections: A: CaO-MnO-Mn<sub>2</sub>O<sub>3</sub> and B: Ca-Mg-Mn-O in reducing conditions. All calculations in the present study were performed with the FactSage [3] software.

	<u>CaO – MgO system</u>	<u>CaO – MnO system</u>	MgO – MnO system
Monoxide	$q_{CaO,MgO}^{11} = 118110 - 18.410T$	$q_{CaO,MnO}^{11} = 15770$	$q_{MgO,MnO}^{11} = 11344.257$
	$q_{CaO,MgO}^{21} = 31380$		$q_{MgO,MnO}^{41} = 2976.457$
Liquid	$\Delta g_{CaO-MgO}^{00} = 45329$	$\Delta g_{CaO-MnO}^{00} = 27006$	$\Delta g_{MgO-MnO}^{00} = 4183.9407$
	$\Delta g_{CaO-MgO}^{10} = -30583$		

Table 5.1: Already optimized model parameters for CaO-MgO [1], CaO-MnO [1] and MgO-MnO [2]

#### A. CaO-MnO-Mn<sub>2</sub>O<sub>3</sub> System

#### 5.2 Phases and thermodynamic models

The following solution phases are found in the CaO-MnO-Mn<sub>2</sub>O<sub>3</sub> system:

Slag (molten oxide phase): CaO-MnO-MnO<sub>1.5</sub>

Monoxide (periclase): CaO-MnO-MnO<sub>1.5</sub>

Cubic spinel (encompassing cubic-Ca $Mn_2O_4$ ,  $Mn_3O_4$ ): Taken as stoichiometric compound which is built from the existing CaO and  $Mn_2O_3$  from FToxide database.

Tetragonal spinel (encompassing tetragonal-Mn<sub>3</sub>O<sub>4</sub>): Taken as stoichiometric compound which has no solubility towards CaO.

Stochiometric Compounds:  $Ca_2MnO_4$ ,  $Ca_3Mn_2O_7$ ,  $Ca_4Mn_3O_{10}$ ,  $CaMnO_3$ ,  $Ca_2Mn_3O_8$ ,  $CaMn_3O_6$ ,  $CaMn_4O_8$  and  $CaMn_7O_{12}$ : built from the existing CaO, MnO, MnO<sub>2</sub> and Mn<sub>2</sub>O<sub>3</sub> from FToxide database.

#### 5.2.1. Molten oxide (slag)

For the slag (molten oxide) phase, the Modified Quasichemical Model [4-7] in the pair approximation (MQM) was used. In this, short-range ordering (SRO) is taken into account by considering second-nearest-neighbor (SNN) pair exchange reactions. For example, for the CaO-MnO-MnO<sub>1.5</sub> slag these reactions are:

$$(Ca^{2+}-Ca^{2+}) + (Mn^{2+}-Mn^{2+}) = 2(Ca^{2+}-Mn^{2+}) \qquad \Delta g_{Ca0,Mn0}$$
(5.1)

$$(Mn^{2+}-Mn^{2+}) + (Mn^{3+}-Mn^{3+}) = 2(Mn^{2+}-Mn^{3+}) \qquad \Delta g_{Mn0,Mn_20_3}$$
(5.2)

$$(Ca2+-Ca2+) + (Mn3+-Mn3+) = 2(Ca2+-Mn3+) \qquad \Delta g_{Ca0,Mn_20_3}$$
(5.3)

where (A–B) represents a second-nearest-neighbour A-B pair. Gibbs energies of these above reaction  $\Delta g_{AB}$  ( $\Delta g_{CaO,MnO}$ ,  $\Delta g_{MnO,Mn_2O_3}$  and  $\Delta g_{CaO,Mn_2O_3}$ ) are the parameters of the model which may be expanded as empirical functions of composition. The Gibbs energy of the solution is given in section 2.15.

The component of the slag is taken as CaO-MnO-MnO<sub>1.5</sub>. Although Mn can have higher oxidation states, only the divalent and trivalent oxidation states, which predominate at oxygen partial pressures less than 1.0 bar, are considered in the present study. The components are written as  $MnO_{1.5}$  rather than  $Mn_2O_3$  simply to show that  $Mn^{3+}$  ions are distributed as independent particles between oxygen in the liquid solution and not as ion pairs.

The binary sub-systems MnO-MnO<sub>1.5</sub> [8] and CaO-MnO [1] has already been critically evaluated and optimized and the optimized model parameters are used as the basis of the present study. All second-nearest-neighbor "coordination numbers" of Ca<sup>2+</sup>, Mn<sup>2+</sup>, Mn<sup>3+</sup> used in the present model for the slag are the same as in previous studies. The binary sub-system CaO-MnO<sub>1.5</sub> has been optimized in the present study which is able to reproduce the available experimental studies. It has been listed in Table 5.2.

The properties of the ternary slag solution were calculated from the binary parameters using a symmetric "Kohler-like" approximation [9] which assumes that the energy  $\Delta g_{AB}$  of reaction (5.1) remains constant as MnO<sub>1.5</sub> is added to an CaO-MnO solution at constant CaO/MnO ratio, and similarly for addition of CaO to MnO-MnO1.5 for reaction (5.2) and of MnO to CaO-MnO1.5 for reaction (5.3). No ternary interaction parameters are needed for CaO-MnO-MnO<sub>1.5</sub> system.

#### 5.2.2. Monoxide solution

Monoxide solution has rock-salt type structure. It was modeled as a simple random mixture of all cations,  $Ca^{2+}$ ,  $Mn^{2+}$ , and  $Mn^{3+}$  ions on cation sites using a simple polynomial excess Gibbs

energy terms [9]. It is assumed that cation vacancies remain associated with  $Mn^{3+}$  to maintain electrical neutrality and so do not contribute to the configurational entropy. The Gibbs energy per mole of the solution is expressed as follow:

$$G_{m} = \sum_{i} X_{i}G_{i}^{o} + RT \sum_{i} X_{i}lnX_{i} + \sum_{i} \sum_{j} X_{i}X_{j}(\frac{X_{i}}{X_{i} + X_{j}})^{m}(\frac{X_{j}}{X_{i} + X_{j}})^{n}q_{ij}^{mn} + g_{ternary}^{ex}$$
(5.8)

where  $G_i^o$  is the Gibbs energy of component like CaO, MnO and MnO<sub>1.5</sub> and X<sub>i</sub> is mole fraction of component. The monoxide solution has been optimized without any binary parameter  $q_{ij}^{mn}$  of CaO-MnO<sub>1.5</sub> system.  $q_{ij}^{mn}$  of MnO-MnO<sub>1.5</sub> [8] and CaO-MnO[1] was optimized previously. The properties of ternary monoxide CaO-MnO-MnO<sub>1.5</sub> were calculated from the binary parameters with asymmetric 'Kohler-like' approximation [9] with MnO<sub>1.5</sub> as the 'asymmetric component'. No ternary excess parameter  $g_{ternary}^{ex}$  was used in the present study.

#### 5.2.3. Stochiometric spinel – CaMn<sub>2</sub>O<sub>4</sub>

The spinel  $CaMn_2O_4$  is optimized by assuming to be a stoichiometric compound. Its heat capacity was assumed to be the weighted sum of the heat capacities of CaO and  $Mn_2O_3$ . Usually the heat capacity,  $C_p$ , of a compound may be separated into a lattice part and a magnetic part in thermodynamic modeling.

$$C_{p} (T) = C_{p}^{\text{lattice}} (T) + C_{p}^{\text{magnetic}} (T)$$
(5.9)

When a compound exhibits ferro- or antiferro-magnetism, the magnetic part is non-zero. In this case,  $C_p^{magnetic}$  (T) is zero.

In the present model,  $C_p^{lattice}$  (T) is assumed to be independent of cation distribution i.e.

$$C_p(T) = C_p^{\text{lattice}}(T) \text{ of normal spinel} = C_p^{\text{lattice}}(T) \text{ of inverse spinel}$$
 (5.10)

With this assumption,  $C_p$  of a hypothetical pure normal compound end-member ( $A^{2+}$ )  $[B^{3+}]_2 O_4$  is taken to be equal to the measured  $C_p$  of the real (mixed) spinel. The value is listed in Table 5.2.

#### **5.2.4. Stoichiometric compound**

 $Ca_2MnO_4$ ,  $Ca_3Mn_2O_7$ ,  $Ca_4Mn_3O_{10}$ ,  $CaMnO_3$ ,  $Ca_2Mn_3O_8$ ,  $CaMn_3O_6$ ,  $CaMn_4O_8$  and  $CaMn_7O_{12}$  are stable within this system, therefore taken as stoichiometric compound.

#### 5.3. Critical evaluation/optimization of experimental data

The experimental data below the liquidus temperature are mainly classified into two groups: thermodynamic data such as enthalpy data and heat capacity data for stoichiometric compounds and phase equilibrium data containing slag, monoxide, cubic spinel (stoichiometric) and all the stoichiometric compounds. During the optimization, all the stoichiometric compounds having thermodynamic data are reproduce first within their experimental error limits. After that, optimization of monoxide and slag are carried out with further slight adjustments of the model parameters for stoichiometric compounds in order to reproduce phase equilibrium data as well as thermodynamic data of stoichiometric compounds. Finally, low temperature stoichiometric compound are optimized to reproduce phase equilibrium data.

Few experimental measurements have been performed for the CaO- $Mn_2O_3$  system. The results of the optimization of the thermodynamic data for stoichiometric compounds are presented first, followed by the phase equilibria for CaO- $Mn_2O_3$  system.

#### 5.3.1. Thermodynamic data

#### CaMnO<sub>3</sub>

According to Riboud and Muan [10], the perovskite-like phase of CaMnO<sub>3</sub> has a solid solution ranging from 20 to 36.7 mol% Mn<sub>2</sub>O<sub>3</sub>. He also states that increase in manganese oxide though the solid solution changes the structure from the tetragonal to distorted cubic. There are, however, three additional phases report in different literatures within this compositional range:  $Ca_2MnO_4$  [11],  $Ca_3Mn_2O_7$  [11], [12] and  $Ca_4Mn_3O_{10}$  [12] which are all perovskite related phases. They all have tetragonal unit cells and their x-ray diffraction patterns are similar to each other as well as to the perovskite CaMnO<sub>3</sub>. So, it seems reasonable to assume that Riboud and Muan [10] mistook the presence of CaMnO<sub>3</sub> solid solution in place of stoichiometric compounds (Ca<sub>2</sub>MnO<sub>4</sub>, Ca<sub>3</sub>Mn<sub>2</sub>O<sub>7</sub> and Ca<sub>4</sub>Mn<sub>3</sub>O<sub>10</sub>), when doing a systematic study for Ca-Mn-O system between 1000 - 1600°C. It has been shown in Figure 5.7. According to Poeppelmeier *et al* [13], the double oxide CaMnO<sub>3</sub> has an orthorhombically distorted perovskite structure (sp gr. Pnma), with four CaMnO<sub>3</sub> formula units per unit cell and its lattice parameters are a = 0.5279 nm, b = 0.7488 nm, and c = 0.5264 nm. As temperature is increased, the stoichiometric calcium manganite, CaMnO<sub>3</sub> having cubic perovskite structure starts deviating from ideal oxygen stoichiometry leading to tetragonal and then orthorhombic lattice distortion which are responsible for CaMnO<sub>3-δ</sub> polymorphism [14, 15].

The CaMnO<sub>3</sub> was prepared by applying the Neumann-Kopp rule from its equilibrium phases CaO and MnO<sub>2</sub>. The heat capacity was modified and fitted from 200 to melting point using one heat capacity functions which reproduces the experimental heat capacity data from 0 K to 600 K as reported by Bakken et al. [16] shown in Figure 5.4. Magnetic disordering is clearly shown at heat capacity measurements at  $T_N = 123$ K [17,18]. The S<sub>298</sub> value of 97.82 Jmol<sup>-1</sup>K<sup>-1</sup> for CaMnO<sub>3</sub> was obtained by integrating the low temperature heat capacity data measured by Bakken et al. [16] and is kept within experimental error limits for current optimization.

Rormark *et al.* [14] measured the total heat capacity from 350 to 630 K by high temperature adiabatic calorimeter. The oxygen stoichiometry of the samples are determined by thermo gravimetric analysis and also confirmed by iodometric titration. Bakken *et al.* [16] measure heat capacities from 10 to 600K by using low temperature and high temperature adiabatic calorimetry. Neumeier *et al.* [17] also measured the heat capacity of CaMnO<sub>3</sub> from 100K to 150K to find the magnetic transition at 124.2 K. Moritomo *et al.* [18] uses quantum design PPMS machine to measure the specific heat of CaMnO<sub>3</sub> from 0 to 200K.

Rormark et al. [14] found out two different enthalpy of oxidation for CaMnO<sub>3</sub> which has been synthesized differently. One is by ceramic method (-  $81.3 \pm 2.8$  kJ/mol) another is by EDTA precursor method (-  $89 \pm 1.6$  kJ/mol) which is in accordance with our optimized result presented in Table 2. High temperature adiabatic calorimeter was used to measure that value. The optimized enthalpy of formation value for CaMnO<sub>3</sub> formed by 1CaO + 0.5 Mn<sub>2</sub>O<sub>3</sub> + 0.5O<sub>2</sub> = CaMnO<sub>3</sub> at 993K is -118.43 kJ/mol which is within experimental error limit (-125.4 ± 7.6) measured by Rormark *et al.* [19].

#### Stoichiometric spinel - CaMn<sub>2</sub>O<sub>4</sub>

According to Riboud *et al.* [10], CaMn<sub>2</sub>O<sub>4</sub> has a solid solution towards Mn<sub>2</sub>O<sub>3</sub> rich side from 50 to 55 mol% Mn<sub>2</sub>O<sub>3</sub> in CaO. The CaMn<sub>2</sub>O<sub>4</sub> compound was created by the algebraic addition of one CaO and Mn<sub>2</sub>O<sub>3</sub> (Neumann-Kopp rule). The low temperature (from 0 to 305K) heat capacity measurement done by White et al. [20] which used thermal relaxation technique in a vibrating sample magnetometer were fitted without any modifications shown in Figure 5.5. A kink shown in the experimental heat capacity measurements done at 217.5  $\pm$  0.6 K shows the Neel temperature i.e. antiferromagnetic to paramagnetic. The S<sub>298</sub> value for CaMn<sub>2</sub>O<sub>4</sub> was obtained similarly by integrating the low temperature heat capacity data measured by White et al. [20] which was found to be 114.87 Jmol<sup>-1</sup>K<sup>-1</sup>. To reproduce the phase diagram data, the S<sub>298</sub> was kept within experimental error limits.

### Ca<sub>2</sub>MnO<sub>4</sub>

The compound  $Ca_2MnO_4$  was formed by algebraic mixing of the equilibrium phases of CaO and  $Mn_2O_3$ . Rormark *et al.* [16] measured enthalpy of oxidation of  $Ca_2MnO_4$  synthesized by ceramic method by in situ oxidation in a high temperature adiabatic calorimeter. The measured value is given in Table 5.2 which is more or less equal to the calculated value

#### CaMn<sub>7</sub>O<sub>12</sub>

The calculated heat capacity data of  $CaMn_7O_{12}$  are shown in Figure 5.6 along with the experimental data from Zhang *et al.* [21] and Volkova *et al.* [22]. Zhang *et al.* [21] uses quantum design PPMS machine to measure the specific heat of  $CaMn_7O_{12}$  from 23 to 112K. The specific heat was also measured by Volkova *et al.* [22] with Termis quasiadiabatic relaxation calorimetry over the range 5-250K.

No thermodynamic data was available for the other compounds  $Ca_3Mn_2O_7$ ,  $Ca_4Mn_3O_{10}$ ,  $Ca_2Mn_3O_8$ ,  $CaMn_3O_6$  and  $CaMn_4O_8$ , but their presence is seen by different authors Horowitz and Longo [23] and Tanida and Kitamura [24] which are well reproduced in the phase diagram in Figure 5.7.

## Table 5.2. Optimized model parameters of solutions in the CaO-Mn<sub>2</sub>O<sub>3</sub> system

## Liquid Phase: CaO-MnO-MnO<sub>1.5</sub>

 $\Delta g^{01}_{CaO\text{-}Mn_2O_3} = \text{-}150624$ 

## **Solid Phases**

$\Delta \mathrm{H_{f}^{\circ}}_{298}(\mathrm{kJ\ mol}^{-1})$			
Compound	Optimized	Experimental	Reference
$Ca_2MnO_4$	- 110.82	$-110.8 \pm 3$	[16]
CaMnO <sub>3</sub>	- 83.71	$-81.3 \pm 2.8$	[16]
		$-89 \pm 1.6$	[16]

## S<sup>°</sup><sub>298</sub> (J mol<sup>-1</sup> K<sup>-1</sup>)

Compound	Optimized	Experimental	Reference
Ca <sub>2</sub> MnO <sub>4</sub>	132.9	-	196.5(mixer)
$Ca_3Mn_2O_7$	236.2	-	355(mixer)
$Ca_4Mn_3O_{10}$	339.5	-	514(mixer)
CaMnO <sub>3</sub>	101.75	97.82	[17]
$Ca_2Mn_3O_8$	333.5	-	438(mixer)
CaMn <sub>2</sub> O <sub>4</sub>	111	114.87	[20]
CaMn <sub>3</sub> O <sub>6</sub>	201.319	-	277(mixer)
CaMn <sub>4</sub> O <sub>8</sub>	291.57	-	398.49(mixer)
CaMn <sub>7</sub> O <sub>12</sub>	329.6	-	515(mixer)

## $C_p \left(J \ mol^{\text{--}1} \ K^{\text{--}1}\right)$

Compound	Optimized	Reference
Ca <sub>2</sub> MnO <sub>4</sub>	$243.862 - 1702.423 T^{-0.5} + 3246.06 T^{-1} - 2294291.965 T^{-2} +$	$C_p = C_p(2CaO) + $
298-2500 K	205957575.728T <sup>-3</sup>	$C_p(1MnO_2)$

Ca <sub>3</sub> Mn <sub>2</sub> O <sub>7</sub>	$428.933 - 3270.942T^{-0.5} + 6492.112T^{-1} - 3441437.947T^{-2}$	$C_p = C_p(3CaO) + $
298-2500 K	$+ 308936363.592 T^{-3}$	C <sub>p</sub> (2MnO <sub>2</sub> )
Ca <sub>4</sub> Mn <sub>3</sub> O <sub>10</sub>	$614.005 - 4839.461 \mathrm{T}^{-0.5} + 9738.168 \mathrm{T}^{-2} - 4588583.929 \mathrm{T}^{-2}$	$C_p = C_p(4CaO) +$
298-2500K	$+ 411915151.456T^{-3}$	C <sub>p</sub> (3MnO <sub>2</sub> )
CaMnO <sub>3</sub>	$185.0711 - 1568.519 T^{-0.5} + 3246.05597843474 T^{-1} -$	$C_p = C_p(1CaO) +$
298-2500K	$1147145.982T^{-2} + 202978787.864T^{-3}$	$C_p(1MnO_2) + 1E8T^{-3}$
Ca <sub>2</sub> Mn <sub>3</sub> O <sub>8</sub>	$479.9 - 4571.653 T^{-0.5} + 9738.168 T^{-1} - 2294291.965 T^{-2} +$	$C_p = C_p(2CaO) +$
298-2500K	205957575.728T <sup>-3</sup>	$C_p(3MnO_2) -$
		16.52
CaMn <sub>2</sub> O <sub>4</sub>	$192.291 + 0.012T^{1} - 133.904T^{-0.5} - 10000T^{-1} - $	$C_p = C_p(CaO) +$
298-2000K	$1433450.744T^{-2} + 102978787.864T^{-3}$	$C_p(Mn_2O_3)$
CaMn <sub>3</sub> O <sub>6</sub>	$313.72 + 0.012T^{1} - 1568.520T^{-0.5} - 6753.944T^{-1} - $	$C_p = C_p(CaO) +$
298-2000K	$1433450.744T^{-2} + 102978787.864T^{-3}$	$C_p(Mn_2O_3) +$
		C <sub>p</sub> (MnO <sub>2</sub> ) - 4.85
CaMn <sub>4</sub> O <sub>8</sub>	$435.2 + 0.012T^{1} - 3003.134T^{-0.5} - 3507.888T^{-1} - $	$C_p = C_p(CaO) +$
298-2000K	$1433450.744T^{-2} + 102978787.864T^{-3}$	$C_p(Mn_2O_3) +$
		C <sub>p</sub> (2MnO <sub>2</sub> ) - 9.6
CaMn <sub>7</sub> O <sub>12</sub>	$585.571 + 0.036 T^1 - 1568.519 T^{-0.5} - 26753.944 T^{-1} - $	$C_p = C_p(CaO) +$
298-2000K	$2006060.267 T^{-2} + 102978787.864 T^{-3}$	$C_p(3Mn_2O_3) +$
		$C_p(1MnO_2)$

#### 5.3.2. Phase diagram data

The studies on the Ca-Mn-O system have reported the existence of the following phases: Slag, Monoxide, Cubic Spinel (Stoichiometric), and  $Ca_2MnO_4$ ,  $Ca_3Mn_2O_7$ ,  $Ca_4Mn_3O_{10}$ ,  $CaMnO_3$ ,  $Ca_2Mn_3O_8$ ,  $CaMn_3O_6$ ,  $CaMn_4O_8$  and  $CaMn_7O_{12}$  as stoichiometric compound.

Figures 5.7 show the phase diagram of the Ca-Mn-O system calculated from the optimized model parameters. Each phase is modeled with the help of one set of model parameters which is able to reproduce all reliable experimental data simultaneously. The compound database was

built from the existing CaO,  $MnO_2$  and  $Mn_2O_3$  from FToxide database in FactSage<sup>TM</sup> [3]. Calculated decomposition temperatures of each stoichiometric compound are listed in Table 3 along with the experimental measured temperature.

#### 5.3.2.1. Phase diagram at air

Figure 5.7(a) shows the calculated phase diagram of the Ca-Mn-O system at air along with the experimental data from the Riboud and Muan [10] and Toussaint [25] which has been optimized quite well. Riboud and Muan [10] did a systematic study in the Ca-Mn-O system using x-ray diffraction (XRD) and microstructural examination of CaCO<sub>3</sub> + MnO<sub>2</sub> mixtures sintered in platinum or 80Pt20Rh containers in air at different temperatures between 1000 and 1600°C. Their phase diagram has three isobarically univariant states: a) CaO, CaMnO<sub>3</sub> and liquid are in equilibrium at 34.75 mol% Mn<sub>2</sub>O<sub>3</sub> (CaO – Mn<sub>2</sub>O<sub>3</sub> phase diagram) at 1588 ± 10°C b) CaMnO<sub>3</sub>, CaMn<sub>2</sub>O<sub>4</sub> and liquid are in equilibrium at 51.58 mol% Mn<sub>2</sub>O<sub>3</sub> at 1455 ± 5°C c) CaMn<sub>2</sub>O<sub>4</sub>, spinel and liquid are in equilibrium at 61.8 mol% Mn<sub>2</sub>O<sub>3</sub> at 1439 ± 5°C. As explained earlier, they mistook the presence of CaMnO<sub>3</sub> solid solution in place of stoichiometric compounds Ca<sub>2</sub>MnO<sub>4</sub>, Ca<sub>3</sub>Mn<sub>2</sub>O<sub>7</sub> and Ca<sub>4</sub>Mn<sub>3</sub>O<sub>10</sub> when doing XRD because they all have perovskite-like phase (see figure 5.7(a)). Toussaint [25] formed mixtures of desired composition and then heats it up to a particular temperature and then quenched. The quenched samples are then analyzed by complexometric titrations and x-rays to find the phases present.

Another set of experimental data [23, 24] for phase equilibria within Ca-Mn-O at air are shown in Figure 5.7(b) along with the optimized calculated phase diagram. Horowitz and Longo [23] did not use ceramic processing route but developed a new procedure which involves formation of solid solution carbonate (Ca<sub>1-x</sub>Mn<sub>x</sub>CO3) precipitation from an aqueous solution of calcium and magnesium nitrates. This helps in achieving complete solid solution at shortest amount of time and lowest possible temperature. These solid solution precursors were reacted to mixed metal oxides by firing them in recrystallized alumina boats at temperature from 800 to 1000°C with 25°C increments from 33 mol% Mn<sub>2</sub>O<sub>3</sub> to 100 mol% Mn<sub>2</sub>O<sub>3</sub> in both air and oxygen atmosphere(  $10^5$  Pa). Careful XRD and TGA are done to identify the phases present and oxygen content of all phases. The new low temperature crystalline phases with their decomposition temperature that are found out from these results are CaMn<sub>7</sub>O<sub>12</sub>, Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, CaMn<sub>3</sub>O<sub>6</sub>, and CaMn<sub>4</sub>O<sub>8</sub>. Tanida and Kitamura [24] in 1980 took CaCO<sub>3</sub> and MnO<sub>2</sub> as starting material and sintered in a Pt crucible for 12 hours in air at two different temperatures: 1100 and 1400 °C for different compositions. High temperature XRD are done to find out the phases present.

#### 5.3.2.2. Phase Diagram at pure oxygen

As described earlier, Horowitz and Long [23] found out new low temperature crystalline phases along with their decomposition temperature at air and at pure oxygen (1 atm). Their data at pure oxygen (1 atm) along with the calculated data are shown in Figure 5.8.

#### B. Ca-Mg-Mn-O System

#### 5.4 Under reducing conditions

For Ca-Mg-Mn-O oxide system, very few experiments are done within this oxide system. The calculated phase diagram for CaO-MgO-MnO along with the experimental data from Woermann and Muan is shown in Figure 5.9. Woermann and Muan [26] prepared mixtures of desired composition within the ternary system CaO-MgO-MnO which were held at 1500°C under reducing conditions (10<sup>-9</sup> atm.) for sufficient length of time(1-5 days) for equilibrium to be attained. The samples were then quenched to room temperature for phase identification by microscopic and X-ray examination.

In this, the optimized model parameters for binary sub-system were used to optimize ternary experimental data without using any ternary model parameters for monoxide solution. That is, the sub-binary systems MgO-MnO, CaO-MgO, CaO-MnO were treated as ideal solutions for both monoxide solution, and no ternary model parameter were used. The properties of ternary slag solution were calculated using a symmetric "Kohler-like" [9] approximation.

#### 5.5. Conclusion

Complete thermodynamic evaluation/optimization of experimental data for CaO-MnO-Mn<sub>2</sub>O<sub>3</sub> system is performed in this study. The optimized model can reproduce all reliable thermodynamic and structural data as well as the phase diagrams of the CaO-MnO-Mn<sub>2</sub>O3 within experimental error limits. The spinel phase is considered as a stoichiometric compound. Many unexplored phase diagrams for the Ca-Mn-O system are predicated by the thermodynamic models with the optimized parameters. No ternary model parameters were required. Proper use

of thermodynamic model for each phase minimizes the number of model parameters required in the optimization and improves the extrapolation of binary and ternary parameters into multicomponent system.

The optimized model parameters can be readily used with general thermodynamic software, such as FactSage [3], to calculate phase equilibria and thermodynamic properties at any given set of conditions and to model various industrial and natural processes.

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Figure 5.1: Calculated CaO-MgO phase diagram by Wu et al. [1]



Figure 5.2: Calculated CaO-MnO phase diagram by Wu et al. [1]



Figure 5.3: Calculated MgO-MnO phase diagram in the previous chapter [2]



Figure 5.4: Calculated heat capacity of CaMnO<sub>3</sub> along with the experimental data [14, 16-18]



Figure 5.5: Calculated heat capacity of CaMn<sub>2</sub>O<sub>4</sub> along with the experimental data [20]



Figure 5.6: Calculated heat capacity of CaMn<sub>7</sub>O<sub>12</sub> along with the experimental data [21-22]


Figure 5.7: Optimized phase diagram of CaO- $Mn_2O_3$  at air compared with experimental data (**a**) compared with experimental data of Riboud and Muan[10] and Toussaint[25], (**b**) compared with experimental data of Horowitz and Longo [23] and Tanida and Kitamura [24]. Here, C-Sp and T-Sp denotes cubic spinel and tetragonal spinel respectively.



Figure 5.8: Optimized phase diagram of CaO- $Mn_2O_3$  at  $p_{O_2} = 1$  atm compared with experimental data from Horowitz and Longo [23]. Here, C-Sp and T-Sp denotes cubic spinel and tetragonal spinel respectively.



Figure 5.9: Optimized CaO-MgO-MnO phase diagram showing isothermal line at  $1500^{\circ}$ C at  $10^{-9}$  atm along with the experimental data from Woermann and Muan [26]

## 6. Conclusions

All the thermodynamic properties and phase diagram of MgO-MnO, MgO-Mn<sub>2</sub>O<sub>3</sub> and CaO- $Mn_2O_3$  systems were critically evaluated and optimized in the present study. As a result one set of optimized model parameters representing the Gibbs energies of all the phases in these binary and ternary systems was obtained.

In the thermodynamic modeling, the Modified Quasichemcial Model (MQM) taking into account a short-range ordering in slag was used to describe the molten oxide. For modeling the  $MgMn_2O_4-Mn_3O_4$  spinel, two-sublattice model in the framework of the Compound Energy Formalism was employed which reproduces all thermodynamic, structural and phase equilibria data. All the reliable experimental data were reproduced within experimental error limits.

These optimized model parameters in conjugation with the existing database in the FactSage will help in the calculation of multicomponent phase diagrams, better understanding of industrial process and help in predicting many unexplored phase diagrams at different conditions.