Thermodynamic Modeling of MgO-P2O5, MnO-P2O5 and CaO-MgO-P2O5 Systems

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DEDICATION

I would like to dedicate this thesis to my grandmother Irene Carmona, for this document is one of the many fruits borne from a seed planted long ago by her, at the cost of great personal sacrifice. I would also like to dedicate this thesis to my mother Sara Curiel, whose sacrifices, work, dedication, resiliency and unflinching vision over the last three decades made possible my reaping the benefits of a good education.

Thank you both,

Gabriel

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ABSTRACT

As part of a sustained effort to model and simulate the thermodynamic behavior of steelmaking slag, binary and ternary phase diagram systems have been modeled using the CALPHAD (CALculation of PHAse Diagrams) approach. The understanding, modeling and thermodynamic simulation of oxide systems including phosphorus oxide are of special importance to the steelmaking industry given requirements for steels with ever lower phosphorus contents while facing the processing of ores with increasing phosphorus content.

In this project, two binary systems (MgO-P₂O₅ and MnO-P₂O₅) and one ternary system (CaO-MgO-P₂O₅) were modeled to extend the oxide database of the Factsage thermodynamic simulation software package. This present study is part of a broader effort conducted to develop a comprehensive thermodynamic database for the CaO-MgO-MnO-FeO-Fe₂O₃-Al₂O₃-Na₂O-P₂O₅ / Fe _{Liq.} system and allow the thermodynamic simulation of steelmaking processes such as dephosphorization.

All available experimental data in the literature were critically assessed and a set of thermodynamic model parameters were developed to simulate reliably the experimental results within experimental error limits. The properties of liquid oxides and solid P_2O_5 compounds were described by thermodynamic models and standard Gibbs energy functions.

The thermodynamic property of the liquid solution (or slag) were described using the Modified Quasi-Chemical Model (MQM) developed by Pelton et. al. (2000). This model allows to simulate short range ordering (SRO). Thermodynamic properties of solid solution phases are described using the Compound Energy Formalism (CEF) by Hillert (2000) which considers the crystal structure of each solid solution.

ABRÉGÉ

Dans le cadre des efforts soutenus pour modéliser le comportement thermodynamique des scories sidérurgiques, des systèmes binaires et ternaires furent modélisés en utilisant l'approche CALPHAD. Les systèmes incluant les oxydes de phosphore sont d'une importance particulière pour l'industrie sidérurgique qui doit satisfaire des demandes pour de l'acier avec des niveaux de phosphore plus bas tout en faisant face à l'exploitation de gisements aux teneures en phosphore chaque fois plus élevés.

Dans ce projet, deux systèmes binaires (MgO-P₂O₅ et MnO-P₂O₅) et un système ternaire (CaO-MgO-P₂O₅) furent modélisés pour développer la base de données du logiciel de simulation thermodynamique Factsage. Cette étude se cadre dans des efforts de développement d'une base de données du système CaO-MgO-MnO-FeO-Fe₂O₃-Al₂O₃-Na₂O-P₂O₅ / Fe_{Liq.} qui pourrais permettre la simulation de procédés sidérurgiques tels que la déphosphorization de l'acier.

Toutes les données expérimentales dans la littérature furent évalués de manière critique et optimisées pour obtenir des paramètres de modèles thermodynamiques pouvant reproduire les données expérimentales à l'intérieur des marges d'erreurs expérimentales. Les propriétés thermodynamiques des oxides liquides et des composantes solides contenant du P₂O₅ furent décrites en utilisant des modèles thermodynamiques ainsi que des fonctions standards d'énergie de Gibbs.

Les propriétés thermodynamiques de la solution liquide furent décrites en utilisant le Modèle Quasichimique Modifié (MQM) développé par Pelton et. al. (2000). Ce modèle tiens compte de l'ordre à courte portée des solutions liquides. Les propriétés thermodynamiques des solutions solides furent décrites par le Formalisme Énergétique des Composés (CEF) par Hillert (2000) qui tiens compte de la structure cristalline de chaque solution.

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1. Introduction

Along with sulfur, phosphorus is a well-known detrimental impurity in steel. Phosphorus typically originates in iron ore but may also be introduced by metallurgical coke or in alloys such as ferromanganese. During ironmaking, in blast furnaces, phosphorus oxide is favorably reduced from its oxidized form to a stable elemental form in the hot metal (liquid iron) where its solubility is high (typically over 1,500 ppm). However, the solubility of phosphorus in iron diminishes during solidification and is pushed towards grain boundaries where it will become detrimental to the toughness of steel, its weldability and make it unsuitable for low temperature applications. Increasing demands in the purities of steel are also coinciding with the ever increasing exploitation of higher phosphorus iron ore resources across the world. The improvement of dephosphorization (or phosphorus removal) methods during steelmaking is thus of great importance and relies on an important and growing body of research.

Crucial in dephosphorization are the relationships of phosphorus with the major slag components such as CaO, AI_2O_3 , Fe_tO and SiO_2 but also the interactions from other oxides such as MgO, MnO, Cr_2O_3 , P_2O_5 etc., amongst themselves.

The relationship of phosphorus between molten metal and multi-component slag (with four oxides or more) has been studied in the past. These works provide observations of the effects of less prevalent slag oxides (such as MgO or MnO) on factors such as the partition ratio of phosphorus between slag and molten metal for given temperature ranges but the use which can be made from these observations is limited since they cannot reproduce exactly the processing conditions of individual steelmaking operations. The advantage of thermodynamic simulation is thus that it offers the possibility of generating thermodynamic predictions tailored to specific operator conditions. These simulations, despite being equilibrium condition simulations, are nevertheless of great importance in the iron, steel and other pyrometallurgical industries given that high processing temperatures often allow the approximation to equilibrium

conditions. They also represent the essential building blocks for the new generation of dynamic simulation tools being developed which combine thermodynamic simulations with fluid flow modeling.

The development of thermodynamic databases containing sufficient model parameters to accurately reproduce operating conditions via Gibbs energy minimization routines (executed by software such as the factsage thermodynamic simulation package) is thus of great industrial importance. At very high temperatures, the kinetics of chemical reaction are often fast enough that results of thermodynamic equilibrium simulations may be applied to the understanding of metallurgical processes. Used in research, in industrial settings and in engineering design, thermodynamic simulations can thus predict equilibrium conditions and identify trends while minimizing the expenditures of resources associated with test programs or campaigns.

It must be noted that the reliability of these simulations is entirely dependent on the suitability of the thermodynamic models applied as well as on the quality of the optimization work. Model parameters must consistently and reliably allow reproducing not only the experimental data available in the literature against which they were optimized in the first place before being added to the databases of Gibbs energy minimization routines software such as Factsage but also, to a certain degree, be able to interpolate the thermodynamic properties which have not yet been tested.

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1.1. Scope of Study

The current work is part of a broader effort sponsored by the steelmaking industry which aims to improve the reliability of thermodynamic simulations by extending the thermodynamic database used in simulating oxide systems commonly found in steelmaking slag. The principal aim of this effort is to be able to reliably and accurately simulate the CaO-FetO-SiO₂-Al₂O₃-MgO-MnO_x-Na₂O-P₂O₅-.../ Fe_{Lig.} system at varying temperatures and compositions and hence allow for the simulation of important steelmaking processes such as dephosphorization. To achieve this, each binary and ternary relationship within this system must be individually modeled before they are used to simulate the higher order systems such as steelmaking slag. In other words, the CaO-MgO, CaO-SiO₂, MgO-SiO₂, CaO-SiO₂ etc. binary systems and all other possible binary combinations must each be modeled by a set of parameters before the higher order system steelmaking slag is reliably simulated. The same is true for ternary systems within steelmaking slag in that every ternary system must also be modeled before the steelmaking slag is reliably simulated.

In this study, the MgO-P₂O₅, MnO-P₂O₅ and the CaO-MgO-P₂O₅ systems are modeled. The present work thus only represents a few pieces of a larger puzzle that is partially completed and being completed in parallel by others. Since they include P₂O₅, these systems are of special importance for the simulation of the dephosphorization process. Besides steelmaking, these systems are also commonly found in the glass and cement industries and will thus be of benefit from this modeling work as well.

1.2. Methodology

In order to model the systems selected for this study, the CALPHAD technique was used (this technique is explained in further detail in Section 2). First, through a literature review, all available phase diagram data within the MgO-P₂O₅ and MnO-P₂O₅ binary systems were collected. The solid compounds stable within the system were identified and the thermodynamic data available from experiments are collected as well for both solids and liquids. Where information was deemed insufficient, experiments were planned and executed. In a given system, solid compounds are represented by the Gibbs energy function (G = H - TS) modeled experimental data (typically Cp or enthalpy of transformation after measurements). Gibbs energy determination between compounds is done by interpolation using empirical models. The same is also the case for the liquid phase of a system. Empirical models (several have been derived since the advent of the CALPHAD method) are typically analogous to the G = H - TSexpression but additionally possess adjustable and expandable parameters to help reproduce bulk thermodynamic interactions between system components. These models are not derived from first principles but are instead limited to modeling bulk interactions in the same way that the G = H - TS expression for a compound represents bulk thermodynamic properties.

Solid compounds are represented by Gibbs energy functions while liquids are represented by empirical thermodynamic models. A thermodynamic simulation software, in this case Factsage, was used to perform the Gibbs energy minimization routines at varying temperatures and compositions. Parameters were subsequently optimized against the critically assessed experimental data. In this Study, a series of experiments were planned and executed. However, given the difficulty experienced in using P_2O_5 as a reactant, the results obtained were not deemed to be sufficiently reliable to be included as part of this Study.

Once the binary systems were modeled, the binary thermodynamic databases were combined to simulate the CaO-MgO-P₂O₅ ternary systems (unpublished

results on the modeling of the CaO- P_2O_5 system by Hudon and Jung were used with permission). The thermodynamic properties of the ternary liquid solution are firstly predicted based on the parameters of binary liquid solutions alone using a carefully selected interpolation technique. Then a small number of ternary adjustable parameters were added to optimize the ternary predictions against the available experimental data. In the case of ternary compounds or ternary solid solutions, these were also modeled to complete the ternary system thermodynamic database.

2. Introduction

2.1. The CALPHAD Technique

In order to optimize the systems in this study, the CALPHAD (CALculations of PHAse Diagrams) approach was used. This technique was first developed by the CALPHAD community in the early 1970's (with the advance of computing power) and has had as its principal focus the characterization of all possible phases within a system by linking thermodynamic properties and phase diagrams (Saunders and Miodownik, 1998). The CALPHAD technique rests principally on the observation that a given phase diagram is the projection of the combined and minimized thermodynamic properties of all existing phases (both solid and liquid) within that system as a function of temperature, composition and pressure also allows to predict the phase diagram. The aim of the CALPHAD method is thus to produce Gibbs energy functions for all the existing phases in a system in order to calculate its phase diagram.

The CALPHAD technique is in itself an iterative method. Reliable thermodynamic data available from experiments and from assumptions (where experimental data are lacking) are coupled with numerical models (pure compound Gibbs energy expressions or empirical Gibbs energy solution models with adjustable parameters) to calculate phase diagrams (Saunders and Miodownik, 1998). Several solution models (and refinements) have been published over the last several decades.. The phase diagrams calculated are in turn compared against existing phase diagram points. Discrepancies between the modeled phase diagram and the experimental points are noted and the Gibbs energy functions (of solid compounds and liquid) are optimized to improve the quality of the modeling. This step is repeated iteratively until the phase diagram is reproduced as reliably as possible and all thermodynamic properties are reproduced with the highest level of confidence. In terms of adjustments, unknown and assumed values are given higher degrees of freedom while experimental values are typically only adjusted within the experimental error range acknowledged by the

author of the experiments (unless an analysis of the experimental technique reveals potential issues affecting the reliability of the results). Phase diagram portions known to be difficult in their measurements can be superseded by available thermodynamic data if these are known to be more reliable. Overall, experimental results are critically assessed and, where they conflict, are ranked in their reliability based on an analysis of factors such as the method used or the conditions prevailing during the experiments.

Figure 1 presents a schematic of the procedure for CALPHAD thermodynamic database development.



Figure 1: Schematic procedure for the CALPHAD thermodynamic database development

It should be mentioned that though the CALPHAD community extends their calculation works to higher pressure systems, the present Study only deals with phases stable at atmospheric pressure.

2.2. Solid Phase Thermodynamic Modeling

To describe the Gibbs energy of pure compounds (G°), the following expression is used:

 $G_T^O = H_T^O - TS_T^O \dots \tag{1}$

where T is temperature in Kelvin, H and S are enthalpy and entropy of pure species expressed as:

$$H_T = \Delta H_{298} + \int_{298}^{T} C_p dT.$$
 (2)
and

$$S_T = S_{298} + \int_{298}^T \frac{C_p}{T} dT.$$
 (3)

where ΔH_{298} is the standard heat of formation, C_p is the heat capacity at standard pressure and S_{298} is the entropy at 298K.

For a given system, the different solid phases are first identified during the literature review. Solids can appear as stoichiometric compounds or terminal solid solutions. In reality, any stoichiometric compound exhibits some degree of solution but in cases where it is immeasurably small, it is, for all practical purpose ignored. Inversely, stoichiometric compounds can sometimes exhibit such a large degree of solid solution behaviour that they are considered independently.

In the case where two components A and B mix ideally (that is, without any interaction between both components), the energy of this newly created system can be described by the proportional contribution of Gibbs energy from A and B (the partial Gibbs energy) and also by the Gibbs energy contribution from the

greater entropy caused by mixing. In this case, the ideal Gibbs energy of mixing of components A and B can be described by:

$$G^{ideal} = G^{0} + G^{ideal}_{mix}$$
(4)
Where,

$$G^{0} = X_{A}G_{A}^{0} + X_{B}G_{B}^{0}.$$
 (5)

The ideal Gibbs energy of mixing (G_{mix}^{ideal}) can be calculated assuming a single lattice where components A and B mix randomly at a given mole fraction of the species X_i :

$$X_A = \frac{N-n}{N} \text{ and } X_B = \frac{n}{N}.$$
 (6)

where N is the total number of lattice sites per mole and n is the total number of moles of B, among N. The ideal entropy change of mixing (also referred to as the configurational entropy) is directly related to the possible configurations of A and B over the lattice sites and can be expressed as:

$$S^{config.} = k. ln \left[\frac{N!}{n!(N-n)!}\right].$$
(7)

where k is the Boltzmann constant. Using Stirling's approximation, this expression reduces to:

$$S^{config} = -Nk(X_A ln X_A + X_B ln X_B) = -R(X_A ln X_A + X_B ln X_B).....(8)$$

It should be noted that this method is done for a two-dimensional system since an expression for a three dimensional system is still unknown. It is thus an approximation. The ideal Gibbs energy of mixing of the solution can thus be expressed as:

$$G_{mix}^{ideal} = RT(X_A ln X_A + X_B ln X_B).$$
(9)

So that,

$$G^{ideal} = (X_A G_A^0 + X_B G_B^0) + RT(X_A ln X_A + X_B ln X_B).$$
 (10)

In reality, however, interactions (attractive or repulsive forces) between two components translate into a deviation from ideality. In thermodynamic modeling, the Gibbs energy contribution from this deviation (the excess Gibbs energy of mixing) is described by the empirical term G_{mix}^{excess} (or simply G^{ex}):

$$G_{mix}^{excess} = \sum \Omega_{ij} X_A^i X_B^j$$
 (11)

The excess Gibbs energy of solution (G_{mix}) can thus be expressed as:

$$G_{mix} = G^o + G_{mix}^{ideal} + G_{mix}^{excess}.$$
(12)

The simplest function to describe the Gibbs energy of mixing is the *regular solution model* where:

$$G_{mix}^{excess} = \Omega X_A X_B.$$
 (13)

Here, Ω is an empirical adjustment coefficient that can be readily extended as a temperature-dependent polynomial. In the Bragg-Williams version of the regular solution model, Ω is typically extended as a function of temperature as: $\omega - \eta T$ (emulating the expression G = H - TS). If, when mixed, components A and B exhibit attractive forces, this will stabilize further the mix (i.e. lower its Gibbs energy) and the adjustment coefficient Ω will be negative. If, on the other hand, repulsive forces between A and B render the mix unstable, Ω will be positive.

The regular solution model is applicable to both solid and liquid solution. However, due to its simplicity, it can only find an analogy in the most basic systems and is thus greatly limited during interpolations from binary to ternary and higher order systems. For more sophisticated systems, different ways of representing $S^{config.}$ and G^{excess}_{mix} must be used.

To extend the thermodynamic model of a random mixing solid solution from a single lattice to two or more sublattice, a formulation known as the Compound Energy Formalism (CEF) (Hillbert, 2000) can be used. In the CEF, the number of sites per lattice remains fixed.

For example, given two components A_2X_3 and B_2Y_3 mixing randomly, 2 sublattices can be considered with sublattice 1 holding two moles of lattice sites (where A and B mix) and sublattice 2 holding three moles of lattices sites (where X and Y mix). A_2X_2 , B_2Y_3 , A_2X_3 and A_2Y_3 are referred to as "end-members". The Gibbs energy of the solution is calculated as:

$$G = \left(y_A y_X G^o_{A_2 X_3} + y_A y_Y G^o_{A_2 Y_3} + y_B y_X G^o_{B_2 X_3} + y_B y_Y G^o_{B_2 Y_3}\right) - TS^{config} + G^{excess} \dots (14)$$

$$S^{config} = -(2R(y_A lny_A + y_B lny_B) + 3R(y_X lny_X + y_Y lny_Y))....(15)$$

$$G^{excess} = \sum_{A,B,X} L_{AB:X} (y_A - y_B) y_X y_A y_B + \sum_{A,B,Y} L_{AB:Y} (y_A - y_B) y_Y y_A y_B + \sum_{A,X,Y} L_{A:XY} (y_X - y_Y) y_A y_X y_Y + \sum_{B,X,Y} L_{B:XY} (y_X - y_Y) y_B y_X y_Y + L_{AB:XY} y_A y_B y_X / \dots (16)$$

Where y_i are site fractions of comonent *i* in a given sublattice:

$$y_A = 1 - y_B = \frac{n_A}{n_A + n_B}$$
 and $y_X = 1 - y_Y = \frac{n_X}{n_X + n_Y}$(17)

 $L_{AB:X}$, $L_{AB:Y}$, $L_{A:XY}$, $L_{B:XY}$ and $L_{AB:XY}$ are interaction parameters between components A and B on one sublattice when the other sublattice is occupied by

X only, interaction parameters between A and B on one sublattice when the other sublattice is occupied by Y only etc. The Gibbs energy of end members and interaction parameters are the model parameters.

In the present study, Hillert's (2000) compound energy formalism (CEF) is explicitly used for solid solutions considering the crystal structure of each solid solution.

2.3. Thermodynamic Modeling of Liquid Solutions (Slag)

2.3.1. Modified Quasichemical Model (MQM)

To account for non-random mixing in liquid slag, an expression that accounts for short-range ordering (SRO) is used. The *quasichemical model for SRO* was developed by Guggenheim (1935) as well as Fowler and Guggenheim (1939) and was further developed to become the Modified Quasichemical Model (MQM) in several works by Pelton and Blander (1984), Blander and Pelton (1986) and Blander and Pelton (1987). The MQM was again further developed by Pelton (2000). The MQM accounts for the formation of nearest neighbour pairs during mixing (i.e. the liquid tends to strongly order around specific compositions) and thus allows simulating certain physical behavior. If A and B are mixed for example, possible pairs formed are A-A, B-B and A-B. The MQM has been used successfully in the modeling of many liquid solutions including liquid oxides.

In the first modification of the Quasichemical Model by Fowler and Guggenheim (1935), freedom was given to determine the composition of maximum short range ordering (lowest entropy of mixing), to turn the Gibbs energy of pair formation into a function of composition and to extrapolate the model to higher order systems Pelton and Blander (1984), Blander and Pelton (1986) and Blander and Pelton (1987). In the subsequent modification of the MQM by Pelton and Chartrand (2001), the Gibbs energy of pair formations (expandable as polynomials) was expressed in terms of pair fractions rather than as component fractions, coordination numbers (the number of pairs existing to a single component) was allowed to vary as a function of composition. Further

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modifications were also made for multi-component systems by Pelton and Chartrand (2001) and for two sublattice modeling by Chartrand and Pelton (2001). A brief summary of the MQM as developed by Pelton et. al. (2000) is presented here.

Considering a liquid oxide binary solution (e.g. two oxides in their liquid states) of components A-O and B-O (where O is oxygen), the Gibbs energy associated with the formation of two A-O-B (or simply A-B) pairs (in a liquid oxide solution two cations share an oxygen anion A-O-B but is simply represented as A-B and the same for all other pairs) is Δg_{AB} and is described by the following reaction:

$$(A - A) + (B - B) = 2(A - B); \Delta g_{AB}$$
.....(18)

where (A - A), (B - B) and (A - B) represent second nearest neighbour (SNN) pairs in liquid oxide solutions (slag). Z_A and Z_B are coordination numbers of A and B such that:

$$Z_A n_A = 2n_{AA} + n_{AB}$$
.....(19)
and,

 $Z_B n_B = 2n_{BB} + n_{AB}.....(20)$

Where n_i is the number of moles of i and n_{ij} is the number of moles of i – j pairs. Pair fractions are described by:

$$X_{ij} = \frac{n_{ij}}{n_{AA} + n_{BB} + n_{AB}}.$$
(21)

Mole fractions of species are described by:

$$X_A = 1 - X_B = \frac{n_A}{n_A + n_B}.$$
(22)

Coordination-equivalent fractions are described by:

$$Y_A = 1 - Y_B = \frac{Z_A n_A}{(Z_A n_A + Z_B n_B)} = \frac{Z_A X_A}{(Z_A X_A + Z_B X_B)} = X_{AA} + \frac{X_{AB}}{2}.....(23)$$

Then the Gibbs energy of the solution is given by:

 ΔS^{config} is the configurational energy of mixing obtained from a purely random mixing of A – A, B – B and A – B pairs. Since no accurate three-dimensional expression for configurational entropy is available, a two-dimensional extension (an approximation) to the one-dimensional Ising model is used.

$$\Delta S^{config} = -R(n_A ln X_A + n_B ln X_B) - R\left[n_{AA} ln\left(\frac{X_{AA}}{Y_A^2}\right) + n_{BB} ln\left(\frac{X_{BB}}{Y_A^2}\right) + n_{AB} ln X_{AB} 2Y_{A} Y_{B} \right]$$
(25)

In its last iteration, to make ΔG_{AB} configuration dependent instead of composition dependent, it is expanded as a pair fraction such that:

Where Δg_{AB}^{o} , g_{AB}^{io} and g_{AB}^{oj} are functions of temperature. To facilitate an extension to ternary systems, a mechanism was put in place so that coordination numbers can vary with composition such that:

$$\frac{1}{Z_A} = \frac{1}{Z_{AA}^A} \left(\frac{2n_{AA}}{2n_{AA} + n_{AB}} \right) + \frac{1}{Z_{AB}^A} \left(\frac{n_{AB}}{2n_{AA} + n_{AB}} \right).$$
(27)

and,

$$\frac{1}{Z_B} = \frac{1}{Z_{BB}^B} \left(\frac{2n_{BB}}{2n_{BB} + n_{AB}} \right) + \frac{1}{Z_{BA}^B} \left(\frac{n_{AB}}{2n_{BB} + n_{AB}} \right).$$
(28)

where,

$$n_A = \frac{2n_{AA}}{Z_{AA}^A} + \frac{n_{AB}}{Z_{AB}^A} \text{ and } n_B = \frac{2n_{BB}}{Z_{BB}^B} + \frac{n_{AB}}{Z_{BA}^B}.$$
 (29)

 Z_{AA}^{A} and Z_{AB}^{A} (same as Z_{BA}^{A}) are the coordination numbers of A when all SNN are A's and B's, respectively. In this way, Z_{AB}^{A} or Z_{BA}^{A} are exclusive to the A – B system while Z_{AA}^{A} remains relevant to all systems containing A.

In the present study, the MQM is explicitly used for the description of the thermodynamic behavior of liquid phases.

1.1.1 Ternary Interpolation Techniques

Once the binary model parameters for liquid solution are optimized, the thermodynamic Gibbs energy of the ternary solution can be predicted using the so-called ternary interpolation techniques.

The methods for interpolation were developed as "geometric" models by Kaufman (1980). Geometric models are classified as "symmetric" or "asymmetric". As a general rule, symmetric models are used when systems are analogous to each other in their behaviour (similarities often dictated by electronic configuration, atomic radii, molecule size etc.). Asymmetric techniques can also be applied to the system where one component behaves differently from the others. In a ternary system, a mix of symmetric and asymmetric extrapolations can be used.

In general terms, the extension to a ternary system with components 1, 2 and 3 can be expressed with the addition of the following Gibbs excess energy term:

$$g^{E} = X_{1}X_{2}\alpha_{12(a)} + X_{2}X_{3}\alpha_{23(b)} + X_{3}X_{1}\alpha_{31(c)} + (adjustable \ parameters)......(30)$$

Ternary terms are empirical fitting parameters that reduce to zero in their binary systems. These terms are to be avoided as much as possible as they find little analogy with actual physical behavior and it is unclear how they can be included in extrapolations to higher order systems and what their meaning is in such cases. An example of a ternary term is given by the following:

The Kohler (symmetric) (1960), Muggianu (symmetric) (1975) and Toop (asymmetric) (1965) geometric interpolation techniques are perhaps of highest significance from a practical standpoint. Figure 2, taken from Pelton (2001), presents some of those models (or functions) to describe α_{ij} .



Figure 2: Selected geometric models used to interpolate three binary systems into a ternary system (Pelton, 2001).

Mathematically, the Kohler, Toop and Muggianu interpolation techniques are represented by the following three functions in MQM, respectively:

and,

$$\alpha_{12(a)} = \sum_{i \ge 0} \sum_{j \ge 0} q_{12}^{ij} X_1^i (1 - X_1)^j.$$
and,
(33)

In the present study, the ternary system CaO-MgO-P₂O₅ used the Toop interpolation technique with P₂O₅ as an asymmetric component. As shown in Figure 2, combinations of models are possible for different values of α_{ij} . For a single ternary system, up to 64 different configurations are possible.

Formalisms for higher order systems have been developed but are not discussed here as the scope of this study limits itself to ternary systems.

3. MgO-P₂O₅ Binary System

A complete literature review of the MgO-P₂O₅ system was made. The Gibbs energies of compounds were optimized iteratively based on experimental data. When the experimental data were unavailable, the Gibbs energies of the compounds were estimated after a systematic analysis of comparable binary systems. The liquid phase of the system was modeled using the MQM based on available thermodynamic data and phase diagram data.

3.1. Literature review

3.1.1. Solid compounds

3.1.1.1. Mg₃(PO₄)₂

Crystal Structure

Magnesium orthophosphate (Mg₃(PO₄)₂) was first synthesized by Berthelot (1897). Nord and Kierkegaard (1968) synthesized the compound by heating to 1400 °C, in platinum tubes, equivalent contents of Mg₂P₂O₇ and MgO. The crystal structure was then characterized by XRD and observed to be monoclinic with space group $P2_1/n$. The structure of the compound was also described as (PO₄) tetrahedra held by Mg ions (Nord & Kierkegaard, 1968). Ben Abdelkader *et al.* (1999) obtained Mg₃(PO₄)₂ by reacting MgO and (NH₄)₂HPO₄ and determined, by XRD, that the structure was monoclinic with space group P2₁/n.

Phase Transformations

Berak (1958) and Bobrownicki and Slawski (1959) observed, by thermal analysis, a polymorphic transition at 1055 °C and 1050 °C, respectively. These two studies

are the only known studies to report a polymorphic transition in $Mg_3(PO_4)_2$. Other extensive characterizations, such as the one by Oetting and McDonald (1963), do not report any such transition.

Stevens and Turkdogan (1954), Berak (1958), Bobrownicki and Slawski (1959) and Oetting and McDonald (1963) observed, by thermal analysis, melting points of 1348 °C, 1357 °C, 1355 °C and 1353 \pm 5 °C, respectively. Oetting and McDonald observed premelting at least 40°C before the melting point. Czupinska (1992a) observed, by DTA, a melting point of 1357 °C.

Thermodynamic Properties

Enthalpy of Formation, $\Delta H^{\circ}_{f, 298.15 \text{ K}}$

Berthelot (1897) measured by, aqueous calorimetry, the $\Delta H^{\circ}_{f, 298.15 \text{ K}}$ of Mg₃(PO₄)₂.The obtained a value was -3 809.95 kJ mol⁻¹ from the elemental components Mg (s), P₂(g) and O₂ (g).The publication of these results dates back to 1897 and details surrounding the experimental technique or any subsequent calculations could not be located. It is also not possible to know if the phosphorus being referred to is in the gaseous or solid form. The difference in the $\Delta H^{\circ}_{f, 298.15 \text{ K}}$ of orthorombic P₂O₅ (o-P₂O₅) depending on whether solid P or gaseous P₂ is used as a reference, is 143.7 kJ mol⁻¹. Given the absence of a specification regarding phosphorus, the value available from Berthelot must be considered to be -3 809.95 ± 143.7 kJ mol⁻¹.

Stevens and Turkdogan (1954) synthesized Mg₃(PO₄)₂ by heating a mixture of MgO and (NH₄)₂HPO₄ in a platinum crucible at 1000 °C. An enthalpy of formation of Mg₃(PO₄)₂ from MgO and o-P₂O₅ from an acid solution calorimeter was -464.2 \pm 2.6 kJ/mol at 348 K. The difference in the enthalpy of formation from 348 K to that of 298 K was ignored.

Using the results from Stevens and Turkdogan (1954), the thermodynamic data of MgO and hexagonal H-P₂O₅ from Factsage's Fact53 database as well as a recent assessment by Jung and Hudon (unpublished results), the $\Delta H^{\circ}_{f, 298 \text{ K}}$ of Mg₃(PO₄)₂ was calculated from its elemental components:

3Mg (s) +2P (s) + 4 O₂ → Mg₃(PO₄)₂ (s)(35) $\Delta H^{\circ}_{298.15K}$: - 3 807 kJ mol⁻¹

This value of $\Delta H^{\circ}_{298.15 \text{ K}}$ is higher than the value calculated by Stevens and Turkdogan (1954) using thermodynamic data available at the time of its publication. Most of the discrepancy is attributable to the use of a different ΔH°_{f} , $_{298.15 \text{ K}}$ value for P₂O₅.

Lopatin and Semenov (1989) investigated the thermodynamic property of $Mg_3(PO_4)_2$ by the Knudsen effusion method and vapor mass spectroscopy. The extrapolated $\Delta H^{o}_{f, 298.15 \text{ K}}$ value for $Mg_3(PO_4)_2$ is -3 895 ± 70 kJ mol⁻¹.

Abdelkader *et al.* (1999) synthesized $Mg_3(PO_4)_2$ by reacting MgO and $(NH_4)_2HPO_4$ with increasing temperatures interrupted by grinding and mixing in acetone. Temperatures used were 500 °C (for 15 hours), 750 °C (for 24 hours) and 900 °C (for 72 hours). IR spectroscopy characterization by Abdelkader *et al.* showed traces of nitrates and water. The heat of solution of $Mg_3(PO_4)_2$ in nitric acid was then measured with a isoperibolic calorimeter. The reaction according to Abdelkader *et al.* and the measured heat of dissolution are as follows:

Mg₃(PO₄)₂(s) + 6(HNO₃; 35.35H₂O) (aq.)→ 3Mg(NO₃)₂ (aq.) + 2H₃PO₄ (aq.)..(36) $\Delta H^{\circ}_{298K} = -232 \pm 2.7 \text{ kJ mol}^{-1}.$

Using the heat of solution values measured in the same study and from other references, Abdelkader *et al.* (1999) calculated a $\Delta H^{\circ}_{f, 298.15 \text{ K}}$ for Mg₃(PO₄)₂ of -3 706 kJ mol⁻¹. This value is the least negative of all measured $\Delta H^{\circ}_{298.15 \text{ K}}$ values of Mg₃(PO₄)₂ and it is a likely possibility that the traces of nitrates and water

observed by IR spectroscopy were responsible for lowering the observed heat of formation.

Heat Capacity, Cp

Oetting and McDonald (1963) used a copper block drop calorimeter to determine the enthalpy change, $H_T - H_{298}$, of Mg₃(PO₄)₂ in the temperature range from 298 to 1700 K. The C_p of the compound can be derived from the experimental points available in the publication. Using a regression formula, the following C_p was obtained for this study:

 $C_p = 632.83 - 0.12978 T + 0.000048 T^2 + 1820000 T^2 - 7012.28 T^{0.5}$(37)

Entropy, S_{298.15 K}

Oetting and McDonald (1963) determined the $S_{298.15 \text{ K}}$ of Mg₃(PO₄)₂ from lowtemperature *heat capacity* measurements (from 17 to 320 K) obtained using an adiabatic calorimeter. The S^{o}_{298} determined by Oetting and McDonald was 189.2 ± 0.6276J mol⁻¹ K⁻¹.

Gibbs Energy, ∆G

Bookey (1952) measured, from 1273 to 1523 K, the equilibrium gas constant for the following reaction:

$$Mg_3(PO_4)_2(s) + 5H_2(g) \rightarrow 3 MgO(s) + P_2(g) + 5H_2O(g) \dots (38)$$

This was achieved by passing H_2 (g) over heated $Mg_3(PO_4)_2$ (s) and determining the H_2O (g) content at the outlet. $Mg_3(PO_4)_2$ was previously synthesized by heating a mixture of MgO and $(NH_4)_2HPO_4$ in a platinum crucible at 1000 °C. The Gibbs energy of the above reaction derived from the equilibrium constant was:

 $\Delta G = 786.59 - 0.26 \text{ T} (\text{kJ mol}^{-1})$ (39)

3.1.1.2. Mg₂P₂O₇

Crystal Structure

The crystal structure of the high temperature polymorph of Mg₂P₂O₇ was first described by Lukaszewicz (1961) by XRD at 80 °C and was described to be isostructural with Sc₂Si₂O₇. Lukaszewicz (1967) studied by XRD the crystal structure of α -Mg₂P₂O₇ and β -Mg₂P₂O₇ and found the density of the β polymorph to be larger than that of the α polymorph (3.145 vs. 3.099 g cm⁻¹ respectively). Calvo (1967a) characterized by X-ray photography the crystal structure of the low temperature polymorph as monoclinic with space group *P*2₁/*c*. Calvo *et al.* (1967b) characterized by XRD α -Mg₂P₂O₇ and β -Mg₂P₂O₇ and determined them to be of space groups *P*2₁/*C* and *C*2/*m*, respectively.

Phase Transformations

The low-temperature polymorphic transition of $Mg_2P_2O_7$ was first detected by DTA at 68 °C by Roy *et al.* (1948). Roy *et al.* reported noticeable changes between 60 and 80 °C. Oetting and McDonald (1963) observed this transition, by low-temperature calorimetry, at 69 °C ±1 with an overlap between the α and β polymorphs being observed over a 20 °C range. Calvo *et al.* (1967b) observed by DTA that only the α phase existed at 61 °C ±1 and that only the β phase was detected at 63 °C ±1. Calvo *et al.* (1967b) detected the transition, using electro spin resonance (ESR), from 59 to 63 °C, but in Mg_2P_2O_7 doped with 0.3 wt.% Mn_2P_2O_7. Calvo (1967a) observed in Mg_2P_2O_7 doped with 0.1% Cu²⁺, using X-ray reflection photography, a polymorphic transition from α to β with a coexistence of both structures between 62 and 65 °C. Czupinska (1992a) observed by DTA, two polymorphic transitions in Mg_2P_2O_7, one at 68 °C and another at 1100 °C. The work of Czupinska is the only study to report this high temperature transition.

Berak (1958) and Oetting and McDonald (1963) reported, from thermal analysis observations, melting points of 1382 °C and 1395 °C, respectively with Oetting

and McDonald observing premelting. Czupinska (1992a) observed, by DTA, a melting point at 1385 °C.

Thermodynamic Properties

Enthalpy of Formation, $\Delta H^{\circ}_{f, 298.15 \text{ K}}$

Lopatin *et al.* (1987) investigated the thermodynamic properties of Mg₃(PO₄)₂, Mg₂P₂O₇ and Mg(PO₃)₂ simultaneously by the Knudsen's effusion method and vapor mass spectroscopy. The following ΔH_{298K} were measured:

 $4Mg(PO_3)_2 (s) \rightarrow 2Mg_2P_2O_7 (s) + P_4O_{10} (g): \Delta H_{298.15 K} = 462 \pm 12 \text{ kJ/mol}.....(40)$

 $3Mg_2P_2O_7 (s) \rightarrow 2Mg_3(PO_4)_2 (s) + 2PO_2 (g) + 1/2 O_2(g): \Delta H_{298.15 K} = 1 \ 135 \pm 12 KJ/mol$ (41)

Heat Capacity, Cp

Oetting and McDonald (1963) used a copper block drop calorimeter to determine the enthalpy change, $H_T - H_{298}$, of Mg₂P₂O₇ in the temperature range from 298 to 1700 K. The C_p of the compound can be derived from the experimental points available in the publication. Using a regression formula, the following C_p was obtained for this study:

 $C_p = 371.24 + 0.00517 T - 430 000 T^2 - 3286.49 T^{0.5}$(42)

Entropy, S_{298.15 K}

Oetting and McDonald (1963) determined the $S_{298.15 \text{ K}}$ of Mg₂P₂O₇ from lowtemperature *heat capacity* measurements (from 14 to 400 K) obtained using an adiabatic calorimeter. The S_{298}° determined was154.89 ± 0.6276J mol⁻¹ K⁻¹.

Gibbs Energy, ΔG

No data were located in the literature.

3.1.1.3. Mg(PO₃)₂

Crystal Structure

Beucher and Grenier (1968) examined the crystal structures of $M_2^{II}P_4O_{12}$ ($M^{II} = Ni$, Mg, Zn, Cu, Co, Mn) by XRD and observed that all the studied tetrametaphosphates were isomorphous, monoclinic with space group *C2/c*. Nord and Lindberg (1975) characterized the crystal structure of Mg₂P₄O₁₂ by X-ray fluorescence spectroscopy and observed it to be monoclinic with space group *C2/c* as well.

Phase Transformations

Thilo and Grunze (1957), Berak (1958), Andrieu and Damient (1964), Bekturov *et al.* (1967), Thonnerieux *et al.* (1968), Kuzmenkov *et al.* (1974), Rakotomahanina-Rolaisoa *et al.* (1979) and Czupinska (1992b) determined the melting point of magnesium metaphosphate (Mg(PO₃)₂) to be 1160 °C, 1165 °C, 1163 °C, 1150 °C, 1140 °C, 1170 °C, 1152 °C and 1165 °C, respectively, by DTA. Sarver and Hummel (1959) observed a melting point of 1165 °C \pm 5 °C by performing quenching experiments. Serazetdinov *et al.* (1970) observed by DTA a melting temperature of 1170 °C upon heating and 1163 °C upon cooling.

Thermodynamic Properties

Enthalpy of Formation, $\Delta H^{\circ}_{f, 298.15 \text{ K}}$

Lopatin *et al.* (1987) investigated the thermodynamic properties of Mg₃(PO₄)₂, Mg₂P₂O₇ and Mg(PO₃)₂ simultaneously by the Knudsen's effusion method and vapor mass spectroscopy. The following $\Delta H^{\circ}_{f, 298.15 \text{ K}}$ was measured:

 $4Mg(PO_3)_2 (s) \rightarrow 2Mg_2P_2O_7 (s) + P_4O_{10}(g): \Delta H^{\circ}_{f, 298.15 \text{ K}} = 462 \pm 12 \text{ kJ/mol....} (43)$

Heat Capacity, Cp

No data were located in the literature.

Entropy, $S_{298.15 K}$ No data were located in the literature.

Gibbs Energy, ΔG No data were located in the literature.

3.1.1.4. MgP₄O₁₁

Crystal Structure

Yakubovich *et al.* (1993) determined the structure of magnesium ultraphosphate, MgP_4O_{11} and observed it to be orthorhombic with space group *Pmc21* while Meyer *et al.* (1994) observed it to be isostructural with ZnP_4O_{11} and with a space group $P2_{1/c}$.

Phase Transformations

Only a single phase transformation reference was located by Meyer *et al.* (1994) who determined the melting point of magnesium MP2 to be 910 °C by DTA.

Thermodynamic Properties

Enthalpy of Formation, ΔH°_{f, 298.15 K}

No data were located in the literature.

Heat Capacity, C_p No data were located in the literature.

Entropy, $S_{298.15 K}$ No data were located in the literature.

Gibbs Energy, ΔG No data were located in the literature.

3.1.2. Liquid phase

The only available experimental data for the MgO-P₂O₅ liquid phase are activity measurements from Iwase *et al.* (1987) determined, at 1673 K, the activity of P₂O₅ in MgO-P₂O₅ slag in equilibrium with phosphorus-containing liquid copper by applying an electrochemical method. Iwase *et al.* determined the activity of P₂O₅ on the MgO-rich side of the MgO-P₂O₅ binary by measuring the oxygen partial pressure of phosphorus-containing liquid copper in equilibrium with molten slag and relating them to available thermodynamic data for the formation of P₂O₅ from oxides Turkdogan and Pearson (1953) as per Equation 44.

 $1/2 P_2 O_5 (I) = 1/2 P_2 (g) + 5/4 O_2 (g) \dots (44)$

The data points show a very low activity around the $Mg_3(PO_4)_2$ composition indicating a strong tendency for short range ordering of the liquid on the MgO-rich side.

3.1.3. Phase diagram

Berak (1958) investigated by DTA the phase diagram of the MgO-P₂O₅ system extensively within the MgO-Mg(PO₃)₂ range. The EMF measurements of liquid slag by Iwase *et al.* (1987) also allowed to produce a liquidus point between MgO and Mg₃(PO₄)₂ at 1400 °C.

3.2. Thermodynamic Optimization

The optimized MgO-P₂O₅ binary phase diagram is presented in Figure 3 along with all phase diagram experimental data. The details of the optimization procedure and optimized model parameters will be presented below. In general, the thermodynamic data for the solid compounds were fixed firstly based on the available thermodynamic data. Then, based on the phase diagram and thermodynamic properties of the liquid phase, the entire solid and liquid parameters were finally optimized to reproduce all reliable experimental data. The optimized model parameters are presented in Table 1.


Figure 3: The optimized phase diagram of the MgO-P₂O₅ binary system.

Table 1:Optimized Thermodynamic Properties and Model Parameters in the Present Study in Comparison withExperimental Data.

Melting and Polymorphic Transition Points of Compounds							
	Temperature						
Compound	(°C)	Transition ¹	Technique ²	Comments	Reference		
					Stevens and		
					Turkdogan		
$Mg_3(PO_4)_2$	1348	MP	ТА		(1954)		
	1357	MP	TA, XRD		Berak (1958)		
					Bobrownicki and		
	1355	MP	TA, XRD		Slawski (1959)		
					Oetting and		
	1353 ±5	MP	ТА		McDonald (1963)		
	1357	MP	DTA, XRD, OM	No polymorphic	Czupinska		
				transition	(1992a)		
	1357	MP	Optimization		This work		
	1055	$PT,\beta\to\alpha$	TA, XRD		Berak (1958)		
					Bobrownicki and		
	1050	PT, $\beta \rightarrow \alpha$	TA, XRD		Slawski (1959)		
		PT, $\beta ightarrow \alpha$		Excluded from this	This work		
				study			
$Mg_2P_2O_7$	1382	MP	TA		Berak (1958)		
	1395 ±5	MP	ТА		Oetting and		

					McDonald (1963)
					Czupinska
	1385	MP	ТА		(1992a)
	1385	MP	Optimization		This work
	940	PT, $\beta \rightarrow \alpha$	ТА		Berak (1958)
					Czupinska
	1100	PT, $\alpha \rightarrow \beta$	ТА		(1992a)
		High-T PT		Excluded from this	This work
				study	
	68	PT, $\alpha \rightarrow \beta$	DTA		Roy (1948)
					Oetting and
	69	PT, $\alpha \rightarrow \beta$	ТА		McDonald (1963)
	62-65	PT, $\alpha \rightarrow \beta$	XRD	with 0.1 % Cu ²⁺	Calvo (1967a)
				with 0.3% $Mn_2P_2O_7$	Calvo <i>et al.</i>
	59-63	PT, $\alpha \rightarrow \beta$	ESR		(1967b)
					Czupinska
	68	$PT,\beta\to\gamma$	ТА		(1992a)
	68	PT, $\alpha \rightarrow \beta$	Optimization		This work
Mg(PO ₃) ₂	1165	MP	TA		Berak (1958)
					Sarver and
	1165 ±5	MP	Quenching		Hummel (1959)
					Andrieu and
	1163	MP	DTA		Diament (1964)
	1150	MP	DTA		Bekturov et al.

					(1967)
					Thonnerieux et
	1040	MP	DTA		<i>al.</i> (1968)
					Rakotomahanina-
					Rolaisoa <i>et al.</i>
	1152	MP	DTA		(1970)
					Urikh <i>et al.</i>
	1160	MP	ТА		(1970)
					Serazetdinov et
	1170	MP	DTA	Upon Heating	<i>al.</i> (1970)
					Serazetdinov et
	1163	MP	DTA	Upon Cooling	<i>al.</i> (1970)
					Rakotomahanina-
					Rolaisoa <i>et al.</i>
	1152	MP	DTA		(1970)
					Kuzmenkov et al.
	1170	MP	DTA		(1974)
					Czupinska
	1165	MP	ТА		(1992b)
	1165	MP	Optimization		This work
					Meyer et al.
MgP ₄ O ₁₁	910	MP	DTA		(1994)
	910	MP	Optimization		This work
¹ MP: Melting Point, F	PT: Polymorphic Transitions. ²	² TA: Thermal Analys	is, XRD: X-Ray Diffraction	on, DTA: Differential	Thermal Analysis,

OM: Optical Microscopy, ESR: Electron Spin Resonance.

ΔH° _{f,298.15}				
	ΔH° _{f,298.15}			
	from oxides*	$\Delta H^{\circ}_{f,298.15}$ from elements		
Compound	(kJ mol⁻¹)	(kJ mol ⁻¹)	Technique	Reference
	-466.4 ± 143.7			
$Mg_3(PO_4)_2$	(calculated)	-3809.95 ± 143.7	Aqueous Calorimetry	Berthelot (1897)
	-398.3 (calculated)	-3741.8	Gas Equilibrium	Bookey (1953)
				Stevens and
				Turkdogan
	-464.2	-3807.7 ± 2.59 (calculated)	Acid Calorimetry	(1954)
	-551.5 (calculated)	-3895 ± 70	Knudsen Effusion	Lopatin (1989)
				Ben Abdelkader
	-362.5	-3706	Aqueous Calorimetry	(1999)
	-457.8	-3801.3	Optimization	This work
-				Lopatin <i>et al.</i>
α -Mg ₂ P ₂ O ₇	-380.2 (calculated)	-3122.2	Knudsen Effusion	(1987)
	-402.2	-3144.2	Optimization	This work
				Lopatin et al.
Mg(PO ₃) ₂	-288.1 (calculated)	-2428.6	Knudsen Effusion	(1987)
	-240.8	-2381.1	Optimization	This work
MgP ₄ O ₁₁	-249.8	-3929.3	Optimization	This work
* Using MgO and	d O-P ₂ O ₅ as reference			

S°298.15

	S° _{298.15}	S° _{298.15} computed			
	experimental	from sum*	Final optimized values		
Compound	(J mol ⁻¹ K ⁻¹)	(J mol ⁻¹ K ⁻¹)	$(J mol^{-1} K^{-1})$	Technique	Reference
CaO		37.75	-		- FACT53
MgO		26.95	-		- FACT53
P ₂ O ₅ (H)*		114.39	-		- FACT53
α -Ca ₃ (PO ₄) ₂	235.978	227.64	-		- FACT53
γ -Ca ₂ P ₂ O ₇	189.024	189.89	-		- FACT53
β- Ca(PO ₃) ₂	146.9421	152.14	-		- FACT53
CaP ₄ O ₁₁	239 (optimized)	266.53	-		- FACT53
					Oetting and
$Mg_3(PO_4)_2$	189.2005 ± 0.6276	-	-	Drop Calorimetry	McDonald (1963)
$Mg_3(PO_4)_2$	-	195.24	189.2	Optimization	This work
					Oetting and
α -Mg ₂ P ₂ O ₇	154.8917 ± 0.6276	-	-	Drop Calorimetry	McDonald (1963)
α -Mg ₂ P ₂ O ₇	-	168.29	154.89	Optimization	This work
Mg(PO ₃) ₂	-	141.34	141.43	Optimization	This work
MgP ₄ O ₁₁	-	255.73	255.73	Optimization	This work

* As S_{298} and C_p for P_2O_5 were experimentally determined only for the hexagonal form of P_2O_5 , H- P_2O_5 was chosen as reference state to estimate unknown C_p and S_{298} of compounds.

C _p experimental							
	$C_{ ho}$ experimental	Final optimized values	Technique	Reference			
Compound	(J mol ⁻¹)	(J mol⁻¹)					
$Mg_3(PO_4)_2$	632.83 - 0.12978 <i>T</i> + 0.000048 <i>T</i> ² +	(same as	Drop Calorimetry	Oetting and			

	1820000 <i>T</i> ² - 7012	.28 <i>T</i> ^{0.5}	experimental)		McDonald (1963)
	371.24 + 0.00517	T - 430000 T ² -	(same as		Oetting and
α -Mg ₂ P ₂ O ₇	3286.49 <i>T</i> ^{0.5}		experimental) 182.54 + 0.04602 <i>T</i> - 4540000 <i>T</i> ² -	Drop Calorimetry	McDonald (1963)
Mg(PO ₃) ₂	-		3286.49 <i>T</i> ^{0.5} 160.90 + 0.382252 <i>T</i> - 8060197 <i>T</i> ² - 22900 T	$C_{\rho} = C_{\rho}(Ca(PO_4)_2)$	This work
MgP ₄ O ₁₁	-		¹ - 0.000112629 <i>T</i> ²	$C_p = C_p(CaP_4O_{11})$	This work
MQM Parameter	rs of MgO-P ₂ O ₅ liquid	l phase			
Mg Liquid Coord	ination Number	P2O3 Liquid Coord	lination Number		
Z ^{Mg} _{MgMg}	= 1.37744375 ;	Z ^{P2O3} P2O3P2O3	= 4.1322000		
MQM Gibbs Ene	rgy Expression:	$\Delta g_{Mg-P2O3}(Kj/mol) =$	(-290.16 + 0.016736 <i>T</i>) - 54	4.392 <i>X_{Mg-Mg}</i> – 225.936 <i>X</i> ,	P203-P203

3.2.1. Compounds

Four compounds are known to exist in the binary system. They are: $Mg_3(PO_4)_2$, $Mg_2P_2O_7$, $Mg(PO_3)_2$ and MgP_4O_{11} .Only one polymorphic transition, for magnesium pyrophosphate ($Mg_2P_2O_7$), was identified consistently within this system. Bookey (1953) studied by XRD the range between MgO and $Mg_3(PO_4)_2$ and did not report any intermediate compounds, such as $Mg_4P_2O_9$, as exist in the CaO-P₂O₅ binary system and summarized by Jung and Hudon (unpublished results).

No compound richer in P_2O_5 than MgP_4O_{11} (such as exist in the CaO- P_2O_5) was found to exist in the literature. However, given some level of symmetry with the CaO- P_2O_5 system, there is a possibility that the MgO- P_2O_5 system may contain P_2O_5 rich compounds.

3.2.1.1. Mg₃(PO₄)₂ Polymorphic Transition

A polymorphic transition for $Mg_3(PO_4)_2$ is reported by Berak (1958) at 1055 °C and by Bobrownicki and Slawski (1959) at 1050 °C. Oetting and McDonald (1963) measured the enthalpy of $Mg_3(PO_4)_2$ from 22 to 1417 °C and reported no such transition. Czupinska (1992) also studied $Mg_3(PO_4)_2$ by thermal analysis and optical microscope and did not report a polymorphic transition. The transitions reported by Berak (1958) and Bobrownicki and Slawski (1959) at 1055 and 1050 °C, respectively, may be due to the presence of an impurity and thus raise the possibility of another compound forming below the $MgO-Mg_3(PO_4)_2$ solidus line. A compound analogous to those observed in the CaO-P₂O₅ binary system. However, the existence of such compounds remains highly speculative at this point and were not identified in the work of Bookey (1953) which analyzed the $MgO-Mg_3(PO_4)_2$ section. A polymorphic transition of $Mg_3(PO_4)_2$ was thus not included in the present modeling.

3.2.1.2. Mg₂P₂O₇ Polymorphic Transitions

The low temperature polymorphic transition of $Mg_2P_2O_7$ is well studied with observations by Roy *et al.* (1948), Oetting and McDonald (1963), Calvo (1967), Calvo *et al.* (1967) and Czupinska (1992). However, only Czupinska reported the higher temperature transition for this compound. Oetting and McDonald performed an enthalpy analysis on $Mg_2P_2O_7$ from 13 °C up to the melting point without reporting another transition. Berak (1958) observed a eutectic temperature between $Mg_2P_2O_7$ and $Mg_3(PO_4)_2$ at 1150 °C and it is thus probable that the high temperature transition observed at 1100 °C by Czupinska may have been caused by contamination with $Mg(PO_3)_2$. For these reasons, the high temperature transition observed by Czupinska was not included from the present modeling work.

Thermodynamic Properties of Compounds

Enthalpy of Formation, $\Delta H^{\circ}_{f, 298.15 \text{ K}}$

The available experimental data were simultaneously optimized against experimental thermodynamic liquid (slag) properties and available phase diagram points. Once experimental data were taken into account, optimization was done iteratively by adjusting each model parameter so as to obtain the best possible fit with the available phase diagram points. Experimental enthalpy of formation data were unavailable for the MP2 compound and its enthalpy of formation was determined as a result of the optimization of the remaining compounds. Optimized values of enthalpy of formation at 298 K of compounds (formed from oxides, MgO (s) and orthorombic P_2O_5 (s)) are presented in Figure 14.

Solid Compounds



Figure 4: Optimized $H_{f, 298 K}$ for compounds in the MgO-P₂O₅ system from MgO and orthorombic o-P₂O₅.

Once the optimized value for the enthalpy of formation of $Mg_3(PO_4)_2$ was obtained, its enthalpy of formation from oxides (at 298 K) was calculated and produced a value of -491.03 kJ mol⁻¹. If the enthalpy of formation from oxides is calculated at 348 K (the temperature for which Stevens and Turkdogan (1954) provides the enthalpy of formation) the value is lower by less than 1 kJ mol⁻¹. Ignoring the temperature difference between the experiments of Stevens and Turkdogan (carried at 348 K) and the optimization done at 298 K, was thus seen as acceptable.

The optimized values are close to the experimental values of both, Berthelot (1897) and Stevens and Turkdogan (1954). Values for the enthalpy of formation of $Mg_2P_2O_7$ and $Mg(PO_3)_2$ are also reasonably close to the experimental values of Lopatin *et al.* (1987).

The final optimized values were presented in Table 2.

Heat Capacity, Cp

Oetting and McDonald (1963) used a copper block drop calorimeter to measure the H_T - $H_{298.15 K}$ of both Mg₃(PO₄)₂ and Mg₂P₂O₇ between 298 and 1700 K. Resulting data was used in this study to generate C_p functions for both compounds.

No data was available for MP and Mg₂P₂O₇. To generate acceptable C_p estimates, an empirical approach was taken. Available data from the CaO-P₂O₅ system was used in the analysis and optimization of the MgO-P₂O₅ binary. In this case, a comparison was made between the known C_p curves of Ca₃(PO₄)₂, Ca₂P₂O₇, Ca(PO₃)₂ and curves generated by adding the C_p functions of the respective oxide components in the CaO-P₂O₅ system. For example, the C_p curve of Ca₃(PO₄)₂ was compared against a curve created by summing: $3xC_p(CaO) + C_p$ (*H*-*P*₂O₅) to see if summing the C_p's yielded estimates reasonably close to those actually measured. As C_p of O-*P*₂O₅ was not determined experimentally, it was assumed to be the same as H-*P*₂O₅ in the previous optimization by Jung and Hudon (unpublished results).

The resulting curves are presented in Figure 5.



Figure 5: C_p of compounds and of sum of oxides in CaO-P₂O₅.

At first glance, the sums of C_p 's are poor predictors of the actual C_p functions of the compounds. The C_p functions of Mg₃(PO₄)₂ and Mg₂P₂O₇ (where there are available data) were compared against the C_p functions of Ca₃(PO₄)₂ and Ca₂P₂O₇, as shown in Figure 6.



Figure 6: C_p of compounds in the CaO-P₂O₅ and MgO-P₂O₅ systems. Solid lines represent modeled C_p functions.

The comparison of these functions shows an acceptable similarity. Based on the data found in Figure 5 and Figure 6, summing the C_p of oxides is a poor predictor of the C_p of the compound themselves but the C_p functions between Mg₃(PO₄)₂ and Ca₃(PO₄)₂ and between Ca₂P₂O₇ and Mg₂P₂O₇ are similar enough that the C_p of Ca₂P₄O₁₂ and CaP₄O₁₁ were used integrally as estimates for the C_p of Mg(PO₃)₂ and MgP₄O₁₁, as shown in Figure 7.



Figure 7: Optimized heat capacities of compounds in the MgO-P₂O₅ system in the present study in comparison to the heat capacities from the sum of oxides. Solid lines represent modeled C_p functions.

The heat capacity functions derived from the experimental data of Oetting and McDonald (1963), for $Mg_3(PO_4)_2$ and $Mg_2P_2O_7$, are presented against the experimental points in Figure 8 and Figure 9.





Figure 8: Optimized H_T - $H_{298.15 K}$ of Mg₃(PO₄)₂ with experimental points from Oetting and McDonald (1963). Solid lines represent modeled functions.





Figure 9: Optimized H_T - $H_{298.15 K}$ of Mg₂P₂O₇ with experimental points from Oetting and McDonald (1963). Solid lines represent modeled functions.

The final optimized values were presented in Table 2.

Entropy, S_{298.15 К}

No data was available for MP and MP2. To generate reasonable first-estimates of $S^{\circ}_{298.15 \ K}$ the same approach was taken as for C_P estimates. The available $S^{\circ}_{298.15 \ K}$ values of known phosphates in the MgO-P₂O₅ and CaO-P₂O₅ systems were compared against the sum of the $S^{\circ}_{298.15 \ K}$ values from their oxides. For example, the available $S^{\circ}_{298.15 \ K}$ value for Mg₃(PO₄)₂ from Oetting and McDonald (1963) (189.2 J mol⁻¹K⁻¹) was compared with the following sum: $3 \times S^{\circ}_{298.15 \ K}$, MgO + $S^{\circ}_{298.15 \ K}$, H-P2O5 (195.2 change J mol⁻¹K⁻¹). The comparison was repeated for MgP₂O₇, Ca₃(PO₄)₂, Ca₂P₂O₇ and Ca(PO₃)₂.

As can be seen in Table 1, it was observed that sum of the $S^{\circ}_{298.15 K}$ of H-P₂O₅ and $S^{\circ}_{298.15 K}$ of CaO or MgO are almost the same as the experimental $S^{\circ}_{298.15 K}$ of several compounds. Therefore, in the present study, the unknown $S^{\circ}_{298.15 K}$ of MP and MP2 compounds were estimated as the sum of the oxides H-P₂O₅ and MgO. $S^{\circ}_{298.15 K}$ of compounds (formed from oxides, MgO (s) and H-P₂O₅ (s))are presented in Figure 10.The final optimized values were presented in Table 2.

Solid Compounds



hexagonal H-P₂O₅.

Gibbs Energy, ΔG

Bookey (1953) produced, from measurements between 1273 to 1523 K, experimental measurement points for the following Gibbs energy function:

$$Mg_3(PO_4)_2(s) + 5H_2(g) = 3 MgO(s) + P_2(g) + 5H_2O(g) \dots (45)$$

Using the thermodynamic data of H₂ (g), MgO (s), P₂ (g) and H₂O (g) available in the Fact53 database, the Gibbs energy of Mg₃(PO₄)₂ was determined for the same reaction. With the C_p function set, the $\Delta H^{\circ}_{298.15 K}$ and $S_{298.15 K}$ of Mg₃(PO₄)₂ were simultaneously adjusted to create a fit (in elevation and inclination) with the experimental points reported by Bookey (1953). The resulting line is shown in Figure 11:



Figure 11: Adjusted $\Delta H^{\circ}_{298.15K}$ and $S_{298.15K}$ of $Mg_3P_2O_8$ to match data from Bookey (1953).

The $\Delta H^{\circ}_{298.15 \text{ K}}$ and $S_{298.15 \text{ K}}$ obtained, so as to match the Gibbs data points produced by Bookey (1953), are thus -3 741.8 kJ mol⁻¹ and 211.5 J mol⁻¹K⁻¹, respectively. It must be noted that the original Gibbs energy function determined by Bookey also poorly correlates with his actual measured points. This may be due to the fact that experiments conducted by Bookey were done over a relatively small temperature range and with few measurement points, thus making the extrapolation very sensitive to experimental errors. The S_{298.15 K} value obtained from this adjustment exercise is also highly sensitive to deviations in the experimental points of Bookey and is likely to be inaccurate. For this reason, it was ignored from the modeling stage.

3.2.2. Liquid

The available activity measurement data from Iwase *et al.* (1987) were adjusted to reflect current energy of formation data available in FactSage (FToxid database for P_2O_5). An adjustment factor was obtained by reducing the difference between both energies of formation at 1673 K to Equation 46 and applying it to the existing activity values as per:

 $1/2 P_2 O_5 (I) = 1/2 P_2 (g) + 5/4 O_2 (g) \dots (46)$

Adjustment factor =
$$-2(\frac{\Delta G_{P_2O_5,[53Tur]}^o - \Delta G_{P_2O_5,FToxid}^o}{RT})$$
.....(47)

So that,

$$\ln a_{P_2O_5,FToxid} = \ln a_{P_2O_5,[87hwa]} - 2\left(\frac{\Delta G^o_{P_2O_5,[53Tur]} - \Delta G^o_{P_2O_5,FToxid}}{RT}\right) \dots (48)$$

At 1673 K, for Equation 46,

 $\Delta G^o_{(1),[53Tur],1673K} = 343\,855$ J/mole

and,

 $\Delta G_{(1), FToxid, 1673K}^{o} = 357\ 620\ J/mole$

The adjustment factor obtained at 1673 K was equal to 0.8596 so that,

 $\ln a_{P_2O_5, FToxid, 1673K} = \ln a_{P_2O_5, [87hwa]} + 0.8596$ (49)

An adjusted set of "activity measurements" were thus produced against which the optimization of the liquid phase was done. The parameters of the MQM liquid model used for this system were modified to fit the adjusted data from Iwase *et al.* (1987). The strong short range ordering around the Mg₃(PO₄)₂ composition was reproduced with the addition of a negative "1-0" parameter. This strong stabilization of the liquid is counterbalanced by the high stability of Mg₃(PO₄)₂ solid compound (i.e. a very negative $\Delta H^{\circ}_{298.15 \text{ K}}$). Both sets of activity data (original and adjusted) are presented in Figure 12 against the activity curves produced at 1673 K by the liquid model optimized for this study.



Figure 12: Activity of $P_2O_5(I)$ at 1673 K from Iwase *et al.* (1987) in comparison with the optimized/calculated activity from the present study. In the optimization, the original experimental data were adjusted using new Gibbs energy liquid P_2O_5 to keep consistency in the database.

The final optimized liquid parameters from the MQM model were presented in Table 2.

3.2.3. Phase diagram

Two polymorphic transitions were ignored for reasons explained previously. However, the phase diagram points could be reproduced confidently with models including the available, estimated and optimized thermodynamic data.

4. MnO-P₂O₅ Binary System

Similarly to the MgO-P₂O₅ binary system, a complete literature review of the MnO-P₂O₅ system was also made. The Gibbs energies of compounds were optimized based on experimental data. When the experimental data were unavailable, the Gibbs energies of the compounds were estimated after the symmetric analysis of similar binary systems such as CaO-P₂O₅ and MgO-P₂O₅. The liquid phase of the system was also modeled using the MQM based on thermodynamic data and phase diagram data available.

4.1. Literature review

4.1.1. Solid compounds

4.1.1.1. Mn₃(PO₄)₂

Crystal Structure

Manganese orthophosphate ($Mn_3(PO_4)_2$) was firstly synthesized by Berthelot (1897). Konstants and Dimante (1977) measured pycnometrically the density of β -Mn_3(PO_4)_2 to be 3.745 g/cm³. Nord (1982) synthesized Mn_3(PO_4)_2 for XRD study but reported to have only obtained the orthophosphate under the β '-Mn_3(PO_4)_2 form (and not under the graftonite structure). Nord reported that the structure, studied at 797 °C, was monoclinic. Massa *et al.* (2005) synthesized Mn_3(PO_4)_2 for XRD study and reported a third structure, identified as γ -Mn_3(PO_4)_2, with a monoclinic symmetry and space group $P2_1/n$.

Phase Transformations

Pearson et al. (1954) observed, by DTA, a melting point for $Mn_3(PO_4)_2$ of 1119 °C. Konstants and Dimante (1977) measured by electrical conductivity measurements the melting temperature of β -Mn₃(PO₄)₂ to be 1117 °C. Nord (1982) reported, from DTA measurements, no polymorphic transitions from room temperature up to the melting point, observed at 1097°C.

Thermodynamic Properties

Enthalpy of Formation, $\Delta H^{\circ}_{f, 298.15 \text{ K}}$

Berthelot (1897) measured by, aqueous calorimetry, the $\Delta H^{\circ}_{f, 298.15 \text{ K}}$ of $Mn_3(PO_4)_2$ and obtained a value of -3 085.7 kJ mol⁻¹ from the elemental components Mn (s), P₂(g) and O₂ (g). The publication of these results dates back to 1897 and details surrounding the experimental technique or any subsequent calculations could not be located. It is also not possible to know if the phosphorus being referred to is in the gaseous or solid form. The difference in the $\Delta H^{\circ}_{f, 298.15 \text{ K}}$ of O-P₂O₅ depending on whether solid P or gaseous P₂ is used, is 143.7 kJ mol⁻¹. Given the absence of a specification regarding phosphorus, the value available from Berthelot must be considered to be -3 085.7 ± 143.7 kJ mol⁻¹.

Stevens and Turkdogan (1954) measured, by acid solution calorimetry, The ΔH°_{f} , _{348 K} of the following reactions:

Mn₃(PO₄)₂ (s) + 6HCl (aq.) → 3MnCl₂ (aq.) + 2H₃PO₄ (aq.)(50) $\Delta H^{\circ}_{348 \, \text{K}}$: -120.954 ± 0.502 kJ mol⁻¹

3MnO (s) + 6HCl (aq.) → 3MnCl₂ (aq.) + 3H₂O (l)(51) $\Delta H^{\circ}_{348 \, \text{K}}$: -342.63 ± 1.4 kJ mol⁻¹

Stevens and Turkdogan (1954) obtained the orthorombic form of P_2O_5 by heating it to 380-390 °C for 2 hours and then reacted the compound with water so as to obtain:

o-P₂O₅ (s) + 3 H₂O (l) → 2H₃PO₄ (aq.)(52) $\Delta H^{\circ}_{348 \, \text{K}}$: -218.61 ± 1.76 kJ mol⁻¹

Stevens and Turkdogan (1954) thus obtained a value of -440.28 ± 2.3 kJ mol⁻¹ for the ΔH°_{f} of Mn₃(PO₄)₂ at 348 K from the oxide components, MnO and P₂O₅. Stevens and Turkdogan then calculated a $\Delta H^{\circ}_{f, 298 \text{ K}}$ of -3136.95 ± 29.29 kJ mol⁻¹

from the elemental components Mn (s), P (s) and O₂ (g), using thermodynamic data available at the time of its publication. If the presently available thermodynamic data for the formation of MnO and orthorombic-P₂O₅ are used (from the FToxid database in Factsage), a value of -3 134.08 ± 29.29 kJ mol⁻¹ is obtained.

Heat Capacity, C_p

No data were located in the literature.

Entropy, $S_{298.15 K}$ No data were located in the literature.

Gibbs Energy, ΔG_f

Similarly to Bookey (1953) who studied $Mg_3(PO_4)_2$ and $Ca_3(PO_4)_2$, Pearson *et al.* (1954) measured the partial pressures of the following reaction:

 $Mn_3(PO_4)_2(s) + 5H_2(g) = 3 MnO(s) + P_2(g) + 5H_2O(g) \dots (53)$

Pearson *et al.* (1954) then determined the equilibrium gas constant at 953, 1023, 1073, 1113 and 1143 K, combined the values from the Gibbs energy relationship from other reactions to produce a Gibbs energy relationship for the following reaction:

 $3MnO(s) + P_2(g) + \frac{1}{2}O_2 \rightarrow Mn_3P_2O_8(s)$ (54)

The Gibbs energy relation determined by Pearson *et al.* for the above reaction was:

 $\Delta G_{f}^{\circ}_{298-1320 \text{ K}}$: - 2 074.9 + 0.652 T kJ mol⁻¹.....(55)

4.1.1.2. Mn₂P₂O₇

Crystal Structure

Lukaszewicz (1967) determined the structure of $Mn_2P_2O_7$ by XRD and observed it to be isostructural with Sc_2SiO_7 and β -Mg_2P_2O_7. Konstants and Dimante (1977) measured pycnometrically the density of $Mn_2P_2O_7$ and determined it to be 3.745 g/cm³.

Phase Transformations

Konstants and Dimante (1977) determined, by conductivity measurements, the melting point of $Mn_2P_2O_7$ to be 1195 °C.

Thermodynamic Properties

Enthalpy of Formation, $\Delta H^{\circ}_{f, 298.15 \text{ K}}$ No data were located in the literature.

Heat Capacity, C_p

No data were located in the literature.

Entropy, $S_{298.15 K}$ No data were located in the literature.

Gibbs Energy, ΔG_{f}

No data were located in the literature.

4.1.1.3. Mn(PO₃)₂ (MP)

Crystal Structure

Bukhalova *et al.* (1975) studied the structure of the MnP_2O_6 compound by XRD and IR spectroscopy and observed that the spectrum obtained was almost identical to that of $Mg_2P_4O_{12}$ suggesting that manganese metaphosphate, $Mn(PO_3)_2$, is in fact manganese tetrametaphosphate, $Mn_2P_4O_{12}$.

Phase Transformations

Thilo and Grunze (1957) reported, from thermal analysis, the melting point to be 1040 °C. Bekturov *et al.* (1970) reported, from DTA measurements, a melting point of 1050 °C.

Bukhalova et al. (1975) synthesized MP by two reactions:

 $MnCO_3 + 2NH_4H_2PO_4 \rightarrow Mn(PO_3)_2 + 2NH_3 + 3H_3O + CO_2.....(56)$ and,

Bukhalova *et al.* (1975) obtained, from the former and latter reactions, sintered products with melting points, observed from DTA experiments, of 1000 \pm 2 °C and 1015 °C, respectively.

Thilo and Grunze (1957) reported its compound to be colorless while Bukhalova et al. (1975) reported obtaining pinkish colors in both cases. No polymorphic transitions were reported by Bukhalova *et al.* (1975). Konstants and Dimante (1977) observed, by electrical conductivity measurements, congruent melting of MP at 1000 °C.

Thermodynamic Properties

Enthalpy of Formation, $\Delta H^{\circ}_{f, 298.15 K}$ No data were located in the literature.

Heat Capacity, C_p No data were located in the literature.

Entropy, $S_{298.15 K}$ No data were located in the literature.

Gibbs Energy, ΔG_f

No data were located in the literature.

4.1.1.4. MnP₄O₁₁ (MP2)

Crystal Structure

Minacheva *et al.* (1975) observed the crystal structure of manganese ultraphophate to be monoclinic with space group $P2_{1/n}$ and isostructural with CaP₄O₁₁ while Murashova and Chudinova (1994) synthesized a different polymorph by reacting manganese(II) oxalate with polyphosphoric acids at a Mn:P ratio of 1:10 and heating to 550 °C for 5 days without stirring. The resulting colorless crystals obtained by Murashova and Chudinova were determined to be triclinic with space group *P*1. Olbertz *et al.* (1994) observed by XRD the crystal structure of MnP₄O₁₁ to be isomorphous with Mg, Zn and Co ultraphophates. Olbertz *et al.* (1995) proposed a redetermination of the crystal structure of magnesium ultraphosphate.

Phase Transformations

No data were located in the literature.

Thermodynamic Properties

Enthalpy of Formation, $\Delta H^{\circ}_{f, 298.15 \text{ K}}$

No data were located in the literature.

Heat Capacity, C_p No data were located in the literature.

Entropy, $S_{298.15 K}$ No data were located in the literature.

Gibbs Energy, ΔG_f

No data were located in the literature.

4.1.2. Liquid Phase

Similarly to the experiments of Iwase *et al.* (1987) in the MgO-P₂O₅ binary, Sobandi *et al.* (1997) determined the activity of P₂O₅ in MnO-P₂O₅ slag at 1573 K using slag equilibrium with liquid copper containing manganese and phosphorus.

Similary to Iwase *et al.* (1987) who studied the activity of P_2O_5 in MgO- P_2O_5 slag, Sobandi *et al.* (1997) determined, at 1573 K, the activity of P_2O_5 in MnO- P_2O_5 slag in equilibrium with phosphorus-containing liquid copper. The chemical content and oxygen partial pressure were measured. Thermodynamic data available in the literature were then used to relate these measurements to activity data. Sobandi *et al.* used the energy of formation of P_2O_5 as per Equation 58 from Barin (1989).

$$1/2 P_2 O_5 (I) = 1/2 P_2 (g) + 5/4 O_2 (g) \dots (58)$$

The experimental data points show a decrease in activity around the $Mn_3(PO_4)_2$ composition, indicating a strong tendency for short range ordering at the $Mn_3(PO_4)_2$ composition.

4.1.3. Phase diagram

Although manganese ultraphosphate, MnP_4O_{11} , is known to exist, no melting temperature could be located in the literature.

Pearson *et al.* (1954) produced a few phase diagram points between MnO and $Mn_3(PO_4)_2$ by thermal analysis. Fischer and Fleischer (1965) reported liquidus and solidus in the MnO-rich using thermal analysis. Konstants and Dimante (1977) determined a phase diagram between $Mn_3(PO_4)_2$ and $Mn(PO_3)_2$ by electrical conductivity measurements. Liquid activity data from Sobandi *et al.* (1997) also allowed to place a liquidus point of MnO at1573 K.

4.2. Thermodynamic Optimization

The optimized MnO-P₂O₅ binary phase diagram is presented in Figure 13 along with all phase diagram experimental data. The details of the optimization procedure and optimized model parameters will be presented below. In general, the thermodynamic data for the solid compounds were fixed firstly based on the available thermodynamic data. Then, based on the phase diagram and thermodynamic properties of the liquid phase, the entire solid and liquid parameters were finally optimized to reproduce all reliable experimental data. The optimized model parameters are presented in Table 2.



Figure 13: The optimized phase diagram of the MnO-P₂O₅ binary system along with experimental data.

Melting Points of Compounds							
Compound	Melting Point (°C)	Technique ¹	Comments	Reference			
				Pearson and Turkdogan			
$Mn_3(PO_4)_2$	1119	ТА		(1954)			
		Electrical					
	1117	conductivity		Konstants and Dimante (1977)			
	1097	DTA		Nord (1982)			
	1118	Optimization		This work			
		Electrical					
$Mn_2P_2O_7$	1195	conductivity		Konstants and Dimante (1977)			
	1195	Optimization		This work			
Mn(PO ₃) ₂	1040	ТА		Thilo and Grunze (1957)			
	1050	DTA		Bekturov et al. (1970)			
	1000	DTA		Bukhalova <i>et al.</i> (1975)			
	1015	DTA		Bukhalova <i>et al.</i> (1975)			
		Electrical					
	1000	conductivity	Congruent melting	Konstants and Dimante (1977)			
	1045	Optimization		This work			
			Excluded from	This work			
MnP_4O_{11}			this study				
¹ TA: ThermalA	Analysis, DTA: Differential Therma	I Analysis.					

Table 2:Optimized Thermodynamic Properties and Model Parameters in the Present Study in Comparison with Experimental Data.

ΔH° _{f,298.15}						
	∆H° _{,298.15} from					
	oxides*	ΔH° _{f,}	298.15 from elements			
Compound	(kJ mol⁻¹)		(kJ mol⁻¹)		Technique	Reference
	-479.8 ± 143.7				Aqueous Calorimetry	Berthelot (1987)
$Mn_3(PO_4)_2$	(calculated)		-3 085.7 ± 143.7			
	-440.2 ± 29.3	-3 134	± 29.3 (calculated)		Aqueous Calorimetry	Stevens and Turkdogan (1954)
	-454.2		-3 148		Optimization	This work
$Mn_2P_2O_7$	-370.3		-2 679.2		Optimization	This work
Mn(PO ₃) ₂	-216.5		-2 140.4		Optimization	This work
MnP ₄ O ₁₁	-		-	E>	cluded from this study	This work
* Using MnO a	and $O-P_2O_5$ as refe	erence				
S ° _{298.15}						
	S° _{298.15}	S° _{298.15} computed				
	experimental	from sum	Final optimized	values		
Compound	$(J mol^{-1} K^{-1})$	(J mol ⁻¹ K ⁻¹)	(J mol ⁻¹ K ⁻¹)		Technique	Reference
Mn ₃ (PO ₄) ₂	-	293	.9	293.9	Optimized	This work
$Mn_2P_2O_7$	-	234	.1	234.1	Optimized	This work
Mn(PO ₃) ₂	-	174	.2	174.2	Optimized	This work
					Excluded from this	
MnP_4O_{11}	-		-	-	study	This work

* As S_{298} and C_p for P_2O_5 were experimentally determined only for the hexagonal form of P_2O_5 , H- P_2O_5 was chosen as reference state to estimate unknown C_p and S_{298} of compounds.

C _p experimental						
	$C_{ ho}$	Final optimized				
	experimental	values	Technique	Reference		
Compound	(J mol ⁻¹)	(J mol ⁻¹)				
$Mn_3(PO_4)_2$	-	201.836 – 0.166021 T - 2092000T ²	$C_{\rho} = C_{\rho}(Ca_3(PO_4)_2)$	This work		
$Mn_2P_2O_7$	-	221.878 – 0.061756 T - 4669000T ²	$C_{p}=C_{p}(Ca_{2}P_{2}O_{7})$	This work		
Mn(PO ₃) ₂	-	182.547 – 0.046024 T - 4544000T ²	$C_{\rho} = C_{\rho}(Ca(PO_4)_2)$	This work		
			Excluded from this			
MnP_4O_{11}	-	-	study	This work		
MQM Parame	eters of MnO-P ₂ O ₅	liquid phase				
Mg Liquid Coo	ordination					
Number		P2O3 Liquid Coordination Number				
Z ^{Mg} _{MgMg}	= 1.37744375 ;	$Z_{P203P203}^{P203P203} = 4.1322000$				
MQM Gibbs E	nergy					
Expression:		$\Delta g_{Mn-P2O3} (kJ/mol) = (-259.052 + 0.00878)$	86T) – 146.44X _{P2O3-P2O3}			

4.2.1. Compounds

Four compounds are known to exist in this binary system: $Mn_3(PO_4)_2$, $Mn_2P_2O_7$ and $Mn(PO_3)_2$ and MnP_4O_{11} . All phases are analogous to those found in the MgO-P_2O_5 system. The crystal structure of manganese ultraphosphate, MnP_4O_{11} , was characterized by Minacheva *et al.* (1975), Olbertz *et al.* (1994) and Olbertz *et al.* (1995) but no thermodynamic data and melting point data were available in the literature. Given the critical importance of thermodynamic and melting point data in modeling, the compound was thus not modeled in this study.

No compound richer in P_2O_5 than MnP_4O_{11} was found to exist in the literature. However, given some level of symmetry with the CaO- P_2O_5 system, there is a possibility that the MnO- P_2O_5 system may contain P_2O_5 rich compounds.

4.2.1.1. Melting Temperature of Compounds

Different polymorphisms exist for $Mn_3(PO_4)_2$ but no transition temperatures are reported. Nord (1982) tried to determine the polymorphic transition of the compound but could not find any such transition until the melting of the compound measured at 1097 °C. $Mn_3(PO_4)_2$ was thus modelled in this study as a single phase using the melting points reported by Pearson *et al.* (1954) and Konstants and Dimante (1977). The melting temperature reported by Nord is also 20 °C lower than the other references raising the prospects of impurities in $Mn_3(PO_4)_2$.

The melting point measurement of $Mn_2P_2O_7$ from Konstants and Dimante (1977), at 1195 °C, was the only available one in the literature. The optimization was thus made to represent this value exactly.

The melting temperature of MP reported by Thilo and Grunze (1957) is 1040 °C, which is higher than those reported by Bukhalova *et al.* (1975) and

Konstants and Dimante (1977) at 1000 and 1115 °C, respectively. However Thilo and Grunze reported, in their experimental procedure, their compound to be colorless while Bukhalova *et al.* reported theirs to be pinkish. In his synthesizing of MP attempt Bukhalova *et al.* obtained a dark violet mass which was then sintered. During sintering, the mass lightened in color turning from dark violet to light pink, the final color at which the mass was evaluated for its melting point. Since the compound of Thilo and Grunze was clear and produced a higher melting temperature, it is thus likely that the compound synthesized by Bukhalova *et al.* retained impurities which would explain the pinkish color reported and could have caused the lower melting temperature observed. The value of 1040 °C obtained by Thilo and Grunze was thus used for modeling.

No melting temperature reference was found for manganese ultraphosphate (MnP_4O_{11}) . Given the fundamental importance of melting point data in optimization, the modeling of this compound was excluded from the present work.

Thermodynamic Properties of Compounds

Enthalpy of Formation, $\Delta H^{\circ}_{f, 298.15 \text{ K}}$

Similarly to the optimization work in the MgO-P2O5 system, the available experimental data were simultaneously optimized against experimental thermodynamic liquid (slag) properties and available phase diagram points. Once experimental data were taken into account, model parameters were adjusted to provide the best possible fit with phase diagram points. Experimental enthalpy of formation data were unavailable for the Mn₂P₂O₇ and MP compounds. Their enthalpies of formation were determined as a result of the optimization of the remaining compounds. Optimized values of enthalpy of formation at 298 K of compounds (formed from oxides, MnO (s)

and orthorombic P_2O_5 (s)) are presented in Figure 14, and compared with the optimized result of the MgO-P₂O₅ system.



Solid Compounds



Once the optimized value for the enthalpy of formation of $Mn_3(PO_4)_2$ was obtained, its enthalpy of formation from oxides (at 298 K) was calculated and produced a value of -485.5 kJ mol⁻¹. If the enthalpy of formation from oxides is calculated at 348 K (the temperature for which Stevens and Turkdogan (1954) provides the enthalpy of formation) the value is lower by less than 1 kJ mol⁻¹. Ignoring the temperature difference between the experiments of Stevens and Turkdogan (carried at 348 K) and the optimization done at 298 K, was thus seen as acceptable. The optimized value, once including the oiquid oxide activity data (discussed later), was slightly more negative than the experimental values from Stevens and Turkdogan.

The final optimized values were presented in Table 2.

Gibbs Energy, ΔG

Pearson *et al.* (1954) studied the Gibbs energy of $Mn_3(PO_4)_2$ from MnO (s), P_2 (g) and O_2 (g) in the temperature range between 953 to 1143 K and proposed the following Gibbs energy of the reaction:

 $\Delta G^{\circ} = -2074.9 + 0.652 \text{ T kJ mol}^{-1}$(59)

Pearson *et al.* (1954) argues that the temperature dependent component in the relationship is similar to the relationships for the formation of magnesium and calcium orthophosphates determined by Bookey (1953). However, the linear regression based on the actual experimental data of Pearson *et al.* produces instead the following relationship:

 $\Delta G^{\circ} = -1.941.8 + 0.113 \text{ T kJ mol}^{-1}$(60)

The smaller temperature-dependent component in the Gibbs energy of the above reaction (0.113 kJ mol⁻¹) is thus very different from those obtained by Bookey (1953) for Mg₃(PO₄)₂ and Ca₃(PO₄)₂ (0.602 and 0.586 kJ mol⁻¹, respectively) for their analogous reactions. The temperature-dependent component of the Gibbs energy is related to the entropy changes and given the similarity of Mn₃(PO₄)₂ to Mg₃(PO₄)₂ and Ca₃(PO₄)₂, a temperature dependent component, similar in magnitude, should be expected as well. Due to this reason, it could be said that the experiments by Pearson *et al.* (1954) may not have reached equilibrium state or contain a possible error in measurement. Moreover, when the data were compared during the optimization, it was found that the data could not be reproduced in a self-consistent way with the other thermodynamic data and phase diagram points. Therefore, the experimental data from Pearson *et al.* was excluded from the
current optimization work. The data from Pearson *et al.* is presented against the calculation from the final optimized data below.



Figure 15: Experimental data from Pearson *et al.* (1954) against calcualted Gibbs energy of reaction for $Mn_3(PO_4)_2$.

Heat Capacity, C_p

No heat capacity data were located in the literature for the MnO-P₂O₅ system. As was done for the MP and MP4 compounds in the MgO-P₂O₅ system modeling, C_p estimates were produced from the CaO-P₂O₅ system. For example, the C_p of Mn₃(PO₄)₂ was lifted from that of Ca₃(PO₄)₂ (available in Factsage's FToxid database). The C_p functions were left unchanged during modeling and are presented in Table 2.

Entropy, S°_{298.15}

No experimental data was found for the entropy of compounds in the MnO- P_2O_5 system. Similarly to the MgO- P_2O_5 system, estimates were generated by

summing the standard entropy values of the oxide components of each compound. For example, the $S^{\circ}_{298.15 \text{ K}}$ of $Mn_3(PO_4)_2$ was estimated by summing 3 $xS^{\circ}_{298.15 \text{ K}}$, MnO and $S^{\circ}_{298.15 \text{ K}, P2O5}$. As was shown during the optimization of the MgO-P₂O₅ compounds, summing the entropy of the oxides can yield reasonably close estimates. Entropy values at 298 K of compounds (formed from oxides, MnO (s) and hexagonal H-P₂O₅ (s)), divided by the number of oxide components (i.e. P₂O₅ or MnO oxides per compound), are presented in Figure 16.



Solid Compounds

Figure 16: ΔS°_{298} of compounds in the MnO-P₂O₅ system from MnO and hexagonal H-P₂O₅.

4.2.2. Liquid Phase Modeling

4.2.2.1. Activity data

Similarly to the experiments of Iwase *et al.* (1987), Sobandi *et al.* (1997) determined the activity of P_2O_5 in MnO- P_2O_5 slag at equilibrium with liquid

copper containing manganese and phosphorus. Sobandi *et al.* determined the activity values of P_2O_5 at 1573 K by quenching equilibrated samples and measuring their contents by spectrophotometry and ICP spectrometry. Thermodynamic data available in the literature were then used to relate these measurements to activity data. Sobandi *et al.* used the energy of formation of P_2O_5 as per Equation 58 from Barin (1989).

As was done in the thermodynamic evaluation of the MgO-P₂O₅ binary system, an adjustment factor was also computed to reflect Gibb's energy of formation of P₂O₅ as it currently exists in Factsage's FToxid database at 1573 K. The adjustment factor was determined as per:

 $\Delta G^o_{(1),\,[89Bar],1573\!K} = 366\,596\,\mathrm{J/mole}$ and,

 $\Delta G^o_{(1), FToxid, 1573K} = 382\ 683\ J/mole$

The adjustment factor obtained, at 1573 K, was equal to 1.0684 so that,

 $\ln a_{P_2O_5, FToxid, 1573K} = \ln a_{P_2O_5, [97Sob]} + 1.0684$ (61)

In the MgO-P₂O₅ system, adjusted activity values for P₂O₅ in MgO-P₂O₅ slags in equilibrium with phosphorus-containing liquid copper yielded reasonably good approximations to the activity generated by the previously optimized model parameters for the liquid MgO-P₂O₅ binary system. Using this observation, the adjusted activity values for P₂O₅ in MnO-P₂O₅ slag at equilibrium with liquid copper containing manganese and phosphorus were used as a further estimating basis for the model parameters of the liquid MnO-P₂O₅ binary system The MQM liquid model parameters were optimized simultaneously against the available compound enthalpy data and melting point measurements. The activity points measured by Sobandi *et al.* (1997), the adjusted activity points and the modeled activity lines are presented in Figure 17.



Figure 17: Activity of $P_2O_5(I)$ at 1573 K from Sobandi *et al.* (1997) in comparison with the optimized/calculated activity from the present study. In the optimization, the original experimental data were adjusted using new Gibbs energy liquid P_2O_5 to keep consistency in the database.

The liquid parameters were simultaneously optimized against the available enthalpy of formation ($\Delta H^{\circ}_{f,298.15}$) of Mn₃(PO₄)₃ and melting point measurements. The finally optimized parameters were in good agreement with the experimental compound enthalpy and liquid activity data.

4.2.3. Phase diagram

The data points from Pearson *et al.* (1954) as well as some data points from Konstants and Dimante (1977) are not followed by the optimization work. As was explained before, the data obtained from Pearson *et al.* and Fischer and Fleischer (1965) are incoherent. The data points from Fischer and Fleischer are also in good agreement with the liquidus point from Sobandi *et al.* (1997) against which the liquid system was modeled and which showed very good agreement with the Mn₃(PO₄)₂ enthalpy of formation data from Stevens and Turkdogan (1954). Some phase diagram points from Konstants and Dimante are also disregarded, especially the solidus points which are more difficult to measure than liquidus points themselves. The experimental method employed by Konstants and Dimante is also uncommon and cannot be cross-checked by other existing data.

5. Ternary CaO-MgO-P₂O₅System

A complete literature review of the CaO-MgO-P₂O₅ system was made. The Gibbs energies of ternary solid solutions were described based on the CEF model by Hillbert (2000). The Gibbs energy of the liquid phase was described using the MQM model with the Toop interpolation technique from the three sub-binary systems with P_2O_5 as asymmetric component. Given the absence of thermodynamic data, the modeling and optimization of the ternary was done mainly based on available sets of phase diagram data.

5.1.1. Ca₃(PO₄)₂ - Mg₃(PO₄)₂ Section

5.1.1.1. Ca₃(PO₄)₂ - Mg₃(PO₄)₂ (C3P-M3P) Phase Diagram Data

The $Ca_3(PO_4)_2$ -Mg₃(PO₄)₂ (C3P-M3P) binary section was investigated by Ando (1958) using DTA and XRD technique from 33 to 83 mol.% M3P. His phase diagram is presented in Figure 18.



Figure 18: Phase diagram of the $Mg_3(PO_4)_2$ -Ca₃(PO₄)₂ system proposed by Ando (1958).

He identified, for the first time, the existence of a ternary orthophosphate $Ca_3Mg_3(PO_4)_4$ (C3M3P2) phase which melted peritectically at 1175 °C and determined the liquidus of $Ca_3(PO_4)_2$, $Ca_3Mg_3(PO_4)_4$ and $Mg_3(PO_4)_2$ solid solutions. The solubility ranges of the solid solutions were also measured using various techniques.

Later, Bobrownicki and Slawski (1960) investigated the C3P-M3P section using DTA and XRD technique. They also reported the existence of a ternary orthophosphate, C3M3P2, having XRD peaks distinctive from those of C3P and M3P. C3M3P2 was reported to melt peritectically, with a significant thermal effect, at 1169 °C. These observations are in good agreement with the observations from Ando (1958). Furthermore, two polymorphic transitions were also identified for $Ca_3Mg_3(PO_4)_4$, at 1104 and at 1006 °C. No attempts to determine solid solubility were made in the study. The proposed phase diagram is shown in Figure 19.



Figure 19: Phase diagram of the Mg₃(PO₄)₂ - Ca₃(PO₄)₂ system according to Bobrownicki and Slawski (1960) from differential thermal analysis data points. Slawski (1966) observed that the solid solubility of C3P extended up to 12.75 mol.% M3P and that that of C3M3P2 extended from 45.87 to 50 mol.% M3P using XRD, DTA and metallography technique. However, the temperature of the sample prepared was not specified, so this data were not used in the present study. Slawski also studied the phase transformation of C3M3P2 compound by DTA and observed polymorphic transitions at 1006 °C, 1104 °C and a melting point at 1170 °C.

McCauley *et al.* (1967) studied the phase stability of C3P-M3P system at 1020 and 1075 °C. The equilibrium phases and solubility limits of solid solutions were identified by XRD technique. The mutual solubility of C3P and M3P was less than 8 mole % at 1200 and 1300 °C. McCauley *et al.* also confirmed by DTA the polymorphic transition observed by Slawski (1966) at 1104 °C and determined by quenching methods the incongruent melting point to be 1175 \pm 5°C.

Schroeder *et al.* (1977) studied the solid solubility range of C3P at 1350 °C using XRD lattice parameter measurement, and reported 14 mol.% M3P can be soluble in C3P at this temperature. Similarly, Terpstra *et al.* (1984) determined the maximum solubility of M3P in C3P solid solution at 1000 °C to be 14.7 mol. % M3P. Later, Terpstra *et al.* studied the entire range of C3P-M3P system by XRD at 1000 °C in air to determine the solid solution ranges of solid phases. They reported that solubility of M3P in C3P to be about 15 mole % of M3P. The C3M3P2 compound was found to have excess solubility toward M3P (the phase was stable up to about 60 mol.%M3P) but almost no excess solubility of C3P. Clement *et al.* (1989) studied the solid solubility of M3P in C3P at 1100 °C by XRD and reported that the solubility range reached up to at least 14 mol.% of M3P.

Goetz-Neunhoeffer *et al.* (2006) re-examined the phase diagram of C3P-M3P section near the C3P region. The maximum solubility of M3P in C3P solid solution was 14 mole % at about 1000 to 1200 °C using XRD lattice parameter measurement. They also determined the transition between β -C3P to α -C3P solid solution and solidus of β -C3P solid solution by DTA. No transformation for α -C3P to α '-C3P was reported. The proposed section of the C3P-M3P phase diagram is presented in Figure 3. No mention of a polymorphic transition α -C3P to α '-C3P at around 1645 °C, as is known to exist (Hudon and Jung, Unpublished results), is made by Goetz-Neunhoeffer *et al.* (2006). The proposed section of the C3P-M3P phase diagram is presented in Figure 20.



Figure 20: Phase diagram points by Goetz-Neunhoeffer *et al.* (2006) from the $Ca_3(PO_4)_2$ rich side drawn on a phase diagram redrawn according to $Mg_3(PO_4)_2$ - $Ca_3(PO_4)_2$ system.

5.1.1.2. Ca₃Mg₃(PO₄)₄ Phase

The only crystal structure data available for this ternary orthophosphate is from Dickens and Brown (1971) who determined by XRD that $Ca_3Mg_3(PO_4)_4$ is in fact $Ca_9Mg_7(Ca,Mg)_2(PO_4)_{12}$ sublattice structure, and has a monoclinic space group C2/c. No thermodynamic data were located in the literature for this compound.

5.1.1.3. Thermodynamic Modelling

Thermodynamic modeling of the solid solution phases were performed to reproduce the experimental solubility of solid solution and liquidus temperature of the $Ca_3(PO_4)_2$ -Mg₃(PO₄)₂ section. During the following sublattice structures were considered for each solid solution:

- (a) Ca₃(PO₄)₂-rich solid solutions (α and β -form): [Ca,Mg]₃P₂O₈
- (b) Mg₃(PO₄)₂-rich solid solutions: [Ca,Mg]₃P₂O₈
- (c) $Ca_3Mg_3(PO_4)_8$ solution: $[Ca,Mg]_3Mg_3P_4O_{16}$

The stable end-member Gibbs energy of each solid solution was taken from the Gibbs energy of each binary system. The Gibbs energy of pseudo endmember was used for model parameter and also if necessary, the interaction parameters were introduced to describe the phase diagram. Small ternary interaction parameters for liquid phase were also needed to reproduce the phase diagram of this section more accurately. The calculated optimized phase diagram of the $Ca_3(PO_4)_2$ -Mg₃(PO₄)₂ section is presented in Figure 21 along with all experimental data. All the experimental data are reasonably well reproduced.



Figure 21: Optimized phase diagram for the Ca₃P₂O₈-Mg₃P₂O₈ system along with all experimental data in literature.

5.1.2. $Ca_2P_2O_7$ - $Mg_2P_2O_7$ section

5.1.2.1. Ca₂P₂O₇- Mg₂P₂O₇ (C2P-M2P) Phase Diagram Data

Bobrownicki and Slawski (1960) studied the $Mg_2P_2O_7$ - $Ca_2P_2O_7$ system by DTA and visual analysis. Bobrownicki and Slawski observed the appearance of a 1:1 ternary pyrophosphate, $CaMgP_2O_7$, with a peritectic melting temperature of 1127 °C at 48 mol.% $Mg_2P_2O_7$. Bobrownicki and Slawski characterized the XRD lines of the $CaMgP_2O_7$ compound and showed them to be distinct from those of $Ca_2P_2O_7$ or $Mg_2P_2O_7$, suggesting a distinct crystal structure. Bobrownicki and Slawski also observed $CaMgP_2O_7$ to have a very low acid solubility compared to samples with compositions in the $Ca_2P_2O_7$ - $CaMgP_2O_7$ or $CaMgP_2O_7$ - $Mg_2P_2O_7$ ranges. The proposed phase diagram from Bobrownicki and Slawski is shown in Figure 22.



Figure 22: Phase diagram of the $Ca_2P_2O_7$ -Mg₂P₂O₇ system according to Bobrownicki and Slawski (1960) with data points from thermal analysis.

Later, Slawski (1967) studied the $Mg_2P_2O_7 - Ca_2P_2O_7$ system again by DTA and visual analysis. Slawski determined by acid solubility tests that the solubility of $Ca_2P_2O_7$ in $Mg_2P_2O_7$ is about 6 mol. % (or the limit is at 94 mol.% $Mg_2P_2O_7$) at 1140 °C. Slawski also identified by microscopic and X-ray analysis a ternary pyrophosphate compound. Slawski reports a stoichiometry of 4:2:3, a formula of $Ca_4Mg_2P_6O_{21}$ (4:2:3) and incongruent melting at 1140 °C. The solid solution of this ternary compound is reported to range from 33.4 to 46.8 mol.% $Mg_2P_2O_7$. Slawski provides XRD lines from samples at both the $Ca_4Mg_2P_6O_{21}$ composition (33.3 mol.% $Mg_2P_2O_7$) and at the $CaMgP_2O_7$ composition (50 mol.% $Mg_2P_2O_7$). Both sets of lines show similarities. Slawski determined by DTA that the solidus temperature on the $Ca_2P_2O_7$ - rich side was 1140°C. Slawski determined by acid solubility tests that the solubility limit of Mg₂P₂O₇ occurs at 98.25 mol.%. The solidus temperature reported on the Mg₂P₂O₇-rich side is 1126 °C.The proposed phase diagram from Slawski is shown in Figure 23.



Figure 23: Phase diagram of the Ca₂P₂O₇-Mg₂P₂O₇ system from Slawski (1967) with data points from visual (circles) and differential (triangles) thermal analysis.

McCauley *et al.* (1967) studied the $Mg_2P_2O_7$ -Ca₂P₂O₇ system by XRD. McCauley *et al.* observed by XRD that the presence of a compound with the formula Ca₄Mg₂P₆O₂₁ (occurring at a 4:2:3 ratio) is highly unlikely and is in fact CaMgP₂O₇ (at 1:1:1). McCauley *et al.* determined by thermal analysis that the incongruent melting temperature of CaMgP₂O₇ is 1120 ±5 °C and reported no solid solution regions for this ternary compound. XRD single-phase analysis was also done on the solid solution range studied by Slawski (1967) for its reported compound Ca₄Mg₂P₆O₂₁. McCauley *et al.* did not report any ternary compound within that range. McCauley *et al.* also noticed, through optical microscopy, the mixed presence of liquid and crystals at compositions ranging between Ca₂P₂O₇-CaMgP₂O₇ and CaMgP₂O₇-Mg₂P₂O₇ with a fully crystalline structure achieved only at the CaMgP₂O₇ composition. CaMgP₂O₇ was determined to melt incongruently at 1120 ± 5 °C by McCauley *et al.* through thermal analysis. McCauley *et al.* determined by DTA that the solidus temperature in the Ca₂P₂O₇-rich side also occurred at 1120 °C.

Terpstra et al. (1984) also studied the Ca₂P₂O₇-Mg₂P₂O₇ system by XRD at 1000 °C. They found from XRD experiments that the solubility of Ca₂P₂O₇ in Mg₂P₂O₇ is immeasurably small at 1000 °C. Terpstra et al. also found by extrapolating XRD peak heights at 1000 °C, a ternary pyrophosphate compound with a solid solution ranging from 15.9 to 27.5 mol.% MgO and mentions that though this region does not clearly enclose CaMgP₂O₇, it does enclose the Ca₄Mg₂P₆O₂₁ compound mentioned by Slawski (1967). Similarly to McCauley et al. (1967), Terpstra et al. performed single-phase characterization by XRD over the $Ca_{2}P_{2}O_{7}$ -Mg₂P₂O₇ ranges. An analysis of 20 peak positions shows a shift in positions between samples at 20.7 and 29.1 mol.% $Mg_2P_2O_7$ and another shift occurring between samples with compositions of 38.1 and 44.85 mol.% Mg₂P₂O₇. Extrapolations of trends by Terpstra et al. give a range of 23.85 – 41.25 mol.% Mg₂P₂O₇. Terpstra et al. recognizes this range as being the solid solution range of a ternary pyrophosphate. Terpstra et al. also notes that this range of shifts encompasses the Ca₄Mg₂P₆O₂₁ composition identified by Slawski (1967). Terpstra *et al.* found by XRD at 1000 °C that the solubility of $Mg_2P_2O_7$ extended from about 98.4-100 mol.% $Mg_2P_2O_7$.

5.1.2.2. Thermodynamic Modelling

The optimized phase diagram calculated in the present study is presented in Figure 24 along with compiled phase diagram data. In the thermodynamic modeling, the following sublattice structure was considered for Mg₂P₂O₇-rich solid solution:

(a) Mg₂P₂O₇-rich solid solutions: [Mg,Ca]₂P₂O₇

The stable end-member Gibbs energy of each solid solution was taken from the Gibbs energy of each binary system. The Gibbs energy of pseudo endmember of $Ca_2P_2O_7$ is used as model parameter for the solution. No solubility of $Mg_2P_2O_7$ in $Ca_2P_2O_7$ is assumed in the present study. The $Ca_4Mg_2P_6O_{21}$ (4:2:3) solid solution phase was considered as a stoichiometric compound, $Ca_4Mg_2P_6O_{21}$ in the present study for the sake of simplicity. The $CaMgP_2O_7$ originally proposed by Bobrownicki and Slawski (1960) were not considered, following the analysis of later studies. As can be seen Fig. 7, all the phase diagram data are well reproduced in the present study except the homogeneity range of $Ca_4Mg_2P_6O_{21}$ (4:2:3) phase.



Figure 24: Optimized phase diagram for the Ca₂P₂O₇-Mg₂P₂O₇ system along with phase diagram experimental data in literature.

5.1.2.3. Other sections

Slawski (1967) performed a visual and thermal analysis on three additional isoplethes in the CaO-MgO-P₂O₅ ternary system. Those sections are the $Ca_3Mg_3(PO_4)_2$ -Mg₂P₂O₇, $Ca_3Mg_3(PO_4)_2$ -Ca₄Mg₂P₆O₂₁ and $Ca_3Mg_3(PO_4)_4$ -CaMgP₂O₇ systems. The proposed phase diagrams are presented in Figure 25.



Figure 25: Phase diagrams proposed by Slawski (1967). (a) $Ca_3Mg_3(PO_4)_4$ -Mg₂P₂O₇, (b) $Ca_3Mg_3(PO_4)_4$ - $Ca_4Mg_2P_6O_{21}$ and (c) $Ca_3Mg_3(PO_4)_4$ - $CaMg_P2O_7$ systems.

5.1.3. CaO-MgO-P₂O₅ Liquidus Projection

Based on the present thermodynamic modeling, the liquidus projection of the CaO-MgO-P₂O₅ system is calculated in Figure 26. The liquid Gibbs energy was calculated using the parameters from all the three sub-binary systems: the parameters for the CaO-P₂O₅ binary determined through the optimization work of Jung and Hudon (unpublished results), the parameters for the CaO-MgO binary available in the Fact53 database and the parameters determined in the present study for MgO-P₂O₅ are used with two ternary parameters.



Figure 26: Predicted liquidus projection for the CaO-MgO-P₂O₅ system from the present study.

Table 3 details the invariant reactions within the CaO-MgO-P₂O₅ calculated with the model parameters developed in this study.

	Invariant Reaction		P_2O_5	CaO	MgO
			(mol. frac.)	(mol. frac.)	(mol. frac.)
1	$L \rightarrow CaO + MgO + Ca_4P_2O_9$	1645	0.1938	0.72609	0.08011
2	$L \rightarrow Ca_4P_2O_9 + \alpha'-Ca_3P_2O_8 + \alpha-Ca_3P_2O_8$	1511	0.23175	0.72144	0.04681
3	$L \rightarrow MgO + Ca_4P_2O_9 + \alpha - Ca_3P_2O_8$	1505	0.23091	0.71754	0.05155
4	$L \rightarrow MgO + \alpha - Ca_3P_2O_8 + \beta - Ca_3P_2O_8$	1486	0.23776	0.62699	0.13525
5	$L \rightarrow Ca_2P_2O_7 + \alpha - Ca_3P_2O_8 + \beta - Ca_3P_2O_8$	1270	0.29248	0.6702	0.03732
6	$L \rightarrow MgO + Ca_3Mg_3P_4O_{16} + \beta - Ca_3P_2O_8$	1169	0.24425	0.39887	0.35687
7	$L \rightarrow \alpha \text{-} Ca_2P_2O_7 + \beta \text{-} Ca_2P_2O_7 + \beta \text{-} Ca_3P_2O_8$	1140	0.30752	0.46413	0.22835
8	$L \rightarrow MgO + Ca_3Mg_3P_4O_{16} + Mg_3P_2O_8$ -rich	1132	0.24515	0.21684	0.53801
9	$L \rightarrow \beta \text{-} Ca_2 P_2 O_7 + Ca_4 Mg_2 P_6 O_{21} + \beta \text{-} Ca_3 P_2 O_8$	1127	0.30771	0.44909	0.2432
10	$L \rightarrow Ca_3Mg_3P_4O_{16} + Mg_2P_2O_7$ -rich + Mg3P2O8-rich	1118	0.26045	0.20456	0.53499
11	$L \rightarrow Ca_3Mg_3P_4O_{16} + Mg_2P_2O_7$ -rich + β - $Ca_3P_2O_8$	1115	0.27417	0.36240	0.36343
12	$L \rightarrow Ca_4Mg_2P_6O_{21} + Mg_2P_2O_7 \text{-rich} + \beta \text{-} Ca_3P_2O_8$	1108	0.30168	0.40144	0.29689
13	$L \rightarrow Ca_4Mg_2P_6O_{21} + Mg_2P_2O_7$ -rich + MgP ₂ O ₆	960	0.43379	0.25915	0.30706
14	$L \rightarrow \beta$ - Ca ₂ P ₂ O ₇ + Ca ₄ Mg ₂ P ₆ O ₂₁ + MgP ₂ O ₆	915	0.45253	0.34998	0.19749
15	$L \rightarrow \beta - Ca_2P_2O_7 + Ca_4P_6O_{19} + MgP_2O_6$	901	0.45947	0.37169	0.16884
16	$L \rightarrow Ca_4P_6O_{19} + CaP_2O_6 + MgP_2O_6$	900	0.46400	0.37486	0.16114
17	$L \rightarrow Ca_2P_6O_{17} + CaP_2O_6 + MgP_2O_6$	737	0.62334	0.28988	0.08679
18	$L \rightarrow Ca_2P_6O_{17} + CaP_4O_{11} + MgP_2O_6$	728	0.63182	0.27455	0.09363
19	$L \rightarrow CaP_4O_{11} + MgP_2O_6 + MgP_4O_{11}$	724	0.64867	0.2273	0.12404
20	$L \rightarrow CaP_4O_{11} + MgP_4O_{11} + O'-P_2O_5$	451	0.84102	0.09131	0.06767

Table 3: Invariant Reactions Within the CaO-MgO-P₂O₅.

5.1.4. CaO-MgO-P₂O₅ Ternary Modeling Parameters

The optimized model parameters for the ternary liquid solution (using the MQM) and solid solutions (using the CEF) are presented in

Table 4 and Table 5, respectively.

Table 4: Optimized Model Parameters for the CaO-MgO-P₂O₅ Ternary Liquid Solution. Liquid solution (Modified Quasichemical model parameters) (J-mol⁻¹)

Coordination numbers: $Z_{Mg Mg}^{Mg} = 1.37744375, Z_{Ca Ca}^{Ca} = 1.37744375, Z_{P2O3 P2O3}^{P2O3} = 4.132200,$

Optimized binary excess Gibbs energy parameters for MgO-P₂O₅ were presented in Table 1. Optimized binary excess Gibbs energy parameters for CaO-P₂O₅ were determined by Hudon and Jung (2013) using the MQM:

$$\Delta g_{Ca-P_2O_3} = (-435194.224 + 41.300264 \text{ T}) - 37530.48 X_{Ca-Ca} - 123900.792 X_{P_2O_3-P_2O_3} + (-186955.19916 + 41.835816 \text{ T}) X_{P_2O_3-P_2O_3}^2 + 76427.09876 X_{P_2O_3-P_2O_3}^4$$

Optimized binary excess Gibbs energy parameters for CaO-MgO were already available in the Factsage solution database. This binary was modeled according to the first extension of the quasichemical model by Dessureault and Pelton (1991). The Gibbs energy parameters for CaO-MgO are:

 $\Delta g_{CaO-MaO} = 45350.4599 - 30595.9 X_{Ca-Ca}$

The ternary excess Gibbs energy parameters (MQM) are:

 $\Delta G_{CaO-MgO-P_2O_5} : q_{CaO,P_2O_5(Mgo)}^{002} = -14\ 650.3 \ \& \ q_{CaO,P_2O_5(Mgo)}^{003} = -6\ 278.7$

Table 5: Optimized CEF Model Parameters for Solid Solutions in the Ternary CaO-MgO-P₂O₅ system.

Solid Solution CEF Parameters in the Ca₃P₂O₈ - Mg₃P₂O₈ system

 α' -Ca₃P₂O₈-rich solution (high temperature polymorph) (α' - [Ca,Mg]₃P₂O₈)

 $\begin{array}{ll} G_{solution} = & y_{Mg} y_{P_2 O_8} G^o_{Mg_3 P_2 O_8} + y_{Ca} y_{P_2 O_8} G^o_{\alpha' - Ca_3 P_2 O_8} + 3RT(y_{Mg} lny_{Mg} + y_{Ca} lny_{Ca}) + G^{excess} \\ G^o_{\alpha' - Ca_3 P_2 O_8} = & G^o_{\alpha' - Ca_3 P_2 O_8} \\ G^o_{Mg_3 P_2 O_8} = & G^o_{Mg_3 P_2 O_8} + 171,618 \text{ (J/mol)} \\ G^{excess} = & L_{Ca,Mg:P_2 O_8}(y_{Mg} - y_{Ca})y_{Ca} y_{Mg} y_{P_2 O_8} \\ 121,388 - 18.84 \text{ T (J/mol)} \end{array}$

 α -Ca₃P₂O₈-rich solution(mid temperature polymorph) (α - [Ca,Mg]₃P₂O₈)

 $\begin{array}{ll} G_{solution} = & y_{Mg} y_{P_2 O_8} G^o_{Mg_3 P_2 O_8} + y_{Ca} y_{P_2 O_8} G^o_{\alpha - Ca_3 P_2 O_8} + 3RT(y_{Mg} lny_{Mg} + y_{Ca} lny_{Ca}) + G^{excess} \\ G^o_{\alpha - Ca_3 P_2 O_8} = & G^o_{\alpha - Ca_3 P_2 O_8} \\ G^o_{Mg_3 P_2 O_8} = & G^o_{Mg_3 P_2 O_8} + 129,760 \text{ (J/mol)} \\ G^{excess} = & L_{Ca,Mg; P_2 O_8}(y_{Mg} - y_{Ca})y_{Ca} y_{Mg} y_{P_2 O_8} = 121,388 - 18.84 \text{ T} \text{ (J/mol)} \end{array}$

 β -Ca₃P₂O₈-rich solution(low temperature polymorph)(β - [Ca,Mg]₃P₂O₈)

 $G_{solution} = y_{Mg} y_{P_2 O_8} G^o_{Mg_3 P_2 O_8} + y_{Ca} y_{P_2 O_8} G^o_{\beta - Ca_3 P_2 O_8} + 3RT(y_{Mg} ln y_{Mg} + y_{Ca} ln y_{Ca}) + G^{excess}$ $G^o_{\beta - Ca_3 P_2 O_8} = G^o_{\beta - Ca_3 P_2 O_8}$

$$\begin{array}{ll} G^o_{Mg_3P_2O_8} = & G^o_{Mg_3P_2O_8} + 79,530 \text{ (J/mol)} \\ G^{excess} = & L_{Ca,Mg;P_2O_8}(y_{Mg} - y_{Ca})y_{Ca}y_{Mg}y_{P_2O_8} = 121,388 - 18.84 \text{ T (J/mol)} \end{array}$$

Mg₃P₂O₈-rich solution ([Mg,Ca]₃P₂O₈)

$G_{solution} =$	$y_{Mg}y_{P_2O_8}G^o_{Mg_3P_2O_8} + y_{Ca}y_{P_2O_8}G^o_{a-Ca_3P_2O_8} + 3RT(y_{Mg}lny_{Mg} + y_{Ca}lny_{Ca}) + G^{excess}$
$G^{o}_{Mg_3P_2O_8} =$	$G^{o}_{Mg_{3}P_{2}O_{8}}$
$G^o_{\alpha-Ca_3P_2O_8} =$	$G^{o}_{\alpha-Ca_{3}P_{2}O_{8}}$ + 100,459 (J/mol)
$G^{excess} =$	0

Ternary Ca₃Mg₃P₄O₁₆ solid solution ([Ca,Mg]₃Mg₃P₄O₁₆)

$G_{solution} =$	$y_{Ca}y_{P_4O_{16}}G^{o}_{Ca_3Mg_3P_4O_{16}} + y_{Mg}y_{P_4O_{16}}G^{o}_{Mg_3Mg_3P_4O_{16}} + 3RT(y_{Mg}lny_{Mg} + y_{Ca}lny_{Ca}) + G^{excess}$
$G^{o}_{Ca_{3}Mg_{3}P_{4}O_{16}} =$	G ^o _{Ca₃P₂O₈ - 31,393 (J/mol)}
$G^{o}_{Mg_{3}Mg_{3}P_{4}O_{16}} =$	$G_{Mg_3P_2O_8}^{o}$ + 5,860 (J/mol)
$G^{excess} =$	$L_{Ca,Mg:Mg:P_4O_{16}}(y_{Mg} - y_{Ca})y_{Ca}y_{Mg}y_{P_4O_{16}} = 73,251 \text{ (J/mol)}$

Solid Solutions in the Ca₂P₂O₇ - Mg₂P₂O₇ system

 α -Mg₂P₂O₇-rich solution ([Ca,Mg]₂P₂O₇)

$G_{solution} =$	$y_{Mg}y_{P_{2}O_{7}}G^{o}_{Mg_{2}P_{2}O_{7}} + y_{Ca}y_{P_{2}O_{7}}G^{o}_{Ca_{2}P_{2}O_{7}} + 2RT(y_{Mg}lny_{Mg} + y_{Ca}lny_{Ca}) + G^{excess}$			
$G^{o}_{Ca_{2}P_{2}O_{7}} =$	G ^o _{Ca2P2O7} + 75,344 (J/mol)			
$G^{o}_{Mg_2P_2O_7} =$	$G^o_{Mg_2P_2O_7}$			
$G^{excess} =$	$L_{Ca,Mg:Mg:P_4O_{16}}(y_{Mg} - y_{Ca})y_{Ca}y_{Mg}y_{P_4O_{16}} = 0$			
Stoichiometric compound				
$Ca_4Mg_2P_6O_{21}$	G of Ca ₄ Mg ₂ P ₆ O ₂₁ = 2 G of γ -Ca ₂ P ₂ O ₇ + G of low-T Mg ₂ P ₂ O ₇ + Δ H - T Δ S			
	∆H = -20,000 (J/mol)			
	$\Delta S = 0 (J/mol-K)$			

6. Conclusion

Based on the CALPHAD approach, the phase diagrams of the MgO-P₂O₅, MnO-P₂O₅ and CaO-MgO-P₂O₅ systems were modeled using numerical models and developing fitting parameters against available experimental data. Where experimental data was unavailable, assumptions, based on similar systems, were made. The resulting thermodynamic parameters were included in the database of the Factsage software package for use in the pyrometallurgical industries. These models, with their parameters, will increase the accuracy of thermodynamic equilibrium calculations involving MgO, MnO, CaO and P_2O_5 and will allow performing a more accurate thermodynamic simulation of industrial processes such as the dephosphorization of steel.

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