A PROCEDURE TO COMPUTE EQUILIBRIUM CONCENTRATIONS IN MULTICOMPONENT SYSTEMS BY GIBBS ENERGY MINIMIZATION ON SPREADSHEETS

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Abstract:
Equilibrium concentrations are traditionally calculated with the help of equilibrium constant equations from selected reactions. This procedure, however, is only useful for simpler problems. Analysis of the equilibrium state in a multicomponent and multiphase system necessarily involves solution of several simultaneous equations, and, as the number of system components grows, the required computation becomes more complex and tedious. A more direct and general method for solving the problem is the direct minimization of the Gibbs energy function. The solution for the nonlinear problem consists in minimizing the objective function (Gibbs energy of the system) subjected to the constraints of the elemental mass-balance. To solve it, usually a computer code is developed, which requires considerable testing and debugging efforts. In this work, a simple method to predict equilibrium composition in multicomponent systems is presented, which makes use of an electronic spreadsheet. The ability to carry out these calculations within a spreadsheet environment shows several advantages. First, spreadsheets are available ‘universally’ on nearly all personal computers. Second, the input and output capabilities of spreadsheets can be effectively used to monitor calculated results. Third, no additional systems or programs need to be learned. In this way, spreadsheets can be as suitable in computing equilibrium concentrations as well as to be used as teaching and learning aids. This work describes, therefore, the use of the Solver tool, contained in the Microsoft Excel spreadsheet package, on computing equilibrium concentrations in a multicomponent system, by the method of direct Gibbs energy minimization. The four phases Fe-Cr-O-C-Ni system is used as an example to illustrate the method proposed. The pure stoichiometric phases considered in equilibrium calculations are: \( \text{Cr}_2\text{O}_3(s) \) and \( \text{FeO}_\text{Cr}_2\text{O}_3(s) \). The atmosphere consists of \( \text{O}_2 \), CO e \( \text{CO}_2 \) constituents. The liquid iron, dissolving \( \text{O}, \text{Cr}, \text{C} \) and \( \text{Ni} \), is modeled with the Unified Interaction Parameter Formalism considering the existence of associates \( \text{Cr}^*\text{O} \) and \( \text{Cr}_2^*\text{O} \), in order to take into account the strong attractive interaction between \( \text{Cr} \) and \( \text{O} \). The thermodynamic conditions found in the production of low carbon stainless steel are analyzed. The thermodynamic equilibrium between dissolved \( \text{Cr} \) and \( \text{O} \) were analyzed at 1873 and 1923 K. The value of the critical chromium in liquid iron is calculated for the temperature of 1873 K. The effects of vacuum level and \( \text{Ni} \) content on decarburization are shown with the proposed method. In this work, the change of variables to overcome the deficiency of the Solver in applying the generalized reduced gradient method (GRG) is also presented. Spreadsheet results are compared with experimental results from the literature and with results determined with the help of FactSage - a commercial software package for solving chemical thermodynamic problems. From the comparison, it can be seen that spreadsheet results are in satisfactory agreement with all others. In addition, it has been shown simultaneously how spreadsheets can be easily used for metallurgical thermodynamics educational purposes.

Keywords: metallurgical thermodynamics, multicomponent systems, Gibbs energy minimization, spreadsheets, engineering education
1. INTRODUCTION

Equilibrium calculations are traditionally made with the help of equilibrium constant equations from selected reactions. However, this procedure is only useful for simpler problems. In many industrially important metallurgical systems, it is usual to find a lot of components and phases. In this way, analysis of the equilibrium state in a multicomponent and multiphase system necessarily involves solution of several simultaneous equations, and, as the number of system components grows, the required computation becomes more complex and tedious. A more direct and general method for solving these complicated problems is the direct minimization of the Gibbs function of the system. The more complex systems have one or more condensed phases, solid or liquid solutions, in addition to the gas phase. The total free energy for such a system is given by [1]:

\[
\frac{G}{RT} = \frac{1}{RT} \sum_{i=1}^{N} n_i G_i^g + \frac{1}{RT} \sum_{i=1}^{N} n_i \ln n_i + \frac{1}{RT} \sum_{i=1}^{N} n_i G_i^l + \frac{1}{RT} \sum_{i=1}^{N} n_i \ln n_i + \frac{1}{RT} \sum_{i=1}^{N} n_i G_i^s + \frac{1}{RT} \sum_{i=1}^{N} n_i \ln n_i + \frac{1}{RT} \sum_{i=1}^{N} n_i \ln n_i
\]

(1)

Where the superscripts g, l and s denote gas, liquid and solid phases.

The problem is to find the different values of \( n_i \) which minimizes the objective function given by equation (1), subject to the constraints of elemental mass balance

\[
\sum_{i=1}^{N} n_i a_{ik} = A_k, \quad K = 1 \text{...} M
\]

(2)

The nonlinear programming model, comprising the objective function (1) to be minimized and the constraints (2), is traditionally solved by the Lagrange multiplier method [2]. However, solving this kind of problem, using the Lagrange method, can be a very difficult task, due to resultant set of equations that can consist in a complex non-linear system. In this way, it is preferable to use direct methods, such as the sequential quadratic programming (SQP) and the generalized reduced gradient (GRG).

To solve such models numerically, usually a computer code is developed, which requires considerable testing and debugging efforts. Instead of developing computer programs, one can also use commercial scientific computer libraries. However, they require driver programs and are machine or software specific. Although there are commercial software packages for solving chemical equilibrium problems, the calculation steps are hidden from the user, and hence they are not suitable to use as teaching and learning aids [2].

In this context, this work presents a simple method to predict equilibrium composition in multicomponent systems, which makes use of an electronic spreadsheet.

The ability to carry out these calculations within a spreadsheet environment shows several advantages. First, spreadsheets are available ‘universally’ on nearly all personal computers. Second, the input and output capabilities of spreadsheets can be effectively used to monitor calculated results. Third, no additional systems or programs need to be learned.

This work describes, therefore, the use of the Solver tool, contained in the Microsoft Excel spreadsheet package, on computing equilibrium concentrations in a multicomponent system, by the method of direct Gibbs energy minimization method.

In addition, this study is aimed at showing how spreadsheets can be used for metallurgical thermodynamics educational purposes. For this reason, the Fe-Cr-O-C-Ni system, which is a basic system in describing the stainless steel production in the steelmaking, is used as an example to illustrate the method proposed.

2. METHOD

The minimization model, consisting of the objective function (1) and the constraints (2), can be directly solved by using Microsoft Excel Spreadsheet’s Solver feature. The Solver applies the Generalized Reduced Gradient (GRG) method to solve nonlinear programming problems.

2.1 Change of variables

One deficiency of the current GRG spreadsheet solver, especially in solving this type of model, is that it seems to violate the non-negativity constraints [2]. This can be due to the fact that GRG algorithm can reach nonfeasible points in trying to get to the optimal solution [3], combined with the involvement of logarithmic functions of the variables.

In this way, in order to overcome this deficiency and to avoid the error message generated by this deficiency, in this work, a change of variables is presented as follows:

Considering, for the sake of simplification, the objective function given by Eq (3):

\[
\frac{G}{RT} = \frac{1}{RT} \sum_{i=1}^{N} n_i G_i^p + \frac{1}{RT} \sum_{i=1}^{N} n_i \ln \frac{n_i}{\sum n_j}
\]

(3)
And doing
\[ n_i = e^{\varphi_i} \tag{4} \]
Combining Eq. (3) and (4) and after rearrangement, we can write:
\[ \frac{G}{RT} = \sum_{i=1}^{N} e^{\varphi_i} \left[ \frac{G_{i}^{0}}{RT} + \varphi_i - \ln \left( \sum_{i=1}^{N} e^{\varphi_i} \right) \right] \tag{5} \]
Remembering the shape of the exponential curve, we can easily see, in Eq. (5), that there will be no more problem with the involvement of logarithmic functions of the variables and, in this way, it is possible to overcome the deficiency of the Solver tool.

2.2 Thermodynamic data

The Gibbs energy description, at normal temperature and pressure, for each species, is calculated from the Gibbs-Helmholtz relation
\[ G = H - TS \tag{6} \]
The temperature dependence of Gibbs energy can be described using the heat capacity, which is often described using an empirical formula, such as:
\[ C_{p} = a + b \cdot 10^{-6}T + \frac{c \cdot 10^{6}}{T^2} + d \cdot 10^{-6}T^2 \tag{7} \]
Enthalpy and entropy can be calculated from heat capacity by:
\[ C_{p} = \frac{\partial H}{\partial T} \tag{8} \]
\[ \frac{C_{p}}{T} = \frac{\partial S}{\partial T} \tag{9} \]
According to Eq. (6) to (9), the Gibbs energy for each specie as a function of temperature is:
\[ G = a_0 - a_1 T + a_2 T(1 - \ln T) - b_1 T^{2} \cdot \frac{c \cdot 10^{6}}{2T} - d_1 10^{-6}T^{3} \tag{10} \]
Where \( a, b, c, d \) are the same constants as in Eq. (7) and \( a_0 \) and \( a_1 \) are constants that can be calculated from the constants \( a, b, c \) and \( d \) and standard values \( H(298) \) and \( S(298) \).

Table I shows the thermodynamic data, obtained from Knacke et al. [4], that were employed in Eq. (10) to compute the Gibbs energy for each specie, in pure standard state, considered in this work.

The liquid iron, dissolving \( O, Cr, C \) and \( Ni \), is modeled with the Unified Interaction Parameter Formalism, considering the existence of associates \( Cr^*O \) and \( Cr_2^*O \), in order to take into account a very strong attractive interaction between \( Cr \) and \( O \). The description of this model can be seen in the work of Bale and Pelton [5] and more details about the associates are presented in the work of Jung et al. [6].

The Gibbs energy for the solution phase (liquid iron), involving the system \( Fe-Cr-O-C-Ni \), is given by Eq. (11).
\[ G = (n_{Fe}G_{Fe}^{0} + n_{Cr}G_{Cr}^{0} + n_{O}G_{O}^{0} + n_{C}G_{C}^{0} + n_{Ni}G_{Ni}^{0} + n_{Cr^*O}G_{Cr^*O}^{0} + n_{Cr_2^*O}G_{Cr_2^*O}^{0}) + RT(n_{Fe}lnG_{Fe} + n_{Cr}lnG_{Cr} + n_{O}lnG_{O} + n_{C}lnG_{C} + n_{Ni}lnG_{Ni} + n_{Cr^*O}lnG_{Cr^*O} + n_{Cr_2^*O}lnG_{Cr_2^*O}) \]
\[ + RT(n_{Fe}lnf_{Fe} + n_{Cr}lnf_{Cr} + n_{O}lnf_{O} + n_{C}lnf_{C} + n_{Ni}lnf_{Ni} + n_{Cr^*O}lnf_{Cr^*O} + n_{Cr_2^*O}lnf_{Cr_2^*O}) \] \( + n_{Cr^*O}lnf_{Cr^*O} + n_{Cr_2^*O}lnf_{Cr_2^*O} \) \( + n_{Cr^*O}lnf_{Cr^*O} + n_{Cr_2^*O}lnf_{Cr_2^*O} \)
In the first- order modified parameter, we have for a solute \( i \):
\[ \ln f_{i} = \ln f_{i}^{0} + \varepsilon_{Cr}X_{Cr} + \varepsilon_{C}X_{C} + \varepsilon_{O}X_{O} \tag{12} \]
Where:
\[ \ln f_{Fe} = -\frac{1}{2} [\varepsilon_{C}X_{C} + \varepsilon_{O}X_{O}^{2} + \varepsilon_{Cr}X_{Cr} + \varepsilon_{Cr_{2}O}X_{Cr_{2}O} + \varepsilon_{Cr_{O}O}X_{Cr_{O}O} + \varepsilon_{Cr_{2}O_{2}O}X_{Cr_{2}O_{2}O}] \tag{13} \]
Similarly to the work of Jung et al. [6], in this work was assumed that:
\[ f_{0} = f_{Cr^*O} = f_{Cr_{2}O} = 1 \tag{14} \]
In order to obtain the standard Gibbs energies in the infinite dilution (Henrian standard state), which is necessary in the description of the Gibbs energy of liquid iron, the following relationship, involving the activity coefficient, was employed:
\[ RT\ln y_{i}^{d} = \frac{g_{i}^{d}(Henrian\text{standard\ state})}{g_{i}^{d}(pure\text{element\ standard\ state})} \tag{15} \]
The activity coefficient of each element dissolved in liquid iron (for applying in the above equation) can be seen in Table II:

<table>
<thead>
<tr>
<th>Table II. The activity coefficient of each element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>Ni</td>
</tr>
</tbody>
</table>
The standard Gibbs energy in Henrian standard state for the associates Cr*O and Cr₂*O is given by:

\[ g_{B, \text{Cr}*O} = -433093 \quad g_{B, \text{Cr}_2*O} = -550665 \]  \hspace{1cm} (16)

Interaction parameters are tabulated by Carvalho et al. [7]

\[ \varepsilon_{\text{CM}} = \varepsilon_{\text{CD}} = \varepsilon_{\text{DM}} = \varepsilon_{\text{BD}} = 0 \]

\[ \varepsilon_{\text{CD}} = \varepsilon_{\text{BC}} = -5.1 \]

\[ \varepsilon_{\text{C}} = 7.8 \quad \varepsilon_{\text{D}} = \varepsilon_{\text{MC}} = 2.9 \]  \hspace{1cm} (17)

### 2.3 Building a spreadsheet and using Solver tool

Fig. 1 shows the spreadsheet that computes equilibrium concentrations, at 1873 K, for a given input of moles of Fe, Cr and O. It is possible to see the number of moles of each specie in liquid iron as well as the amount of the solid oxides Cr₂O₃ and FeO.Cr₂O₃ and number of moles of O₂ in the atmosphere. In Fig. 1, we can also see how to introduce data in a Solver dialogue box. It is necessary only to specify the objective function to be minimized, that is, the target cell, given by the cell B10, which corresponds to the total Gibbs energy of the system divided by RT. In the next step, the user adds the equations related to the elemental mass balance in the space of the dialogue box named “Subjected to the Constraints”. These equations can be seen in the spreadsheet by the formulas entered in A13, A14 and A15 cells, which correspond to the mass balance given by Eq. (2) of Fe, Cr and O, respectively. The cells to be changed in the minimization process are from B2 to B9, indicated in dialogue box as “By Changing Cells”. The values of these cells, \( n' \), are negative, due to the change of variables presented in section 2.1. The cells C2 to C9 show the respective number of moles of the species, obtained calculating \( e^{n'} \).

<table>
<thead>
<tr>
<th>Species</th>
<th>H(298) Jmol⁻¹</th>
<th>S(298) Jmol⁻¹K⁻¹</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>( a₀ )</th>
<th>( a₁ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0</td>
<td>27.280</td>
<td>46.024</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-10828</td>
<td>-245.456</td>
</tr>
<tr>
<td>Cr (S)</td>
<td>0</td>
<td>23.640</td>
<td>24.514</td>
<td>2.050</td>
<td>-0.18</td>
<td>5.950</td>
<td>-8056</td>
<td>-117.919</td>
</tr>
<tr>
<td>C(graphite)</td>
<td>0</td>
<td>5.740</td>
<td>24.435</td>
<td>0.435</td>
<td>-3.163</td>
<td>-</td>
<td>-16019</td>
<td>-146.304</td>
</tr>
<tr>
<td>Ni (L)</td>
<td>0</td>
<td>29.874</td>
<td>38.911</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-2198</td>
<td>-193.932</td>
</tr>
<tr>
<td>CO (g)</td>
<td>-110528</td>
<td>-197.65</td>
<td>30.962</td>
<td>2.439</td>
<td>-0.280</td>
<td>-</td>
<td>-120809</td>
<td>18.937</td>
</tr>
<tr>
<td>CO₂(g)</td>
<td>-393521</td>
<td>213.794</td>
<td>51.128</td>
<td>4.368</td>
<td>-1.469</td>
<td>-</td>
<td>-413886</td>
<td>-87.078</td>
</tr>
<tr>
<td>O₂(g)</td>
<td>0</td>
<td>205.146</td>
<td>29.154</td>
<td>6.477</td>
<td>-0.184</td>
<td>-1.017</td>
<td>-9589</td>
<td>36.116</td>
</tr>
<tr>
<td>Cr₂O₃(s)</td>
<td>-1458605</td>
<td>81.170</td>
<td>109.650</td>
<td>15.456</td>
<td>-</td>
<td>-</td>
<td>-1173938</td>
<td>-548.181</td>
</tr>
<tr>
<td>FeO.Cr₂O₃(s)</td>
<td>-1458605</td>
<td>146.858</td>
<td>163.009</td>
<td>22.343</td>
<td>-3.188</td>
<td>-</td>
<td>-1518892</td>
<td>-806.493</td>
</tr>
</tbody>
</table>

Table I: Thermodynamic data of pure substances considered in this work. Data from Knacke et al. [4].
Once a solution has been generated, Solver permits the user to keep or reject the solution found. Additionally, Solver can create reports that summarize the sensitivity, answer, and limits of the solution found. The sensitivity report gives the values of Lagrange multipliers associated to each restriction associated to the elemental mass balance. This information is very useful, since it is possible to predict the activity of a specie through the following relationship:

\[
\ln a_i = \left( -\frac{G^o_i}{RT} \right) + \sum \frac{\lambda_k}{RT} a_{i,k}
\]

The extent of the deviation from unity of an activity for a stoichiometric condensed phase is a measure of its thermochemical instability. For values of activity smaller than unit, this phase is not in equilibrium. A value close to unity indicates that even small changes in temperature, pressure and or composition can make this phase appear at equilibrium.

Fig. 2 shows, on top, a Solver dialogue box, where is possible to select the option ‘Sensitivity’. On bottom, the sensitivity report shows the values of Lagrange multipliers associated to elemental mass balances of Fe, Cr and O.

<table>
<thead>
<tr>
<th>cell</th>
<th>Name</th>
<th>Final Value</th>
<th>Lagrange Multiplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$11</td>
<td>Fe</td>
<td>0.00</td>
<td>-7.40</td>
</tr>
<tr>
<td>$A$12</td>
<td>Cr</td>
<td>0.00</td>
<td>-9.18</td>
</tr>
<tr>
<td>$A$13</td>
<td>O</td>
<td>0.00</td>
<td>-26.34</td>
</tr>
</tbody>
</table>

Fig. 3 shows the experimental values of Itoh et al. [8] and Kimoto et al. [9] along with the curve calculated using the model proposed by Jung et al. [6]. Those authors calculated the curves using reactions and equilibrium constant equations, that is, they employed the stoichiometric method.

3 RESULTS AND DISCUSSION

3.1 System Fe-Cr-O

This is the most basic system to control Cr in the stainless steel production in a steelmaking.

Thermodynamic information on the equilibrium between dissolved Cr and O (known as ‘deoxidation equilibrium’, in literature) is the basic knowledge to control Cr content in the stainless steel. Due to such importance, many researches have been made in the past on the thermodynamic study in Fe-Cr-O system, in order to provide reliable thermodynamic data. In more recent works, Itoh et al. [8] and Kimoto et al. [9] used very accurate experimental techniques to measure Cr and O content in equilibrium in liquid iron at 1873 and 1923 K.

To perform the computations in this work, it was selected the Unified Interaction Parameter Formalism, considering the existence of associates Cr*O and Cr2*O, as described in the work of Jung et al. [6]. This model was chosen, because it is in satisfactory agreement with experimental values. Fig. 3 shows the experimental values of Itoh et al. [8] and Kimoto et al. [9] along with the curve calculated using the model proposed by Jung et al. [6]. Those authors calculated the curves using reactions and equilibrium constant equations, that is, they employed the stoichiometric method.

In this work, the equilibrium between Cr and O in liquid iron was calculated with the GRG method, using the Solver tool and the spreadsheet shown in Fig. 1. As can be seen in Fig. 4, the values obtained with the methodology of the present work are in satisfactory agreement with the curve of Jung et al. [6]. Note that the axes, in Fig. 3 and 4, show the total content of Cr dissolved (as Cr + Cr*O + Cr2*O) and O dissolved (as O + Cr*O + Cr2*O).

The deoxidation equilibrium may be written as

\[
2\text{Cr} + 3\text{O} = \text{Cr}_2\text{O}_3(s).
\]

With an equilibrium constant written as

\[
K_{\text{Cr}_2\text{O}_3} = \frac{1}{(x_1^2 \cdot x_2^3) (x_1^2 - x_2^3)}
\]
In an ideal Henrian solution of only unassociated Cr and O, then, one would expect the oxygen content to decrease continuously as the dissolved Cr content increases (see Eq. (20)). This is indeed the case for low Cr contents where most of the oxygen is dissolved as free O. However, at higher Cr contents, most of the dissolved oxygen is in the form of Cr*O associates, and the principal deoxidation equilibrium becomes

$$3\text{Cr}^*\text{O} = \text{Cr}_2\text{O}_3 + \text{Cr}$$

With an equilibrium constant written as

$$K = \frac{\left(\frac{X_{\text{Cr}^*\text{O}}}{f_{\text{Cr}^*\text{O}}}\right)}{\left(\frac{X_{\text{Cr}_2\text{O}_3}}{f_{\text{Cr}_2\text{O}_3}}\right)}$$

Since \(f_{\text{Cr}}\) and \(f_{\text{Cr}^*\text{O}}\) are equal to unity, an increase in the total dissolved Cr content results in an increase in \(X_{\text{Cr}^*\text{O}}\) and thus in an increase in the total dissolved oxygen. Hence, a ‘deoxidation minimum’ is observed in the curves presented in Fig. 3 and 4. Fig. 5 shows molar fractions of O and Cr*O dissolved in liquid iron. Note the agreement with the explanation given before: at low Cr dissolved, most of the oxygen is dissolved as free O; increasing Cr content dissolved, molar fraction of Cr*O increases. The point where the curves of molar fraction of free O and Cr*O cross each other corresponds to the minimum of the curves presented in Fig. 3 and 4.

The chromium content in liquid iron, where FeOCrO and CrO are together in equilibrium, is known as critical chromium. Using Eq. (18) and the Lagrange multipliers obtained from Solver sensitivity reports (as shown in Fig. 2), activities of the condensed stoichiometric phases FeO-CrO and CrO were computed. Fig. 6 shows the activity of FeO-CrO and CrO in function of total dissolved chromium in liquid iron. At low Cr contents, the activity values of CrO are smaller than unity, while the activity value of FeO-CrO is equal to unity, what means that only FeO-CrO is in equilibrium with liquid iron and the atmosphere (O2). Increasing Cr content in liquid iron, the values of activity of CrO also increases. When both CrO and FeO-CrO have activity value equal to unity, these two solid phases are in equilibrium together with liquid iron and the atmosphere (O2). The Cr concentration that corresponds to this situation is the critical chromium, and, in the present work, this point is calculated at log [total wt pct Cr] = 0.68 (wt pct Cr = 4.78). Jung et al. [6] found, for critical chromium, log [total wt pct Cr] = 0.65 (wt pct Cr = 4.5).

The Fe-Cr-O system was also analyzed with the help of FactSage - a commercial software package for solving chemical thermodynamic problems. Table III shows a comparison between values calculated by FactSage and the GRG method proposed in the present work.
Table III. Comparison between values computed by FactSage and GRG, at 1873 K. Input (moles): Fe=1.785E-2, Cr=1.923E-2 and O=0.00625.

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles (FactSage)</th>
<th>Moles (GRG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.01790</td>
<td>0.01790</td>
</tr>
<tr>
<td>Cr</td>
<td>0.01497</td>
<td>0.01498</td>
</tr>
<tr>
<td>O</td>
<td>4.498E-6</td>
<td>2.84E-6</td>
</tr>
<tr>
<td>Cr*O</td>
<td>2.787E-5</td>
<td>3.03E-5</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>6.744E-5</td>
<td>5.33E-5</td>
</tr>
<tr>
<td>CrO₂</td>
<td>0.00205</td>
<td>0.00205</td>
</tr>
<tr>
<td>FeO.Cr₂O₃</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>O₂</td>
<td>2.4E-13</td>
<td>6.1E-13</td>
</tr>
</tbody>
</table>

3.2 System Fe-Cr-O-C-Ni

Austenitic stainless steels classically contains the elements iron, chromium and nickel; chromium (typically 18 wt %) to give corrosion resistance and nickel (typically 8 wt %) to improve the ductility of the Fe-Cr alloys. Unfortunately, higher carbon contents lead to the formation of M₂C₆ carbides mainly containing chromium, thereby reducing the corrosion resistance. It is, therefore, necessary to establish a production process that yields Fe-Cr-Ni-C alloys with low carbon and high chromium contents. In the converter, oxygen is blown through the liquid iron, thus removing carbon as CO gas. However, chromium also has a high affinity for oxygen, and oxidation of chromium from the melt is quite probable. The engineering solution can be either reduction of the total gas pressure level, a process that is called Vacuum Oxygen Decarburization (VOD), or reduction of the partial pressure of CO by strong dilution in the gas phase, called Argon Oxygen Decarburization (AOD) [10].

Using a spreadsheet similar to that presented in Fig. 1, the effect of vacuum level was analyzed. As can be seen in Fig. 7, the lower the value of total pressure, the lower the carbon concentration in the iron bath.

In Fig. 7, can be seen the solid lines calculated with GRG method along with the values calculated using the software FactSage. Table IV shows a comparison between values calculated by FactSage and the GRG method proposed in the present work (note that the atmosphere is composed mainly by CO):

Table IV. Comparison between values computed by FactSage and GRG, at 1873 K, P=101.3 KPa. Input (moles): Fe=1.446, Cr=0.346, O=0.1875 and C=0.0833.

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles (FactSage)</th>
<th>Moles (GRG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.446</td>
<td>1.446</td>
</tr>
<tr>
<td>Cr</td>
<td>0.262</td>
<td>0.259</td>
</tr>
<tr>
<td>O</td>
<td>5.09E-4</td>
<td>5.48E-4</td>
</tr>
<tr>
<td>C</td>
<td>2.09E-2</td>
<td>3.48E-2</td>
</tr>
<tr>
<td>Cr*O</td>
<td>9.91E-4</td>
<td>1.072E-3</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>7.54E-4</td>
<td>5.48E-4</td>
</tr>
<tr>
<td>FeO-Cr₂O₃</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>O₂</td>
<td>5.346E-13</td>
<td>5.08E-13</td>
</tr>
<tr>
<td>CO</td>
<td>6.189E-2</td>
<td>4.8E-2</td>
</tr>
<tr>
<td>CO₂</td>
<td>4.362E-4</td>
<td>3.7E-4</td>
</tr>
</tbody>
</table>

It is known from literature [11] that Ni affects the decarburization. In this way, the effect of Ni on decarburization was analyzed with the GRG method. As can be seen, in Fig. 8, Ni favors decarburization. According to Campos [11], Ni is an element that increases henrian carbon activity in the steel.

Fig. 8 Effect of Ni content in decarburization of steel.

4. CONCLUSIONS

In this work, the use of spreadsheet Solver, as a tool to compute equilibrium concentration by Gibbs energy minimization method, was presented. The change of variables, in order to run the Solver continuously, without the error messages being generated due to the violation of non-negativity constraints, was described. In this way, there was no difficulty with the involvement of logarithmic
functions of the variables. The approach is easy to understand, apply and provides a direct procedure. The Fe-Cr-O and Fe-Cr-O-C-Ni systems were analyzed in order to illustrate the method. The thermodynamic equilibrium between dissolved Cr and O were analyzed at 1873 and 1923 K. The value of the critical chromium in liquid iron was calculated at 1873 K and the effects of vacuum level and Ni content on decarburization were shown with the proposed method. The results were compared with those presented in literature and with results determined with the commercial software FactSage. The results obtained in this work are found to be in good agreement with all others. In this way, the proposed procedure can be also used for metallurgical thermodynamics educational purposes.

**Notation**

- \( G \): Gibbs energy of the system
- \( G^i \): Gibbs energy of specie \( i \) at normal P and T
- \( n_i \): Moles of the specie \( i \)
- \( R \): Gas constant
- \( T \): Temperature
- \( P \): Pressure
- \( a_{K^i} \): Number of gram atoms of component \( K \) in a mole of the specie \( i \)
- \( A_K \): Total number of moles of the component \( K \)
- \( \lambda_K \): Lagrange multiplier of the component \( K \)
- \( a_i \): Activity of the specie \( i \)
- \( M,N \): Total number of components and species, Respectively

**REFERENCES**


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