



A Thermodynamic Analysis of the Mo-V and Mo-V-C Systems

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Abstract. A new thermodynamic evaluation of the binary *Mo-V* system and the ternary *Mo-V-C* system using thermodynamic models for the Gibbs energy of individual phases is presented. The CALPHAD method has been used, with predictions of unknown thermodynamic quantities, to optimize a set of thermodynamic parameters taking related experimental information into consideration. The predictions are based on regularities in bonding properties and vibrational entropy of 3d-transition metal carbides. The results are summarized in tables of thermodynamic parameters, calculated binary phase diagrams and isothermal sections of the ternary phase diagram compared with experimental information. Finally the influence of ternary interaction parameters, especially in the fcc phase, on calculations of equilibria in multicomponent systems is discussed. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The thermodynamic properties of the transition metal alloys and compounds are a subject of considerable practical and theoretical interest. The CALPHAD method [1,2] has been used in the present work to evaluate thermodynamic parameters for the ternary *Mo-V-C* system. The compound energy model [3] was selected to describe the Gibbs energy for the individual phases. Some of the adjustable parameters involved in that model of multicomponent solid solution phases represent the Gibbs energy of compounds, which are not stable in the binary system. The Gibbs energy of those metastable compounds can only be predicted. That has been done in this present work by a method developed by Fernández Guillermet and Grimvall [4].

Miedema's formula [5] has been very successful in accounting for the enthalpy of formation of various groups of compounds, but it does not treat the entropy part of the Gibbs energy, which is important in a consideration of the phase equilibria at high temperatures. The problem of estimating Gibbs energy at high temperatures led Fernández Guillermet and Grimvall [4] to a systematic study of the thermodynamics of various 3d-transition metal compounds. They have reported various correlations, which allowed the estimation of e.g. the room temperature entropy, and the enthalpy of formation of various stable carbides, nitrides and oxides. Besides, their correlation's have been used in studying the properties of various stable and metastable phases, e.g. a phase with the (cF8) *NaCl*-structure in the *Cr-C* system [6], the metastable (cF8) *NaCl*-structure phase, *NiN*, and other nitride phases in the *Ni-N* system [7], and the metastable (oP16) (cementite-structure) phase *Cr₃C* of the *Cr-C* system [8].

In the present work the estimation procedures introduced in references [4,6-8] have been combined with the CALPHAD method [1,2] to gain information on the thermodynamics of the metastable η -VC phase which is not known from experiments. A new thermodynamic evaluation of the binary Mo -V system, and an addition to the binary V -C system which originates from the work of Huang [9] have been performed. The binary Mo -C system is taken from the thermodynamic assessment by Andersson [10]. How the interaction parameters, specially the ternary interaction parameter in the fcc phase, from the present work influence the calculated result in multicomponent systems is investigated through comparison with experimental data from Wisell [11]. The present work is organized as follows. In section 2 the thermodynamic models for the Gibbs energy of the various phases in the ternary Mo -V-C system are defined. All the experimental information from the literature is shown in section 3 and the procedure to evaluate the model parameters is described in section 4. Section 5 is devoted to the analysis of lattice stabilities. Finally, in section 6 binary phase diagrams and isothermal sections of the ternary phase diagram are compared with experimental information, and in section 7 the work is summarized.

2. Thermodynamic Models

2.1 Gibbs Energy of the Liquid Phase

The Gibbs energy of the liquid phase was described by adopting a substitutional solution model. The molar Gibbs energy as a function of temperature and composition is described as follows,

$$\begin{aligned} G_m^{liq} = & x_C {}^0G_C^{liq} + x_{Mo} {}^0G_{Mo}^{liq} + x_V {}^0G_V^{liq} \\ & + RT(x_C \ln x_C + x_{Mo} \ln x_{Mo} + x_V \ln x_V) \\ & + x_C x_{Mo} L_{C,Mo} + x_C x_V L_{C,V} + x_{Mo} x_V L_{Mo,V} + x_C x_{Mo} x_V L_{C,Mo,V} \end{aligned} \quad (1)$$

where x_{Mo} , x_V and x_C are the atomic fraction of the components Mo , V and C in the liquid phase. The quantities ${}^0G_{Mo}^{liq}$, ${}^0G_V^{liq}$ and ${}^0G_C^{liq}$ were taken from references [10], [9] and [13], respectively. All the interaction parameters in equation (1) can be composition dependent according to the Redlich-Kister [14] phenomenological power series. The interaction parameters can also be temperature dependent and $L_{Mo,C}$ and $L_{V,C}$ originate from the binary Mo -C [10] and V -C [9] systems. The interaction parameter $L_{Mo,V}$, assessed in the present work, is discussed in sections 4 and 6. Only one ternary interaction term, $L_{Mo,V,C}$, was included in equation (1) because of the lack of information and is also discussed in section 4 and 6.

2.2 Gibbs Energy of Solid Solution Phases

The solid phases were described by using a two-sublattice version of the compound energy model (CEM) [3], $(Mo,V)_a(C,Va)_c$, where Va denotes vacancies. The Gibbs energy as a function of temperature and composition is described by the expression,

$$G_m^\phi = \sum_M \sum_I y_M y_I {}^0G_{M:I}^\phi + RT(a \sum_M y_M \ln y_M + c \sum_I y_I \ln y_I) + {}^E G_m^\phi + G_m^{\phi,mg} \quad (2)$$

where M represents the elements on the first sublattice and I the elements on the second sublattice. The y parameters denote the mole fraction of an element on a sublattice. The quantity ${}^0G_{M:I}^\phi$ represents the Gibbs energy of the compound $M_a I_c$ and is referred to the enthalpy of the stable element reference (SER) that is defined as the stable state of the elements at 298.15 K and 0.1 Mpa. The term ${}^E G_m^\phi$ in equation (2) represents

the excess Gibbs energy and the term G_m^{mg} represents the contribution due to magnetic ordering. The excess Gibbs energy, $^E G_m$, represents the non-ideal contributions to mixing. It was expressed as follows,

$$^E G_m = y_{Mo} y_V (y_C L_{Mo,V,C} + y_{Va} L_{Mo,V,Va}) + y_C y_{Va} (y_{Mo} L_{Mo,C,Va} + y_V L_{V,C,Va}) \quad (3)$$

Where the L parameters are composition dependent according to the so-called Redlich-Kister [14] phenomenological power series, i.e.,

$$L_{Mo,V,j} = \sum_{k=0}^n L_{Mo,V,j}^k (y_{Mo} - y_V)^k \quad (4)$$

with $j = C$ or Va , and

$$L_{i,C,Va} = \sum_{k=0}^n L_{i,C,Va}^k (y_C - y_{Va})^k \quad (5)$$

with $i = Mo$ or V .

The term, G_m^{mg} , describes the magnetic contribution to the Gibbs energy.

2.3 Phases and Structures

Mo and V were assumed to occupy the first sublattice, whereas C atoms and vacancies, Va , were assumed to substitute for each other on the second sublattice, which represent the interstitial sites. In the two-sublattice model $(Mo,V)_a(C,Va)_c$ the symbols a and c denote the number of sites on each sublattice. The phases that have been studied in the present work are the bcc phase in the binary $Mo-V$ and ternary $Mo-V-C$ systems, the fcc/hcp phase in the ternary $Mo-V-C$ system and the metastable $\eta-VC$ phase because available experimental data shows that there is a solubility range of V in $\eta-MoC$. Experimentalists have considered the $\eta-MoC$ carbide as a non-stoichiometric phase with a deficit of carbon. Furthermore the $\eta-MoC$ carbide is of a hexagonal type where all interstitial octahedral sites can be occupied with carbon. In table 1 the phases modeled in the present work are summarized.

Table 1. Models for the Phases.

Phase	Model	Comment
	$(Mo,V)_a(C,Va)_c$	
bcc	$a = 1, c = 3$	
fcc	$a = 1, c = 1$	
hcp	$a = 1, c = 0.5$	
$\eta-MC$	$a = 1, c = 1$	Hexagonal carbide

2.4 Gibbs Energy of the Metastable η -MC Phase

The carbide $\eta-MoC$ originates in the binary $Mo-C$ system [10] and the thermodynamic description for the $\eta-MoC$ carbide is also taken from there. In the present work Mo and V atoms are allowed to substitute for each other in the η phase since available experimental data [15,16] shows that there is a solubility range of V in the $\eta-MoC$ carbide. Therefore it is necessary to evaluate the parameters $^0 G_{V,Va}^\eta$, the Gibbs energy of $\eta-V:Va$, and $^0 G_{V,C}^\eta$, the Gibbs energy of the stoichiometric $\eta-VC$ carbide with hcp structure,

where all interstitial sites are filled with C atoms. The function ${}^0G_{V:Va}^\eta - {}^0H_V^{bcc}$ was estimated and given same value as ${}^0G_{V:Va}^{hcp} - {}^0H_V^{bcc}$, whereas the quantity ${}^0G_{V:C}^\eta$ was referred to the enthalpy of the elements V and C in their reference state as,

$${}^0G_{V:C}^\eta - {}^0H_V^{bcc} - {}^0H_C^{graphite} = \Delta^0 G_m^{\eta-VC}(T) \quad (6)$$

and the temperature dependent function $\Delta^0 G_m^{\eta-VC}(T)$ was expressed as,

$$\Delta^0 G_m^{\eta-VC}(T) = a + bT + cT \ln T + dT^{-1} \quad (7)$$

with coefficients determined as explained in section 4 and 6.

To be able to fit the available experimental data [15,16] of the V solubility in the η - MoC carbide it is necessary to use a ternary interaction parameter between Mo , V and C . That parameter belongs to the excess Gibbs energy. The whole term was treated using the regular solution approximation.

$${}^E G_m^\eta = y_V y_{Mo} {}^0L_{V,Mo:C} \quad (8)$$

The interaction parameter ${}^0L_{V,Mo:C}$ is discussed in Section 4 and 6.

3. Experimental Information

3.1 The Binary Mo-V System

The binary $Mo-V$ system is characterized by complete solid solution of bcc structure and the phase diagram is rather simple with only two phases, bcc and liquid. Smith [17] has summarized the relevant experimental work on the $Mo-V$ system. Zheng [18] has reassessed the $Mo-V$ system with the use of MTDATA [19] as well as evaluating experimental data that were not used in the previous assessment. The experimental data has its origin from three different groups of researchers. Baron [20] gave the first phase diagram and continued to improve their measurements of the solidus temperature, over the entire composition range, by using pure elements [21]. However, their results have been ignored due to the effect of the impurities. Rudy [22] reexamined the system. The melting point given for pure Mo was 2619 ± 4 °C, while that of V was 1926 ± 3 °C. These are in quite good agreement with those accepted by SGTE, even though no information about the purity of the materials used by Rudy are available in the report. The latest determination was made by Kocherzhinskii and Vasilenko [23,24] using alloys made from 99.95 % Mo and 99.5 % V . The results gave positive curvature to the liquidus and solidus lines, disagreeing with the shapes previously reported. Again considering the impurity effect, Smith [17] rejected their results although they are the latest available.

In the evaluation of Kocherzhinskii and Vasilenko [23,24] a partial excess Gibbs energy expression given by Brewer [25] was used. In the addition to the usual contributions to the enthalpy of mixing of internal pressure differences, that expression also considered the effect of strain energy of the solid solution and the utilization of the empty d orbital for the $Mo-V$ system. The values from those expressions together with $\Delta H_{fus}^0 / R = 2270 \pm 90$ K for the enthalpy of fusion of V from Berezin [26] fit the solidus curve determined by Rudy [22], with an average deviation of ± 0.01 for the mole fraction. However, the calculated liquidus shows a smaller gap than that given by Rudy. Three sets of thermodynamic data for the binary system [27,28,29] were combined with above phase diagram data and used in an attempt by Zheng [18] to optimize the $Mo-V$ system using the Lukas program [30]. Unfortunately, this was unsuccessful, probably due to the insufficient experimental data, the impurities in the elements that were used in some of the investigations, and the large differences in the observations reported by the different researchers.

Zheng [18] therefore took the partial excess Gibbs energy expression given by Brewer [25], which agreed reasonably with the experimental work of Rudy [22], as the best values and combined them with the latest values for the enthalpy of fusion of *V* and *Mo* [17], which were accepted by SGTE [12]. The combinations were then used to calculate the phase diagram using MTDATA [19].

A new assessment of the binary *Mo*–*V* system has been performed in the present work, using only experimental information. The objective was also to reduce the number of variables for the thermodynamic descriptions. The experimental data from Rudy [22] were used in the present work to optimize the defined variables, because we judged the reliability of those values to be high. The optimizations have been performed with different numbers of variables for the thermodynamic descriptions of the liquidus and the bcc phase.

3.2 The Binary V-C and Mo-C Systems

The binary *V*–*C* system originates from an assessment by Huang [9]. The stoichiometric V_3C_2 phase has been treated as a separated phase in the present work due to results of Lee [32] who predicted that the V_3C_2 phase has a different structure than the M_3C_2 phase in the *Fe*–*Cr*–*V*–*C* system. Except from that addition Huang's description is used consistently.

The binary *Mo*–*C* system is completely intact from the thermodynamic assessment by Andersson [10].

3.3 The Ternary Mo-V-C System

Very few experimental investigations or thermodynamic assessments have been done on the ternary *Mo*–*V*–*C* system. Holleck [15] presented three isothermal sections at 1500, 1800 and 2000 °C, which are mainly based on a report by Rudy [16]. In the work of Rudy 48 different alloys from the ternary system has been produced and later investigated with x-ray diffraction. The alloys were heat treated at two different temperatures, namely 1500 and 1800 °C, and then cooled rapidly to room temperature. The phase distribution was analyzed and the solubility of *V* in the η –*MoC* phase was found to be approximately 10 weight percent at 1800 °C. Furthermore the tielines have been experimentally investigated and drawn.

Another experimental investigation concerning the ternary *Mo*–*V*–*C* system and specially the *Mo* corner of that ternary system has been presented by Kiseleva and co workers [33]. In that work the *Mo* corner of the ternary *Mo*–*V*–*C* system (up to 0.5 mol percent *C* and 1.2 mol percent *V*) was studied by metallography, X-ray diffraction, electron diffraction and by measuring the solidus temperatures. Isothermal sections were constructed for 2100, 1600 and 1200 °C and a section of *Mo*– V_2C (from the *Mo* side). They showed that addition of *V* significantly reduces the solid solubility of *C* in *Mo* particularly at high temperatures. For example, at 2100 °C the solid solubility of *C* is reduced from about 0.09 mol percent (in the binary *Mo*–*C* system) to 0.035 mol percent with a *V* content over 0.2 mol percent, and at 1600 °C from 0.04 to 0.02 mol percent. Finally, the *Mo*– V_2C section in the ternary *Mo*–*V*–*C* system has at 2250 °C the greatest combined solubility of *V* and *C* in *Mo*, namely about 0.24 mol percent (0.18 mol percent *V* and 0.06 mol percent *C*) and it decreases significantly when the temperature is lowered.

3.4 Phase Equilibria Compositions in Multicomponent Model Alloys

A study by Wisell [11] presents compositional data obtained after long equilibration heat treatments on multicomponent model alloys. Wisell prepared a number of model alloys with varying composition. The phase compositions and volume fractions of the austenite and of the carbide phases in these alloys were measured by Wisell after equilibration in 240 to 270 hours at 1273 and 1473 K. In the present work we have made ThermoCalc calculations for three of these alloys at 1473 K. The alloy composition which were chosen can be seen in table 2. The results of these calculations are compiled in section 6 where they are compared to Wisell's experimental data.

Table 2. Composition in Weight Percent of Model Alloys Investigated by Wisell [11].

Alloy number	C	Si	Cr	Mo	V
1	0.57	0.12	4.10	9.00	1.80
2	1.07	0.53	4.00	8.70	2.20
3	1.41	0.56	4.00	8.80	3.80

4. Evaluation of Model Parameters

The thermodynamic parameters were evaluated using the PARROT module [34] in the Thermo-Calc software package [35]. This module works by minimizing an error sum where each piece of information is given a certain weight according to its estimated accuracy and allows the simultaneous consideration of various types of thermodynamic and phase diagram data. The best-fit criterion follows the maximum likelihood principle and that principle as a criterion for best fit is most efficient when the amount of data is large.

For the binary $Mo-V$ system first an optimization with the same amount of variables, for describing the L parameters, as in the work from Zheng [18] was done. The calculated diagram fits the experimental data quite well with those values, but at the V side of the diagram the curves have an unreasonable appearance. Also the very bad relative standard deviation value of the variables is a reason to try to reduce the number of variables. After some trial and error work it finally resulted in only one constant variable for the liquid phase, ${}^0L(liq, Mo, V; 0)$, and one constant variable for the bcc phase, ${}^0L(bcc, Mo, V; Va; 0)$. The calculated phase diagram with those variables gives an acceptable agreement to the experimental values from Rudy [22]. The relative standard deviation values for the variables lie within the acceptable limits. Furthermore the value of the L parameter in liquid is quite small and that is in accordance with the theoretically calculated enthalpy value of the heat of mixing, ΔH_{MoV}^{mix} , from Miedema [5] that determined it to zero. The optimized value can be assumed to lie within the margin of error of the theoretical value from Miedema.

The quantity ${}^0G_{V,C}^{\eta}$ as described in section 2.4 was evaluated with use of the enthalpy and entropy values which have been determined through the method described in section 5. To be able to fit the experimental information about the ternary $Mo-V-C$ system it was necessary to introduce three different ternary interaction parameters. The parameter ${}^0L(eta, Mo, V; C; 0)$ describes the V solubility in the $\eta-MoC$ phase, whereas the parameters ${}^0L(liq, Mo, V, C; 0)$ and ${}^0L(bcc, Mo, V; C; 0)$ describes the information from Kiseleva and co workers [33]. All the above ternary interaction parameters were defined as a constant value with no temperature dependence.

The ternary parameter ${}^0L(fcc, Mo, V; C; 0)$ is discussed in section 6 because it influences the composition in separate phases in multicomponent systems. This ternary interaction parameter was assessed by Gustafsson [31] and is now again fitted to experimental data from Wisell [11]. Finally the ternary parameter ${}^0L(hcp, Mo, V; C; 0)$ which is predicted from experimental investigated tielines from Rudy [16] is discussed in section 6, and how it influences the shape of the tielines in the isothermal sections.

5. Analysis of the $\eta-VC$ Phase

The quantity $\Delta^0 G_m^{\eta-VC}(T)$ (section 2.4) which belongs to the total Gibbs energy function for the $\eta-VC$ phase is determined in the present work. To be able to estimate the temperature dependent variables in equation (7), b , c and d , a method based on the work of Fernández Guillermet and Grimvall [4] was used. The first variable, a , in the same equation was determined from the enthalpy of formation at 298.15 K.

The various correlation's between quantities related to the strength of chemical bonding in 3d-transition metal carbides and the average number of valence electrons per atom, n_e , have been reported by Fernández Guillermet and Grimvall [4]. The first variable in equation (7), a , can be described using the correlation between the room temperature enthalpy of formation per atom and n_e . The lattice vibrations, which may be described by a properly defined Debey temperature, θ , usually dominate the temperature dependent part of

equation (7). It is obtained from the $\theta_s(T)$ function that it reproduces the vibrational entropy $S_{vib}(T)$ per atom of the compound if $\theta_s(T)$ is inserted in the Debey model expression S_D for entropy.

$$S_{vib}(T) = S_D(\theta_s(T)/T) \quad (9)$$

The prediction of θ_s^0 is based on the use of trends in information on related compounds, and the correlations presented in [4] were used in the present work to predict a value for θ_s for η -VC. In table 3 the properties of the metastable η -VC phase estimated with the method from reference [4] are presented.

Table 3. Properties of the Metastable η -VC Phase. Where Ω is the Average Volume per Atom, E_s the Entropy Related Characteristic Energy in Rydberg/Atom and k_s an Effective Force Constant with the Dimension N/m.

Compound	Structure	n_e	Ω	E_s	k_s	θ_s^0
η -VC	Hcp	4.5	9.058	7.794	391	745

The estimation of the enthalpy of formation value for the metastable η -VC phase has been done as follows. In reference [10] the binary Mo -C system is assessed and in that work the η -MoC phase have got an experimental enthalpy of formation value, namely $\Delta^0 H_m^{\eta-MoC}(T_0) = -20$ kJ/mol. The calculated enthalpy of formation value is -17.5 kJ/mol. From the correlation in reference [4] the enthalpy of formation of cubic MoC was estimated. Assuming the same difference for cubic VC and η -VC, as for the Mo carbides, the enthalpy of formation of the metastable η -VC phase was estimated to $\Delta^0 H_m^{\eta-VC}(T_0) = -45$ kJ/mol. This value can be compared with the value for the stable VC phase from Fernández Guillermet and Grimvall [4], $\Delta^0 H_m^{VC}(T_0) = -50.4$ kJ/mol, and the value (stable phase) predicted by Miedema and co-worker [5], $\Delta^0 H_m^{VC}(T_0) = -42$ kJ/mol.

Once the probable θ_s^0 value has been established, one approximates the total entropy (per mole of formula units) of η -VC, ${}^0 S_m^{\eta-VC}(T)$, from the entropy (per mole of atoms) $S_{vib}(T)$, which is obtained from equation (9), with $\theta_s(T)$ evaluated at $T = \theta_s$ i.e. θ_s^0 .

$${}^0 S_m^{\eta-VC}(T) = S_D(\theta_s^0/T) \quad (10)$$

6. Results and Discussion

The final result of the thermodynamic analysis of the binary Mo -V system involves two temperature independent variables. This set of parameters gave the best accordance between the calculated phase diagram and the experimental data, with good relative standard deviation values of the parameters. Furthermore, the binary interaction parameter in liquid is quite small, and agrees with the theoretical value predicted by Miedema [5]. In appendix 1 the values of the binary interaction parameters are shown, and in figure 1 the calculated binary Mo -V system is drawn with the experimental data from Rudy [22], Baron [20] and Kocherzhinskii [23] included.

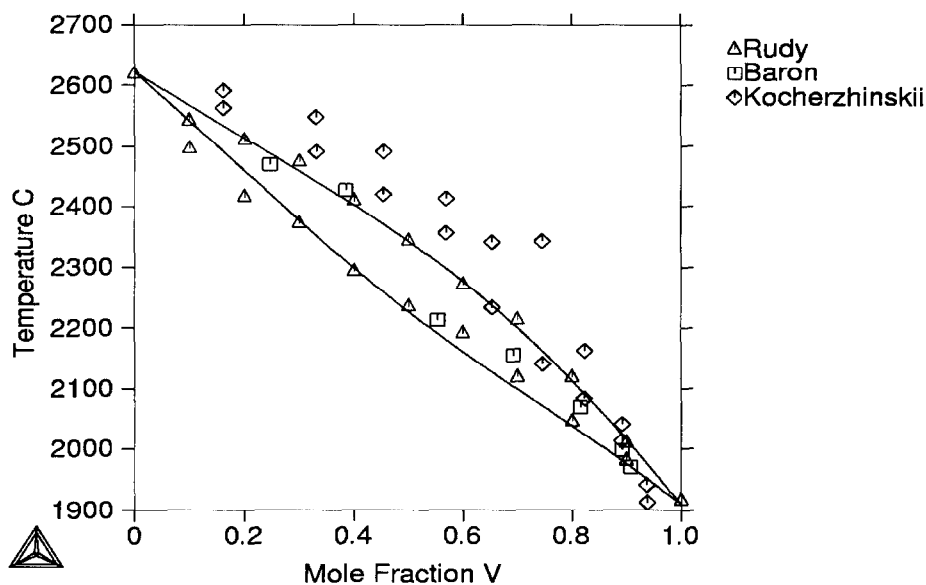


Figure 1. The calculated $Mo-V$ system compared with the experimental information from Rudy [22], Baron [20] and Kocherzhinskii [23].

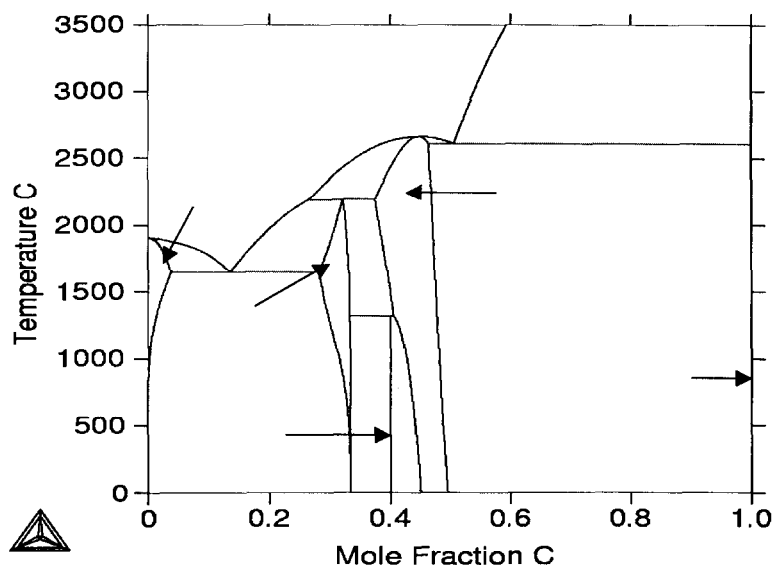


Figure 2. The calculated $V-C$ system.

The binary $V-C$ system which originates from an assessment done by Huang [9] is shown in figure 2. However the stoichiometric V_3C_2 phase is taken from the work of Beyong-Joo Lee [32], see section 3.2. The thermodynamic parameters for that phase can be seen in appendix 1. The $\eta-VC$ phase was included in the calculation presented in figure 2 and the estimated parameters successfully predict $\eta-VC$ to be metastable in the binary system. Furthermore the binary $Mo-C$ system is shown in figure 3 based on a completely intact thermodynamic description from Andersson [10].

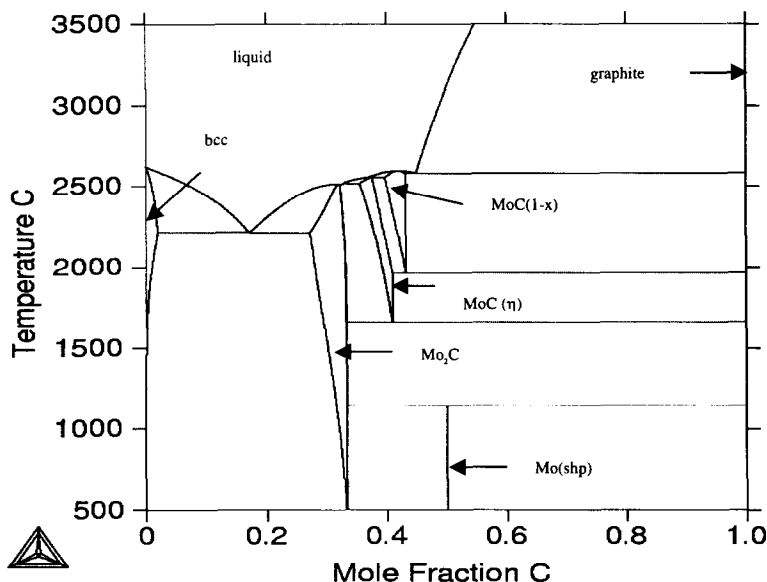


Figure 3. The calculated $Mo-C$ system.

In figures 4, 5 and 6 three isothermal sections calculated with the thermodynamic parameters from the present work are shown. The thermodynamic parameters describing the quantities ${}^0G_{V,C}^\eta$ and ${}^0G_{V,Va}^\eta$ can be found in appendix 1. Those quantities actually describe the binary $\eta-VC$ phase but that phase is metastable in the binary $V-C$ system, see figure 2. However, that phase was defined and a ternary interaction parameter introduced (see section 4) to be able to describe the V solubility in the $\eta-MoC$ phase in the ternary $Mo-V-C$ system. The value after optimization of the ternary interaction parameter is also shown in appendix 1. Without a ternary interaction parameter the V solubility in the $\eta-MoC$ phase was low compared with the experimental information [15,16]. Isothermal sections in the ternary $Mo-V-C$ system at 2000 and 1800 °C calculated with the thermodynamic parameters developed in present work describe the experimental data from Holleck [15] satisfactorily. At 1500 °C thermodynamic parameters predict a ternary compound $\eta-(Mo,V)C_{1-x}$ with a V solubility around 15 weight percent. There is no experimental information at this temperature, and this result was therefore accepted. The experimental tielines presented by Rudy [16] indicate that a ternary interaction parameter in the hcp phase should be used with a negative value. This value is shown in appendix 1. Furthermore the tielines in the calculated isothermal sections at 1500 °C and 1800 °C are in quite good agreement with those calculated by Rudy [16] at the Mo rich side of the isothermal sections but at the Mo poor side the agreement is poor. The comparison between the calculated tielines in this present work and the experimental investigated tielines from Rudy [16] is shown in figure 7.

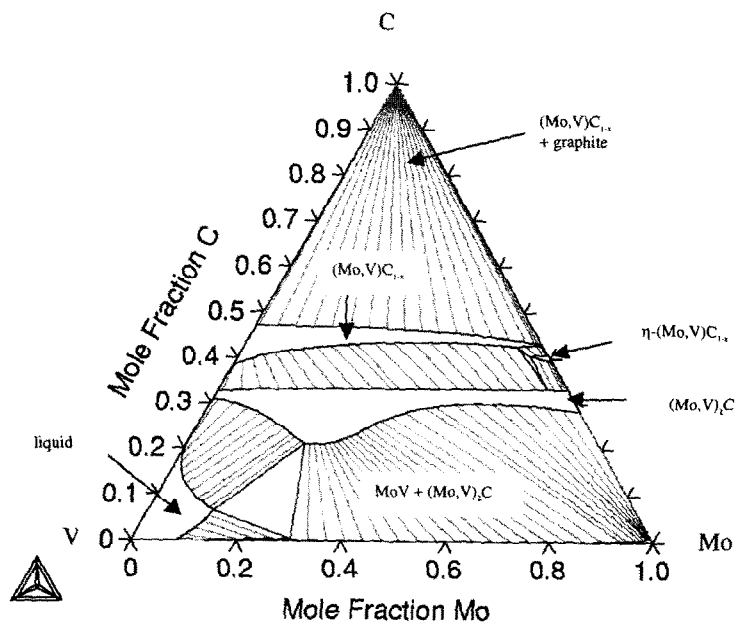


Figure 4. Isothermal section of the ternary $Mo-V-C$ system at 2000 °C.

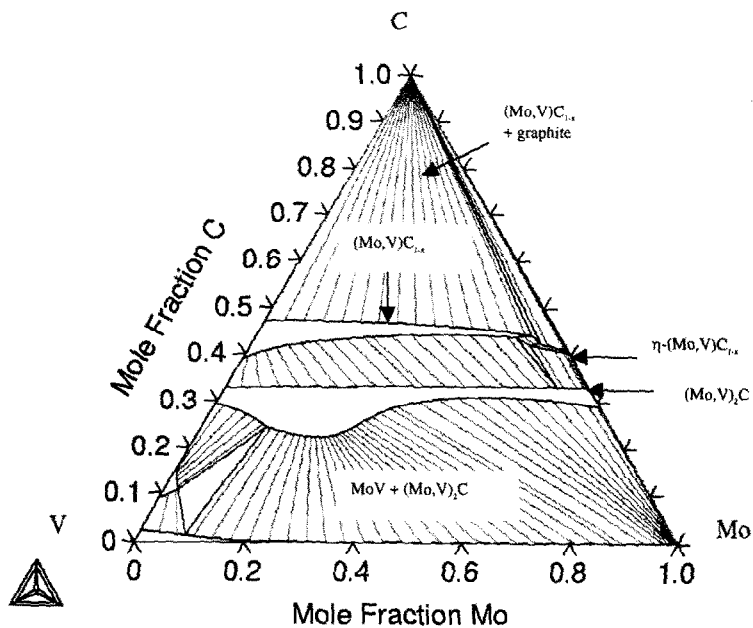


Figure 5. Isothermal section of the ternary $Mo-V-C$ system at 1800 °C.

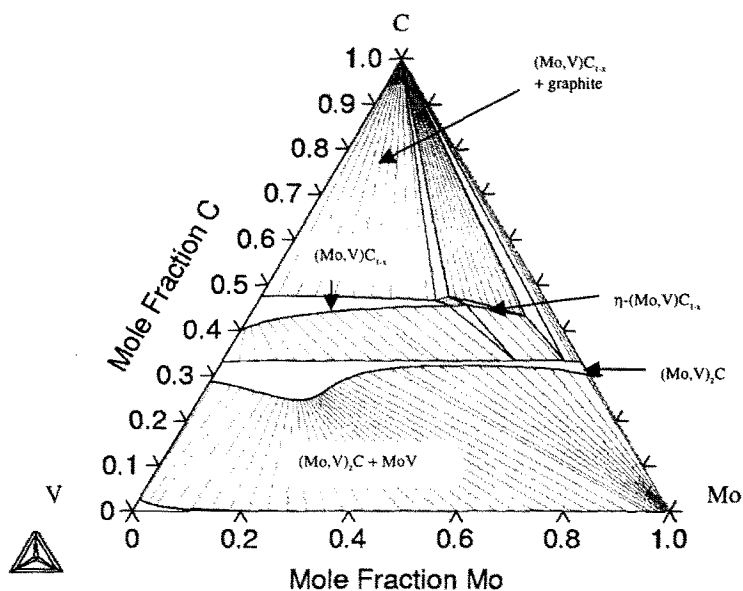


Figure 6. Isothermal section of the ternary $Mo-V-C$ system at 1500 °C.

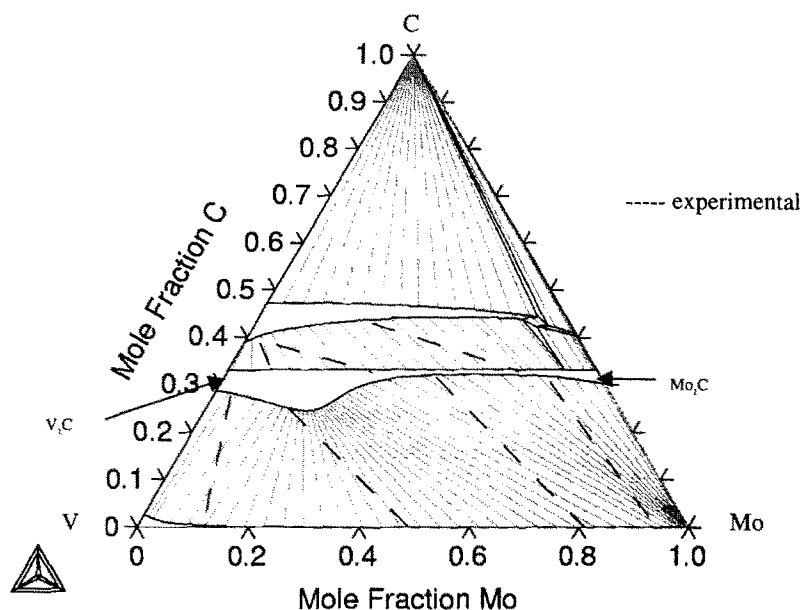


Figure 7. Comparison between calculated and experimental tielines in the isothermal section of the ternary $Mo-V-C$ system at 1500 and 1800 °C. The $V-Mo-Mo_2C-V_2C$ part of the diagram is from the section at 1500 °C and the Mo_2C-V_2C-C part of the diagram is from the section at 1800 °C.

To fit the experimental information from Kiseleva and co workers [33] it was necessary to optimize two ternary interaction parameters as described in section 4. The value of those ternary parameters can be seen in appendix 1. In figure 8 the calculated section of $Mo-V_2C$ is shown compared with the experimental data from Kiseleva [33]. It was also possible to use a ternary interaction parameter between Mo, V and C in the hcp phase to facilitate the thermodynamic assessment, but that attempt did not affect the earlier description appreciably. The ternary interaction parameter in the bcc phase had to be quite large and positive to describe the experimental information from Kiseleva [33]. This was accepted due to a satisfactory description of the experimental information.

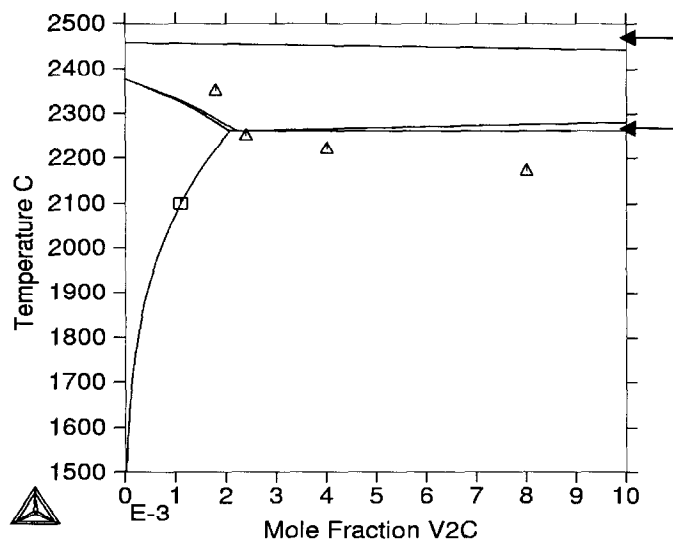


Figure 8. Section of $Mo-V_2C$ from the Mo side compared with the experimental information from Kiseleva and co workers [33].

The phase equilibria calculations in the multicomponent model alloys which were chosen from Wisell's work [11] are compiled in table 4 where they can be compared to experimental values. The thermodynamic calculations were made with two different values on the ternary interaction parameter ${}^0L(fcc, Mo, V : C; 0)$ where $L1$ was assessed by Gustafson [31] and is fitted to all experimental data from Wisell [11]. In the present work thermodynamic calculations were made and fitted to three of these alloys, see section 3.4, and resulted in a best ternary interaction parameter in the fcc phase with the $L2$ value. The latter value was chosen in the present work. Comparisons in new model alloys with different composition ranges compared to Wisell's model alloys are planned in the future to be able to fit this ternary interaction parameter better. These results indicated that even small differences in the ternary interaction parameters in the fcc phase influence the thermodynamic calculations in multicomponent systems.

Table 4. The Results of Calculations for Model Alloys Compared with Experimental Data from Wisell [11] in Mole Fraction at 1473 K. There $L1$ Means that the Parameter ${}^0L(fcc, Mo, V : C; 0) = -18000$ and $L2$ Stands for ${}^0L(fcc, Mo, V : C; 0) = -28000$.

a) Phase Compositions in Mole Fraction at 1473 K.

Alloy number	Composition	Austenite			M ₆ C carbide			MC carbide		
		exp.	calc. L1	calc. L2	exp.	calc. L1	calc. L2	exp.	calc. L1	calc. L2
1 0.12 Si	C	2.29	1.92	1.88	14.29	14.29	14.29	45.94	0	43.81
	Mo	3.90	3.43	3.46	32.82	33.83	33.89	8.34	0	13.95
	V	1.79	1.79	1.75	5.88	5.08	4.98	41.58	0	39.66
	Cr	4.36	4.51	4.51	4.25	3.57	3.58	2.37	0	1.93
	Fe	87.34	88.09	88.13	41.95	43.23	43.26	1.77	0	0.64
2 0.53 Si	C	2.92	2.92	2.74	14.29	14.29	14.29	45.94	44.58	44.56
	Mo	3.39	2.95	3.01	33.70	33.98	34.16	13.70	12.69	16.39
	V	1.36	1.05	0.92	4.65	3.08	2.75	34.90	38.59	36.18
	Cr	4.27	4.33	4.37	3.97	3.38	3.44	3.30	3.11	2.12
	Fe	87.00	87.61	87.82	40.20	45.28	45.37	2.16	1.03	0.75
3 0.56 Si	C	3.45	2.73	2.52	14.29	14.29	14.29	45.94	44.50	44.45
	Mo	3.07	2.97	3.05	32.97	33.99	34.16	15.30	12.48	16.05
	V	1.35	1.09	0.98	4.89	3.29	3.02	33.73	39.00	36.70
	Cr	4.06	4.32	4.41	4.09	3.36	3.45	2.99	3.02	2.07
	Fe	86.85	87.65	87.82	40.59	45.07	45.08	2.04	1.00	0.73

b) Volume Fractions of Equilibrium Phases at 1473 K.

Alloy number	M ₆ C carbide			MC carbide		
	exp.	calc. L1	calc. L2	exp.	calc. L1	calc. L2
1	4.4	6.1	6.0	0.5	0	0.6
2	5.0	5.6	4.7	2.7	3.3	3.9
3	1.8	4.2	2.7	8.5	7.6	8.5

7. Summary and Conclusions

A new thermodynamic assessment of the binary $Mo-V$ system has been presented. Furthermore the V_3C_2 phase in the binary $V-C$ system has been treated as a separated phase compared to the M_3C_2 phase description, because of different structures. In the ternary $Mo-V-C$ system has it been accepted that V solves in the $\eta-MoC$ phase based on available experimental information. To be able to describe the thermodynamics of the ternary η phase in the $Mo-V-C$ system it was necessary to treat the thermodynamic properties of the binary metastable $\eta-VC$ phase. This was done using the quantities ${}^0G_{V:C}^\eta$ and ${}^0G_{V:Va}^\eta$ which were estimated. Together with four different ternary interaction parameters, see section 4, the experimental information could be described satisfactorily. The calculated tielines in this present work agree with those experimentally produced at 1500 °C and 1800 °C at the Mo rich side. Finally the ternary interaction parameter in the fcc phase was assessed and thermodynamic calculations in multicomponent model alloys were compared to experimental data with satisfactory result. It was also shown how much this parameter influences the composition in separated phases and also on the amount of different phases in multicomponent systems.

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9. Appendix 1

The thermodynamic properties of the ternary $Mo - V - C$ system. Parameters marked by * were optimized in this work.

Pure element data

Element for pure data is taken from SGTE unary database [12]. The functions are valid in the temperature range 298.15 K to 6000 K.

GRAPHITE

$${}^0G_C^{GRAPHITE} - H_C^{SER} = +GHSERCC + GPCGRA$$

LIQUID

$${}^0G_C^{LIQUID} - H_C^{SER} = +GCLIQ + GPCLIQ$$

$${}^0G_{Mo}^{LIQUID} - H_{Mo}^{SER} = +GMOLIQ + GPMOLIQ \quad 298.15 < T < 5000.00$$

$${}^0G_V^{LIQUID} - H_V^{SER} = +GVLIQ \quad 298.15 < T < 4000.00$$

$${}^0L_{C,Mo}^{LIQUID} = -217800 + 38.41T$$

$${}^1L_{C,Mo}^{LIQUID} = +30000$$

$${}^2L_{C,Mo}^{LIQUID} = +47000$$

$${}^0L_{C,Mo,V}^{LIQUID} = +120000 *$$

$${}^0L_{C,V}^{LIQUID} = -284196 + 38.952T$$

$${}^1L_{C,V}^{LIQUID} = +96335 - 17.775T$$

$${}^2L_{C,V}^{LIQUID} = +102050$$

$${}^0L_{Mo,V}^{LIQUID} = +17784 *$$

BCC A2

2 Sublattices, sites 1 : 3

Constituents: Mo, V : C, Va

$${}^0G_{Mo:C}^{BCC_A2} - H_{Mo}^{SER} - 3H_C^{SER} = +331000 - 75T + GHSEMO + 3GHSECC$$

$${}^0G_{V:C}^{BCC_A2} - H_V^{SER} - 3H_C^{SER} = +GHSEVV + 3GHSECC$$

$${}^0G_{Mo:Va}^{BCC_A2} - H_{Mo}^{SER} = +GHSEMO + GPMOBCC \quad 298.15 < T < 5000.00$$

$${}^0G_{V:Va}^{BCC_A2} - H_V^{SER} = +GHSEVV \quad 298.15 < T < 4000.00$$

$${}^0L_{Mo,V:C}^{BCC_A2} = +330000 *$$

$${}^0L_{Mo:C,Va}^{BCC_A2} = -50000$$

$${}^0L_{V:C,Va}^{BCC_A2} = -297868$$

$${}^0L_{Mo,V:Va}^{BCC_A2} = +19245 *$$

FCC A1

2 Sublattices, sites 1 : 1

Constituents: Mo, V : C, Va

$${}^0G_{Mo:C}^{FCC_A1} - H_{Mo}^{SER} - H_C^{SER} = -7500 - 8.3T - 750000T^{-1} + GHSEMO + GHSECC$$

$${}^0G_{V:C}^{FCC_A1} - H_V^{SER} - H_C^{SER} = -117302 + 262.57T - 41.756T \ln T - 0.00557101T^2 + 590546T^{-1}$$

$${}^0G_{Mo:Va}^{FCC_A1} - H_{Mo}^{SER} = +15200 + 0.63T + GHSEMO + GPMOBCC \quad 298.15 < T < 5000.00$$

$${}^0G_{V:Va}^{FCC_A1} - H_V^{SER} = +7500 + 1.7T + GHSEVV \quad 298.15 < T < 4000.00$$

$${}^0L_{Mo,V:C}^{FCC_A1} = -28000 *$$

$${}^0L_{Mo:C,Va}^{FCC_A1} = -41300$$

$${}^0L_{V:C,Va}^{FCC_A1} = -74811 + 10.201T$$

$${}^1L_{V:C,Va}^{FCC_A1} = -30394$$

HCP A3

2 Sublattices, sites 1 : 0.5

Constituents: Mo, V : C, Va

$${}^0G_{Mo:C}^{HCP_A3} - H_{Mo}^{SER} - 0.5H_C^{SER} = -24150 - 3.625T - 163000T^{-1} + GHSEMO + 0.5GHSECC$$

$${}^0G_{V:C}^{HCP_A3} - H_V^{SER} - 0.5H_C^{SER} = -85473 + 182.441T - 30.551T \ln T - 0.00538998T^2 + 229029T^{-1}$$

$${}^0G_{Mo:Va}^{HCP_A3} - H_{Mo}^{SER} = +11550 + GHSEMO + GPMOBCC \quad 298.15 < T < 5000.00$$

$${}^0G_{V:Va}^{HCP_A3} - H_V^{SER} = +4000.00 + 2.4T + GHSEVV \quad 298.15 < T < 4000.00$$

$${}^0L_{Mo,V:C}^{HCP_A3} = -30000 *$$

$${}^0L_{Mo:C,Va}^{HCP_A3} = +4150$$

$${}^0L_{V:C,Va}^{HCP_A3} = +12430 - 3.986T$$

M3C2

2 Sublattices, sites 3 : 2

Constituents: Mo, V : C

$${}^0 G_{MoC}^{M3C2} - 3H_{Mo}^{SER} - 2H_C^{SER} = +3GHSEMO + 2GHSECC + 27183$$

$${}^0 G_{V:C}^{M3C2} - 3H_V^{SER} - 2H_C^{SER} = -222500 + 16.6545T + 3GHSERVV + 2GHSECC$$

M7C3

2 Sublattices, sites 7 : 3

Constituents: Mo, V : C

$${}^0 G_{MoC}^{M7C3} - 7H_{Mo}^{SER} - 3H_C^{SER} = +7GHSEMO + 3GHSECC - 140415 + 24.24T$$

$${}^0 G_{V:C}^{M7C3} - 7H_V^{SER} - 3H_C^{SER} = -454245 + 1518.48T - 250.981T \ln T + 2148692T^{-1}$$

MC ETA

2 Sublattices, sites 1 : 1

Constituents: Mo, V : C, Va

$${}^0 G_{MoC}^{MC-ETA} - H_{Mo}^{SER} - H_C^{SER} = +GHSEMO + GHSECC - 9100 - 5.35T - 750000T^{-1}$$

$${}^0 G_{V:C}^{MC-ETA} - H_V^{SER} - H_C^{SER} = -115426.29 + 299.799T - 47.012T \ln T + 210127.634T^{-1} *$$

$${}^0 G_{MoVa}^{MC-ETA} - H_{Mo}^{SER} = +GHSEMO + 15200 + 0.63T$$

$${}^0 G_{V:Va}^{MC-ETA} - H_V^{SER} = +4000 + 2.4T + GHSERVZ *$$

$${}^0 L_{Mo,V:C}^{MC-ETA} = -70000 *$$

$${}^0 L_{Mo:C,Va}^{MC-ETA} = -59500$$

MC SHP

2 Sublattices, sites 1 : 1

Constituents: Mo : C

$${}^0 G_{MoC}^{MC-SHP} - H_{Mo}^{SER} - H_C^{SER} = -32983 + 2.5T + GHSEMO + GHSECC$$

V3C2

2 Sublattices, sites 3 : 2

Constituents: V : C

$${}^0 G_{V:C}^{V3C2} - 3H_V^{SER} - 2H_C^{SER} = -260341 + 16.897T + 3GHSERVV + 2GHSECC *$$

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