

# Thermodynamic Computation of the Mo-V Binary Phase Diagram

F. Zheng, B.B. Argent, and J.F. Smith

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The available phase diagram and thermodynamic data for the Mo-V system has been reviewed and an attempt made to optimize the system using the Lukas program. This was unsuccessful, probably due to insufficient and inconsistent experimental data. The best fit to the experimental phase diagram data was obtained using Brewer and Lamoreaux's Gibbs energy expressions and the pure element data recommended by SGTE. Equations are given for the temperature/composition dependence of the liquidus and solidus curves.

## 1. Introduction

Owing to the importance of Mo-V in alloy steels, [92Smi] has summarized the relevant experimental work on the Mo-V system and has included a calculated phase diagram. In order to (a) make it consistent with other alloy systems assessed using the pure element data recommended by SGTE [91Din], (b) to correct a minor error, and (c) to enable one to model higher-order systems containing this binary, the present authors have reassessed the Mo-V system, with the use of MTDATA [91Dav] as well as evaluating experimental data that were not used in the previous assessment.

## 2. Thermodynamic Models

The Mo-V system contains two phases, the names of which are identical with the names of their structures: body-centered cubic (bcc) and liquid (liq). The Gibbs energies of individual phases were treated with a subregular solution model that gives the following expression for the Gibbs energy per mole of atoms:

$$G_m^\Phi = X_{\text{Mo}} {}^0G_{\text{Mo}}^\Phi + X_{\text{V}} {}^0G_{\text{V}}^\Phi + RT(X_{\text{Mo}} \ln X_{\text{Mo}} + X_{\text{V}} \ln X_{\text{V}}) + G_m^{\text{ex},\Phi} + G_m^{\text{mag},\Phi} \quad (\text{Eq 1})$$

where  $X_i$  ( $i = \text{Mo}, \text{V}$ ) is the mole fraction of component  $i$  in  $\Phi$  ( $\Phi = \text{bcc}$  or  $\text{liq}$ ).  ${}^0G_i^\Phi$  is the molar Gibbs energy of the pure element  $i$  with the structure  $\Phi$  in a hypothetical nonmagnetic state, the thermodynamic description of  ${}^0G_i^\Phi$  was taken from the SGTE database.  $R$  is the gas constant,  $T$  is temperature, and  $G_m^{\text{ex},\Phi}$  is the molar excess Gibbs energy of the phase  $\Phi$ , expressed in Redlich-Kister polynomials [48Red]:

**F. Zheng\*** and **B.B. Argent**, Thermodynamics Group, Department of Engineering Materials, The University of Sheffield, Mappin St., P.O. Box 600, Sheffield, S1 4DU, U.K.; and **J.F. Smith**, Iowa State University, Ames, IA, USA. Contact e-mail: b.argent@sheffield.ac.uk.

\*On leave from Anshan Iron & Steel School, 77 Youth St., Anshan, Liaoning, 114002, P.R. China.

$$G_m^{\text{ex},\Phi} = X_{\text{Mo}} X_{\text{V}} \sum_{n=0}^{n=i} {}^nL_{\text{Mo,V}}^\Phi (X_{\text{Mo}} - X_{\text{V}})^n \quad (\text{Eq 2})$$

The interaction parameters,  ${}^nL_{\text{Mo,V}}^\Phi$ , can be both concentration and temperature dependent. When  $n = 0$ , it corresponds to the regular solution model and when  $n \geq 1$  it corresponds to the subregular solution model.

The magnetic term,  $G_m^{\text{mag},\Phi}$ , is set to zero as Mo and V are not ferromagnetic and because there is no experimental evidence of a ferromagnetic transition in the alloys.

## 3. Available Experimental Data

### 3.1 Liquidus and Solidus Data

Three different groups have investigated the phase diagram data of the Mo-V system. [58Bar] gave the first phase diagram and continued to improve their measurement of the solidus temperature, over the entire composition range, by using purer elements [60Bar]. However, their results have been ignored due to the effect of the impurities. The purity of the elements they used were 99.00% Mo, 95.5% V and 99.99% Mo, 99.4% V, respectively.

[69Rud] reexamined the system. The melting point given for pure Mo was  $2619 \pm 4^\circ\text{C}$ , while that of V was  $1926 \pm 3^\circ\text{C}$ . These are in quite good agreement with those accepted by SGTE, even though no information about the purity of the materials used by [69Rud] are available in the report.

The latest determination was made by [85Koc1, 85Koc2] using 99.95% Mo, 99.5% V and gave positive curvature to the liquidus and solidus lines disagreeing with the shapes previously reported. Again considering the impurity effect, the present authors have rejected their results, although they are the latest available.

### 3.2 Thermodynamic Data

In addition to the usual contributions to the enthalpy of mixing of internal pressure difference, [80Bre] also considered the effect of strain energy of the solid solution and the utilization of the empty  $d$  orbital for Mo-V system and gave the following estimated molar partial excess Gibbs energy for bcc solid solutions with an uncertainty of  $\pm 0.2$ :

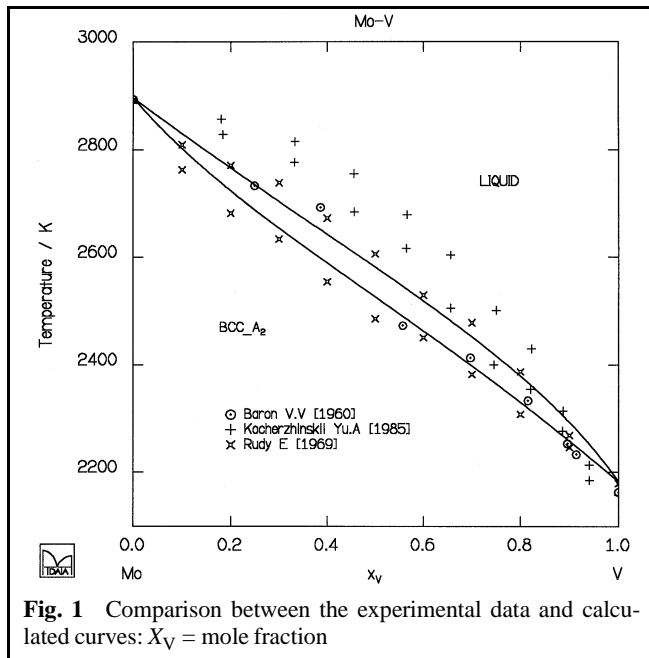
$$G_V^{\text{ex, bcc}} / RT X_{\text{Mo}}^2 = 0.1 - 550 T^{-1} + (0.1 + 90 T^{-1}) X_{\text{Mo}} \quad (\text{Eq 3})$$

$$G_{\text{Mo}}^{\text{ex, bcc}} / RT X_V^2 = 0.25 - 415 T^{-1} - (0.1 + 90 T^{-1}) X_V \quad (\text{Eq 4})$$

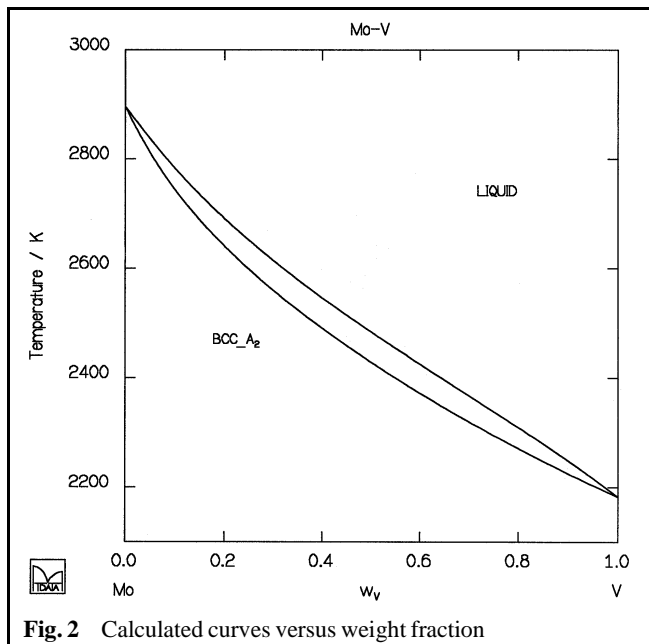
and for liquid:

$$G_V^{\text{ex, liq}} / RT X_{\text{Mo}}^2 = 0.015 - 138 T^{-1} + (0.05 + 75 T^{-1}) X_{\text{Mo}} \quad (\text{Eq 5})$$

$$G_{\text{Mo}}^{\text{ex, liq}} / RT X_V^2 = -0.06 - 250 T^{-1} + (0.05 + 75 T^{-1}) X_V \quad (\text{Eq 6})$$



**Fig. 1** Comparison between the experimental data and calculated curves:  $X_V$  = mole fraction



**Fig. 2** Calculated curves versus weight fraction

These values, [80Bre] claimed, together with  $\Delta H_{\text{fus}}^0 / R = 2270 \pm 90$  K for the enthalpy of fusion of the V [75Ber] fit the solidus curve determined by [69Rud], with an average deviation of  $\pm 0.01$  for the mole fraction. However, the calculated liquidus shows a smaller gap than that given by [69Rud].

Three sets of thermodynamic data for the binary system [87Ero, 89Ero1, 89Ero2] have been combined with above phase diagram data and have been used in an attempt to optimize the Mo-V system using the Lukas program [77Luk]. Unfortunately, this was unsuccessful, probably due to 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.

**Table 1** Parameters describing the thermodynamic properties of the Mo-V system

**Liquid; 1 sublattice, sites 1; constituents, Mo, V**

**Mo**

$$298.15 < T < 2896.00 \quad G\text{-HSER}_{\text{Mo,liq}} = 34,085.045 + 117.224788 T - 23.56414 T \ln(T) - 0.003443396 T^2 + 5.662834 \times 10^{-7} T^3 - 1.309265 \times 10^{-10} T^4 + 65,812.39 T^{-1} + 4.24519 \times 10^{-22} T^7$$

$$2896 < T < 4000 \quad G\text{-HSER}_{\text{Mo,liq}} = 3538.963 + 271.6697 T - 42.63829 T \ln(T)$$

**V**

$$298.15 < T < 790 \quad G\text{-HSER}_{\text{V,liq}} = 12,833.687 + 123.890501 T - 24.134 T \ln(T) - 3.098 \times 10^{-3} T^2 + 0.121750 \times 10^{-6} T^3 + 69,460 T^{-1} - 5.19136 \times 10^{-22} T^7$$

$$790 < T < 2183 \quad G\text{-HSER}_{\text{V,liq}} = 12,796.275 + 133.835541 T - 25.9 T \ln(T) + 0.0625 \times 10^{-3} T^2 - 0.68 \times 10^{-6} T^3 - 5.19136 \times 10^{-22} T^7$$

$$2183 < T < 4000 \quad G\text{-HSER}_{\text{V,liq}} = -19,617.510 + 311.055983 T - 47.43 T \ln(T)$$

$${}^0L_{\text{Mo,V}}^{\text{liq}} = -1612.9936 - 0.187074 T(a)$$

$${}^1L_{\text{Mo,V}}^{\text{liq}} = -157.9736 - 0.10393 T(a)$$

**Body-centered cubic; 2 sublattice, sites 1:3; constituents, Mo,V:Va where Va = vacancies**

**Mo**

$$298.15 < T < 2896 \quad G\text{-HSER}_{\text{Mo,bcc}} = -7746.302 + 131.9197 T - 23.56414 T \ln(T) - 0.003443396 T^2 + 5.66283 \times 10^{-7} T^3 + 65,812 T^{-1} - 1.30927 \times 10^{-10} T^4$$

$$2896 < T < 4000 \quad G\text{-HSER}_{\text{Mo,bcc}} = -30,556.41 + 283.559746 T - 42.63829 T \ln(T) - 4.849315 \times 10^{33} T^{-9}$$

**V**

$$298.15 < T < 790 \quad G\text{-HSER}_{\text{V,bcc}} = -7930.43 + 133.346053 T - 24.134 T \ln(T) - 0.003098 T^2 + 1.2175 \times 10^{-7} T^3 + 69,460 T^{-1}$$

$$790 < T < 2183 \quad G\text{-HSER}_{\text{V,bcc}} = -7967.842 + 143.291093 T - 25.9 T \ln(T) + 6.25 \times 10^{-5} T^2 - 6.8 \times 10^{-7} T^3$$

$$2183 < T < 4000 \quad G\text{-HSER}_{\text{V,bcc}} = -41,689.864 + 321.140783 T - 47.43 T \ln(T) + 6.4439 \times 10^{31} T^{-9}$$

$${}^0L_{\text{Mo,V:Va}}^{\text{bcc}} = -4011.698 + 1.45502 T(a)$$

$${}^1L_{\text{Mo,V:Va}}^{\text{bcc}} = +187.074 + 0.20786 T(a)$$

Note: Values are given in SI units and correspond to 1 mole of formula unit. The Gibbs energy of pure element  $i$ ,  ${}^0G_i^{\Phi}(T)$ , referred to the enthalpy for its stable state  $\Phi$  at 298.15 K and 1 bar,  ${}^0H_i^{\Phi}(298.15 \text{ K})$ , is denoted by G-HSER, e.g.,  $G\text{-HSER}_{\text{Mo,liq}} = {}^0G_{\text{Mo}}^{\text{liq}}(T) - {}^0H_{\text{Mo}}^{\text{bcc}}(298.15 \text{ K})$ . (a) Parameters modified in the present work

## Section I: Basic and Applied Research

The present authors have therefore taken the partial excess Gibbs energy expressions given by [80Bre], which agreed reasonably with the experimental work of [69Rud], as the best values and combined them with the latest values for the enthalpy of fusion of V and Mo [92Smi], which were accepted by SGTE. The combinations were then used to calculate the phase diagram using MTDATA.

From Eq 2 to 4, the excess Gibbs energy for bcc phase can be expressed as:

$$G^{\text{ex, bcc}} = X_{\text{Mo}}X_{\text{V}}[-4011.698 + 1.45502 T + (187.074 + 0.20786 T)(X_{\text{Mo}} - X_{\text{V}})] \quad (\text{Eq } 7)$$

An analogous expression for the excess Gibbs energy of the liquid phase was derived with Eq 5 and 6 giving:

$$G^{\text{ex, liq}} = X_{\text{Mo}}X_{\text{V}}[-1612.9936 - 0.187074 T + (-157.9736 - 0.10393 T)(X_{\text{Mo}} - X_{\text{V}})] \quad (\text{Eq } 8)$$

with  $R = 8.3144 \text{ J/K} \cdot \text{mol}$  in the above algebraic operations.

## 4. Results and Conclusions

Table 1 summarizes the thermodynamic data for the Mo-V binary system in SI units and for 1 formula unit.

A comparison between the experimental data [58Bar, 69Rud, 85Koc1, 85Koc2] and calculated curves is shown in Fig. 1 and the calculated curves in terms of weight fraction in Fig. 2. It is believed that the calculated phase diagram is within the experimental uncertainty of the experimental data.

The liquidus and solidus have the following temperature/composition dependence, respectively:

$$X_{\text{V}}(\text{bcc}) = 9.184 \times 10^{-3}(2896 - T) + 1.688 \times 10^{-6}(2896 - T)^2 - 1.43 \times 10^{-9}(2896 - T)^3 \quad (\text{Eq } 9)$$

$$X_{\text{V}}(\text{liq}) = 1.4396 \times 10^{-3}(2896 - T) + 8.9828 \times 10^{-7}(2896 - T)^2 - 1.3923 \times 10^{-9}(2896 - T)^3 \quad (\text{Eq } 10)$$

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