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# Critical Evaluation of the Thermodynamic Properties of Molybdenum

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The thermodynamic properties and the pressure–temperature phase diagram of pure Mo have been evaluated from experimental information using thermodynamic models for the Gibbs energy of the individual phases. A set of parameters describing the Gibbs energy of the various phases as a function of temperature and pressure is presented. The agreement between experimental data and calculated values is satisfactory.

**KEY WORDS:** enthalpy; equation of state; heat capacity; high pressure; high temperature; molybdenum; thermodynamic properties.

## 1. INTRODUCTION

The thermodynamic properties of Mo have been studied experimentally in considerable detail. Most of the studies have been undertaken at atmospheric pressure and consist of measurements of thermodynamic properties and the thermal expansion of the bcc phase. Some data obtained at higher pressures concerning the effect of pressure on the volume of the condensed phases and the melting point have also been published.

The thermodynamic data have been reviewed several times after the publication of the works by Hultgren and co-workers [1, 2]. Ditmars et al. [3] reviewed the data concerning bcc Mo and presented new experimental values for its heat capacity and heat content. Selected values of the thermodynamic properties of bcc Mo between 273 and 2800 K were also presented by Ditmars et al. Later, Brewer and Lamoreaux [4] assessed the thermodynamic data on bcc, liquid, and gaseous Mo. In that assessment,

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the properties of bcc Mo were defined by giving a high weight to the selected values of Ditmars et al., while the properties of liquid Mo were evaluated from the levitation calorimetry data presented by Treverton and Margrave [5] and Berezin et al. [6]. All values presented by Brewer and Lamoreaux were based on the IPTS-48 temperature scale. The most recent assessment of the thermodynamic properties of Mo was made by Chase et al. [7]. For bcc Mo they also gave a high weight to the values selected by Ditmars et al. Due to the lack of additional experimental data, they defined the properties of liquid Mo by adopting values for the enthalpy of fusion and the heat capacity in agreement with Brewer and Lamoreaux.

New experimental data concerning the properties of bcc and liquid Mo have become available after the publication of the work by Chase et al. [7]. Betz and Frohberg [8, 9] presented values for the heat content of bcc and liquid Mo determined between 2200 and about 3400 K by levitation calorimetry. Additional $C_P$ measurements performed on bcc Mo using pulse-heating techniques by Cezairliyan [10] and by Righini and Rosso [11] are also available. Finally, values of the heat capacity of bcc Mo at lower temperatures have been presented in the recent papers by Khriplovich and Paukov [12] and by Oetting and West [13].

In addition to the thermodynamic data, other thermophysical properties have been studied. The thermal-expansion data on bcc Mo were compiled by Touloukian et al. [14]. The measurements by Petukhov and Chekhovskoi [15] were the most recent data included in their compilation. Additional data due to Waseda et al. [16] and Pethukov et al. [17] are now available.

The effect of pressure on the volume of bcc Mo has been studied using various techniques. Values of the molar volume for pressures up to 200 GPa have been reported by Carter et al. [18], whereas Vaidya and Kennedy [19] and Ming and Manghnani [20] have recently obtained data on the low-pressure range. Finally, information concerning the effect of pressure on the melting point of Mo has been reported by Fateeva and Vereshchagin [21, 22].

In view of this wealth of new information it seems appropriate again to assess the properties of Mo. In principle, thermodynamic information can be evaluated from all these various types of experimental data by applying thermodynamic models for the Gibbs energy of the individual phases as a function of temperature and pressure and optimizing the parameters involved. When using this procedure, the model parameters may be evaluated from selected experimental data. As a consequence, thermodynamic values obtained from the optimization may be taken as assessed values, consistent with the most reliable information. This procedure has now been applied to the evaluation of the thermodynamic properties of bcc, liquid, and gaseous Mo and the results of the assessment are presented in this report.

The main purpose of this work was to provide the Gibbs energy functions for pure Mo which are necessary in the evaluation of binary and higher-order phase diagrams involving Mo.

## 2. THERMODYNAMIC MODELS

When evaluating the thermodynamic properties of pure Fe, Fernández Guillermet and Gustafson [23] established analytical expressions for the Gibbs energy $[G_m(T, P)]$ per mole (m) of the various phases from the temperature and pressure dependency of those derivatives of $G_m(T, P)$ which have been studied experimentally.

In the present case, the available data consist of measurements of heat capacity $(C_P)$, heat content $(H_T - H_{298.15})$, and molar volume $(V_m)$ at atmospheric pressure $(P_0)$ and some measurements of $V_m(T, P)$ performed at higher pressures. Accordingly, an expression for $G_m(T, P)$ will be obtained by integrating the relations

$$\left(\frac{\partial^2 G_m}{\partial T^2}\right)_P = -\frac{C_P(T, P)}{T}, \qquad \left(\frac{\partial G_m}{\partial P}\right)_T = V_m(T, P) \tag{1}$$

where $C_P(T, P)$ and $V_m(T, P)$ are functions chosen to represent the experimental data. The analytical form of these functions is now considered.

### 2.1. Description of the Heat Capacity

#### 2.1.1. Solid (bcc) Phase

The following expression was adopted for describing the heat capacity of bcc Mo at zero pressure and form 200 K to the melting point:

$$C_P = -(c + 2dT + 6eT^2 + 12fT^3 + 2gT^{-2}) \tag{2}$$

where the quadratic and cubic terms were included in order to describe the deviation from the linear behavior which is noticeable in the proximity of the melting point. The term with $T^{-2}$ was included in order to describe the variations shown by $C_P$ between 200 K and about 500 K.

The description of $C_P$ for the solid phase will be complete if a method of extrapolation outside the range of stability is defined. A model with a sound physical basis has not been developed yet but a simple procedure has been adopted by the SGTE (Scientific Group Thermodata Europe)

[24]. Its purpose is to make sure that the stability of the solid phase relative to the liquid does not change unintentionally at higher temperatures. This could be accomplished by making $C_P$ of the solid phase above the melting point, $T_f$, equal to the $C_P$ of the liquid. In order to avoid a discontinuous change of $C_P$ for the solid phase at the melting point, it is instead made to approach $C_P$ of the liquid phase at high temperatures by applying the following expression at zero pressure above the melting point:

$$C_P^{\mathrm{bcc}} = C_P^{\mathrm{liq}}(T) + [C_P^{\mathrm{bcc}}(T_f) - C_P^{\mathrm{liq}}(T_f)] \left(\frac{T}{T_f}\right)^{-10}, \qquad T > T_f \qquad (3)$$

The exponent $-10$ was chosen in order to make the difference in $C_P$ less than 2% at $T = 1.5\,T_f$. Equation (3) was adopted in this work for extrapolating $C_P$ of bcc Mo above the melting point.

### 2.1.2. Liquid Phase

The properties of the liquid phase have been studied only between the melting point and 3383 K. For this reason Eq. (2) was simplified by assuming a temperature-independent heat capacity. For the extrapolation of $C_P$ below the melting point, the procedure adopted by the SGTE was again adopted. In this case the heat capacity of the liquid below $T_f$ was assumed to approach $C_P$ of the bcc phase according to the expression

$$C_P^{\mathrm{liq}}(T) = C_P^{\mathrm{bcc}}(T) + [C_P^{\mathrm{liq}}(T_f) - C_P^{\mathrm{bcc}}(T_f)] \left(\frac{T}{T_f}\right)^{6}, \qquad T_f < T \qquad (4)$$

The exponent 6 was chosen in order to make the difference in $C_P$ less than 2% at $T = 0.5\,T_f$. It should be emphasized that the purpose is not to describe as well as possible the real properties of the supercooled liquid and its glass transition. It is rather to obtain a reasonable reference for the description of the liquid phase in low-melting Mo alloys.

### 2.1.3. Gas Phase

The properties of the gas phase are known from calculations based on the electronic levels of monoatomic Mo. The most recent evaluation of the heat capacity of Mo(g) has been performed by Chase et al. [7]. These assessed values have recently been described by Rand [25] by means of the following expression

$$C_P = -(c + 2dT + 6eT^2 + 2gT^{-2}) \qquad (5)$$

When fitting Eq. (5) to the assessed $C_P$ values between 298.15 and 6000 K, the required goodness of fit was achieved by dividing the temperature range in three intervals. Rand's description was considered adequate for the present purpose, and it was accepted in this evaluation.

## 2.2. Description of the Molar Volume

### 2.2.1. Condensed Phases

The results of compression studies made on solid [26] and liquid [27] phases have been described by expanding the isothermal bulk modulus $[B(T, P)]$ in powers of $P$ and retaining only the linear term

$$B(T, P) = B(T, 0) + nP \tag{6}$$

where $B(T, 0)$ is the bulk modulus at zero pressure. By integrating Eq. (6), the following expression for the pressure dependence of the molar volume can be obtained:

$$V_{\mathrm{m}}(T, P) = \frac{V_{\mathrm{m}}(T, 0)}{[1 + nK(T, 0)P]^{1/n}} \tag{7}$$

where $V_{\mathrm{m}}(T, 0)$ and $K(T, 0)$ are the molar volume at zero pressure and the isothermal compressibility at zero pressure, respectively. Equation (7), first suggested by Murnaghan [28], was accepted in this work for describing the effect of pressure on the molar volume of bcc and liquid Mo. The effect of temperature on $V_{\mathrm{m}}(T, P)$ was described through the temperature dependence of the quantities $V_{\mathrm{m}}(T, 0)$ and $K(T, 0)$, while the parameter $n$ was considered temperature independent. Furthermore, its value was assumed to be the same for bcc and liquid Mo. This assumption was made because of the lack of experimental data on the pressure dependence of $V_{\mathrm{m}}$ for liquid Mo.

The effect of temperature on $V_{\mathrm{m}}(T, 0)$ was described in the following way:

$$V_{\mathrm{m}}(T, 0) = V_{\mathrm{m}}(T_0, 0) \cdot \exp\left[\int_{T_0}^{T} \alpha(T, 0)\, dT\right] \tag{8}$$

where $\alpha(T, 0)$ is the thermal expansivity at zero pressure and $T_0$ is the reference temperature. The available data suggested the following expression, which was adopted for the temperature dependence of $\alpha(T, 0)$ in the case of bcc Mo:

$$\alpha(T, 0) = \alpha_0 + \alpha_1 T + \alpha_2 T^2 \tag{9}$$

Due to the lack of experimental data concerning the thermal expansion of the liquid phase, it was assumed to be the same as for the bcc phase. Hence, the expansivity of liquid Mo was described by using Eq. (9) with the same coefficients as for bcc Mo.

Very little is known about the effect of temperature on the compressibility to bcc Mo. The results presented by Bridgman in his book [29] show an increase in the compressibility with temperature, but the temperature range studied by him was too limited to give information about the form of the temperature dependence. On the other hand, the temperature range considered in his work is large and it seemed unrealistic to assume the compressibility of Mo to be temperature independent. However, information now available on the compressibility of bcc W [30, 31] may be used for making reasonable estimates. These data suggested the following expression for the compressibility of bcc W at zero pressure:

$$K(T, 0) = K_0 + K_1 T + K_2 T^2 \tag{10}$$

The same expression was adopted for bcc Mo in this work and the values of $K_1$ and $K_2$ were taken from W, whereas $K_0$ was evaluated from data on the compressibility of Mo at room temperature [18–20]. Due to the lack of information on the properties of liquid Mo, its compressibility was also described using Eq. (10) with the same coefficients as for bcc Mo.

### 2.2.2. Gas Phase

In this evaluation, the available information on the vapor pressure of solid and liquid Mo was considered in order to define the properties of the gaseous phase. These pressures are low enough for the ideal gas approximation to be valid. Hence, these data were analyzed by assuming the following expression for the molar volume of gaseous Mo:

$$V_m(T, P) = \frac{RT}{P} \tag{11}$$

where $R$ is the gas constant.

The description of the nonideal behavior of the gas phase was not a purpose of the present evaluation. For this reason, no attempt was made to modify Eq. (11) in order to describe the molar volume of the gaseous Mo under higher pressures.

### 2.3. Description of the Gibbs Energy

The contributions to the Gibbs energy discussed in the preceding sections give, when combined, the following type of expression for the Gibbs energy of bcc and liquid Mo as a function of temperature and pressure:

$$G_m(T, P) - H_m^{SER} = a + bT + cT\ln(T) + dT^2 + eT^3 + fT^4 + gT^{-1} + jT^{(i+1)} + \int_0^P V_m(T, P)\,dP \qquad (12)$$

where

$$\int_0^P V_m(T, P)\,dP = \frac{A\exp(\alpha_0 T + (1/2)\alpha_1 T^2 + (1/3)\alpha_2 T^3}{(K_0 + K_1 T + K_2 T^2)(n-1)} \times \{[1 + nP(K_0 + K_1 T + K_2 T^2)]^{1-1/n} - 1\} \qquad (13)$$

and $A$ is a parameter of the dimension volume. The exponent $i$ is equal to $-10$ for bcc Mo above $T_f$ and equal to 6 for the liquid below $T_f$. $j$ is equal to 0 for bcc Mo below $T_f$ and for liquid Mo above $T_f$. $H_m^{SER}$ is the enthalpy of Mo in a special reference state recommended by the SGTE [24]. This state, denoted by the superscript SER (stable element reference), is defined as the stable state at 298.15 K and $P_0 = 0.1$ MPa.

For the gas phase we obtain

$$G_m(T, P) - H_m^{SER} = a + bT + cT\ln(T) + dT^2 + eT^3 + gT^{-1} + RT\ln(P) \qquad (14)$$

## 3. SELECTED EXPERIMENTAL INFORMATION

The selection of values for the optimization procedure was made after a consideration of the works mentioned in the Introduction together with earlier data. The inclusion of a given piece of information in the optimization was decided after analyzing the accuracy of the experimental technique and its agreement with results obtained by other methods. All values included in the optimization were based on IPTS-68. Temperatures and calorimetric data were corrected to this temperature scale by means of the tables presented by Douglas [32] and Ditmars et al. [8].

### 3.1. Thermochemical Data

#### *3.1.1. bcc Phase*

Values for the heat content of bcc Mo have been determined by different authors. The data considered in this evaluation consist of the measurements performed by Jaeger and Veenstra [33] between 670 and 1828 K, Lazareva et al. [34] between 1154 and 2462 K, Kirillin et al. [35] between 972 and 2610 K, Conway et al. [36] between 1267 and 2628 K, Chekhovskoi and Petrov [37] between 972 and 2834 K, Chekhovskoi et al. [38] between 2094 and 2864 K, Ditmars et al. [3] between 323 and 2102 K, and Betz and Frohberg [8] between 2282 and 3383 K. From this experimental information, the following values were selected for the optimization.

Values for the heat content were selected between 373.15 and 973.15 K from the measurements performed by Ditmars et al. using a Bunsen ice calorimeter. Between 1198.6 and 2102.4 K enthalpy values were selected from the values determined by Ditmars et al. using an adiabatic receiving calorimeter. One value at 2215.15 K was selected from the data obtained by Kirillin et al. by the method of mixtures using a massive calorimeter with an isothermal shell, and values at 2632.2 and 2834.2 K from the results obtained by Chekhovskoi and Petrov using the same equipment and procedure. Finally, from the results obtained by Betz and Frohberg by levitation heating and drop calirimetry, values measured at 2500, 2604, and 2761 K were selected and included in the optimization.

In addition to the heat content data, heat capacity values were also selected. This was considered necessary since the heat content data are usually not enough to define the shape of the $C_P$ function in the regions where it varies rapidly with temperature, in particular at very high temperatures and below room temperature.

The $C_P$ data considered in this work consist of the measurements reported by Clusius and Franzosini [39] between 10 and 271 K, by Lowenthal [40] between 1200 and 2100 K, by Taylor and Finch [41] between 200 and 2860 K, by Makarenko et al. [42] between 1100 and 2400 K, by Chekhovski and Kalinkina [43] between 464 and 833 K, by Oetting and West [13] between 200 and 700 K, by Cezairliyan [10] between 1500 and 2800 K, by Righini and Rosso [11] between 1300 and 2500 K, and by Khriplovich and Paukov [12] between 5 and 302 K. From this experimental information, the following data were selected. $C_P$ values at 200, 250, and 298.15 K were selected from the measurements performed by Khriplovich and Paukov using an adiabatic calorimeter. From the measurements performed by Oetting and West by adiabatic calorimetry, values were selected between 300 and 700 K. A value measured at 1200 K by Makarenko et al. using a modulation method was also selected. The $C_P$ values measured by Righini and Rosso using pulse-heating technique are in good agreement with the values previously determined by Cezairliyan using the same technique. $C_P$ values in agreement with these sources were selected between 1500 and 2500 K and included in the optimization. Between

2600 and 2800 K, $C_P$ values were taken from Cezairliyan's pulse-heating data. Finally, the entropy and enthalpy at 298.15 K evaluated by Khriplovich and Paukov were accepted and included in the optimization.

### *3.1.2. Liquid Phase*

According to Kenisarin et al. [44], pure Mo melts at 2896 K at atmospheric pressure. This value, recently included in a list of secondary reference points [45], was accepted in this evaluation.

The heat content of liquid Mo has been measured by levitation calorimetry and by dynamic techniques. Treverton and Margrave [5], Berezin et al. [6], and Betz and Frohberg [8, 9] used levitation calorimetry, whereas Dikhter and Lebedev [46] and Shaner et al. [47] used dynamic techniques. The values obtained by levitation calorimetry are considered first.

The heat content values presented by Treverton and Margrave are considerably lower than those reported by Berezin et al. and by Betz and Frohberg. The discrepancy may be explained by considering the heat lost by the specimen during the drop into the calorimeter. Treverton and Margrave did not report how they took into account the heat losses or whether such correction was done at all. For this reason their values were not used in this work.

The measurements presented by Berezin et al. cover a rather small temperature range, while Betz and Frohberg determined the heat content of liquid Mo up to about 3383 K. A comparison of the values reported at the melting point indicates that Berezin's values is about 3.5% lower. On the other hand, Betz and Frohberg's data show a larger scatter just above the melting point than at higher temperatures. Hence, values for the heat content of the liquid were primarily selected only for the region between 3040 and 3383 K. A linear extrapolation of these selected heat content values to the melting point gave about 127 $\mathrm{kJ \cdot mol^{-1}}$, while Betz and Frohberg evaluated 128.1 $\mathrm{kJ \cdot mol^{-1}}$ from their points, and Berezin et al. about 124.5 $\mathrm{kJ \cdot mol^{-1}}$. The value of 127 $\mathrm{kJ \cdot mol^{-1}}$ may thus be considered a weighted average of both pieces of information, and it was included in the optimization.

The heat content values obtained by Dikhter and Lebedev using dynamic techniques are much higher than those obtained by levitation calorimetry. Dikhter and Lebedev's values were considered uncertain and not used in this work. The heat content values presented by Shaner et al. were determined by a pulse-heating technique. They indicate a very high value for $C_P$ of liquid Mo. In a more recent paper, the existence of a systematic error in the temperature measurement of [47] has been communicated [48], but the corrected values are not available. For this reason, the heat content values presented by Shaner et al. were not used in this evaluation.

### 3.1.3. *Gas Phase*

The already mentioned $C_P$ functions for gaseous Mo obtained by Rand [25] were accepted in this work and were not modified during the evaluation. The entropy value at 298.15 K computed by Chase et al. [7] was also accepted. Experimental data on the vapor pressure of the solid and liquid phases were used for defining the enthalpy of gaseous Mo. Values of the vapor pressure for bcc Mo between 2154 and 2400 K were selected from the measurements by Edwards et al. [49]. From the data presented by Vozzella et al. [50], a value at 2500 K was also selected. Finally, for the vapor pressure of liquid Mo, values at 2945, 2955, and 2995 K were selected from the work by Koch and Anable [51].

## 3.2. Thermophysical Data

### 3.2.1. *Thermal Expansion Data*

Information concerning the temperature dependence of the volume of bcc Mo at atmospheric pressure can be obtained from two sources, dilatometric measurements and X-ray determinations of the lattice parameters. The dilatometric data examined in this work consist of the measurements performed by Nix and MacNair [52] between 86 and 298 K, by Conway and Losenkamp [53] between 298 and 2773 K, by Petukhov and Chekhovski [15] between 2073 and 2819 K, and by Petukhov et al. [17] between 1547 and 2700 K. The X-ray data examined in this evaluation consist of the measurements performed by Edwards et al. [54] between 1126 and 2073 K, by Ross and Hume-Rothery [55] between 1173 and 2005 K, by Straumanis and Shodhan [56, 57] between 288 and 338 K, and by Waseda et al. [16] between 1073 and 2614 K. From these data, the following pieces of information were selected. First, values for the molar volume at 273.15, 298.15, 318.15, and 338.15 K were evaluated from the X-ray work by Straumanis and Shodhan and included in the optimization. The value $6.0220940 \cdot 10^{23}\ \mathrm{mol}^{-1}$ for Avogadro's constant was used in these evaluations.

Molar volume values were selected at 1163, 1512, abd 1821 K from the work by Edwards et al. A value at 1681 K was selected from Waseda et al., and values at 2008 and 2149 K from Pethukov et al. Finally, values from the work by Pethukov and Chekhovskoi were selected between 2453 and 2819 K.

A value for the molar volume of liquid Mo at the melting point has been presented by Kostikov et al. [58]. However, no information on their experimental methods was given. For this reason, their value was not used in this work. In the work by Shaner et al. [47] values for the molar volume of liquid Mo and Ta at 0.2 and 0.1 GPa, respectively, were also presented. Obviously, the systematic error in the measurement of temperature reported by Gathers [48] affected these values also. He did not present the corrected values for Mo but he did for Ta, and that information was used by us to estimate the corrections to the molar volume of liquid Mo by assuming the error in the temperature measurement to be the same in both cases. The high melting point of Ta allowed this correction to be made only at the highest temperatures. Values for the molar volume of liquid Mo could thus be estimated at 3839, 4098, 4473, and 4736 K. They were included in the optimization.

### 3.2.2. *Compression Data*

Data concerning the effect of pressure on the volume of bcc Mo have been obtained at low pressures by Bridgman [59] and by Vaidya and Kennedy [19] using piston-cylinder techniques and by Ming and Manghnani [20] using an X-ray technique, and at high pressures by Carter et al. [18] from an analysis of shock-wave data. At low pressures, the values reported by Ming and Manghnani at 2.4 and 3.4 GPa were accepted and included in the optimization. They are in good agreement with the results reported by Vaidya and Kennedy and Bridgman. At higher pressures, the data obtained by Carter et al. between 5 and 200 GPa were used and included in the optimization.

## 3.3. Experimental Data on the Temperature–Pressure Phase Diagram

The only source of data on the P–T phase diagram is the work by Fateeva and Vereshchagin [21, 22]. They determined the melting point of Mo between 0.1 MPa and 9 GPa by a method based on the measurement of the thermal radiation and evaluated the liquids line by fitting a straight line to some selected points. However, the selection was made in such a way that the evaluated liquidus line came out with a very small slope, suggesting a difference of about 1 % between the molar volume of solid and that of liquid Mo. That volume difference seems too small when compared with the values for Ta presented by Gathers [48]. Furthermore, when Fateeva and Vereschagin described their data on the liquidus lines of W

[22, 60] and Ta [22, 61], they adopted larger slopes. For these reasons, their recommended values for the melting point of Mo between 3 and 9 GPa were given a low weight in the present optimization.

## 4. RESULTS

The evaluation of the various parameters was made by means of a computer program for the optimization of thermodynamic parameters developed by Jansson [62, 63]. All the parameter values obtained in the present evaluation are presented in Table I.

Comparisons with experimental data are given in Figs. 1 to 11. In Figs. 1 and 2 the calculated heat content of bcc Mo is compared with the experimental data examined in this evaluation. The agreement is very good, even for those data that were not used in the optimization. The heat content of bcc Mo at higher temperatures and of liquid Mo are compared with experimental data in Fig. 3. The agreement is again very good. The enthalpy of fusion evaluated in this work is presented in Table II and compared with values according to various authors. The present value is higher than previous recommendations, agrees fairly well with the value obtained by Berezin et al., and is lower than the value reported by Betz and Frohberg.

In Figs. 4 and 5 the optimized heat capacity of bcc Mo is compared with experimental data obtained using various techniques. The agreement is very good. The present values of $C_P$ for bcc Mo close to the melting point are lower than those reported by Taylor and Finch but in good agreement with recent data by Cezairliyan. The value of $C_P$ for liquid Mo according to this evaluation is compared in Table III with the values according to various authors. The agreement with the value by Betz and Frohberg and with a value suggested by Hultgren et al. [1] is good.

In Fig. 6, the vapor pressure of bcc and liquid Mo according to the present evaluation is compared with experimental data. The agreement is very good. This diagram may be regarded as a $T$–$P$ phase diagram for Mo, with the pressure axis showing $RT \ln P$. The extension of the calculated bcc/liquid phase boundary toward higher pressures is shown later. First, the molar volumes of bcc and liquid Mo according to the present work are considered. In Figs. 7 and 8 the molar volume of bcc Mo at atmospheric pressure according to the present work is compared with experimental data. The agreement is very good. In Figs. 9 and 10 the pressure dependence of the molar volume of bcc Mo at room temperature according to the present evaluation is compared with the available data. The optimized values are slightly higher than Bridgman's [59] but in good agreement with more recent data. In particular, the shock-wave data are well

**Table I.** Summary of Optimum Parameters for Molybdenum
All Data in SI Units (J, Mol, K)

| Element, | Stable element reference (SER), | Mass, | $H_{298.15} - H_0$, | $S_{298.15}$, |
|---|---|---|---|---|
| Mo | bcc Mo at 298.15 K and 0.1 MPa | 95.94 | 4589 | 28.56 |

Solid

$298.15 < T < 2896$ K

$$G_m^{bcc} - H_m^{SER} = -7747.257 + 131.9197\,T - 23.56414\,T\ln(T) - 0.003443396\,T^2 + 5.662834 \times 10^{-7}\,T^3 - 1.309265 \times 10^{-10}\,T^4 + 65812.39\,T^{-1} + \textstyle\int_0^P V_m(T, P)\,dP$$

$2896 < T < 4000$ K

$$G_m^{bcc} - H_m^{SER} = -30{,}724.08 + 283.6116\,T - 42.6329\,T\ln(T) - 4.610447 \times 10^{33}\,T^{-9} + \int_0^P V_m(T, P)\,dP$$

Liquid

$298.15 < T < 2896$ K

$$G_m^{liq} - H_m^{SER} = 33{,}869.51 + 117.3112\,T - 23.56414\,T\ln(T) - 0.003443396\,T^2 + 5.662834 \times 10^{-7}\,T^3 - 1.309265 \times 10^{-10}\,T^4 + 65812.39\,T^{-1} + 4.035826 \times 10^{-22}\,T^7 + \int_0^P V_m(T, P)\,dP$$

$2896 < T < 4000$ K

$$G_m^{liq} - H_m^{SER} = 3538.018 + 271.6697\,T - 42.63829\,T\ln(T) + \int_0^P V_m(T, P)\,dP$$

where

$$\int_0^P V_m\,dP = \frac{A\exp(\alpha_0 T + (1/2)\alpha_1 T^2 + (1/3)\alpha_2 T^3)}{K(T, 0)(n-1)} \{[1 + nK(T, 0)P]^{1-1/n} - 1\}$$

and

$$K(T, 0) = K_0 + K_1 T + K_2 T^2$$

The constants in these equations have the following values:

$\alpha_0 = 1.43780 \times 10^{-5}$, $K_0 = 3.5027 \times 10^{-12}$, $n = 3.25$;
$\alpha_1 = 4.66062 \times 10^{-10}$, $K_1 = 1.5 \times 10^{-16}$, $A = 9.34372 \times 10^{-6}$ for bcc Mo;
$\alpha_2 = 3.44061 \times 10^{-12}$, $K_2 = 3.9 \times 10^{-20}$, $A = 9.75079 \times 10^{-6}$ for liquid Mo.

Gas

$298.15 < T < 1550$ K

$$G_m^{gas} - H_m^{SER} = RT\ln(P) + 654{,}894.5 - 137.2814\,T - 20.2972241\,T\ln(T) + 2.0577132 \times 10^{-4}\,T^2 - 3.7855145 \times 10^{-8}\,T^3 + 3716.8083\,T^{-1}$$

$1550 < T < 3550$ K

$$H_m^{gas} - H_m^{SER} = RT\ln(P) + 638{,}221.2 - 17.80267\,T - 37.27552\,T\ln(T) + 0.007391151\,T^2 - 6.3943702 \times 10^{-7}\,T^3 + 324{,}7589.4\,T^{-1}$$

$3550 < T < 6000$ K

$$G_m^{gas} - H_m^{SER} = RT\ln(P) + 968{,}833.2 - 1190.181\,T + 106.69409\,T\ln(T) - 0.020544187\,T^2 + 3.7923253 \times 10^{-7}\,T^3 - 1.3950975 \times 10^8\,T^{-1}$$

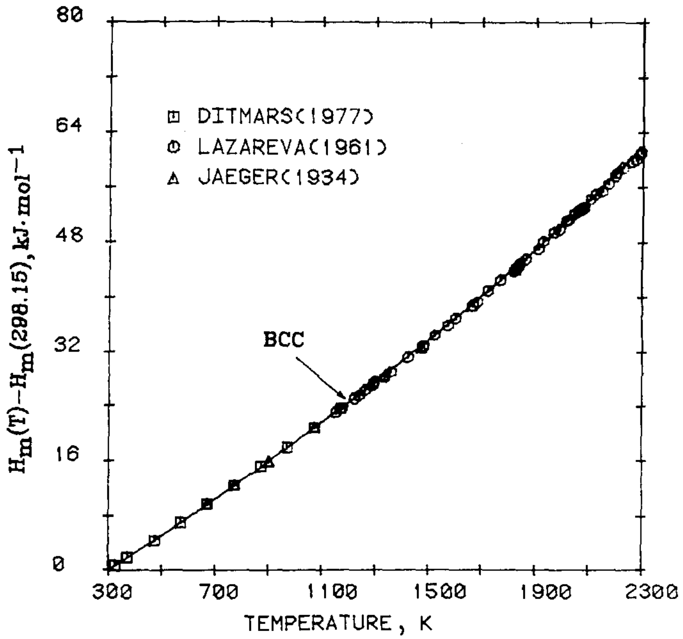

**Fig. 1.** The heat content of bcc Mo at low temperatures according to experimental data and the present evaluation.

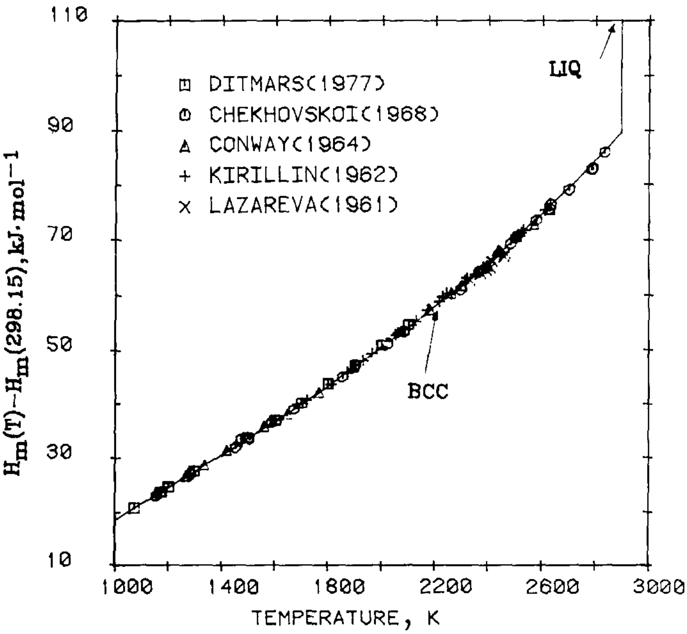

**Fig. 2.** The heat content of bcc Mo at high temperatures according to experimental data and the present evaluation.

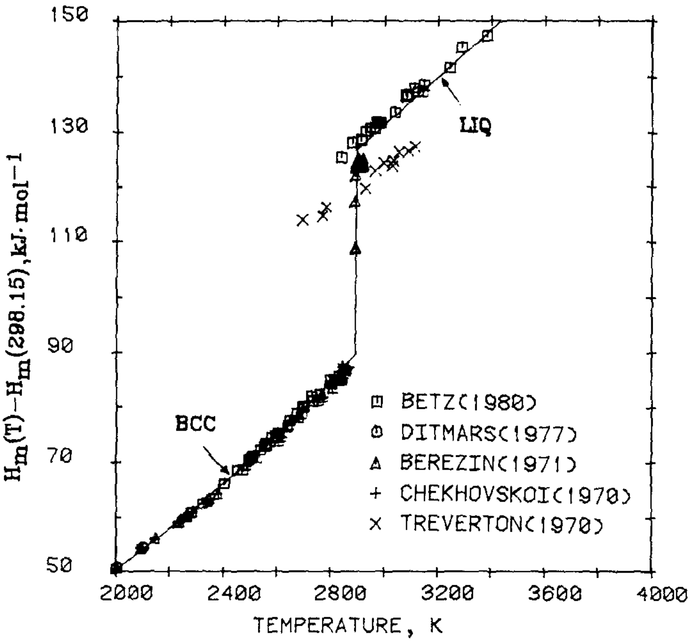

Fig. 3. The beat content of bcc and liquid Mo according to experimental data and the preset evaluation.

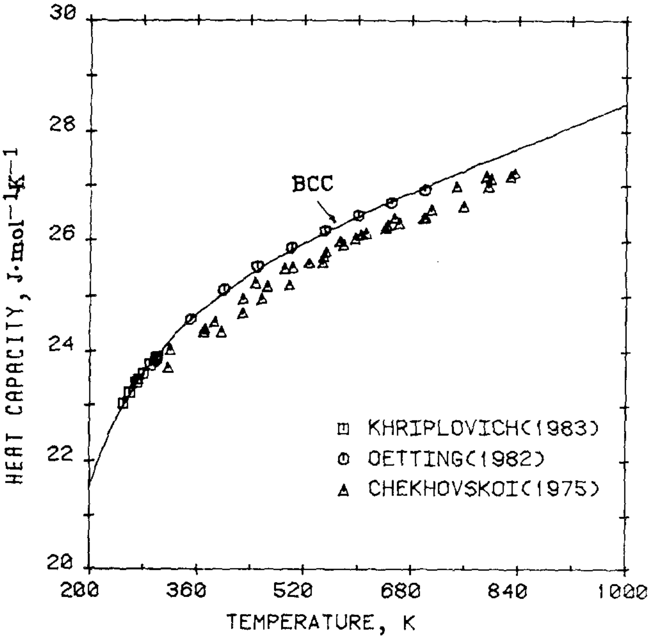

Fig. 4. The heat capacity of bcc Mo at low temperatures according to experimental data and the present evaluation.

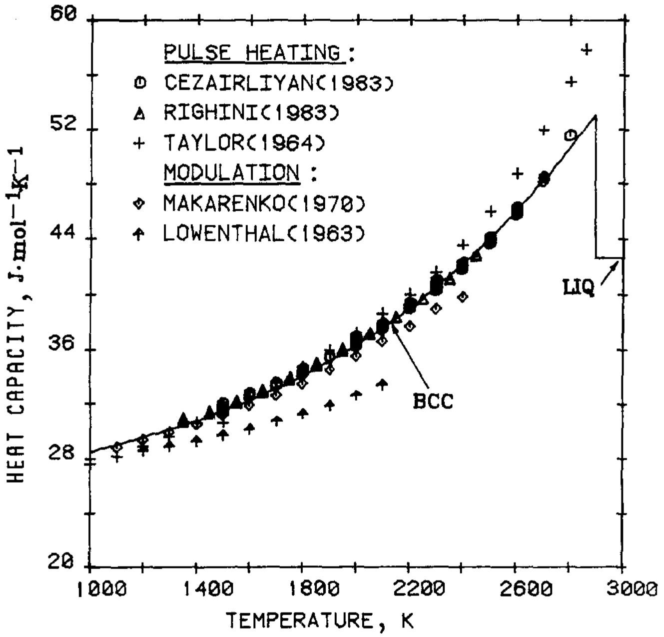

Fig. 5. The heat capacity of bcc and liquid Mo according to experimental data and the present evaluation.

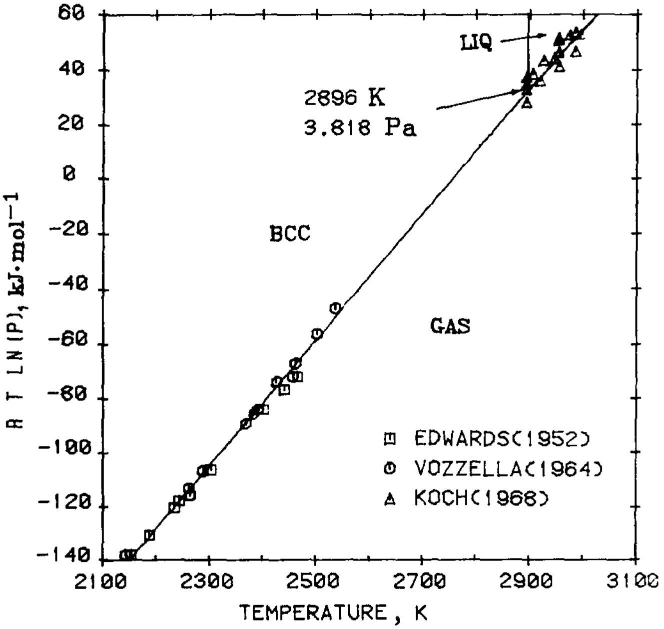

Fig. 6. Experimental vapor pressure of bcc and liquid Mo compared with the calculated $T$–$P$ phase diagram, with the pressure axis showing $RT \ln P$.

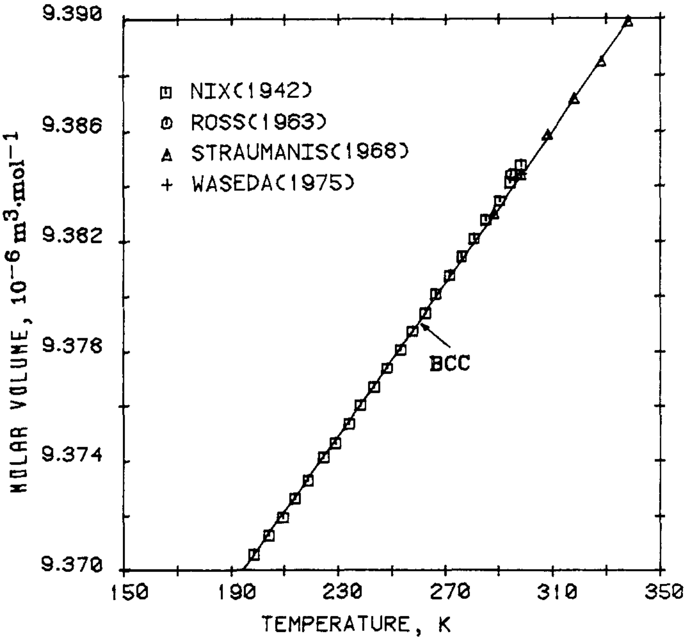

**Fig. 7.** The molar volume of bcc Mo at low temperatures according to experimental data and the present evaluation.

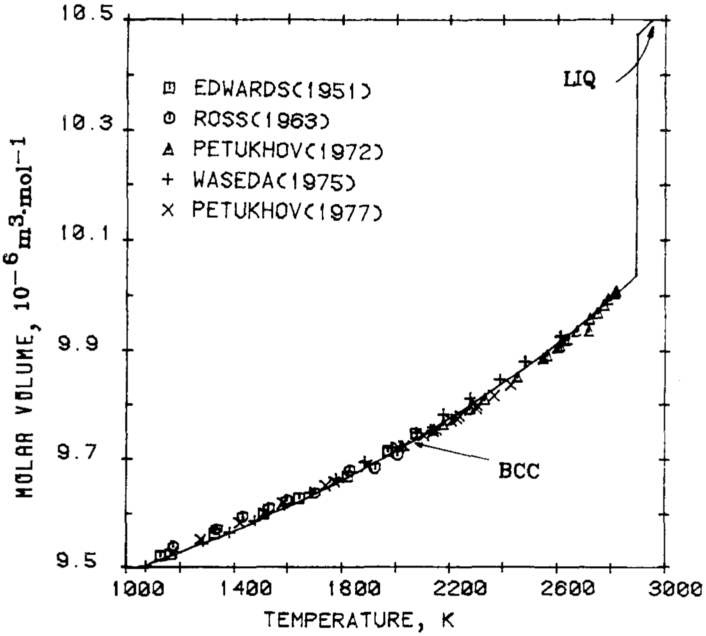

**Fig. 8.** The molar volume of bcc and liquid Mo according to experimental data and the present evaluation.

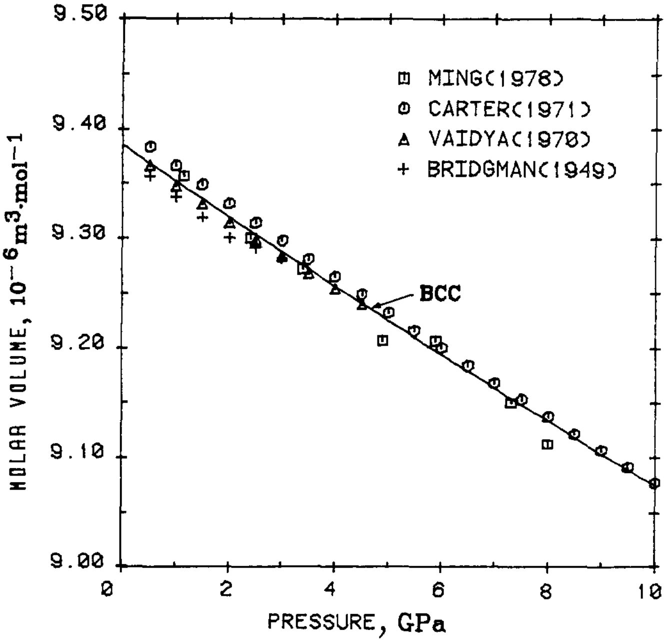

**Fig. 9.** The molar volume of bcc Mo at room temperature and high pressures according to experimental data and the present evaluation.

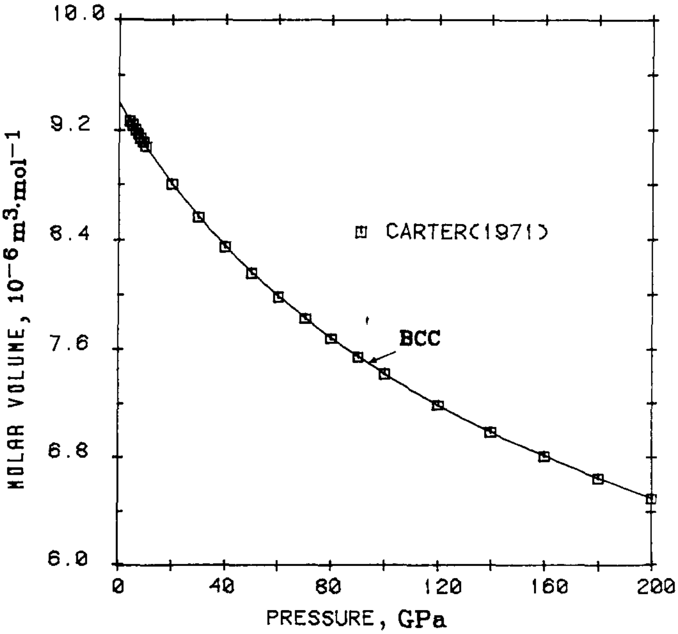

**Fig. 10.** The molar volume of bcc Mo at room temperature and high pressures according to the shock-wave data by Carter et al. [18] and the present evaluation.

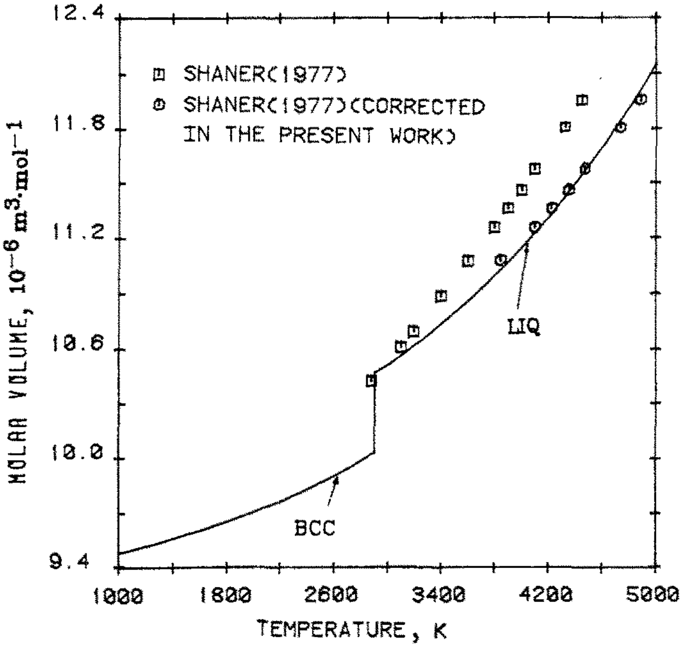

**Fig. 11.** The molar volume of solid and liquid Mo at 0.2 GPa according to experimental data by Shaner et al. [47] corrected in this work and the present evaluation.

reproduced up to 200 GPa. The present values for the isothermal bulk modulus of bcc Mo and its pressure derivative are presented in Table IV and compared with the available experimental data. Values for the pressure derivative of the bulk modulus according to the predictions of various suggested relations [67–70] between this derivative and the Grüneisen parameter are also presented. This was considered interesting because these relations are sometimes used for making estimates of lacking data [26]. The present value for the bulk modulus agrees with the one according to Bridgman [71] but is higher than the other values. Its pressure derivative according to this work is in fair agreement with the value evaluated by McQueen et al. [66] from shock-wave data. It is much lower than the value obtained by Vaidya and Kennedy. It is also lower than the value from ultrasonic data, but the difference $4.46-3.25=1.26$ agrees with differences from 0.5 to 1 found by Anderson [72] by comparing the ultrasonic and the very-high-pressure derivatives of the bulk modulus of various substances. Furthermore, the present value is lower than the one calculated using Dugdale and MacDonald's relation [68] and the Grüneisen parameter evaluated in the present work at 298.15 K and

**Table II.** The Enthalpy of Fusion of Pure Mo According to Various Authors and the Present Evaluation

| Author(s) | Year | Value ($J \cdot mol^{-1}$) | Observations |
|---|---|---|---|
| Hultgren et al. [1] | 1963 | 27,824 | Estimated value |
| Treverton and Margrave [5] | 1970 | 34,811 (±300) | Determinated by levitat. calorim. |
| Berezin et al. [6] | 1971 | 36,585 (±1300) | Determined by levitat. calorim. |
| Dikther and Lebedev [46] | 1971 | 40,295 | Determined by a dynamic method |
| Hultgren et al. [2] | 1973 | 32,540 (±4100) | Assessment |
| Shaner et al. [47] | 1977 | 35,786 | Determined at 0.2 GPa by a dynamic method |
| Brewer and Lamoreaux [4] | 1980 | 35,730 | Assessment |
| Betz and Frohberg [8] | 11980 | 39,116 (±200) | Determinated by levitat. calorim. |
| Chase et al. [7] | 1982 | 35,982 (±5400) | Assessment |
| This work | | 37,479.8 | Evaluation |

**Table III.** The Heat Capacity of Liquid Mo According to Various Authors and the Present Evaluation

| Author(s) | Year | Value ($J \cdot mol^{-1} \cdot K^{-1}$) | Operations |
|---|---|---|---|
| Hultgren et al. [1] | 1963 | 41.84 | Estimated value |
| Treverton and Margrave [5] | 1970 | 34.27 (±2) | Determined by levit. calorim. |
| Dikhter and Lebedev [46] | 1971 | 58.5 | Determined by a dynamic method |
| Hultgren et al. [2] | 1973 | 34.27 | Assessment |
| Shaner et al. [47] | 1977 | 69.8 | Determined at 0.2 GPa by a dynamic method |
| Brewer and Lamoreaux [4] | 1980 | 37.7 (±2) | Assessment |
| Betz and Frohberg [8] | 1980 | 40.35 (±1) | Determined by levit. calorim. |
| Chase et al. [7] | 1982 | 37.7 | Assessment |
| This work | | 42.64 | Evaluation |

**Table IV.** The Isothermal Bulk Modulus of bcc Mo and Its Pressure Derivative According to Experimental Data, the Predictions of Various Relations Between $(\partial B/\partial P)$ and the Grüneisen Parameter, and the Present Evaluation[a]

| Source of information | Bulk modulus (GPa) | $(\partial B/\partial P)$ | Observations |
|---|---|---|---|
| Köster and Franz [64] | 274.584 | | Value selected in Ref. 64 |
| Bridgman [71] | 283.44 | | Evaluated in this work from the polynomial fit to Bridgman's data presented in Ref. 19 |
| Vaidya and Kennedy [19] | 253.1 | 13.2979 | Evaluated by Vaidya and Kennedy [19] from a polynomial fit to their own data |
| | 266.037 | 11.963 | Evaluated by Vaidya and Kennedy [19] from the application of Murnaghan's model to their own data |
| Katahara [65] | 260.8 | 4.46 | Evaluated in Ref. 65 from ultrasonic data |
| Ming and Manghnani [20] | 267 (±11) | 4.46 | Evaluated in Ref. 20 by accepting the value for $(\partial B/\partial P)$ presented by Katahara [65] |
| McQueen et al. [66] | 261 | 3.96 | Values quoted in Ref. 20; evaluated from shock-wave data |
| This work | | 3.64 | Calculated in this work using Slater's [67] relation |
| | | 4.30 | Calculated in this work using Dugdale and McDonald's [68] relation |
| | | 2.65 | Calculated in this work using Cook and Rogers' [69] relation |
| | | 3.30 | Calculated in this work using Bohlin's [70] relation |
| | 281.62 | 3.25 | Evaluated in this work from experimental data |

[a] The estimates of $(\partial B/\partial P)$ According to the Suggested Relations [67–70] were based on the value 1.6527 for the Grüneisen parameter at 298.15 K and 101325 Pa, obtained in this present work.

101325 Pa. Its agreement with the prediction of Slater's [67] relation is better than the one found by Vaidya and Kennedy [19] and by Gilvarry [73] in his study of the Grüneisen parameter of various substances. Finally, the present value is in good agreement with the one calculated using the Grüneisen parameter at 298.15 and 101325 Pa according to this work and the relation recently presented by Bohlin [70].

The temperature dependence of the isothermal compressibility adopted in this work is now considered. In Table V the present value for the temperature derivative of the compressibility at room temperature and zero pressure is compared with a value evaluated in this work from data by Bridgman [29] and with values calculated from various suggested relations [74–76] between the thermophysical properties of solids. These values are the only independently produced data which can be used for comparison with the estimates made in the present work. The value calculated with the present parameters is reasonably close to the one evaluated from Bridgman's [29] data, and it is close to those given by the relations suggested by various authors. The compressibility at high temperatures remains to be considered. Drapkin [74] has observed that the compressibility of many metals at the melting point is about 20 to 30% higher than at 0 K. The third law of thermodynamics precludes a linear temperature dependence for the compressibility to be used when approaching 0 K. A linear extrapolation to 0 K would give a value lower than the real one, but the difference may not be too high. The value obtained with the present set of parameters is about 22% lower than the value at the melting point. This value seems to agree with the trend observed by Drapkin [74].

**Table V.** The Temperature Derivative of the Isothermal Compressibility of bcc Mo at 298.15 K and Zero Pressure According to Various Sources and the Present Evaluation

| Source of information | $(\partial K/\partial T)$ $(10^{-16}\,\mathrm{m^2 \cdot N^{-1} \cdot K^{-1}})$ | Observations |
|---|---|---|
| Bridgman [29] | 2.12 | Evaluated in this work from data presented by Bridgman [29] |
| This work | 1.18 | Calculated in this work using a relation presented by Drapkin [74] |
| | 1.71 | Calculated in this work using a relation presented by Rodionov [75] |
| | 1.46 | Calculated in this work using a relation presented by Schramm [76] |
| | 1.73 | Calculated using the present parameters |

**Table VI.** The Molar Volume of Liquid Mo at the Normal Melting Point According to Various Sources and the Present Evaluation

| Source of information | Molar volume ($10^{-6}$ m$^3$·mol$^{-1}$) | Observations |
|---|---|---|
| Kostikov et al. [58] | 10.54 | Measured value, Ref. 58 |
| Allen [77] | 10.26 | Estimated value, Ref. 77 |
| This work | 10.50 | Calculated in this work using Kubaschewski's [78] relation |
| | 10.16 | Calculated in this work from Fateeva and Vereshchagin's [22] equation |
| | 10.473 | Evaluated in this work from experimental data |

The calculated molar volume of liquid Mo at 0.2 GPa is compared in Fig. 11 with the experimental data considered in this work. The agreement is satisfactory. In Table VI the calculated molar volume of liquid Mo at the normal melting point is compared with the values according to various authors. The present value is lower than the one presented by Kostikov et

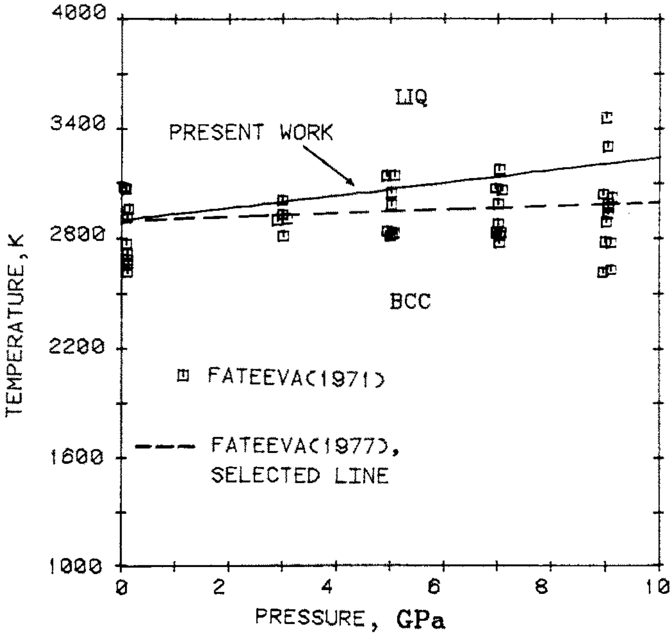

**Fig. 12.** The bcc/liquid phase boundary calculated in the present work and experimental data by Fateeva and Vereshchagin [21, 22].

al., higher than a value estimated by Allen [77], and in reasonable agreement with an estimate according to the empirical relation between the entropy of melting and the change in molar volume proposed by Kubaschewski [78]. A value calculated from Vereshchagin and Fateeva's equation for the pressure dependence of the melting point is also included in Table IV. It is lower than the present value. As a consequence, the liquidus line calculated in the present work lies above the one suggested by Fateeva and Vereshchagin. However, as can be seen in Fig. 12, the present line falls well within the experimental scatter band.

## 5. CONCLUSIONS

The results presented in the present report show that the models used in this work are capable of describing the information available on pure Mo within the experimental accuracy. However, the empirical nature of these models and the simplifications introduced in describing the temperature and pressure dependencies of the derivatives of $G_m(T, P)$ limit the possibilities of making reliable extrapolations outside the range studied experimentally. For instance, the present assessment gives a rapid increase with temperature of the thermal expansivity of liquid Mo because of the use of Eq. (9), and this results in a drastic decrease with pressure of its heat capacity in view of the following Maxwell relation:

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V_m}{\partial T^2}\right)_P \tag{15}$$

Reasonable extrapolations of the phase boundaries and the thermodynamic properties of the condensed phases may be obtained from the present work only up to 4000 K and 20 GPa. For the gaseous phase, these limits are 6000 K and 0.1 MPa. Extrapolations to higher pressures and temperatures are dangerous. Such extrapolations can be safe only if models with a sounder physical basis are used. The application of Eq. (3) to $C_P$ of bcc Mo prevents it from becoming stable at high temperatures but may not give realistic values.

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calculations were performed using the computer programs PARROT and POLY, respectively, both developed by Bo Jansson at the Division of Physical Metallurgy [62, 63, 79].

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