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Critical parameters and equation of state for heavy liquid metals

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Abstract

Heavy liquid metals (HLM), such as mercury (Hg), lead (Pb), bismuth (Bi) and lead–bismuth eutectic (Pb–Bi), have been studying in several countries as potential materials for spallation neutron sources. However, experimental data on their thermal properties in the temperature range of interest are rare. In this case, an equation of state (EOS) developed on the basis of the fundamental thermodynamics and limited experimental data can play a very important role. Different approaches to construction of EOS are considered in the present work: the generalized van der Waals equation, the Redlich–Kwong equation and the concept of internal pressure of liquids. The results of calculation of the critical temperature, the critical pressure and the critical density of Hg, Pb, Bi and Pb–Bi obtained with these models and available experimental data on thermal properties of these HLM at lower temperatures and normal pressure are presented and discussed. An EOS is proposed which allows to estimate densities of liquid and vapour phases of HLM at high temperatures and pressures.

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1. Introduction

Spallation neutron sources (SNS) are considered as an important tool in many fields of research and for development of new techniques using neutrons. Heavy liquid metals (HLM), such as mercury (Hg), lead (Pb), bismuth (Bi) and lead–bismuth eutectic (Pb–Bi), have being studied in several countries as potential materials for spallation neutron sources driven by proton or electron accelerator because of a high neutron yield per incident high energy particle. The most illustrative example is the Spallation Neutron Source facility that has just started its operation in Oak Ridge (USA) [1]. In few ADS projects HLM are used for both spallation target and core coolant [2]. The detailed knowledge of HLM thermodynamic properties is a necessary step for design of a spallation source and its behaviour modelling under representative conditions. However, experimental data on HLM properties in the temperature range of interest are rare. Therefore the prediction of these properties with the help of an adequate equation of state (EOS) developed on the basis of the fundamental thermodynamics and limited experimental data can be an alternative way. Once EOS is known for a fluid, one can

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determine its various thermodynamic (TD) properties at equilibrium at different conditions, such as the density, heat capacity, thermal expansion, etc. Different types of EOS were used for modelling of the liquid metals: the equations of the van der Waals (VDW) family (such as the Redlich–Kwong (RK) equation [3] and its later modifications by Soave [4], Martynyuk [5], Fischer [6], and by others), and the liquid phase EOS based on the concept of the internal pressure (CIP) proposed by Srinivasan and Ganesan [7]. A variant of EOS was proposed and applied to the considered HLM: Hg, Pb, Bi, and Pb–Bi.

2. Equations of state

Considerable progress has been achieved in the development of empirical, semi-empirical and mechanistic EOS for fluids during the last years. Two types of EOS are usually used: caloric and thermal. The first expresses a thermodynamic (TD) potential through TD variables, such as pressure (p), molar volume (V) and temperature (T). For fluid, the potential of Helmholtz (G) or enthalpy (H) are often used as the potential depending on temperature and pressure: $G = G(p,T)$, $H = H(p,T)$. The second type EOS binds the TD variables between themselves: $f(p,V,T) = 0$. These EOS determine the main parameters of a fluid and can be expressed one through another:

$$V(P,T) = \left(\frac{\partial G(P,T)}{\partial p}\right)_T \quad \text{or}$$

$$G = G(p_0,T) + \int_{p_0}^{p} V(p,T)\mathrm{d}p.$$

The most known EOS of the second type was developed by van der Waals in 1873. For one mole it can be presented as follows:

$$p = \frac{RT}{V-b} - \frac{a}{V^2}, \tag{1}$$

where $R = 8.314\ \mathrm{J\ mol^{-1}}$ is the universal gas constant and parameters a and b are related with the critical molar volume (V_c), temperature (T_c) and pressure (p_c) of the considered fluid:

$$a = 3P_c \cdot V_c^2 \quad b = V_c/3. \tag{2}$$

The VDW EOS is a two-parametric equation with the fixed reduced critical compressibility:

$$\chi_c \equiv \frac{p_c \cdot V_c}{RT_c} = \frac{p_c \cdot M}{RT_c \cdot \rho_c} \quad \chi_{c(\mathrm{VDW})} = 0.375, \tag{3}$$

where M is molecular mass and ρ_c – density in the critical point. The main drawback of the VDW EOS is that it can be applied only to fluids with $\chi_{c(\mathrm{VDW})} = 0.375$. Moreover, its simplified description of the attractive and repulsive terms does not work well at the molecular packing fractions higher than 0.1. Since, many modifications were proposed to take into account the molecular repulsive and attractive forces in a more precise manner. Many studies were devoted the virial EOS in which the attractive term is present as a power series over V^{-n}. However, in the design and industrial applications, different semi-empirical equations of the VDW-family are widely used with success.

In 1949, Redlich and Kwong [3] proposed to introduce the explicit dependence on temperature in the attractive term of Eq. (1):

$$p = \frac{RT}{V-b} - \frac{a}{V \cdot (V+b) \cdot T^{0.5}}. \tag{4}$$

Trying to improve the prognosis capacity of this two-parameter Redlich–Kwong (RK) equation for mixtures, Soave [4] proposed to replace the coefficient $a/T^{0.5}$ with a more general temperature dependence $a(T)$ and presented the EOS in the following dimensionless form:

$$\chi^3 - \chi^2 + (A - B - B^2) \cdot \chi - A \cdot B = 0, \tag{5}$$

where $\chi \equiv \frac{p \cdot V}{RT}$ is the dimensionless compressibility and the coefficients A and B depend on temperature, pressure and related with the coefficients a and b of the RK EOS (4):

$$A \equiv \frac{a \cdot p}{R^2 T^2}, \quad B \equiv \frac{b \cdot p}{RT}. \tag{6}$$

A modification by introducing a variable power n for V in the attractive term was proposed by Martynyuk [5], in order to calculate with a better precision the critical parameters of the metallic substances:

$$p = \frac{RT}{V-b} - \frac{a}{V^n}. \tag{7}$$

The last equation provides a possibility to consider fluids with different values of the critical compressibility, which is a function of n:

$$\chi_c = \frac{n^2 - 1}{4n}. \tag{8}$$

A more complicated four-parameter EOS, based on the statistical mechanics perturbation theory, was developed by Ihm et al. [8] and applied to Hg by Mehdipour and Boushehri [9].

Morita and Fischer [10] extended the modification of RK EOS [6] to a reacting system where vapour can consist of dimer and monomer components. A dimer molar fraction (x_d) was introduced in the repulsive term:

$$p = \frac{RT}{(V-b)\cdot(1+x_d)} - \frac{a(T)}{V\cdot(V+b)}. \qquad (9)$$

A simple EOS for liquid phase, based on the CIP concept of liquids, and assuming that data on density (ρ), isobaric and isochoric heat capacities (C_p *and* C_v) and sound velocity (v_s) are known, was proposed by Srinivasan and Ganesan [7]:

$$\frac{p+p_i}{T} = v_s\cdot\alpha_p\cdot\rho\cdot\frac{C_p}{C_v}, \qquad (10)$$

where p_i is the internal pressure. The right side of Eq. (10) has been described with the linear empirical function:

$$\frac{p+p_i}{T} = C - D\cdot T. \qquad (11)$$

3. Critical parameters

The critical temperature, critical pressure and critical density (or molar volume) are the most important parameters of EOS, which allows estimating the thermophysical properties of the given substance. Among HLM, they were measured rather well only for Hg. Some results are also available for Pb and Bi. Only theoretical estimations were found in the open literature for the critical parameters of Pb–Bi.

3.1. Mercury

The critical temperature and pressure of Hg were first experimentally determined by Birch [10] in 1952. He found $T_{c(Hg)} = 1733 \pm 50$ K, $p_{c(Hg)} = 160.8 \pm 5$ MPa and $\rho_{c(Hg)} = 5.00$ g cm^{-3}. Grosse [12] calculated the Hg critical density of 4.70 g cm^{-3} with the law of rectilinear diameter [13], using the earlier experimental data on the Hg density (liquid and vapour at high pressures and temperatures) and $T_{c(Hg)}$ measured by Birch [11].

In 1983, Martynyuk communicated the measured critical constants of Hg as follows [14]: $T_{c(Hg)} = 1756 \pm 10$ K, $p_{c(Hg)} = 159.3 \pm 5.0$ MPa and $\rho_{c(Hg)} = 5.27 \pm 0.70$ g cm^{-3}. The same publication also presented the calculated values: $T_{c(Hg)} = 1762$ K, $p_{c(Hg)} = 157.8$ MPa and $\rho_{c(Hg)} = 5.00$ g cm^{-3}, which were obtained by using the extrapolated temperature dependence of the saturated vapour pressure and the heat of sublimation/evaporation. Later he calculated the critical parameters of Hg using the generalized VDW EOS proposed by himself earlier [5] and obtained $T_{c(Hg)} = 1720$ K, $p_{c(Hg)} = 127.6$ MPa and $\rho_{c(Hg)} = 4.730$ g cm^{-3} [15]. Precision of the calculated values was estimated to be ±50% for p_c, ±15% for T_c and ±20% for ρ_c.

Measurement performed by Hensel [16] in the critical point region gave $T_{c(Hg)} = 1751$ K, $p_{c(Hg)} = 167.3$ MPa and $\rho_{c(Hg)} = 5.80$ g cm^{-3}.

In the present article, the Hg critical temperature was also calculated with the semi-empirical method of Watson [17] proposed for non-polar polar liquids and with the correlation of Kopp [18].

The Watson's semi-correlations bind the ratio of the specified equilibrium temperature (T_e) to the critical temperature with the liquid molar volume (V') at the boiling temperature (T_b):

$$\frac{T_e}{T_c} = 0.283\cdot(V'(T_b))^{0.18}. \qquad (12)$$

With a correlation to calculate (T_e) deduced from the Clapeyron-Clausius equation [17]:

$$\ln T_e = \frac{9.8T_e}{T_b} - 4.2. \qquad (13)$$

Using $T_{b(Hg)} = 629.9$ K, $\rho'_{(Hg)}(T_b) = 12.737$ g cm^{-3} from [12], one can obtain $T_{c(Hg)} = 1485$ K, which is about 15% lower than the measure value.

The Kopp's relationship [18] is based on the general hypothesis about correlation between the critical temperature and the enthalpy of vaporization (ΔH):

$$\begin{aligned} T_c\ (\mathrm{K}) &= 0.112\Delta H\ (\mathrm{cal\ mol^{-1}}) \\ &= 0.02675\Delta H\ (\mathrm{J\ mol^{-1}}). \end{aligned} \qquad (14)$$

Using $\Delta H_{(Hg)} = 59.1$ J mol^{-1} from [19] one can obtain $T_{c(Hg)} = 1581$ K. This is about 9% smaller than the experimental values. All data for Hg presented above are listed in Table 1.

3.2. Lead

In 1990, Pottlacher and Jäger [20] published a summary of experimentally determined and theoretically estimated parameters for the critical point of

Table 1
Summary of the critical point parameters for Hg (experimental data are in bold)

Reference	T_c	p_c (MPa)	ρ_c (kg m^{-3})	χ_c	Eq.
Birch [11]	**1733**	**160.8**	5000	0.448	–
Grosse [12]	(1733)	–	4700	–	–
Martynyuk [14]	**1756**	**159.3**	**5270**	0.415	–
	1762	157.8	5000	0.432	–
Martynyuk [15]	1720	127.6	4730	0.378	–
Hensel [16]	**1751**	**167.3**	5800	0.397	–
Watson's method	1485	–	–	–	(12), (13)
Kopp's correlation	1581	–	–	–	(14)

Pb available in the literature by this time. They considered sixteen sets of data as well as their own estimations based on the experimental results obtained with the pulse-heating technique. Their summary shows that the experimental and theoretical data on the critical temperature of Pb lie within the range of 3584–6000 K, while their own estimation on a basis of experimental investigations at elevated static pressure of Pb obtained by a pulse-heating method yields $T_{c(Pb)} = 5400 \pm 400$ K.

Martynyuk [15] estimated the critical parameters of Pb by determining parameters of the generalized VDW equation and using the experimental data on the Pb liquid phase density and heat of vaporization in the temperature range from the melting point to the normal boiling point. $T_{c(Pb)} = 4766$ K, $p_{c(Pb)} = 90$ MPa, $\rho_{c(Pb)} = 2259$ kg m^{-3} were obtained for the critical point of Pb. The calculated results were compared with the data obtained using the pulsed-heating experiments and a relationship between the critical temperature and the heat of sublimation [14]. A rather poor agreement between the theoretical and experimental values on the critical pressure and density was explained by low accuracy in the experiment.

Grosse [12] estimated the Pb critical temperature $T_{c(Pb)} = 5400$ K using the principle of corresponding states (Hg was used as reference) and entropy of the vaporization at the boiling point.

Recently, Azad [21] estimated the critical temperatures of Pb, Bi and Pb–Bi with the above-described CIP model. The estimation for Pb indicates a quite low value of the critical temperature ($T_{c(Pb)} = 3369$–3391 K) in comparison with most of other theoretical and experimental estimations. This can be explained by errors of extrapolation of the used experimental data on the sound velocity and heat capacity of Pb to high temperatures.

The Watson's method yields $T_{c(Pb)} = 4967$ K, if the liquid phase density of Pb at the boiling point is calculated with the correlation recommended in [22]. Then the law of rectilinear diameter [13] allows to obtain the Pb critical density of $\rho_{c(Pb)} = 2463$ kg m^{-3}. With $\chi_{c(Pb)} = 0.21$ from [15] one can obtain $p_{c(Pb)} = 103$ MPa. The Kopp's Eq. (11) yields $T_{c(Pb)} = 4756$ K if the molar enthalpy vaporization at normal boiling temperature is taken from [23].

A summary of data on the critical point of Pb extracted from the cited above literature is presented in Table 2 (the data reviewed by Pottlacher and Jäger [20] are not included – only their recommendation is reproduced in Table 2). One can see that Watson method and Kopp's correlation give T_c values rather close to the experimental results.

3.3. Bismuth

Only a few sets of the critical point data are available for bismuth. Grosse [12] calculated the Bi critical temperature ($T_{c(Bi)} = 4620$ K) by application of the principle of corresponding states to the entropy of vaporization at the normal boiling point taken from [24].

Cahill et al. [25] compared this value with one estimated by the method of rectilinear diameter

Table 2
Summary of the critical point parameters for Pb (experimental data are in bold)

Reference	T_c	p_c (MPa)	ρ_c (kg m^{-3})	χ_c	Eq.
Grosse [12]	5400	–	–	–	–
Martynyuk [14]	**4460**	**160**	**2950**	0.30	–
Pottlacher and Jäger [20]	**5400**	**250**	**3200**	0.36	–
Martynyuk [15]	4776	90	2259	0.21	–
Azad [21]	3369–3391	–	–	–	–
Watson's method and the law of rectilinear diameter (p_c obtained with $\chi_c = 0.21$)	4967	(103)	2463	(0.21)	(12), (13)
Kopp's correlation	4756	–	–	–	(14)

Table 3
Summary of the calculated parameters for the critical point of Bi (the experimental data are in bold)

Source	T_c	p_c (MPa)	ρ_c (kg/m^3)	χ_c	Eq.
Grosse [12]	4620	–	–	–	–
Cahill et al. [25]	5000	–	–	–	–
Fortov et al. [26]	4200	126	2660	0.28	–
Martynyuk [14]	**3780**	**132**	**3010**	0.29	–
Azad [21]	2042–2106	–	–	–	–
Morita [35]	4720	77	2040	0.20	–
Watson's method and the law of rectilinear diameter (p_c obtained with $\chi_c = 0.29$)	4420	(139)	2720	(0.29)	(12), (13)
Kopp's correlation	4842	–	–	–	(14)

($T_{c(Bi)} \sim 5000$ K), which assumes that the average density of the liquid and the saturated vapour changes linearly with temperature.

Fortov et al. [26] calculated the theoretical values of the critical temperature ($T_{c(Bi)} = 4200$ K), pressure ($p_{c(Bi)} = 126$ MPa) and density ($\rho_{c(Bi)} = 2660$ kg m^{-3}) of Bi, based on the traditional approaches such as used by Grosse [12] and on the method of rectilinear diameter.

Martynyuk [14] estimated the parameters of the critical point of Bi based on the results of pulsed-heating experiments and a relationship between the critical temperature and the heat of sublimation and obtained $T_{c(Bi)} = 3780$ K, $p_{c(Bi)} = 132$ MPa and $\rho_{c(Bi)} = 3010$ kg m^{-3}.

The method proposed by Martynyuk [15] was also used in [27]. The constants of the generalized VDW Eq. (7) were expressed through the melting and boiling temperatures, the molar enthalpies of vaporization, and the liquid molar volume at the melting and boiling points. The liquid Bi density was taken from Cahill and Kirshenbaum [28] and the heat of vaporization was calculated with the Clapeyron-Clausius equation using the vapour pressure curve based on the data from Hultgren et al. [29]. The resultant critical parameters of Bi are $T_{c(Bi)} = 4720$ K, $\rho_{c(Bi)} = 2040$ kg/m^3 and $p_{c(Bi)} = 77$ MPa.

The estimation of the critical parameters using the Watson's method with the liquid Bi density from [23] and the law of rectilinear diameter yields: $T_{c(Bi)} = 4354$ K and $\rho_{c(Bi)} = 2705$ kg m^{-3}. Similar estimate performed with the density taken from [28] yields $T_{c(Bi)} = 4420$ K and $\rho_{c(Bi)} = 2720$ kg m^{-3}. (Using these values with $\chi_{c(Bi)} = 0.29$ from [15] one can obtain $p_{c(Bi)} = 139$ MPa).

The Kopp's correlation (14) yields $T_{c(Bi)} = 4842$ K if the molar enthalpy vaporization at normal boiling temperature is taken from [23].

The critical temperature of Bi estimated by Azad [21] with CIP method ($T_{c(Bi)} = 2042$–2106 K) is lower than values recommended by other authors.

A summary of the critical point parameters for Bi, available in the literature, is presented in Table 3. There is still a very large uncertainty in the available data for the critical point of Bi even if the values given by Azad would be discarded.

3.4. Lead–bismuth eutectic

Only two sets of the critical parameters for Pb–Bi were found: one was estimated by Morita et al. [27] and another by Azad [21]. Both were estimated theoretically on the basis of some known or estimated properties of Pb–Bi. No publications were found with the results of measurement of the Pb–Bi critical parameters.

The method proposed by Martynyuk [15] was used in [27]. The liquid Pb–Bi density was taken from Alchagirov et al. [30] and the heat of vaporization was estimated with the Clapeyron-Clausius equation using the estimated vapour pressure curve. The obtained critical parameters of Pb–Bi are $T_{c(Pb–Bi)} = 4890$ K, $\rho_{c(Pb–Bi)} = 2170$ kg m^{-3} and $p_{c(Pb–Bi)} = 87.8$ MPa.

Azad [21] estimated the Pb–Bi critical temperatures using CIP method described above. The gas phase was modelled with the perfect gas equation. In order to determine the constants, the Pb–Bi melt density was taken from the measurements of Alchagirov et al. [30], the Pb–Bi heat capacity and the sound velocity were found with the Vegard's law using the literature data on heat capacities [31] and sound velocities [32,33] of the molten Pb and Bi. The obtained values for the Pb–Bi critical temperature and pressure are $T_{c(Pb–Bi)} = 2411$ K and $p_{c(Pb–Bi)} = 244$ MPa. The critical temperature

Table 4
Summary of the calculated parameters for the critical point of Pb–Bi eutectic

Reference	T_c	p_c (MPa)	ρ_c (kg/m^3)	χ_c	Eq.
Morita et al. [27]	4890	87.8	2170	0.21	–
Azad [21]	2411	244	–	–	–
Kopp's correlation	4880	–	–	–	(14)
Watson's method	4720	–	–	–	(12), (13)
	4750	–	–	–	

obtained by Azad [21] is more than by factor 2 lower and the critical pressure is 3 times higher than those calculated by Morita et al. [27] with the generalized VDW equation of Martynyuk [15].

The Kopp's correlation (14) yields $T_{c(\text{Pb–Bi})} = 4880$ K using the value of the evaporation enthalpy at the normal boiling temperature of Pb–Bi from [27]. The Watson method [17] with the liquid density at the normal boiling temperature from [30] gives $T_{c(\text{Pb–Bi})} = 4750$ K and with that from [23] $T_{c(\text{Pb–Bi})} = 4720$ K.

A summary of the critical parameters of Pb–Bi is given in Table 4. A very large uncertainty exists. More data and estimates are needed to reduce it.

4. Equation of state for HLM

Considering the problems of safety analysis of the accelerator driven systems cooled by liquid Pb–Bi, Morita et al. [27] proposed to apply the modified RK (MRK) Eq. (6) extended to a liquid metal with vapour consisting of dimer and monomer components. The functional form of Eq. (6) can be rewritten using specific volume υ as follows:

$$p = \frac{RT}{M \cdot (1 + x_d) \cdot (\upsilon - b)} - \frac{a(T)}{\upsilon(\upsilon + c)}, \tag{15}$$

where b and c are the model parameters.

The temperature dependent constant $a(T)$ is presented as a power function of temperature:

$$a(T) = a_c \cdot \left(\frac{T}{T_c}\right)^n \quad \text{at } T \leqslant T_c$$
$$\text{and} \quad a(T) = a_c + \left.\frac{da}{dT}\right|_{T_c} (T - T_c) \quad \text{at } T > T_c. \tag{16}$$

From the definition, x_d is related to the equilibrium constant K_e:

$$K_e = \frac{p_2}{(p_1)^2} = \frac{x_d}{(1 - x_d)^2 \cdot p}. \tag{17}$$

The total pressure p is a sum of the monomer pressure p_1 and the dimer pressure p_2:

$$p = p_1 + p_2. \tag{18}$$

The equilibrium constant K_e can be determined if the partial pressures of vapour as a function of temperature are known. The parameters a_c and n can be found by fitted to the saturated vapour pressure curve in the region of the critical temperature. Parameters b and c can be found from the estimated values of the critical point parameters based on the fact that the critical isotherm on a p–υ diagram has an inflection point at $\upsilon = \upsilon_c$.

Eqs. (15)–(18) have been applied to Pb–Bi and Bi, taking into account that in both the monatomic and diatomic molecules of Bi are present in vapours (there is no experimental evidence on the presence diatomic Pb molecules in Pb–Bi vapour).

The equilibrium constants K_e for both Bi and Pb–Bi was evaluated using the 'best estimate' values of vapours pressures tabulated by Hultgren et al. [29,34]. The results available in the temperature range 600–2000 K were fitted to the following equations:

$$K_{e(\text{Bi})} = \exp\left(-24.264 + \frac{24344}{T}\right), \tag{19}$$

$$K_{e(\text{Pb})} = \exp\left(-24.611 + \frac{23511}{T}\right). \tag{20}$$

For Bi and Pb–Bi, the critical parameters given in [35,27] were used, respectively. The calculated coef-

Table 5
Constants of MRK EOS for Hg, Pb, Bi and Pb–Bi

	Pb–Bi	Bi	Pb	Hg
a_c	159.328	141.178	203.243	14.3774
b	6.26824×10^{-5}	6.76609×10^{-5}	3.39179×10^{-5}	7.49883×10^{-5}
c	8.11866×10^{-4}	7.71091×10^{-4}	7.50986×10^{-4}	-3.14362×10^{-5}
n	0.378359	0.712600	0.0489557	−0.0284127
x_d	$\neq 0$	$\neq 0$	0.0	(0.0)?

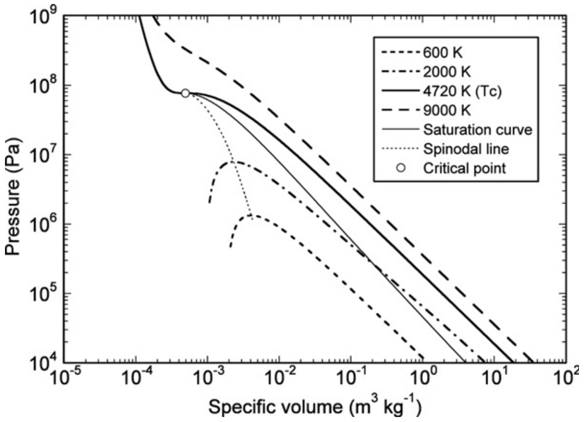

Fig. 1. Bi vapor isotherm shapes on a *p*–*υ* diagram calculated by the MRK equation.

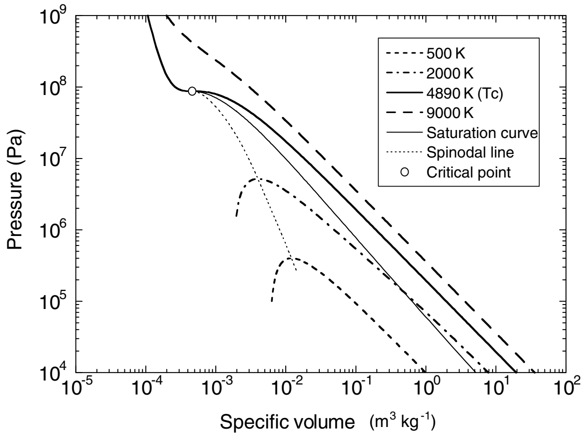

Fig. 2. Pb–Bi eutectic vapor isotherm shapes on a *p*–*υ* diagram calculated by the MRK equation.

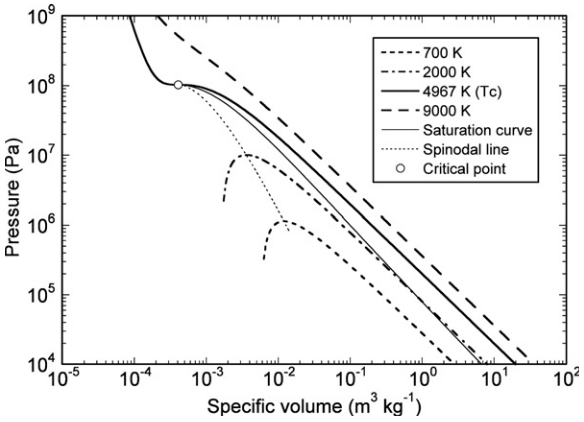

Fig. 3. Pb vapor isotherm shapes on a *p*–*υ* diagram calculated by the MRK equation.

ficients of EOS (15) are presented in Table 5. Figs. 1 and 2 show the calculated vapor isotherms of Bi and Pb–Bi respectively on a *p*–*υ* diagram. The spinodal line and the saturation curve are also presented in the figures.

The similar approach was applied for Pb and Hg but in these cases it was assumed that $x_d = 0$. The coefficients presented in Table 5 were calculated with $T_{c(Pb)} = 4967$ K, $p_{c(Pb)} = 103$ MPa, $\rho_{c(Pb)} = 2463$ kg m^{-3} and $T_{c(Hg)} = 1762$ K, $p_{c(Hg)} = 158$ MPa, $\rho_{c(Hg)} = 5270$ kg m^{-3}. The calculated Pb vapor isotherms are presented in Fig. 3.

5. Conclusions

The critical parameters of HLM of interest (Hg, Pb, Bi and Pb–Bi) given in the literature were analyzed and compared aiming to develop more reliable recommendation. It was shown that semi-empirical Watson method and Kopp's correlation can give good approximation for the critical temperature, and the rectilinear diameter law for the critical density of HLM in many cases.

The modified four-parametric Redlich–Kwong EOS can in principle be applied for Hg, Pb, Bi and Pb–Bi. However, supplementary experimental data are needed to fit better the constants.

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