

Thermodynamic properties and equation of state of liquid lead and lead–bismuth eutectic

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Abstract

Since the 1950s, liquid lead (Pb) and lead–bismuth eutectic (Pb–Bi) have been studied in the USA, Canada and in the former-USSR as potential coolants for nuclear installations due to their very attractive thermophysical and neutronic properties. However, experimental data on the thermal properties of these coolants in the temperature range of interest are still incomplete and often contradictory. This makes it very difficult to perform design calculations and to analyse the normal and abnormal behaviour of nuclear installations where these coolants are expected to be used. Recently, a compilation of heavy liquid metal (HLM) properties along with recommendations for its use was prepared by the OECD/NEA Working Party on Fuel Cycle (WPFC) Expert Group on Lead–Bismuth Eutectic Technology. A brief review of this compilation and some new data are presented in this article. A set of correlations for the temperature dependence of the main thermodynamic properties of Pb and Pb–Bi(e) at normal pressure, and a set of simplified thermal and caloric equations of state for the liquid phase are proposed.

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1. Introduction

Since the mid 1950s, interest in and active studies of heavy liquid metals (HLM) – Pb–Bi(e), Pb, and Hg, – have been growing, due to the potential for their use as coolants in a new generation of fast spectrum nuclear (subcritical and critical) reactors [1,2]. Detailed knowledge of HLM thermodynamic properties is needed for reactor design and modelling under representative normal and abnormal conditions.

The main properties of HLM have been measured primarily at normal atmospheric pressure and at relatively low temperatures in many laboratories. A rather complete review of the main thermophysical properties of Pb and Pb–Bi(e) and a comparison with those of sodium and sodium–potassium eutectic was performed by Imbeni

et al. [3,4]. The available information on the thermophysical properties of Pb–Bi(e), Pb and Bi was recently collected by the OECD/NEA WPFC Expert Group on Lead–Bismuth Eutectic Technology in the “Handbook on Lead–Bismuth Eutectic Alloy and Lead Properties, Materials Compatibility, Thermal Hydraulics and Technologies” (Version 0 was issued in May 2007) [5]. Some results of this Handbook on thermophysical properties of molten Pb and Pb–Bi(e) were also presented at the Spring 2006 Meeting of the European Materials Research Society EMRS-2006 and published in the Proceedings [6].

To address the missing thermodynamic properties at high temperatures and pressures, work is underway to develop a relevant equation of state (EOS) based on the available experimental data and proven physical models. This article gives a brief review of the compilation results on the main thermodynamic properties of the molten Pb and Pb–Bi(e) (i.e. density, thermal expansion, heat capacity, compressibility, surface tension and saturated vapour pressure) and presents a simplified EOS.

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2. Temperature range

The temperature range for normal operation of an HLM-cooled system is determined by the coolant melting and boiling temperatures. The melting temperatures of chemically pure Pb and Pb–Bi(e) (>99.99%), have been measured with a high precision at normal atmospheric pressure. However, for these reactor grade metals (~99.5%), the uncertainty on the determination of the melting point can be a few tenths of kelvin [5]. The melting temperature increases when pressure increases (e.g., for Pb, the rate of this increase is $7.92 \times 10^{-8} \text{ K Pa}^{-1}$ in the pressure range of 15–200 MPa [7]). The boiling temperatures of these HLM coolants have been measured with a lower precision than the melting temperatures. The uncertainty in the boiling temperature ranges from 10 to 20 K for Pb and Pb–Bi(e). The most probable values of the normal melting ($T_{M,0}$) and boiling ($T_{B,0}$) temperatures of Pb and Pb–Bi(e), together with their latent enthalpies of melting and boiling as recommended in [5], are presented in Table 1. The difference between melting and boiling temperatures of these liquid metals is also shown.

The boiling temperature T_B increases when pressure increases. The equilibrium boiling line (p_s, T_s) = 0 can be found using the available experimental data on the saturated vapour pressure as a function of temperature. For Pb and Pb–Bi(e) these measurements were performed mainly at temperatures below the normal boiling point. The available experimental data and recommendations analysed in [5] are presented in Fig. 1.

At low pressures, metal vapour behaves as a perfect gas and the evaporation enthalpy (ΔH_E) is about constant. Therefore the temperature dependence of the saturated vapour pressure should be exponential (as deduced from Clapeyron–Clausius equation of vapour–liquid equilibrium [8]):

$$p_s(T) = p_\infty \cdot \exp(-\Delta H_E/RT), \quad (1)$$

where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal gas constant. The “best fit” of the coefficients of correlation (1) to the available data [5] yields $p_{\infty(\text{Pb})} = 6.189 \times 10^9 \text{ Pa}$, $\Delta H_{E(\text{Pb})} = 184.7 \text{ kJ mol}^{-1}$ for Pb and $p_{\infty(\text{Pb-Bi})} = 11.1 \times 10^9 \text{ Pa}$, $\Delta H_{E(\text{Pb-Bi})} = 187.5 \text{ kJ mol}^{-1}$ for Pb–Bi(e). For Pb, the uncertainty of this correlation is about 12%. For Pb–Bi(e), the uncertainty of 12% is observed at temperatures higher than 900 K, however, it becomes more than 50% when the temperature decreases to 700 K. At lower temperatures the saturated vapour pressure is too low to be measured correctly. The obtained values of ΔH_E are in satisfactory agreement with the measured ΔH_B recom-

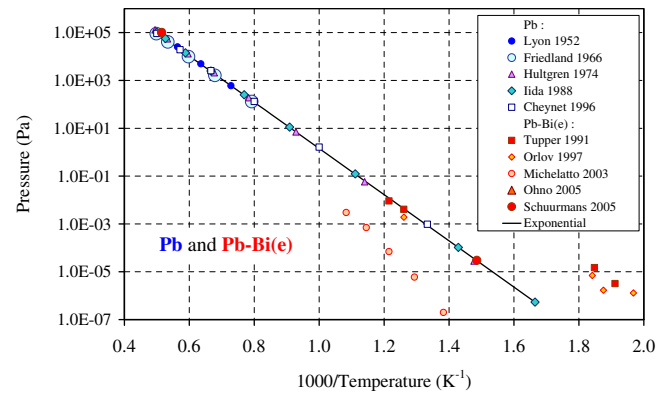


Fig. 1. Saturated vapour pressure of Pb and Pb–Bi(e) (references from [6]).

mended in [5] (Table 1). An extension of correlation (1) to higher temperatures and pressures is limited by the fact that the evaporation enthalpy decreases and the density of the vapour phase becomes non-negligible. Application of (1) to the region close to the critical point leads to underestimation of the saturated vapour pressure. More sophisticated correlations, taking into account the above mentioned effects, should be used in this region.

Under accidental conditions, the coolant temperature can locally increase up to fuel melting temperatures (>3000 K) and the local coolant pressure can increase up to the cladding failure limit (>20 MPa). Therefore, coolant properties must be known within larger range of temperature and pressure. For development of the EOSs of HLM coolants, needed for the correct extension of the properties recommendations to higher temperatures and pressures, the critical parameters (temperature, pressure and density) should be known. A very large uncertainty still exists in the critical temperatures, pressures and densities of the HLMs of interest. Many results were obtained for Pb but with a large dispersion. Only theoretical estimations were found in the open literature for the critical parameters of Pb–Bi(e). The mean values of the measured and calculated critical parameters as collected in [9] are presented in Table 2.

Table 2
Critical parameters of Pb and Pb–Bi(e)

		T_c (K)	p_c (MPa)	ρ_c (kg m ⁻³)
Pb	Measured	4900 ± 500	200 ± 50	3100 ± 300
	Calculated	4800 ± 700	120 ± 40	2500 ± 500
Pb–Bi(e)	Measured	No	No	No
	Calculated	2410–4890	88–244	~2200

Table 1
Characteristic temperatures and temperature ranges of liquid Pb and Pb–Bi(e) [5]

	$T_{M,0}$ (K)	$\Delta H_{M,0}$ (kJ mol ⁻¹)	$T_{B,0}$ (K)	$\Delta H_{B,0}$ (kJ mol ⁻¹)	$T_{B,0} - T_{M,0}$ (K)
Pb	600.6 ± 0.1	4.9 ± 0.2	2016 ± 10	177.8 ± 0.4	1415
Pb–Bi(e)	397.7 ± 0.6	8.1 ± 0.1	1943 ± 20	178.0 ± 0.4	1545

3. Properties and recommendations

Almost all of the main thermodynamic properties of the HLM (such as density, thermal expansion, heat capacity, enthalpy, surface tension and sound velocity) are measured with a satisfactory precision in the region close to the melting temperature. The recommended values of the above mentioned parameters, calculated for the considered HLM coolants at the normal melting temperatures using the correlations given hereafter, are presented in Table 3.

At normal atmospheric pressure, density was measured better than other properties. For Pb the experimental data are available from the normal melting point up to the normal boiling point. For Pb–Bi(e), the recommendations are given up to 1273 K (Fig. 2) [6].

With an uncertainty of 0.7–0.8%, the temperature dependence of the Pb and Pb–Bi(e) density $\rho(T, p_0)$ can be described by the following linear correlation:

$$\begin{aligned} \rho(T, p_0) &= \rho_{M,0} - A_{\rho,0}(T - T_{M,0}) \\ &= \rho_{M,0} + \frac{\partial \rho(T, p_0)}{\partial T} (T - T_{M,0}), \end{aligned} \quad (2)$$

where $\rho_{M,0}$ is given in Table 3 and $A_{\rho,0} = 1.2795 \text{ kg m}^{-3} \text{ K}^{-1}$ for Pb and $1.293 \text{ kg m}^{-3} \text{ K}^{-1}$ for Pb–Bi(e) (both are obtained using data presented in [5]). The isobaric volumetric thermal expansion coefficient (α_p) is evaluated by its definition:

$$\alpha_p(T, p) \equiv -\frac{1}{\rho(T, p)} \left(\frac{\partial \rho(T, p)}{\partial T} \right)_p = \frac{A_\rho(p)}{\rho(T, p)}. \quad (3)$$

The compressibility of the liquid Pb and Pb–Bi(e) have not yet been measured directly. However, it can be expressed through the velocity of propagation of sound waves which was measured at the normal atmospheric pressure, mainly close to the melting temperature. Only two measurements of the sound velocity in liquid Pb–Bi(e) were found in open literature [10,11], which give results from $T_{M,0}$ up to 680 K. In a limited temperature range close to melting (from $T_{M,0}$ to $T_{M,0} + 400$ K), the sound velocity (u_{sound}) decreases with temperature in a fashion that is almost linear [12]:

$$u_{\text{sound}}(T, p_0) = u_{\text{sound}}(T_{M,0}, p_0) - A_{u,0}(T - T_{M,0}). \quad (4)$$

Values of $u_{\text{sound}}(T_{M,0}, p_0)$ are given in Table 3. For the temperature coefficient, the following values were deduced from Ref. [5]: $A_{u,0} = 0.23 \text{ m s}^{-1} \text{ K}^{-1}$ for Pb and $0.24 \text{ m s}^{-1} \text{ K}^{-1}$ for Pb–Bi(e).

At high temperatures, the sound velocity can deviate from a linear temperature dependence [13] (Fig. 3). The following parabolic correlation can be obtained using data

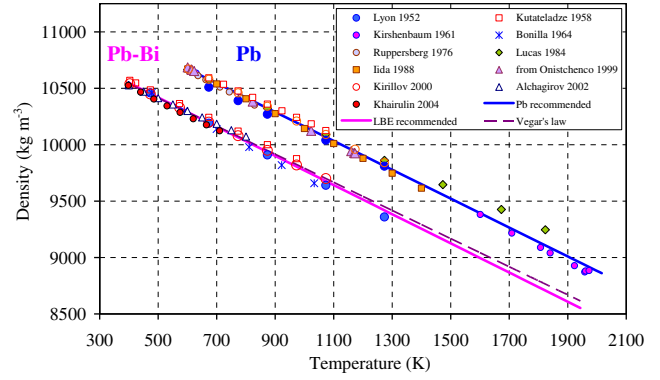


Fig. 2. Density of liquid Pb and Pb–Bi(e) at $p \approx p_{\text{atm}}$ (references from [6]).

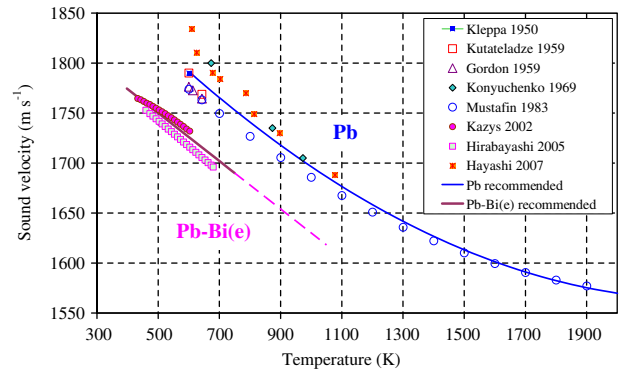


Fig. 3. Temperature dependence of the sound velocity in the molten Pb and Pb–Bi(e) at $p \approx p_{\text{atm}}$ (references from [6,11,12]).

presented in [5,12,13] for the sound velocity of liquid Pb in the temperature range from $T_{M,0}$ to $T_{B,0}$:

$$\begin{aligned} u_{\text{sound}}(\text{Pb})(T, p_0) &= 1791 - 0.27 \cdot (T - T_{M,0}) \\ &\quad + 7.95 \times 10^{-5} \cdot (T - T_{M,0})^2. \end{aligned} \quad (5)$$

The available results on heat capacity of liquid Pb and Pb–Bi(e), reproduced from the review presented in [6], show little consistency and are sometimes even contradictory (Fig. 4).

The theoretical calculation of the Pb isobaric heat capacity (C_p) indicates that it should decrease with temperature after melting and after passing, through a large plateau start increasing with temperature [14]. Usually, an empirical correlation is used that is deduced from the ‘standard’ thermodynamic polynomial applied for enthalpy [15]:

$$C_p(T, p_0) = \left(\frac{\partial H}{\partial T} \right)_{p_0} = a + b \cdot T + c \cdot T^2 + d \cdot T^{-2}. \quad (6)$$

Table 3

Recommended values of the main thermodynamic parameters of liquid Pb and Pb–Bi(e) at the normal atmospheric pressure and melting temperatures

	M_a (g mol ⁻¹)	$T_{M,0}$ (K)	ρ (kg m ⁻³)	α_p (10 ⁻⁵ K ⁻¹)	u_{sound} (m s ⁻¹)	C_p (J mol ⁻¹ K ⁻¹)	p_s (Pa)
Pb	207.20	600.6	10673	12.0	1791	30.7	5.3×10^{-7}
Pb–Bi(e)	208.18	397.7	10551	12.3	1774	30.8	2.6×10^{-15}

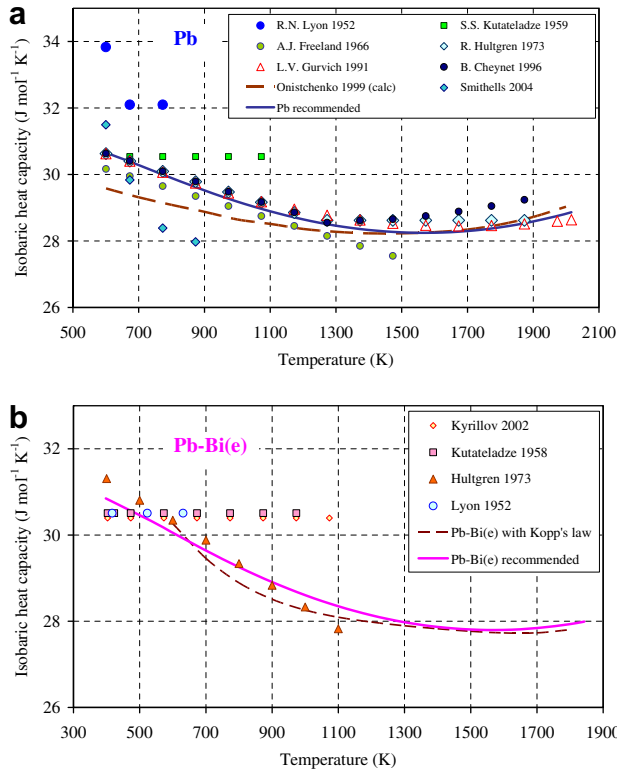


Fig. 4. Isobaric molar heat capacity of Pb (a) and Pb–Bi(e) (b) at $p \approx p_{\text{atm}}$ (references from [6]).

Table 4
Recommended coefficients of correlation (6) for heat capacity

	a ($\text{J K}^{-1} \text{mol}^{-1}$)	b ($\text{J K}^{-2} \text{mol}^{-1}$)	c ($\text{J K}^{-3} \text{mol}^{-1}$)	d ($\text{J K}^2 \text{mol}^{-1}$)
Pb	36.50	-1.020×10^{-2}	3.2×10^{-6}	-3.158×10^5
Pb– Bi(e)	34.30	-8.20×10^{-3}	2.6×10^{-6}	-9.5×10^4

The recommended values for the coefficients of correlation (6) for the isobaric molar heat capacity (obtained on the basis of data presented in [5]) are given in Table 4. The uncertainty is about 5–7% up to $T = 1200\text{--}1400$ K and increases at higher temperatures where no experimental data were found in open literature.

4. Equation of state

The correlations presented above for the main thermodynamic properties of liquid Pb and Pb–Bi(e) at normal atmospheric pressure, allow to construct thermal and caloric EOS. From here, predictions of thermodynamic properties at higher pressures can be made.

A simple thermal EOS is frequently used to bind the main thermodynamic variables: pressure, temperature and density: $F(p, T, \rho) = 0$. Such an EOS can be constructed using the known temperature and pressure dependence of the density:

$$\begin{aligned} \rho(T, p) &= f(T, p) \approx \int_{T_0}^T \left(\frac{\partial \rho}{\partial T} \right)_p dT + \int_{p_0}^p \left(\frac{\partial \rho}{\partial p} \right)_T dp \\ &= \rho(T, p_0) + \int_{p_0}^p \left(\frac{\partial \rho}{\partial p} \right)_T dp. \end{aligned} \quad (7)$$

The first term on the right hand side of expression (7) is calculated with correlation (2). The partial derivative of the density with respect to the pressure at constant temperature can be expressed through other thermodynamic parameters using known thermodynamic relationships [8]:

$$\left(\frac{\partial \rho(T, p)}{\partial p} \right)_T = \left(\frac{1}{u_{\text{sound}}^2(T, p)} + \frac{M \cdot T \cdot \alpha_p^2(T, p)}{C_p(T, p)} \right), \quad (8)$$

where M is molecular mass.

The results of the calculation of the density derivative with respect of the pressure are presented in Fig. 5. They show that the variation of the density as a function of pressure does not exceed 0.1% per 1 MPa in the region of the normal operation of nuclear installations.

In the general case, the caloric EOS of a liquid thermodynamic system can be presented by considering enthalpy as a function of temperature and pressure:

$$\begin{aligned} H(T, p) &= H(T_M, p_0) + \int_{T_M}^T C_p(T, p_0) dT \\ &+ \int_{p_0}^p \left(\frac{\partial H(T, p)}{\partial p} \right)_T dp, \end{aligned} \quad (9)$$

where $H(T_M, p_0)$ is the tabulated value of enthalpy at the normal conditions, $C_p(T, p_0)$ is the isobaric heat capacity calculated with correlation (6). The partial derivative of the enthalpy with respect to the pressure at constant temperature is expressed through the density (7) and molar mass M .

$$\left(\frac{\partial H}{\partial p} \right)_T = \frac{M}{\rho(T, p)}. \quad (10)$$

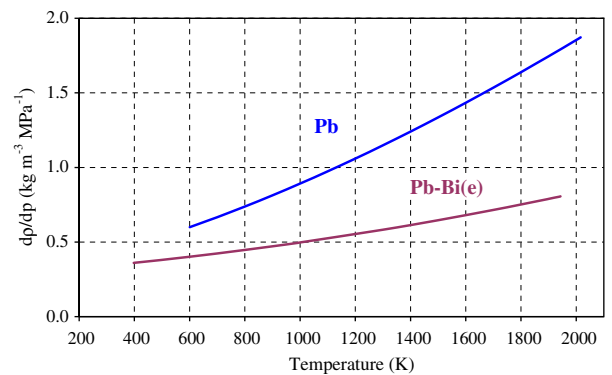


Fig. 5. Pressure correction factor for the density of Pb and Pb–Bi(e) ($p \approx p_{\text{atm}}$).

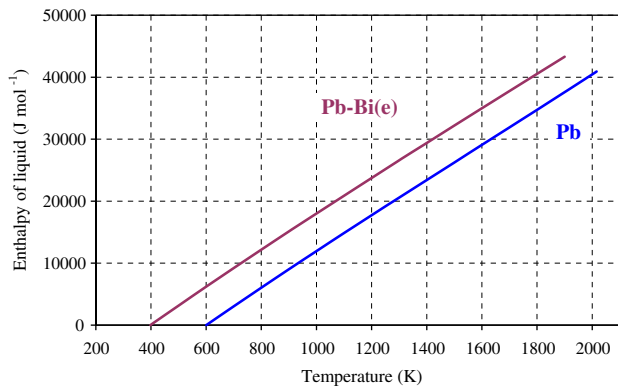


Fig. 6. Pb and Pb–Bi(e) molar enthalpy as a function of temperature ($p \approx p_{\text{atm}}$).

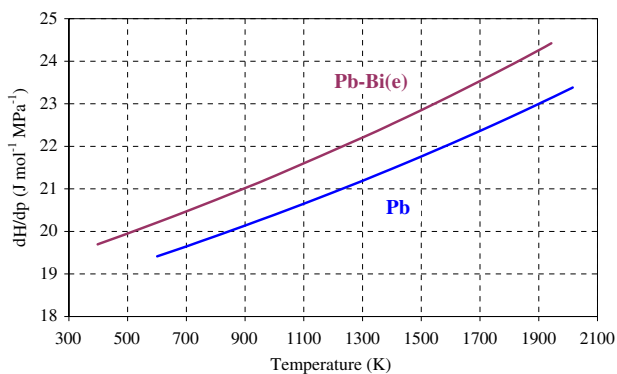


Fig. 7. Pressure correction factor for the enthalpy of Pb and Pb–Bi(e) ($p \approx p_{\text{atm}}$).

The Pb and Pb–Bi(e) molar enthalpy as a function of temperature in the region from $T_{M,0}$ to $T_{B,0}$ is presented in Fig. 6. The derivative of the enthalpy with respect to the pressure as a function of temperature at the normal pressure is presented in Fig. 7.

From Figs. 6 and 7 one can see that the pressure correction of the enthalpy is important only at temperatures close to the melting point.

The estimation performed above is only valid for the liquid phase (i.e., in the temperature range from T_M to T_B) and under the condition that the thermodynamic coefficients do not depend on the pressure. More sophisticated EOSs should be used at high pressures and temperatures close to the critical point and for the two phase region [9].

5. Conclusions

For liquid Pb and Pb–Bi(e), the experimental data are available for most of the thermodynamic parameters of interest in the temperature region that encompasses the

normal operation of nuclear installations, albeit only at atmospheric pressure. A set of correlations was proposed to describe the density, thermal expansion, sound velocity, heat capacity and saturated vapour pressure of liquid Pb and Pb–Bi(e) as a function of temperature. A simplified EOS was deduced for prediction of Pb and Pb–Bi(e) thermodynamic properties at higher pressures. However, a large uncertainty in the critical parameters of Pb and Pb–Bi(e) given in the literature restrains its application to pressures which are significantly below the critical pressure.

Coordinated international and national R&D programs (*experimental and theoretical*) are needed to complete the available database on thermal properties of Pb and Pb–Bi(e).

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