STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ÉTUDE DE L'ÉNERGIE NUCLÉAIRE

Thermodynamic Properties and Equation of State of HLM

(brief review)

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1. Introduction

1. Since middle 1990's, interest to and intensive studies of HLM (**Pb-Bi** eutectic, **Bi**, **Pb**, and **Hg**) are growing, due to perspective of their application in intensive spallation neutron sources and in fast reactors of the new generation (subcritical and critical):
   a) SNS with **Hg** target of 1 MW and 1.3 GeV LINAC in USA (started in 2006).
   b) MEGAPIE experience with **Pb-Bi** target of 1 MW (2006)
   c) MYRRHA XT-ADS (**Pb-Bi**) design at SCK·CEN in Belgium together with EU partners. EDT ADS conceptual design in EU (**Pb**). ADS studies in Japan, Korea, USA (**Pb, Pb-Bi**).
   d) **Pb-Bi** and **Pb**-cooled critical fast reactor projects in GIF, Euratom FP6 (ELSY) and in Russia (BREST, SVBR).

1. Introduction

2. Main properties of the **HLM** were measured at relatively low temperatures in many laboratories and information is recently collected by WPFC Expert Group on LBE Technology in the OECD Handbook on HLMC Properties (Version 0 will be issued in 2007; Ed. C. Fazio).

3. For prognosis of the missing thermodynamic properties at high temperatures and pressures (required for safety studies of nuclear installations with HLM), a work is under way to develop a relevant equation of state (**EOS**) based on available experimental data and proved physical models.

2. Properties of interest

Heavy metals for spallation targets should preferably have the following properties:

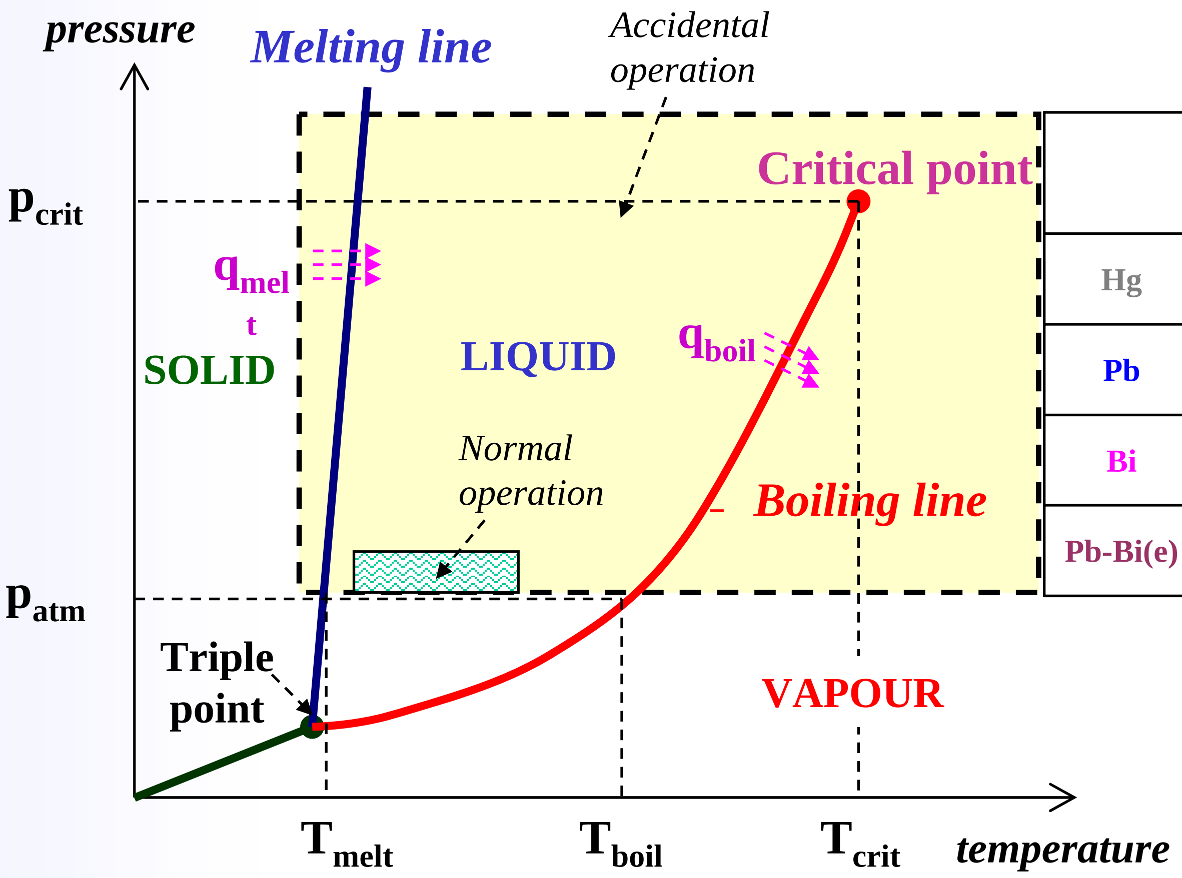
- high neutron yield per proton in unit volume
- radiation stability → *long operation time and safety*
- low chemical activity → *long operation time and safety*
- low melting temperature → *easy operation conditions*
- high boiling temperature → *large temperature range*
- low saturated vapour pressure → *low evaporation*
- large heat capacity → *good heat removal*
- small viscosity → *lower power for circulation*
- large thermal expansion → *natural convection*

2. Properties of interest:

Comparison ($T = T_{m\ 0}$)

Parameter	Hg	Pb	Bi	Pb-Bi (e)
M_a (g mol^{-1})	200.59	207.20	208.98	208.18
T_{melt} (K)	234.2	600.6	544.1	397.7
Q_{melt} (kJ mol^{-1})	2.3	4.9	11.0	8.01
T_{boil} (K)	629.7	2016	1806	1943
Q_{boil} (kJ mol^{-1})	59.1	177.8	181.0	178.0
ρ (kg m^{-3})	13691	10673	10062	10570
α_{vol} (10^{-5} K^{-1})	17.7	22.7	24.1	23.0
C_p (J mol^{-1} K^{-1})	28.3	30.6	30.5	31.1
σ (10^{-3} N m^{-1})	498.1	451.1	382.0	410.8
η (10^{-4} Pa s)	21.0	27.0	18.7	32.9
p_s (Pa)	$3.4 \cdot 10^{-4}$	$5.7 \cdot 10^{-7}$	$1.4 \cdot 10^{-8}$	$3 \cdot 10^{-15}$

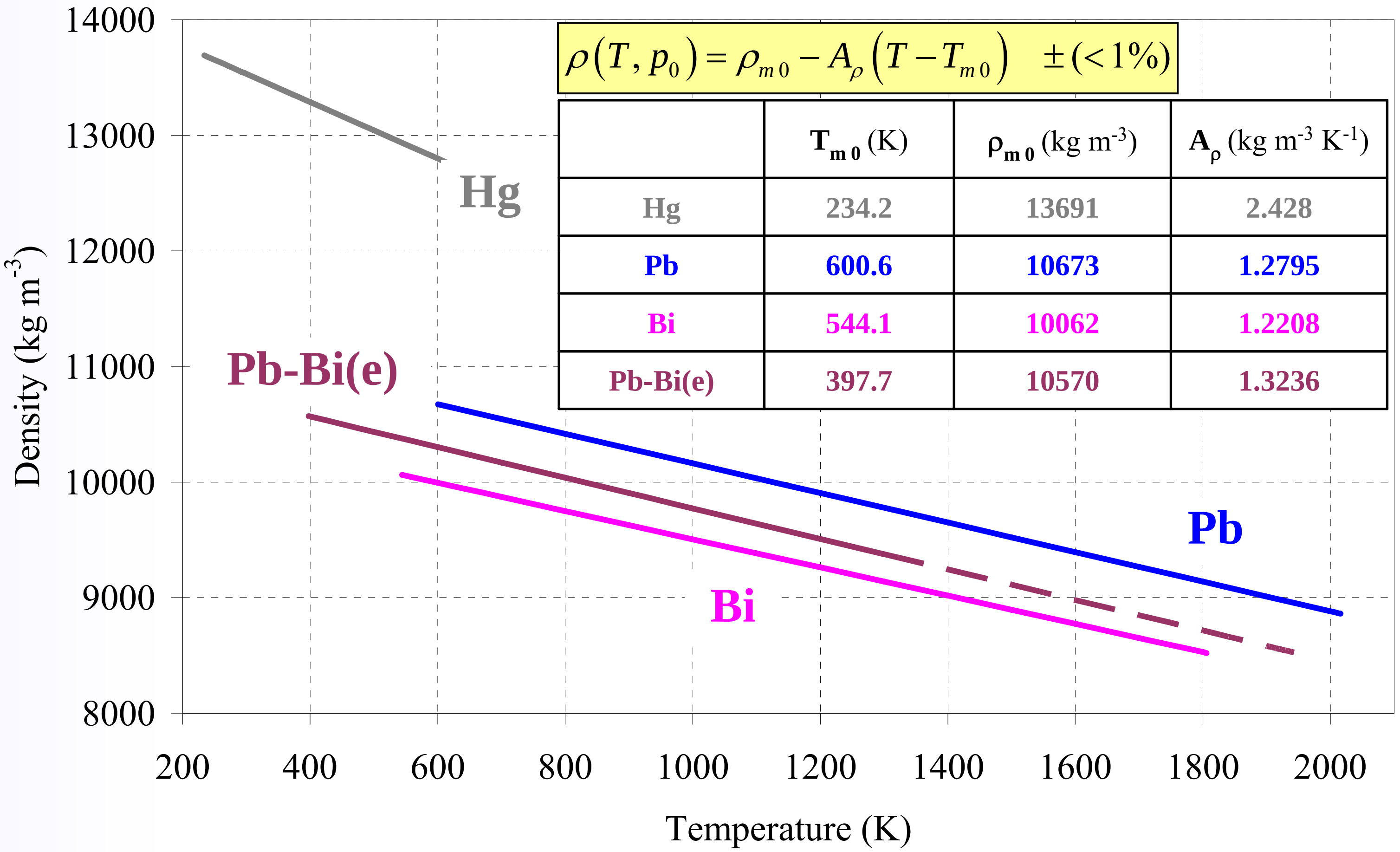
3. Temperature range



	T_{M0} (K)	$T_{B0} - T_{M0}$ (K)	$T_c - T_{M0}$ (K)
Hg	234.2	396	> 1480
Pb	**600.6**	**1415**	**> 2770**
Bi	**544.1**	**1264**	**> 1550**
Pb-Bi(e)	**97.7**	**1845**	**> 2300**

4. Available recommendations:

Density

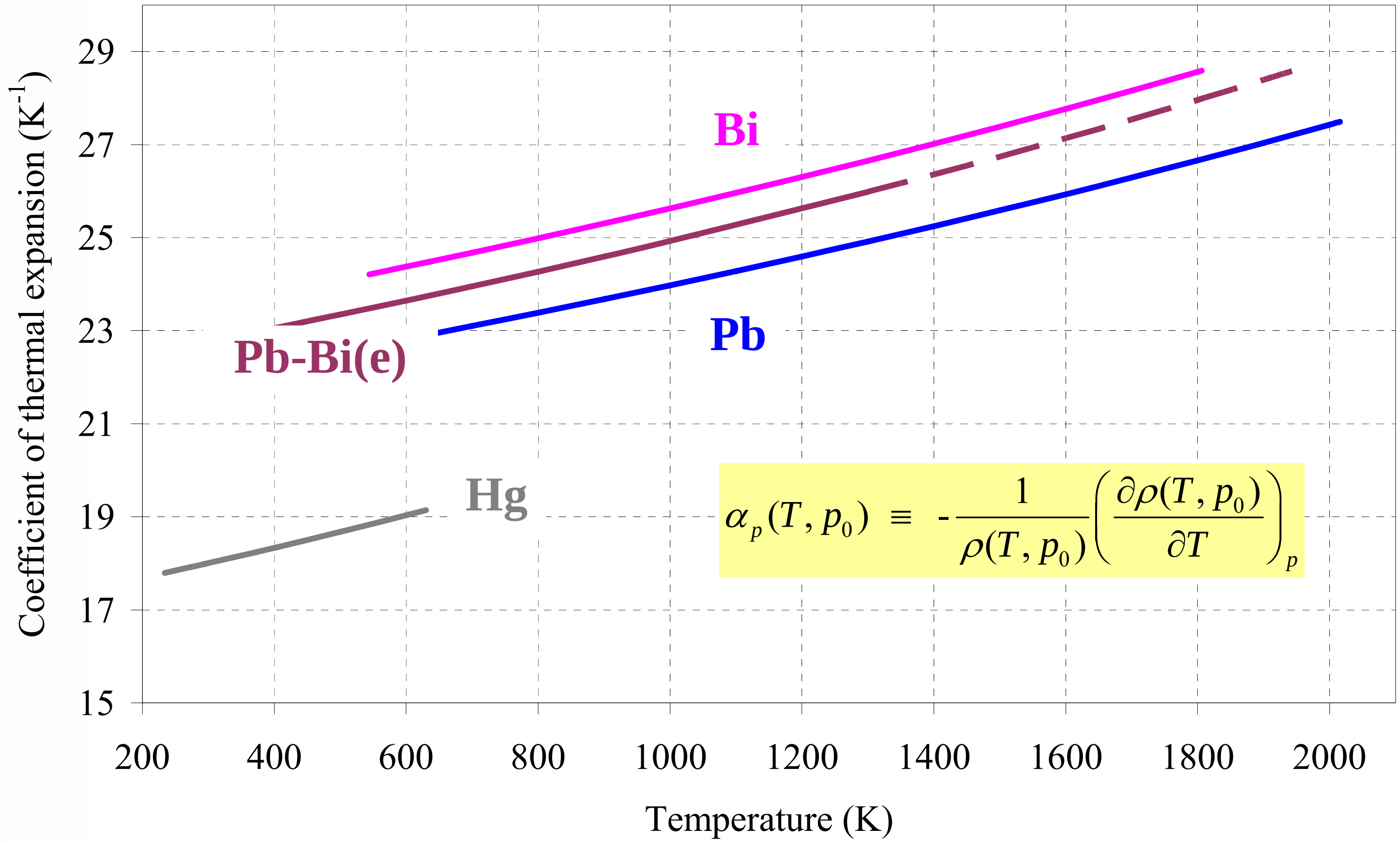


$$\rho(T,p_0)=\rho_{m0}-A_\rho\left(T-T_{m0}\right)\quad\pm(<1\%)$$

	T_{m0} (K)	**ρ_{m0} (kg m^{-3})**	**A_ρ (kg m^{-3} K^{-1})**
Hg	**234.2**	**13691**	**2.428**
Pb	**600.6**	**10673**	**1.2795**
Bi	**544.1**	**10062**	**1.2208**
Pb-Bi(e)	**397.7**	**10570**	**1.3236**

4. Available recommendations:

Volumetric thermal expansion

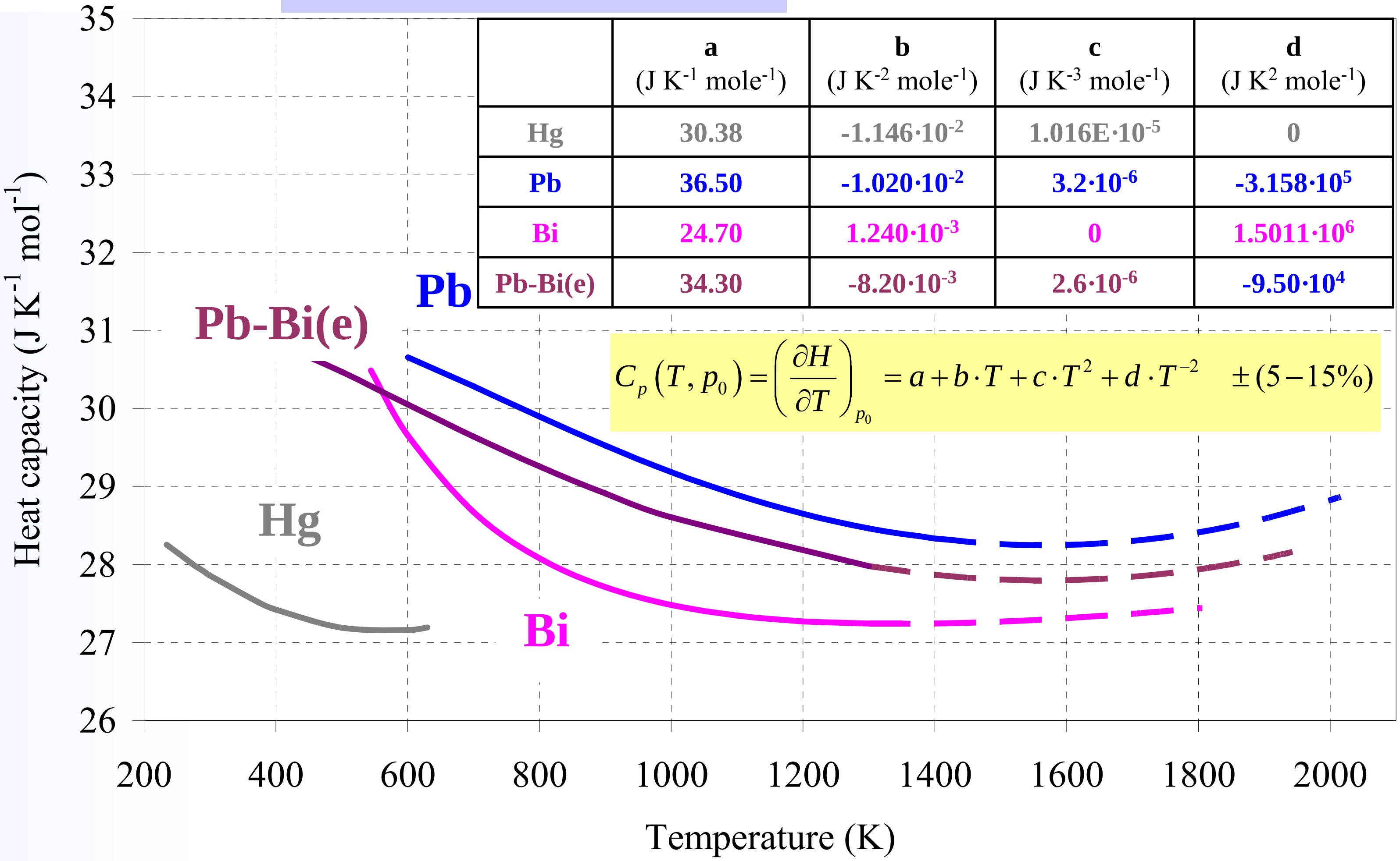


$$\alpha_p(T,p_0) \equiv -\frac{1}{\rho(T,p_0)}\left(\frac{\partial \rho(T,p_0)}{\partial T}\right)_p$$

Fifth International Workshop on the Utilisation and Reliability of High Power Proton Accelerators, HPPA-5
Topic: Spallation target development and coolant technology. Mol, Belgium, May 6-9, 2007

4. Available recommendations:

Isobaric heat capacity

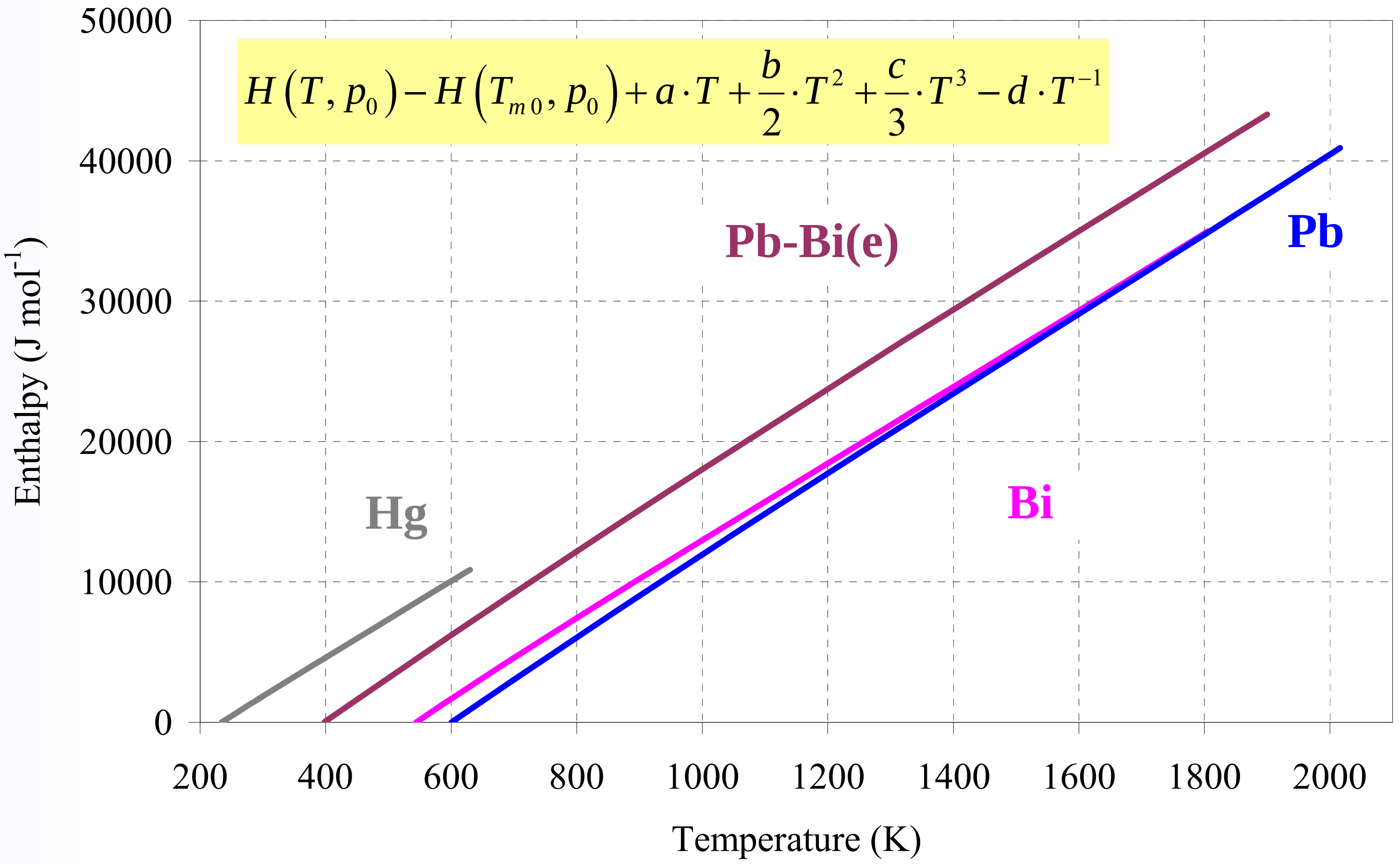


	a (J K^{-1} mole^{-1})	**b** (J K^{-2} mole^{-1})	**c** (J K^{-3} mole^{-1})	**d** (J K^{2} mole^{-1})
Hg	**30.38**	**$-1.146\cdot10^{-2}$**	**$1.016\text{E}\cdot10^{-5}$**	**0**
Pb	**36.50**	**$-1.020\cdot10^{-2}$**	**$3.2\cdot10^{-6}$**	**$-3.158\cdot10^{5}$**
Bi	**24.70**	**$1.240\cdot10^{-3}$**	**0**	**$1.5011\cdot10^{6}$**
Pb-Bi(e)	**34.30**	**$-8.20\cdot10^{-3}$**	**$2.6\cdot10^{-6}$**	**$-9.50\cdot10^{4}$**

$$C_p(T,p_0) = \left(\frac{\partial H}{\partial T}\right)_{p_0} = a + b\cdot T + c\cdot T^2 + d\cdot T^{-2} \qquad \pm(5-15\%)$$

4. Available recommendations:

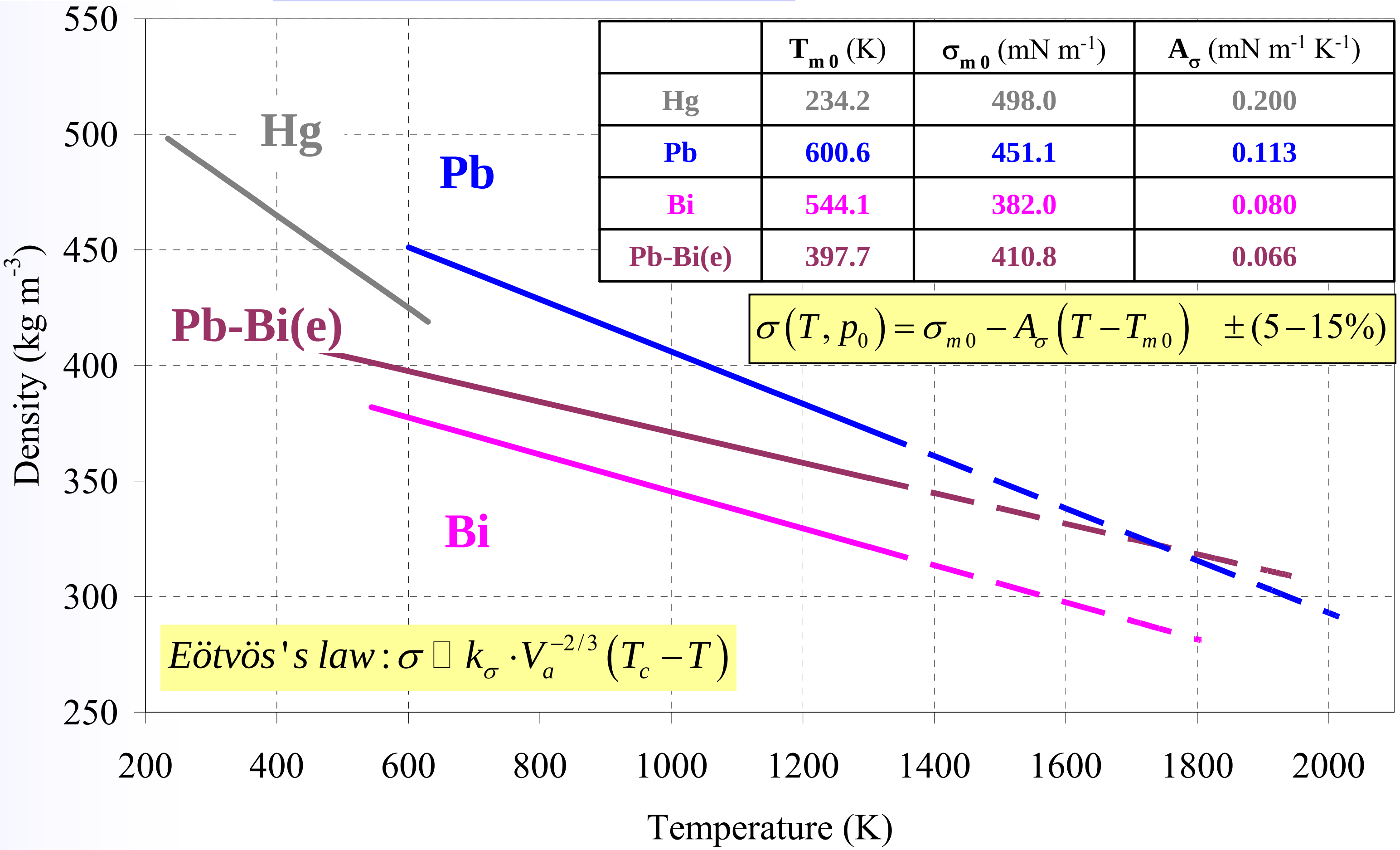
Enthalpy increase



$$H\left(T,p_0\right)-H\left(T_{m0},p_0\right)+a\cdot T+\frac{b}{2}\cdot T^2+\frac{c}{3}\cdot T^3-d\cdot T^{-1}$$

4. Available recommendations:

Surface tension



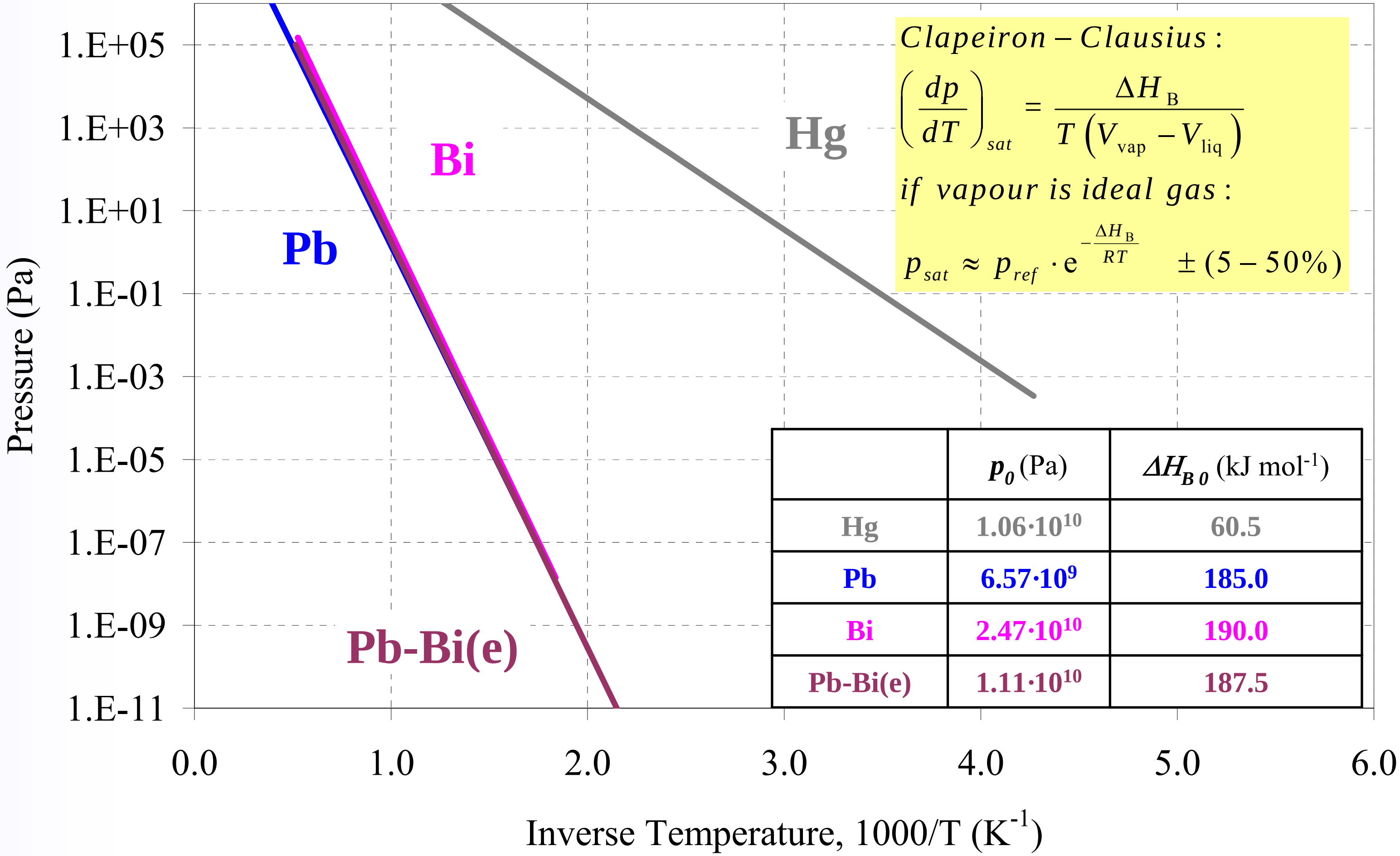
	T_{m0} (K)	σ_{m0} (mN m^{-1})	A_σ (mN m^{-1} K^{-1})
Hg	234.2	498.0	0.200
Pb	**600.6**	**451.1**	**0.113**
Bi	**544.1**	**382.0**	**0.080**
Pb-Bi(e)	**397.7**	**410.8**	**0.066**

$$\sigma(T, p_0) = \sigma_{m0} - A_\sigma (T - T_{m0}) \quad \pm (5 - 15\%)$$

$$Eötvös's\ law: \sigma \approx k_\sigma \cdot V_a^{-2/3} (T_c - T)$$

4. Available recommendations:

Saturated vapour pressure



Clapeiron – Clausius :

$$\left(\frac{dp}{dT}\right)_{sat} = \frac{\Delta H_B}{T\left(V_{vap} - V_{liq}\right)}$$

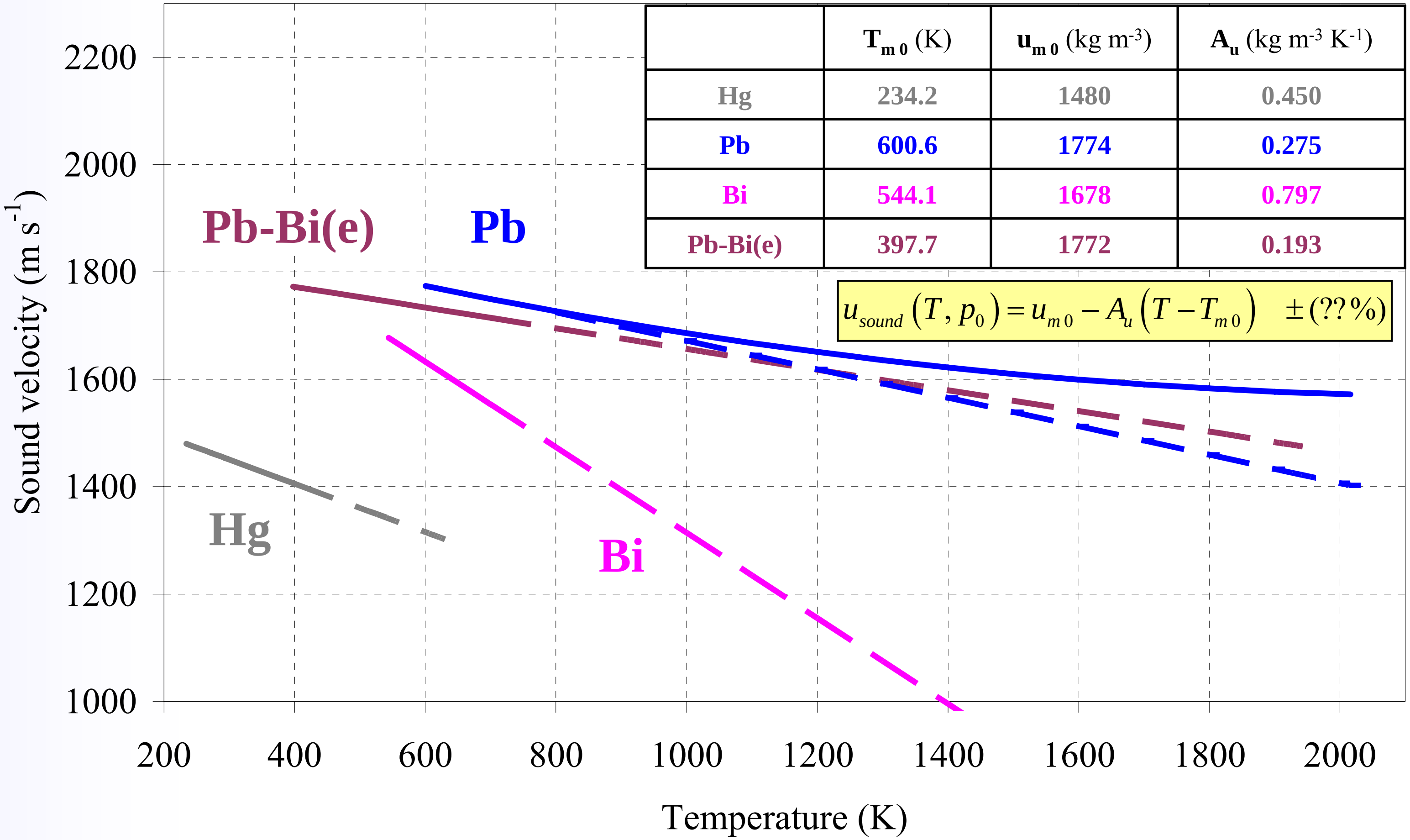
if vapour is ideal gas :

$$p_{sat} \approx p_{ref} \cdot e^{-\frac{\Delta H_B}{RT}} \pm (5 - 50\%)$$

	p_0 (Pa)	$\Delta H_{B\,0}$ (kJ mol^{-1})
Hg	**$1.06 \cdot 10^{10}$**	**60.5**
Pb	**$6.57 \cdot 10^{9}$**	**185.0**
Bi	**$2.47 \cdot 10^{10}$**	**190.0**
Pb-Bi(e)	**$1.11 \cdot 10^{10}$**	**187.5**

4. Available recommendations:

Sound velocity

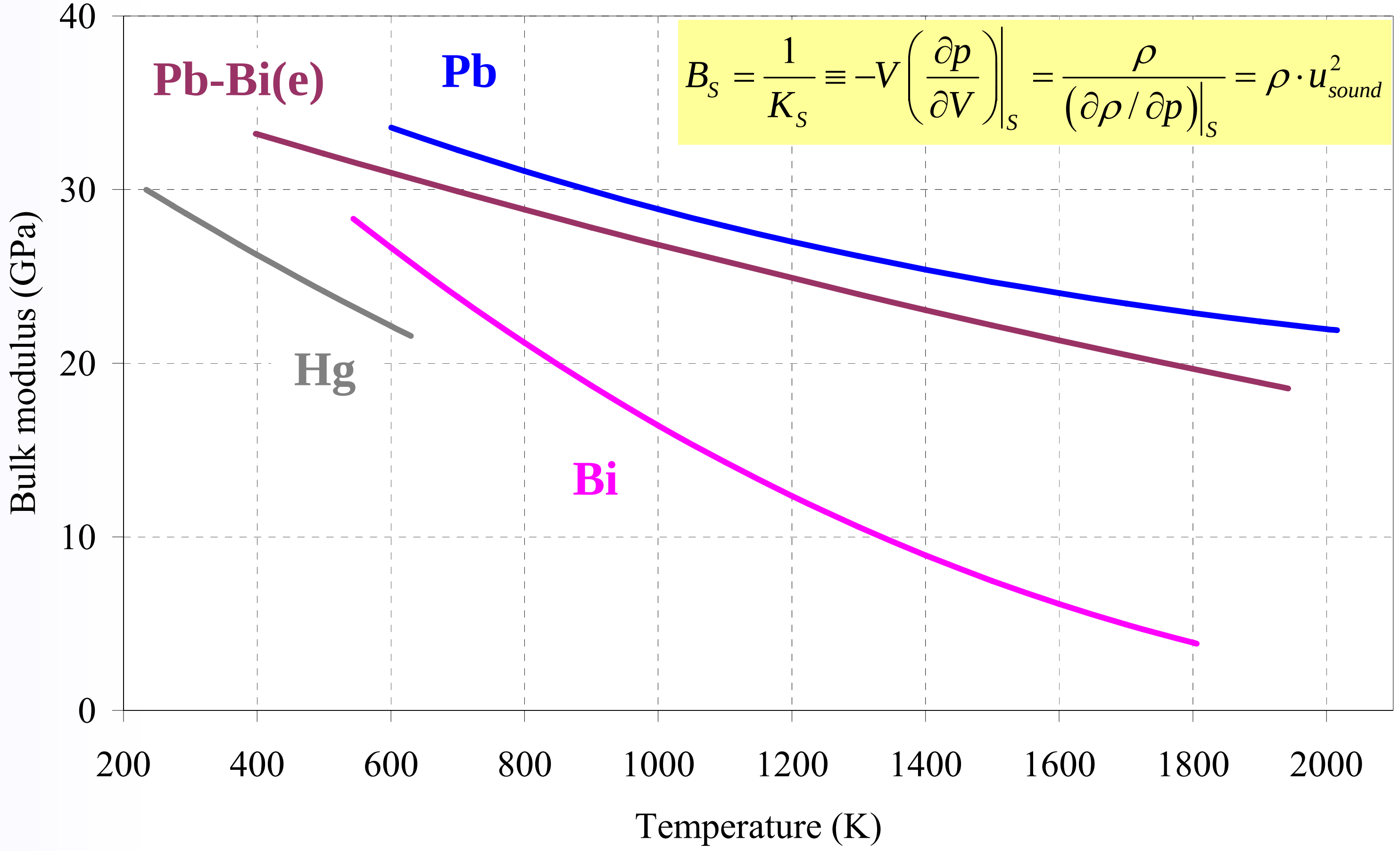


	T$_{m0}$ (K)	**u$_{m0}$** (kg m^{-3})	**A$_u$** (kg m^{-3} K^{-1})
Hg	**234.2**	**1480**	**0.450**
Pb	**600.6**	**1774**	**0.275**
Bi	**544.1**	**1678**	**0.797**
Pb-Bi(e)	**397.7**	**1772**	**0.193**

$$u_{sound}(T, p_0) = u_{m0} - A_u(T - T_{m0}) \quad \pm(??\%)$$

4. Available recommendations:

Bulk modulus (compressibility)



$$B_S = \frac{1}{K_S} \equiv -V\left(\frac{\partial p}{\partial V}\right)\bigg|_S = \frac{\rho}{\left(\partial\rho/\partial p\right)\big|_S} = \rho\cdot u_{sound}^2$$

5. Equations of state:

Simplified EOS for p > p_{atm}

$$\rho(p,T)=\rho(p_0,T)+\int_{p_0}^{p}\left(\frac{\partial\rho}{\partial p}\right)_T\cdot dp$$

Taking into account that

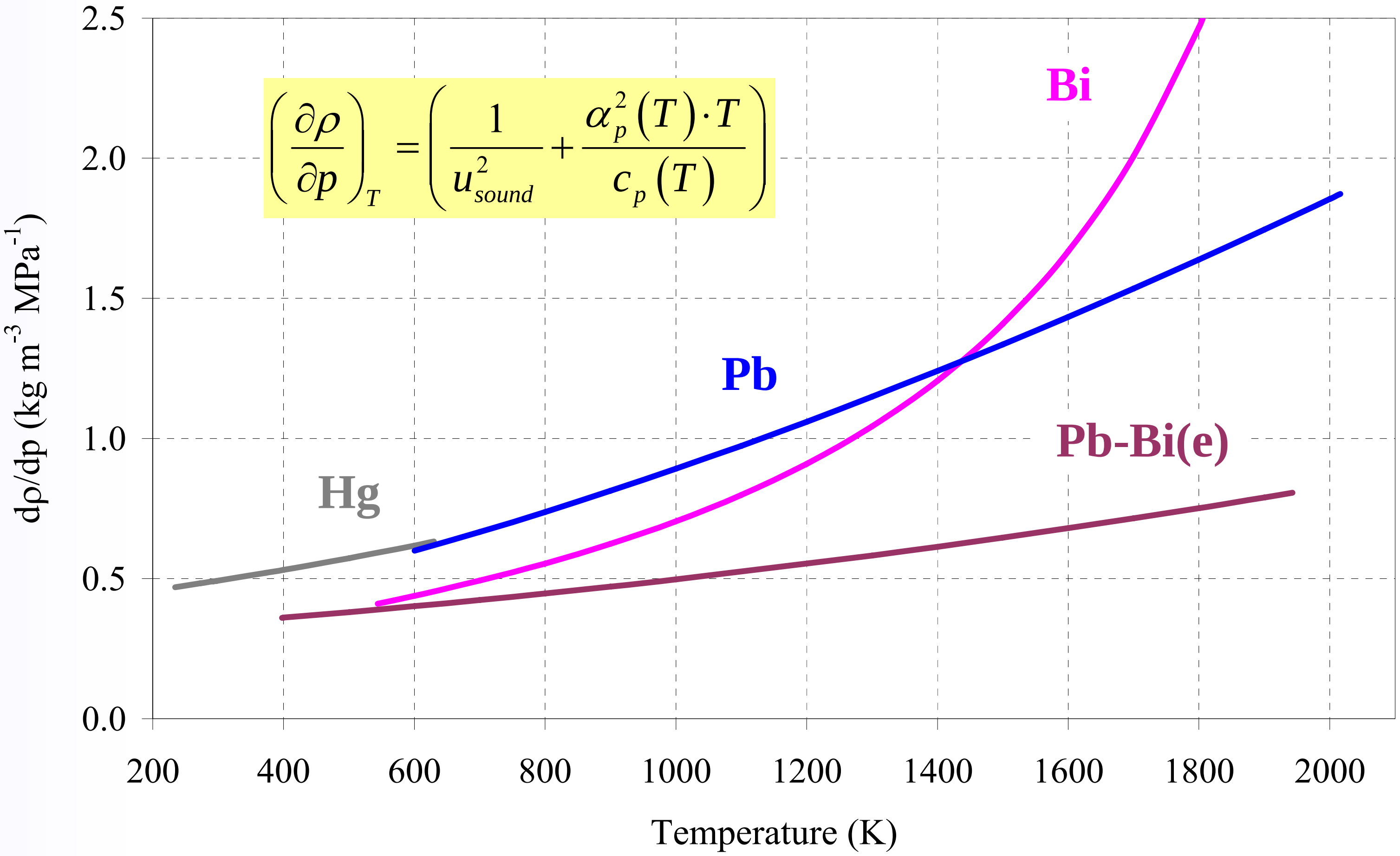
$$\left(\frac{\partial\rho}{\partial p}\right)_T=\left(\frac{1}{u_{sound}^2}+\frac{\alpha_p^2\cdot T}{c_p}\right)$$

one can obtain at pressures close to p_0:

$$\boxed{\rho(p,T)\approx\rho(p_0,T)+(p-p_0)\cdot\left(\frac{1}{u_{sound}^2(T)}+\frac{T\cdot\alpha_p^2(T)}{c_p(T)}\right)}$$

5. Equations of state:

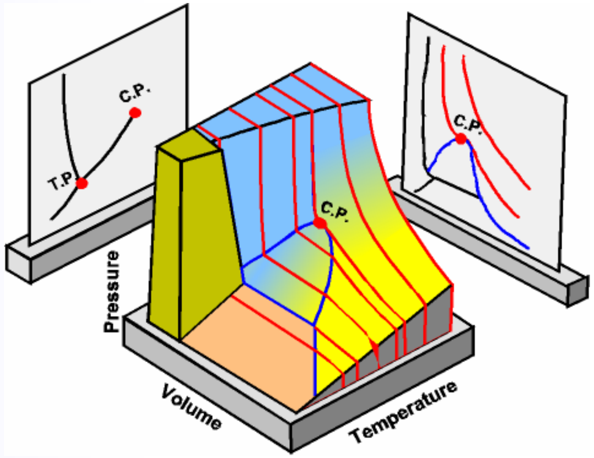
Correction for $p > p_{atm}$

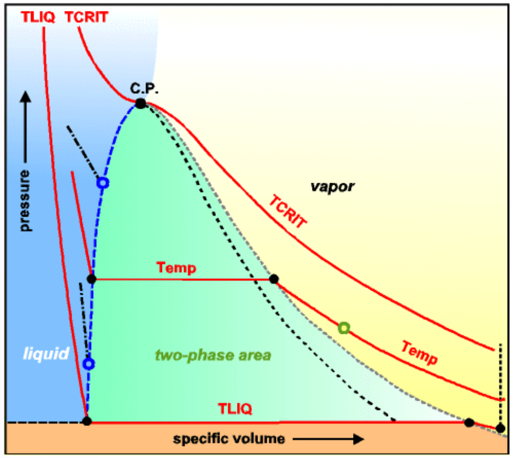


$$\left(\frac{\partial \rho}{\partial p}\right)_T = \left(\frac{1}{u_{sound}^2} + \frac{\alpha_p^2(T)\cdot T}{c_p(T)}\right)$$

5. Equations of state:

Thermal EOS (high *p* and *T*)





- General thermal EOS:

$$p = f\left(\rho, T\right)$$

- The most know is the 2-parameter EOS of Van der Waals:

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

$$a = 3 \cdot p_c \cdot V_c^2 = \frac{9R \cdot T_c \cdot V_c}{8}; \quad b = \frac{V_c}{3}$$

$$Z_c \equiv \frac{p_c \cdot V_c}{R \cdot T_c} = \frac{3}{8} = 0.375$$

- T_c, p_c, V_c (ρ_c) to determine…

5. Equations of state:

EOS of the Van der Waals family

Redlich and Kwong (1949):
(two parameters, $Z_c = 0.333$)

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

Soave (1972):

(two parameters and one function of temperature)

$$p = \frac{RT}{V-b} - \frac{a(T)}{V\cdot(V+b)}$$

Fisher *et al.* (1992) :

(three parameters and one function of temperature, $Z_c = f(c)$; was applied to Na)

$$p = \frac{RT}{(V-b)} - \frac{a(T)}{V\cdot(V+c)}$$

Morita *et al*. (2005):

(four parameters and temperature function); $Z_c = f(c,y)$

$$p = \frac{RT}{(1-y_d)(V-b)} - \frac{a(T)}{V\cdot(V+c)}$$

5. Equations of state:

Determination of T_c, p_c and ρ_c

1. Direct measurement of T_c, p_c and V_c *(measured rather well only for Hg; limited results for Pb; no results for Bi, Pb-Bi)*
2. Watson's semi-empirical correlations to estimate T_c ($\rho_{B\,0}$ should be known)
3. Kopp's empirical correlation to estimate T_c from $\Delta H_{B\,0}$.
4. Extrapolation of $\Delta H_B(T)$ or $\sigma(T)$ to temperatures close to T_c where $\Delta H_B \to 0$ and $\sigma \to 0$
5. The "corresponding states" principle and $\Delta H_{B\,0}$ to determine T_c (reference material is needed)
6. The law of "rectilinear diameter" to determine ρ_c (densities of vapour and liquid phases in function of temperature and T_c are expected to be known)
7. Concept of internal pressure to determine T_c ($u_{sound} \alpha_p \rho C_p / C_V$ should be known)

5. Equations of state:

Critical parameters

		T_c (K)	p_c (MPa)	ρ_c (kg m^{-3})	Z_c (-)
Hg	**measured** *calculated*	**1747**±30 *1656(7%)*	**162**±5 *143(10%)*	**5357**±700 *4885(4%)*	**0.419**±0.040 *0.426(21%)*
Pb	**measured** *calculated*	**5400**±400 *4808(14%)*	**250**±30 *118(36%)*	**3200**±300 *2468(19%)*	**0.361**±0.050 *0.247(59%)*
Bi	**measured** *calculated*	- *4457(15%)*	- *119(25%)*	- *2688(34%)*	- *0.249(84%)*
Pb-Bi(e)	**measured** *calculated*	- *4830(3%?)*	- *166(47%?)*	- *2170(??)*	- *0.396(>50%?)*

5. Equations of state:

First and higher approximations

1. Taking into account a large uncertainty in the estimated critical parameters of Hg, Pb, Bi and Pb-Bi(e), the classic V-d-W EOS can be used as the zero approach at very high pressures.
2. Better results can be obtained with the Redlich-Kwong (RK) EOS or with its extensions using (3-4)-parameters:
   - Recently, Morita *et al.* (JNM, 2007) applied a modified Redlich and Kwong equation (MRK-EOS, proposed by Fisher *et al*. for Na -…), to Hg and Pb.
   - For Bi and Pb-Bi(e), an advanced variant of MRK-EOS, which takes into account the presence of two-atomic molecules in vapour phase, was used.

5. Equations of state:

MRK of Morita *et al.*

$$p = \frac{RT}{M(1+y_2)(\upsilon - b)} - \frac{a(T)}{\upsilon(\upsilon + c)}$$

y_2 is a fraction of M_2 molecules in M-vapour. It is determined by the equilibrium constant:

$$K_e = \frac{p_2}{p_1^2} = \frac{y_2}{(1-y_2)^2 \cdot p}$$

The equilibrium constant is found using the available experimental data on vapour composition.

The temperature dependent coefficient *a(T)* was presented as follows:

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

The constants ***a_c*, *b*, *c*** are determined using the "best estimated" values of the critical parameters*;* ***n*** is fitted to the slope of the vapour pressure curve at the critical temperature.

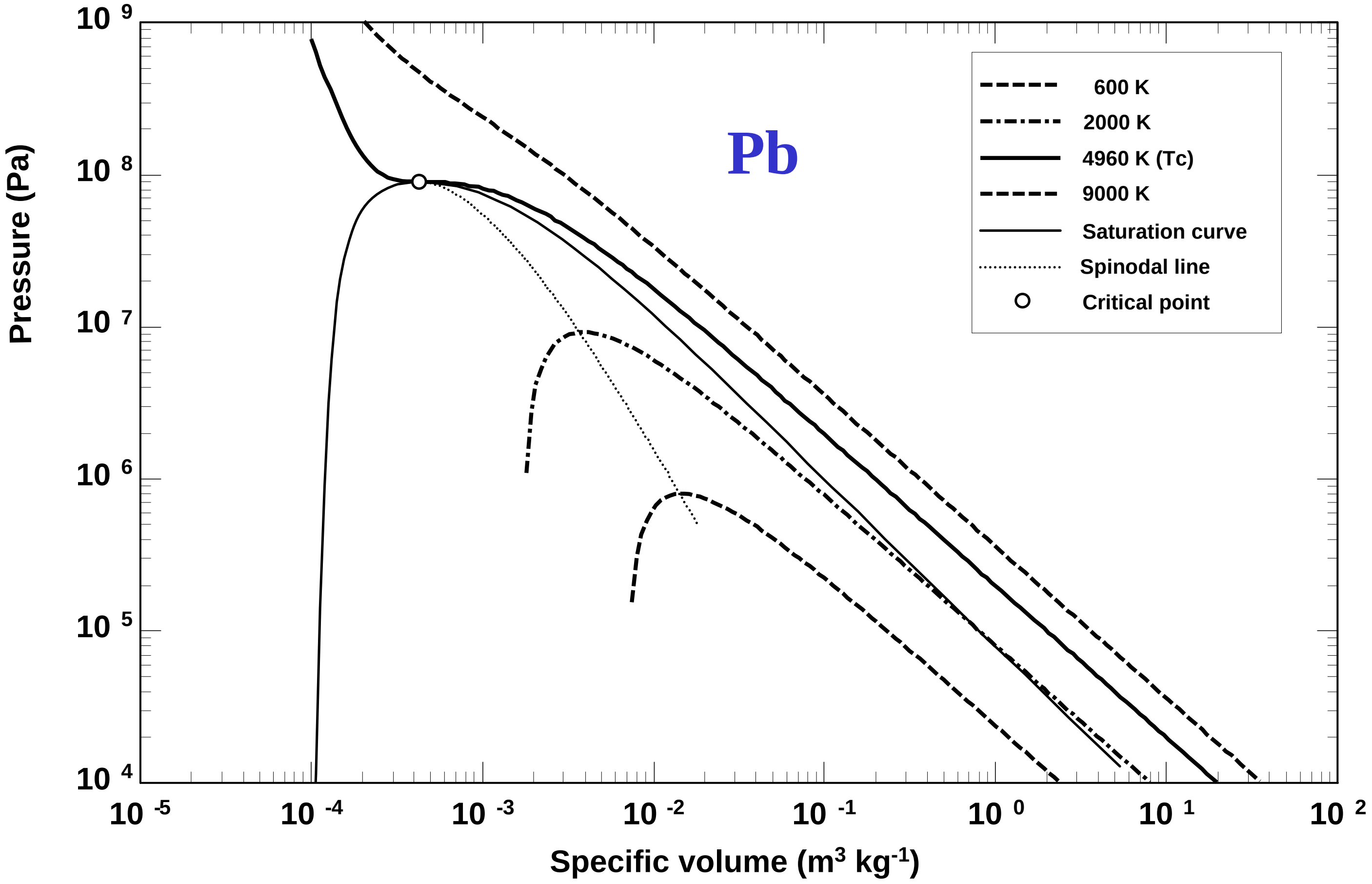
5. Equations of state:

Constants of MRK EOS for HLM

	Hg	**Pb**	**Bi**	**LBE**
a_c	14.377	203.24	49.064	159.33
b	7.4988×10^{-5}	3.3918×10^{-5}	1.8448×10^{-4}	6.2682×10^{-5}
c	-3.1436×10^{-5}	7.5099×10^{-4}	-5.8218×10^{-5}	8.1187×10^{-4}
n	-0.028413	0.048956	0.14618	0.37836
y_2	(0.0) ?	0.0	$\neq 0$	$\neq 0$

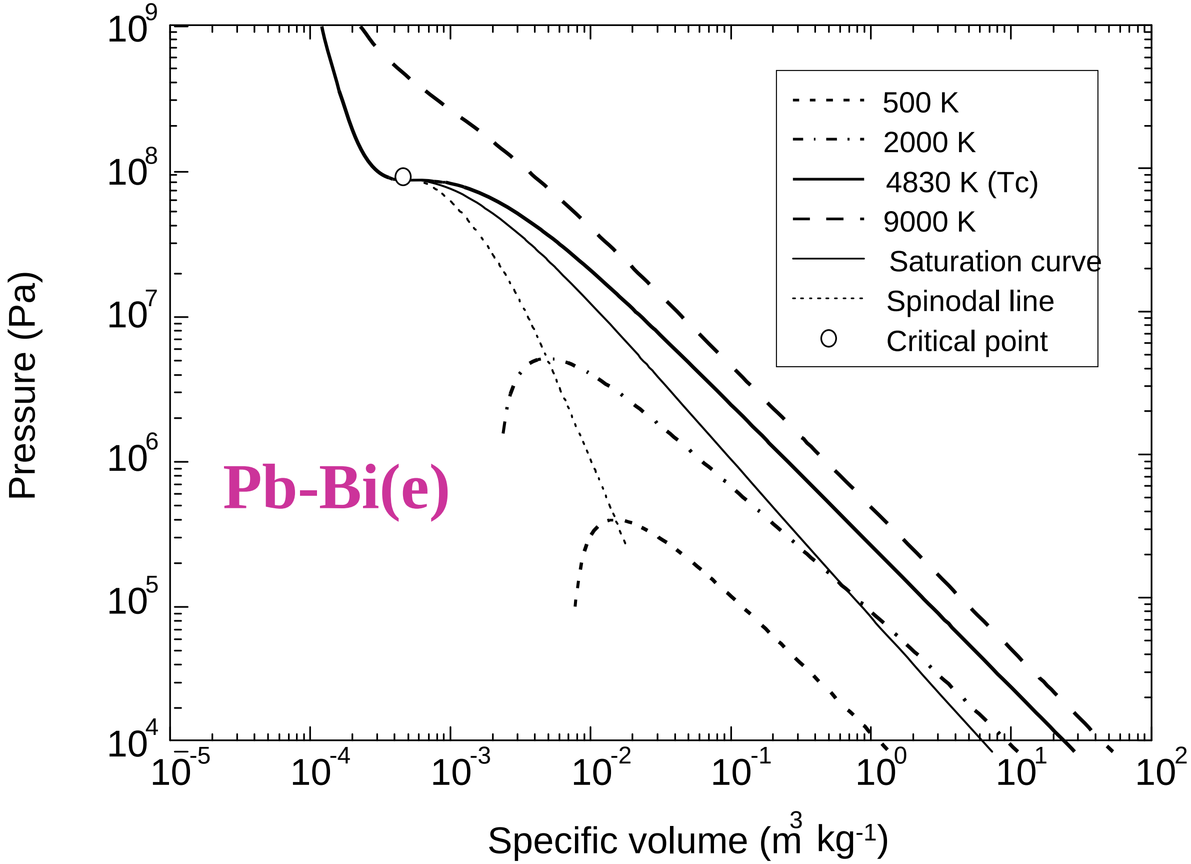
5. Equations of state:

Pb-vapour isotherms



5. Equations of state:

Pb-Bi(e)-vapour isotherms



6. CONCLUSIONS

- For molten **Hg, Pb Bi and Pb-Bi(e)**, experimental data are available for most of thermodynamic parameters of interest in the temperature region of normal operation of nuclear installations, but only at the atmospheric pressure. Moreover, some of these parameters (heat capacity, saturated vapour pressure, sound velocity, the critical point) have not yet been determined with the needed accuracy.
- The modified Redlich-Kwong EOS could be applied for prognosis of thermodynamic properties of the **HML** at high temperatures and pressures, however, new experimental results are necessary for the EOS validation.
- Coordinated international and national R&D programs (*experimental and theoretical*) are needed to develop a more reliable and complete **HLM** properties database.

Acknowledgement

- This work was supported by funds of the MYRRHA project (SCK•CEN) and EURATOM FP6 ELSY project.
- Thermodynamic properties for Pb, Bi and Pb-Bi(e) were mainly extracted from Chapter 2 of the OECD Handbook on HLMC written by G. Benamati (ENEA) and V. Sobolev (SCK·CEN) with the support of many members of WPFC EG on HMLC Technology.
- Special acknowledgement to Dr. K. Morita (Kyushu University) and to Dr. M. Flad (representing FZK) for the MRK EOS calculations.