



The solubility of helium in lead–lithium eutectic alloy

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ABSTRACT

The helium production rates in liquid metals (Pb–Li eutectic alloy, LLE and others) Blanket Breeders (BB) are nearly mol-to-mol linked to tritium and intimately associated with the compulsory requirement of high tritium self-sufficiency of next fusion reactors. When LLE is oversaturated and the helium solubility limit is exceeded, helium atoms can nucleate in the form of bubbles. The presence of helium bubbles within LLE channels could have severe impact on the diverse BB designs, in particular on tritium transport permeation and its recovery. Even though He is an inert gas assumed to be insoluble, the helium Henry's constant (K_H) in a liquid metal is not zero. The very low K_H and difficulties to measure it has historically driven to the absence of basic data. A semi-empirical correlation is proposed providing the helium solubility (i.e.: the helium Henry's constant) based on Kumar's cohesion model using the available thermo-physical experimental solubility data for lithium, sodium, potassium, mercury. The proposed expression for eutectic lead–lithium is:

$K_H (\text{at.fr.Pa}^{-1}) = 5.99 \cdot 10^{-4} \exp(-1.16 \cdot \delta_k) \exp(-54.23/RT)$, being K_H the Henry's constant; T [K], R [$8.314 \cdot 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$] and δ_k the Kumar's cohesive parameter. From a δ_k justified value of $18.2 \text{ MPa}^{1/2}$ in LLE the values for K_H range from $1.14 \cdot 10^{-17}$ to $1.35 \cdot 10^{-15} \text{ at.fr.Pa}^{-1}$ for temperatures between 350 and 870C. The helium solubility should integrate the lead–lithium eutectic nuclear material database for fusion systems design.

1. Introduction

The helium molar production rate in tritium breeding liquid metal (LM) alloys is linked to tritium, through $n({}_3^6\text{Li}, {}_1^3\text{H})_2\text{He}$, $n({}_3^7\text{Li}, {}_1^3\text{H}, {}_2^4\text{He})n'$ reactions, and then intimately associated to the compulsory requirement of high tritium self-sufficiency of next fusion reactors [1,2]. The singular case of helium in the LM Breeding Blankets (BB) relies on its relatively high helium concentration with respect to expectable low solubility as inert insoluble gas, i.e. on the potential LM gas super-saturation. Under supersaturated conditions, helium can nucleate and forms bubbles. However, super-saturation is a necessary but not sufficient condition for bubble nucleation. Extra “sufficiency” conditions for bubble nucleation and bubble stability (i.e.: bubbles non/re-dissolution) are needed. According to a limited database for the noble gases in liquid metals the Henry's constant (K_H) is not zero nor immeasurably small. Measures were obtained in the past for Helium in liquid lithium, potassium, sodium, mercury and others. However, the difficulties to measure it makes such fundamental data scarce.

The value of helium solubility is the key primary input to assess the

helium state of solution in a liquid metal and the characteristics of nucleated bubbles and their evolution: *migration, interaction or coalescence probabilities* and *their stability* (growth or implosive decay) under given LM BB channel conditions. The final state of solution of helium should certainly impact on: (1) the potential “foaming-like” modification of LM bulk thermo-physical properties, (2) the possible change of LM/wall heat, mass, electrical coefficients by the development of helium interfacial phenomena, (3) a LM channel over pressurization and (4) complementary helium induced cavitation issues in EM (ElectroMagnetic) pumping systems. In addition, if helium bubbles are nucleated; (5) bubbles may act as sinks for the tritium flowing in solution in the LM, i.e. play on tritium transport characteristics in the LM channel. This point would be of paramount importance in Nuclear Fusion Technology systems because it would impact tritium fuel management: material inventories, permeation fluxes & recovery kinetics, dwelling-times and therefore self-sufficiency assessments [3,4].

A semi-empirical correlation is proposed for the helium solubility (i.e.: the helium Henry's constant) in lead–lithium eutectic alloy based on Kumar's cohesion model using the available thermo-physical

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experimental data for lithium, sodium, potassium, mercury. Values for lead are derived by using the same semi-empirical correlation and the resulting value for solubility in the PbLi eutectic alloy is obtained by computing its own cohesion parameter.

2. Henry's law and solvent–solvent cohesion parameters

Henry's law describes the solubility of a dissolved gaseous solute of a lighter component (gas or liquid) "j" in a denser liquid state as solvent ("i") at low molar fractions of solute (for $x_j \ll 1$):

$$x_j = (K_H)_{ji} \cdot y_i \cdot p \quad (1)$$

being y_i the molar fraction in the gas phase at pressure p (i.e. $y_i \cdot p$ is the gas pressure of i). The proportionality constant $(K_H)_{ji}$ is known as the *solubility constant* or as the *Henry's constant*. The Henry's constant value for a solute depends on temperature T and the relative cohesion forces solvent–solvent and on the singular interaction between the solvent and solute.

Inert gases are special types of solutes in terms of interaction even though rare helium chemistry with highly reactive atoms (case of alkali) forming "helides" is thermodynamically not forbidden.

When determining the Henry's constant of Helium in the LM the correct assessment of the cohesive force between the eutectic alloy atoms results crucial.

The cohesion solvent–solvent forces are quantified by a cohesion parameter (δ_C): $\delta_C = (U/\nu)^{1/2}$ i.e. the ratio between specific cohesive energy U (J/mol) and the specific volume (m^3/mol).

These cohesion forces or the cohesion energies could be expressed parametrically by using different approximations appearing in the literature.

The two most outstanding are that of Hildebrand's ((δ_H) ; [5]) and Kumar's ((δ_K) ; [6]) one. The specific cohesive energy can be expressed as the vaporization energy ΔU_{vap} plus the energy required to expand the liquid–vapor pressure to zero: ΔU_{∞} . In other words: $U = \Delta U_{\text{vap}} + \Delta U_{\infty} = \Delta H_{\text{vap}} + \Delta H_{\infty} - RT - p_s \cdot V$ being p_s the vapor saturation pressure at T and R the constant of gases ($8.314 \cdot 10^{-3}$ kJ/K/mol).

Commonly well below the liquid metal boiling temperature (1750 °C) both ΔH_{∞} and $p_s \cdot V$ terms could be neglected when compared with latent melting heat (ΔH_{melt}) and thermal energy so: $\delta_C = (\Delta H_{\text{vap}} - RT/\nu)^{1/2}$. The Hildebrand's cohesion parameter is ad-hoc defined and referred to room temperature.

When Kumar's assessed the cohesion parameter (δ_K) [6] of binary alloys; he pointed out how liquid metals in terms of structural order and atomic correlations (density, packing, structural factors...) are closer to quasi-crystals than to a condensed-gas. Thus, in Kumar's model, the melting enthalpy (ΔH_{melt}) replaces full vaporization energy (ΔH_{vap}) driving to significantly lower cohesion parameter values.

Both Hildebrand's and Kumar's cohesion parameters are computed in Table 1 from thermo-physical values discussed and tabulated in [7].

2.1. Semi-empirical correlations and experimental data analytics

Semi-empirical correlation for Henry's constant applies for parametric fitted expressions including cohesive parameter and

Table 1
Thermo-physical ([7]), Hildebrand's ([5]) and Kumar's ([6]).cohesion parameters.

	Melt. / Boil.[K] (@1bar)	Mol. W. [g/mol]	Spec vol. [cm ³ /mol]	ΔH_{MELT} [kJ/mol]	ΔH_{VAP} [kJ/mol]	Hildebrand δ_H [MPa ^{1/2}]	Kumar δ_K [MPa ^{1/2}]
Li	453/1603	6.9	13.5	2.88	136	98.7	14.6
K	336/1032	39.1	47.2	2.34	77	40.3	7.1
Hg	234/629.8	200.6	14.82	2.29	59.11	62.1	12.4
Na	370.9/1156	22.9	24.7	2.6	97.42	61.8	10.3
Pb	600/2022	207.2	27.8	4.76	179.5	97.6	16.1
LLE	508/—	173.1	17.6	5.86	174.05	98.07	18.2

temperatures.

$$\ln(1/K_H) = A_1 + A_2/T + A_3 \quad (2)$$

(A_1, A_2, A_3 to be determined and the δ_C as the cohesion parameter).

Marathe & Prausnitz [8] proposed a correlation of Helium Henry's ($A_{1,H} = 15.06$; $A_{2,H} = 85.489 \text{ K}^{-1}$; $A_{3,H} = 0.305 \text{ [MPa}^{-1/2}]$) and $\delta_C = \delta_H$ in a wide variety of non-hydrogen- strongly bonded and hydrogen-bonded solvents. Such correlation shows max. deviations of few percentiles (<7 %) and root-square linear correlation coefficient [COR > 0.97] driving to a K_H numerical scattering lower than 50 %. None of those data points are liquid metals and the validity of extrapolation to liquid metals should be questioned.

Considering there is not know data for boiling enthalpy of LLE we propose the following approach based on action mass rule: $\Delta H_{\text{VAP}} [\text{Pb-15.7Li}] = 0.157 (\Delta H_{\text{VAP}} [\text{Li}] - \Delta H_{\text{MELT}} [\text{Li}]) - + 0.843 (\Delta H_{\text{VAP}} [\text{Pb}] - \Delta H_{\text{MELT}} [\text{Pb}]) = 174,05 \text{ kJ/mol}$, accounting that both alloying elements can vaporize separately from the molten phases. Such action mass rule can not be applied directly to assess the value of cohesion parameter in the eutectic phase; e.g: $\delta_K [\text{LLE}] = 0.157 \delta_K [\text{Li}] + 0.843 \delta_K [\text{Pb}] = 15.8 \text{ [MPa}^{1/2}]$ is incorrect as corresponding to a fully segregated immixed mixture. The correct value: $\delta_K (\text{LLE}) = (\Delta H_{\text{MELT}}/\nu)^{1/2} = 18,23 \text{ [MPa}^{1/2}]$ (Table 1).

The use of Marathe & Prausnitz correlation to liquid metals and Hildebrand's cohesion parameter drives to K_H values from $10^{-12} \text{ at.fr. Pa}^{-1}$ in the case of potassium to $10^{-15} \text{ at.fr. Pa}^{-1}$ in the case of sodium or mercury and to low $10^{-20} \text{ at.fr. Pa}^{-1}$ in liquid Li, Pb for the range $400\text{--}600$ °C making unreliable a general semi-empirical correlation for liquid metals.

Furthermore, even the purpose of a correlation would be unreliable according to ranges shown by the experimental data in Table 2. Reversely, the use of Kumar's [5] with Marathe & Prausnitz parameters drives to K_H values within two orders of magnitude in accordance with empirical results.

Thus, the obtaining of a new set of coefficients [$A_{1,K}$; $A_{2,K}$; $A_{3,K}$] for a semi-empirical correlation using experimental data in Table 2 (experimental quality is assumed not possible to be checked) but now with: $\delta_C = \delta_K$ is naturally suggested.

When experimental data is considered for potassium, sodium, mercury, lithium and lead. the available experimental data is consistent with the semi-empirical correlation in eq. (2): [$\delta_K (\text{K}) < \delta_K (\text{Na}) < \delta_K (\text{Hg}) < \delta_K (\text{Li}) < \delta_K (\text{Pb}) < \delta_K (\text{LLE})$]. Last relationship is fully consistent with the eutectic condition. Accordingly the solubility of helium in lead and in

Table 2
Historic experimental data points for Helium solubility in liquid metals (Li, K, Na, Hg).

Ref., Author, Year	(G)/ (M)	T (°C);P (Atm.)	K_H [at.fr. Pa ⁻¹]
[9], H. Slotnik, 1965	He/Li	649–871 °C; 1–3 atm	$[5.0 - 7.0] \cdot 10^{-14}$
	He/K	482–704 °C; 1–3 atm	$[2.0 - 7.0] \cdot 10^{-11}$
[10], K. Thormeier 1970	He/Na	500 °C; 1 atm.	$1.53 \cdot 10^{-12}$
[11], S. Fukase 1976	He/Na	500 °C; 1 atm.	$9.74 \cdot 10^{-13}$
[12], M. Francis 2008	He/Hg	500 °C; 1 atm.	$9.87 \cdot 10^{-14}$
[13], E. Veleckis 1971	He/Na	350–550 °C; 6 atm.	$[1.26 - 25.8] \cdot 10^{-13}$

lead–lithium eutectic should take lower values: [$K_H(K) > K^H(Na) > K^H(Hg) > K^H(Li) > K^H(Pb) > K^H(LLE)$].

The least-square fitting in K, Na, Li and Hg drives into a general semi-empirical fitting liquid metals for the available data points:

$$A_1 = 7.42; A_2 = 6523; A_3 = 1.16 \quad (3)$$

2.2. Helium solubility in molten lead

From [eq. (3)] the values of Helium solubility in molten lead ($\delta_K(Pb) = 16.1 \text{ MPa}^{1/2}$) could be assessed. Lead values range from $K_H(Pb) = 1.34 \cdot 10^{-16}$ (350 °C) up to $K_H(Pb) = 1.55 \cdot 10^{-14}$ (870 °C) [at.fr. Pa⁻¹]. Unfortunately, there is not open experimental data known to confirm the soundness of this assessment. Thus, these values are proposed for the material database of Lead.

3. Helium solubility in lead–lithium eutectic

The semi-empirical approach has reproduced lithium, Sodium, Potassium data and predicted that of lead (Fig. 1). Following the proposed approach the obtained values for the Helium solubility in lead–lithium eutectic alloy (Pb-15.7(2)Li) are:

$$K_H(\text{Pa}^{-1}) = 5.99 \cdot 10^{-4} \exp(-1.16 \cdot \delta_K) \exp(-54.23/RT) \quad (4)$$

K_H being the Henry's constant expressed in [at.fr. Pa⁻¹]; T [K], R [8,314 10⁻³ kJ mol⁻¹ K⁻¹] and δ_K the Kumar's cohesive parameter in lead–lithium. For $\delta_K = 18.2 \text{ MPa}^{1/2}$ the correlation approximates: $1.14 \cdot 10^{-17}$ (350 °C) up to $1.35 \cdot 10^{-15}$ (870 °C) [at.fr. Pa⁻¹].

4. Discussion

It has been proven how an general semi-empirical correlation is able to fit the scarce database for the helium solubility in liquid metals; just four metals (Li, Na, K, Hg) and three authors ([9,10,11,12,13]).

The sequence of K_H values obtained appears fully consistent with thermo-physical values and Kumar's approach: [$\delta_K(K) < \delta_K(Na) < \delta_K(Hg) < \delta_K(Li) < \delta_K(Pb) < \delta_K(LLE)$] and accordingly: [$K_H(K) > K_H(Na)$

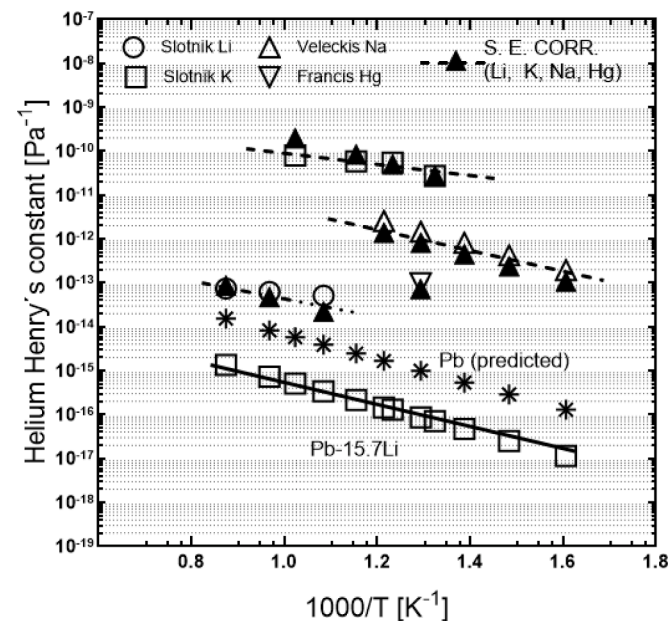


Fig. 1. Available experimental data points for helium solubility (Li, K, Hg, Na) [9,12,13] and regression from (eq.2 and 3) using Kumar's cohesion model [6]. Proposed prediction for Pb ($\delta_K(Pb) = 16.1 \text{ MPa}^{1/2}$) and LLE (Pb15.7Li) ($\delta_K(LLE) = 18.2 \text{ MPa}^{1/2}$) values by taking profit from the semi-empirical correlation (Eq. (2)) with coefficients in (eq.3).

$> K_H(Hg) > K_H(Li) > K_H(Pb) > K_H(LLE)$]. The soundness for the semi-empirical correlations with respect to the available historic published experimental measurements is reported in the right column in Table 3. The experimental quality of historical database for Helium in liquid metals could not be questioned here. There is a maximum deviation between the semi-empirical correlation proposed and data for Potassium @ 704C ([9] Slotnik data, 1965) with a value of 153%: i.e. a factor 2.5 between the correlation and the experimental value. The soundness of this proposed semi-empirical correlation should also be taken in the context of the experimental difficulty to obtain the very low values of Helium solubility in the liquid metals. *Strictu sensu*; such 153% deviation for Potassium @ 704C (Slotnik data, 1965) should be taken as the maximum deviation supported by data in our correlation (eq. (4)).

Similar deviations could be justified following a more rigorous procedures by differentiating K_H with respect to (δ_K) and T in eq.(4):

$$\Delta K_H/K_H = |(-1.16\Delta\delta_K) + (54.23\Delta T/RT^2)| \quad (5)$$

The temperature term could be assumed as being negligible. The maximum ad-hoc deviation value in of the cohesion term in the semi-empirical correlation (max. $\Delta\delta_K$); needed to fit exactly the experimental data is around $1.25 \text{ [MPa]}^{1/2}$ (K. Slotnik @704C), that is: $\Delta\Delta K_H/K_H \sim 145 \%$, that could be taken to proof the fully consistency.

Therefore, a factor of 2.5 for eq. (4) should be taken even if this value could be clearly overestimated.

5. Concluding remarks

Helium solubility should integrate the lead–lithium eutectic material database for nuclear systems design. Values for the Helium solubility in lead–lithium eutectic alloys are proposed based on a semi-empirical correlation fitting the available experimental data points and Kumar's cohesion model. Further validation and refinement of semi-empirical correlation need of the extension of the He solubility experimental database in liquid metals and alloys. Conventional experimental measurements (Gas Isovolomic Desorption techniques) appear challenging considering such low solubility values, the required sensitivities and the need to load eutectic sample at very high pressures. New experimental techniques and measuring principles are probably needed to confirm the soundness of the proposed values at such low ranges.

The proposed correlations here anticipate as blind predictions near-term prospected measurement confirming the Helium Henry's constant in lead–lithium eutectics.

Table 3

Helium solubility experimental data (Li, K, Na, Hg) by the semi-empirical correlation in eq. (2).

[9], H. Slotnik, 1965 K_H [at.fr. Pa ⁻¹] ($\delta_K(Li)$: 14.6 MPa ^{1/2})	°C	Experimental	Semi-Empirical approx.	Deviat. (Δ)
	649	5.19E-14	2.24E-14	56.8%
	769	6.28E-14	4.78E-14	23.8%
	841	7.53E-14	8.83E-14	17.2%
[9], H. Slotnik, 1965 ($\delta_K(K)$: 7.1 MPa ^{1/2})	482	2.73E-11	2.81E-11	2.9%
	538	5.51E-11	5.10E-11	7.4%
	593	5.92E-11	8.50E-11	43.5%
	704	7.97E-11	2.00E-10	153.1%
[13], E. Veleckis 1971 ($\delta_K(Na)$: 10.3 MPa ^{1/2})	550	2.58E-12	1.40E-12	45.7%
	499	1.47E-12	8.36E-13	43.5%
	447	8.23E-13	4.54E-13	44.8%
	400	4.28E-13	2.42E-13	43.4%
	349	1.96E-13	1.09E-13	44.3%
	349	1.96E-13	1.09E-13	44.3%
[12], M. Francis, 2008 ($\delta_K(Hg)$: 12.4 MPa ^{1/2})	500	9.87E-14	7.35E-14	25.5%

$$\text{Deviation } \Delta (\%) = 100 \times |\text{val. exp.} - \text{val. corr.}| / \text{val. exp.}$$

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Signe don behalf of research team by the corresponding author (Prof. LUIS A. SEDANO).

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