



**Comments on the Hydrogen Solubility Data for  
Liquid Lead, Lithium and Lithium-Lead Alloys  
and Review of a Tritium Solubility Model for  
Lithium-Lead Alloys**

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## Introduction

The projected use of a lithium-lead alloy as the tritium breeding blanket and heat transfer agent in fusion reactors requires data on the solubility of hydrogen isotopes in the alloys at the temperatures of interest. In the fusion design studies NUWMAK<sup>(1)</sup> and WITAMIR-I<sup>(2)</sup>, lithium-lead blankets were proposed, and the available data base for hydrogen solubility in lithium, lead and lithium-lead alloys was thoroughly analyzed. In the absence of available experimental data in the desired temperature range, estimates were made on the hydrogen isotope solubility in the lithium-lead alloys. In NUWMAK, solubility estimates were based on activity studies of lithium in lithium-lead while in WITAMIR the solubility was extrapolated from deuterium measurements in the alloy at higher temperatures. In this note we summarize the existing data and review our methods of estimating the tritium solubility in the desired temperature range.

## Hydrogen Solubility in Lead

There exists some controversy over the subject of hydrogen solubility in liquid lead. An investigation by Opie and Grant<sup>(3)</sup> found appreciable hydrogen solubility over the temperature range 500-900°C with the solubility increasing with temperature according to the equation:

$$\log_{10} S = - \frac{2450}{T} + 2.19$$

where S is the solubility in cc H<sub>2</sub> per 100 g Pb. The value reported by Opie and Grant at 600°C, 0.25 cc H<sub>2</sub> per 100 g Pb, was not corroborated by Hofmann and Maatsch<sup>(4)</sup> who found a lower solubility, less than 0.01 cc H<sub>2</sub> per 100 g Pb, at this temperature (Table 1).

Table 1  
Hydrogen Solubility in Liquid Lead

<u>Investigator</u>	Solubility (cc/100 g Pb) at 600°C	Sievert's Constant, $K_S$ (appm H/torr <sup>1/2</sup> ) 600°C
Opie and Grant <sup>(3)</sup>	0.25	1.68
Hofmann and Maatsch <sup>(4)</sup>	< 0.01*	< 0.067*

\*Established by the limit of detection of the technique used.

There are additional data which indicate a very low solubility for hydrogen in liquid lead. Cerjak and Erdmann-Jesnitzer<sup>(5)</sup> observed that the amount of gas released in the temperature range 300-600°C from lead samples exposed to hydrogen was very low; near the background limits of their experiment. Mannchen and Baumann<sup>(6)</sup> observed that lead did not absorb hydrogen on melting in a hydrogen atmosphere. Experiments on evaporated and sintered lead films<sup>(7,8)</sup> have shown that gas phase hydrogen atoms ( $10^{-3}$  -  $10^{-2}$  torr) are absorbed to a maximum bulk composition of  $PbH_{0.19}$  at 0°C, but when the hydride is heated, 25% of the hydrogen is desorbed by 140°C<sup>(6)</sup> and 50% is desorbed by 190°C.<sup>(7)</sup>

The high solubility observed by Opie and Grant has been attributed<sup>(9)</sup> to an oxygen impurity in the lead, which combines with the hydrogen to form water. On the basis of the data available at this time, the work of Hofmann

and Maatsch<sup>(4)</sup> are the most reliable even though considerable uncertainty remains in the actual value for hydrogen solubility in liquid lead.

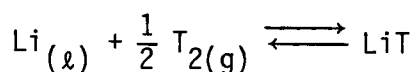
#### Hydrogen Solubility in Lithium

Several investigators have determined the solubility of hydrogen isotopes in pure liquid lithium. The results, summarized in Fig. 1 and Table 2, are shown to be in good agreement.

#### Hydrogen Solubility in Lithium-Lead

The lithium activity in lithium-lead alloys has been studied by both electrochemical<sup>(15-17)</sup> and vapor pressure techniques<sup>(18)</sup> at temperatures ranging from 477 to 800°C. The measurements of activity of lithium in the Li<sub>17</sub>Pb<sub>83</sub> eutectic as a function of temperature (Fig. 2) are in very good agreement. Following the solubility model in NUWMAK<sup>(1)</sup>, the above activity data and the solubility of tritium in pure lithium have been used to estimate the solubility of hydrogen isotopes in Li<sub>17</sub>Pb<sub>83</sub>.

The solubility of tritium in pure liquid lithium may be defined by the equation



for which the equilibrium constant is

$$K_{\text{eq}} = \frac{[\text{a}_{\text{LiT}}]}{[\text{a}_{\text{Li}}][\text{a}_{\text{T}_{2(\text{g})}}]^{1/2}}, \text{ where } a \text{ denotes activity.} \quad (1)$$

At very low concentrations of tritium, the activity of Li<sub>(ℓ)</sub> is unity, and the activities of LiT and T<sub>2(g)</sub> may be taken as the concentration of LiT in lithium, C<sub>LiT</sub>, and the partial pressure of T<sub>2</sub> above the liquid, P<sub>T<sub>2</sub></sub>. The

Table 2  
Hydrogen Isotope Solubility in Liquid Lithium

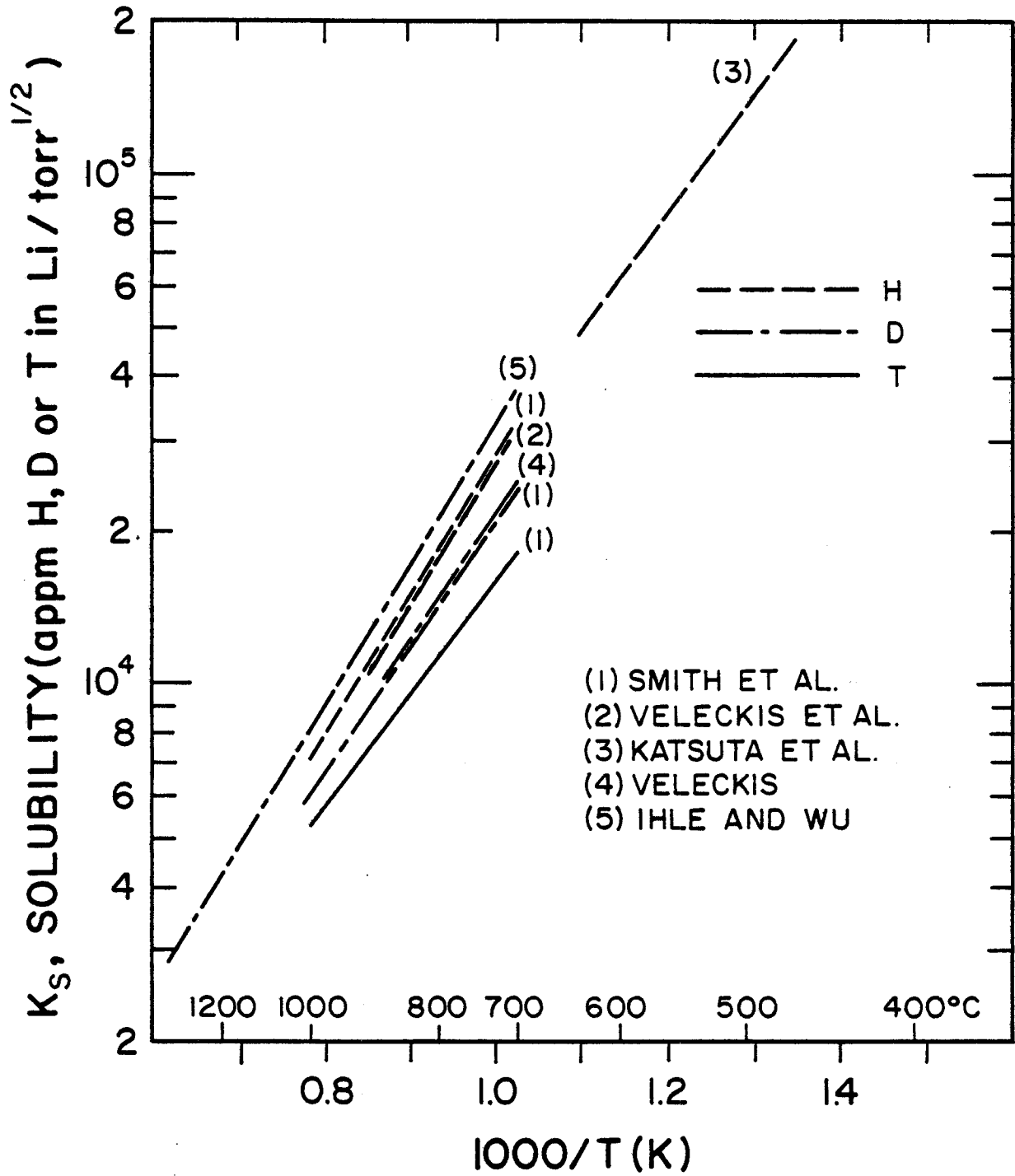
<u>Isotope</u>	<u>Mole Fraction</u>	<u>Sievert's Constant, <math>K_s</math> (appm, H,D,T/torr<sup>1/2</sup>)</u>	<u>References</u>
H	0.01 -0.1	exp (3.974 + 6242/T(K))	Smith et al.(10)
H	0.005 -0.99	exp (4.001 + 6182/T(K))*	Veleckis et al.(11)
H	0.002 -0.012	exp (4.93 + 5340/T(K))	Katsuta et al.(12)
D	0.01 -0.1	exp (4.301 + 5644/T(K))	Smith et al.(10)
D	0.01 -0.99	exp (4.361 + 5599/T(K))*	Veleckis(13)
D	5x10 <sup>-7</sup> -10 <sup>-4</sup>	exp (4.0 + 6381/T(K))	Ihle and Wu(14)
T	0.01 -0.1	exp (4.590 + 5085/T(K))	Smith et al.(10)

\*Equations valid for dilute solutions only.



Figure 1

# SIEVERT'S CONSTANT FOR HYDROGEN ISOTOPES IN LIQUID LITHIUM



# LITHIUM ACTIVITY IN 17 Li: 83 Pb

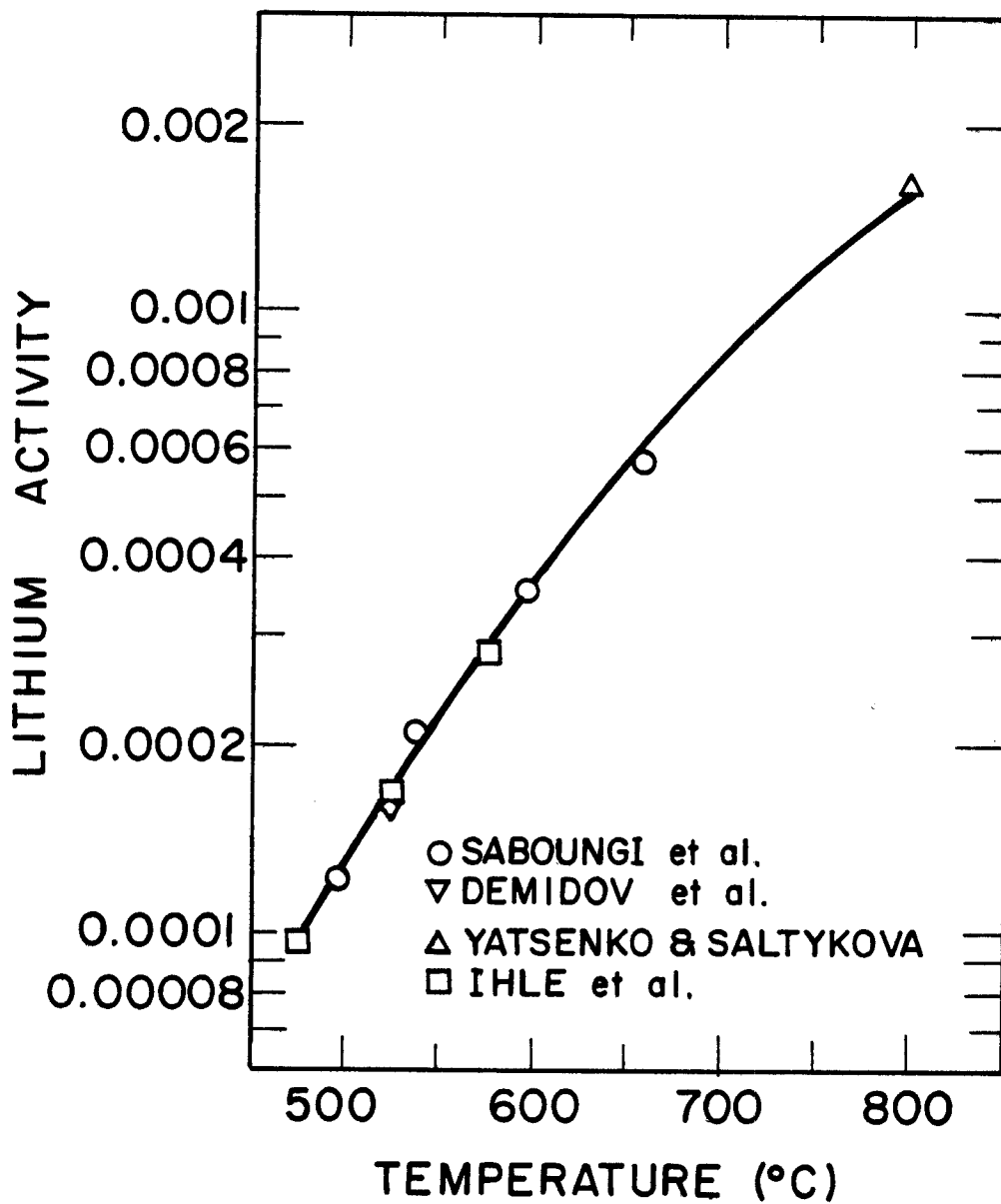
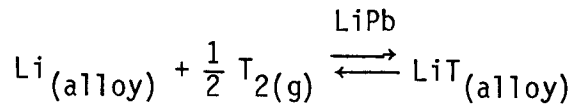


Figure 2

resulting equilibrium constant, referred to as Sievert's constant, is then

$$K_s = \frac{[C_{LiT}]}{[P_{T_2(g)}]^{1/2}} \quad (2)$$

In the lithium-lead alloy system an equivalent equation may be written



for which

$$K'_{eq} = \frac{[a_{LiT(alloy)}]}{[a_{Li(alloy)}][a_{T_2(g)}]^{1/2}} \quad (3)$$

Again at very low concentrations of tritium, the activity of LiT and  $T_2(g)$  in the alloy may be considered to equal the concentration and partial pressure, respectively. The activity of liquid lithium in the alloy is no longer unity, but fortunately has been experimentally determined. So Eq. (3) becomes

$$K'_{eq} = \frac{[C_{LiT(alloy)}]}{[a_{Li(alloy)}][P_{T_2(g)}]^{1/2}} \quad (4)$$

To relate the solubility of tritium in the alloy to the solubility of tritium in lithium,  $K'_{eq}$  is set equal to  $K_s$ , which upon rearrangement yields Eq. (5)

$$K'_s = \frac{[C_{LiT(alloy)}]}{[P_{T_2(g)}]^{1/2}} = a_{Li(alloy)} K_s \quad (5)$$

where  $K'_S$  is a postulated Sievert's constant for tritium in the lithium-lead alloy.

Several assumptions are involved in the above derivation:

- (1) This model assumes that tritium dissolves in the alloy by association with the lithium. Any lead-tritium interaction is assumed to be negligible. This behavior is expected from periodic trends<sup>(19)</sup>; lithium is capable of forming hydride bonds while lead-hydrogen interactions are weak. A comparison of the hydrogen solubility in lithium and lead to that in other metals<sup>(4,10,20-22)</sup> (Fig. 3) shows that lithium has one of the highest hydrogen solubilities of any known metal while lead has one of the lowest hydrogen solubilities. It has also been observed that when small amounts of lithium (0.03 wt%) are added to pure lead, the amount of hydrogen absorbed is significantly increased.<sup>(5)</sup>
- (2) The manner in which the lead enters into the lead-lithium-tritium equilibrium is to chemically bond the lithium making it less available to interact with the tritium. The degree to which the lithium is available for bonding is related to the lithium activity ( $a_{Li}$ ) in Li-Pb.
- (3) The lithium activity is unaffected by ppm quantities of tritium.

Plots of the postulated Sievert's constant calculated from Eq. (5) are shown in Fig. 4 for deuterium in lithium-lead alloys. Also plotted are the experimental solubility data of Ihle et al.<sup>(18)</sup> and Veleckis<sup>(24)</sup>, and the data on the pure components. (Note in Fig. 4 the data are plotted such that the Sievert's constant is directly proportional to the solubility, rather than inversely as in Ihle's paper. Also, there is no attempt to plot the theoretical solubility in regions where solid phases occur.) It can be seen that the

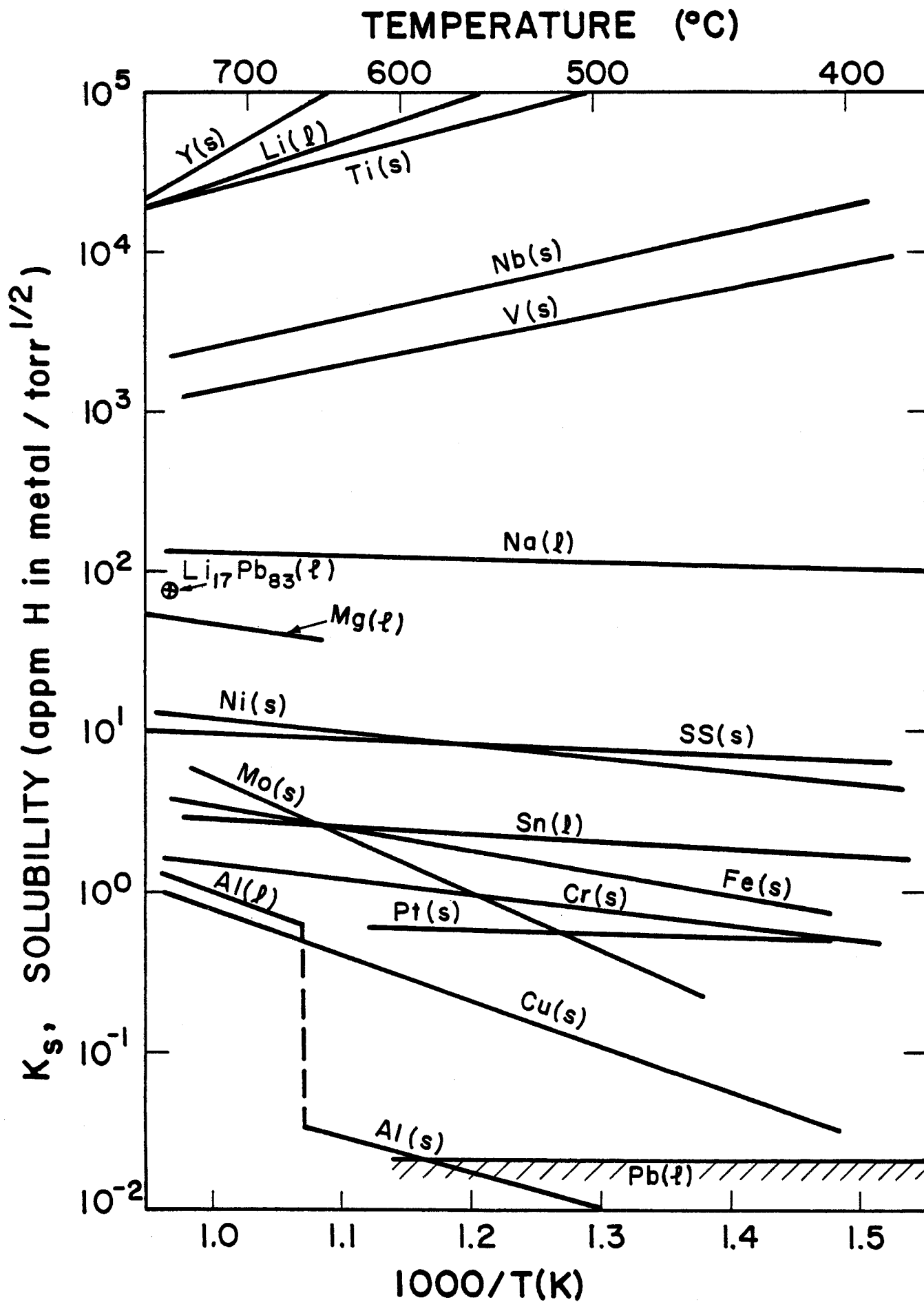


Figure 3. THE SOLUBILITY OF HYDROGEN IN SELECTED METALS AND ALLOYS AS A FUNCTION OF TEMPERATURE.

# SOLUBILITY OF DEUTERIUM IN LIQUID Li-Pb ALLOYS

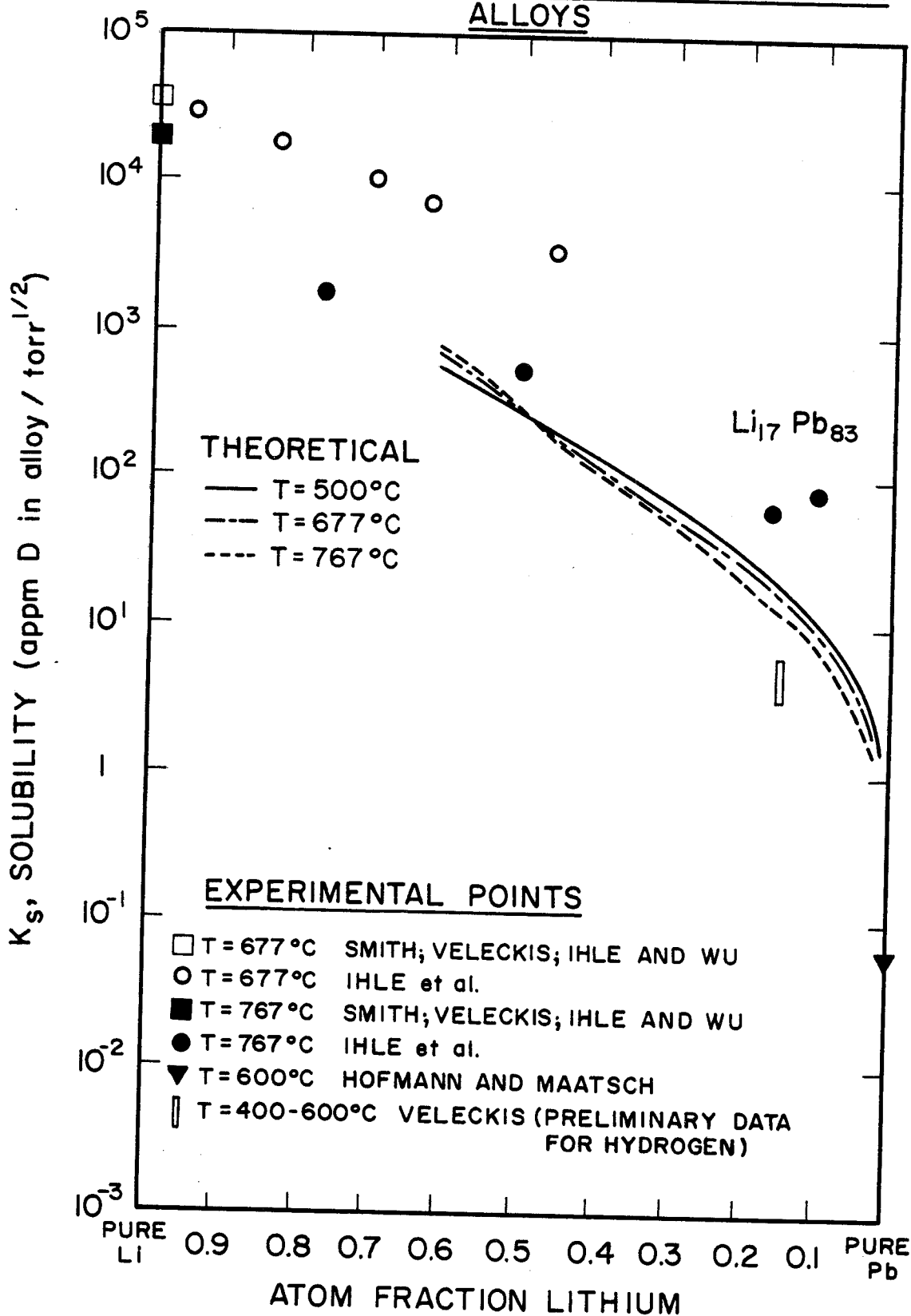


Figure 4

model predicts lower deuterium solubility in lithium-lead than that observed by Ihle et al.

The theoretical model also shows only a very slight temperature dependence. This occurs because  $K'_S$  is proportional both to the solubility of deuterium in pure lithium and to the activity of lithium in Li-Pb alloys (Eq. 4). These two effects nearly cancel one another since the solubility decreases with increasing temperature and the activity increases with increasing temperature. The temperature dependence observed in the work by Ihle et al. is much greater than has been observed for any other metal or alloy system and, therefore, does not appear credible. On the other hand, the theoretical model predicts only a slight temperature dependence which would be expected on examination of Fig. 2. Lithium dissolves hydrogen exothermically while metals with low hydrogen solubilities (such as lead) generally dissolve hydrogen endothermically, which probably leaves Li-Pb alloys in an intermediate category showing little temperature dependence. This invariance with temperature was used in both NUWMAK<sup>(1)</sup> and WITAMIR<sup>(2)</sup> as a basis for the estimation of tritium solubility. NUWMAK utilized the  $\text{Li}_{62}\text{Pb}_{38}$  eutectic as the breeding material and the tritium solubility was calculated using Eq. (5). WITAMIR utilized  $\text{Li}_{17}\text{Pb}_{83}$  as the breeding material and the tritium solubility was estimated by assuming the solubility value of deuterium in  $\text{Li}_{17}\text{Pb}_{83}$  obtained by Ihle et al. at 767°C to be valid. This value was then extrapolated to the temperature region of interest (329-500°C) by assuming that the solubility was independent of temperature.

In the absence of reliable experimental data, the model outlined in this paper, predicting a low solubility and slight temperature dependence, is felt

to be superior to both the extrapolation proposed in WITAMIR and to those proposed by others.<sup>(23)</sup>

To resolve the issue of hydrogen solubility in lithium-lead, E. Veleckis is presently conducting experiments.<sup>(24)</sup> Preliminary results on the  $\text{Li}_{17}\text{Pb}_{83}$  eutectic indicate a Sievert's constant of  $5.1 \pm 1.1$  appm H in alloy/torr<sup>1/2</sup> that is independent of temperature in the range 400-600°C. The solubility is slightly lower than predicted by the model (Fig. 4), but consistent with the prediction of temperature independence. The low solubility of tritium is favorable for lithium-lead fusion blanket designs, resulting in low tritium inventories and simplified tritium extraction schemes.

#### Acknowledgement

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