

KfK 3269
Dezember 1982

The Solubility of Hydrogen, Deuterium and Tritium in Liquid Lead-Lithium Alloys in the Temperature Region 500-1500 K

M. Hoch
Institut für Neutronenphysik und Reaktortechnik

Kernforschungszentrum Karlsruhe

KERNFORSCHUNGSZENTRUM KARLSRUHE

Institut für Neutronenphysik und Reaktortechnik

KfK 3269

The Solubility of Hydrogen, Deuterium and Tritium in
Liquid Lead-Lithium Alloys in the Temperature Region
500-1500 K

Michael Hoch⁺

⁺Department of Materials Science and Metallurgical
Engineering, University of Cincinnati, Ohio, USA

Kernforschungszentrum Karlsruhe GmbH, Karlsruhe

Als Manuskript vervielfältigt
Für diesen Bericht behalten wir uns alle Rechte vor

Kernforschungszentrum Karlsruhe GmbH
ISSN 0303-4003

THE SOLUBILITY OF HYDROGEN, DEUTERIUM AND TRITIUM IN LIQUID LEAD-LITHIUM ALLOYS IN THE TEMPERATURE REGION 500-1500 K

ABSTRACT

The solubility of H_2 , D_2 and T_2 in liquid Pb-Li alloys was calculated, using the thermodynamic data in the binary systems. In the temperature range of 500 to 1500K and composition range $.01 < x_{Li} < 0.6$, the solubility is almost temperature independent, and is not strongly influenced by the solubility of H_2 in pure lead. In the 17 at % Li alloy, at 500K the D_2 solubility is $\log K = 1.49 \pm .213$, K in appm. $\text{torr}^{-1/2}$, that of H_2 is $1.565 \pm .213$, and that of T_2 is $1.446 \pm .213$.

DIE LÖSLICHKEIT VON WASSERSTOFF, DEUTERIUM UND TRITIUM IN BLEI-LITHIUM-LEGIERUNGEN IM TEMPERATURBEREICH 500 BIS 1500K

ZUSAMMENFASSUNG

Die Löslichkeit von H_2 , D_2 und T_2 in flüssigen Pb-Li-Legierungen wird unter Benutzung der thermodynamischen Daten der linearen Systeme berechnet. Die Löslichkeit ist im Temperaturbereich von 500K bis 1500K und bei einem Li-Gehalt von 1 % bis 60 % von der Temperatur nahezu unabhängig. Sie wird von der Löslichkeit von H_2 in reinem Pb fast nicht beeinflusst. Für eine Legierung mit einem Li-Gehalt von 17 Atom-% ist der Wert der D_2 -Löslichkeit bei 500K $\log K = 1.49 \pm 0.213$. Die Einheit von K ist appm. $\text{Torr}^{-1/2}$. Der entsprechende Wert ist für H_2 1.565 ± 0.213 und der für T_2 1.446 ± 0.213 .

ABSTRACT

The solubility of H_2 , D_2 and T_2 in liquid Pb-Li alloys was calculated, using the thermodynamic data in the binary systems. In the temperature range of 500 to 1500K and composition range $.01 < x_{Li} < 0.6$, the solubility is almost temperature independent, and is not strongly influenced by the solubility of H_2 in pure lead. In the 17 at % Li alloy, at 500K the D_2 solubility is $\log K = 1.49 \pm .213$, K in appm. $\text{torr}^{-1/2}$, that of H_2 is $1.565 \pm .213$, and that of T_2 is $1.446 \pm .213$.

INTRODUCTION

The aim of this paper is to calculate, from the available thermodynamic data, the solubility of H_2 , D_2 and T_2 in Pb-Li alloys in the temperature range 500-1500 K. The aim more specifically is to obtain the Sievert's law constant K as a function of composition and temperature.

The approach is to calculate the thermodynamic functions from the available data in the binary systems Li-LiH (Li-LiD, Li-LiT), Li-Pb and Pb-H and calculate the thermodynamic function of the ternary Pb-Li-H (Pb-Li-D, Pb-Li-T) system.

We are interested in the pressure at low concentration of H_2 (D_2 and T_2) and over a large temperature range. The available thermodynamic data in the binary systems do not cover the temperature and composition range in question. We, therefore, use a thermodynamic model to calculate the various parameters which then permit a satisfactory extrapolation of the data to compositions and temperatures where no experimental data are available. The model approach has the advantage that a large number of experimental data from various authors using different methods are combined to determine the energy parameters.

The model we use is the model described by Hoch and Arpshofen [1] which is a quasichemical regular solution model similar to that one used by Guggenheim [3]. The approach by Hoch and Arpshofen [1] involves associates i.e., compounds in the solution of various complexities such as A_n , B_m where (A and B are the two species and n and m are their coefficients in the compound). The model provides various compounds in solution (such as A_3B , A_2B_2 and AB_3) and the relationship of the heat and free energy of formation of those compounds can be calculated from first principles i.e., the relation between the heat and free energy of formations of the various compounds obey a relatively simple formula. This permits us for one system i.e., the Pb-Li to describe the thermodynamic activity in terms of one constant, the interaction parameter Ω_0 . The model takes into account the deviation of the atomic distribution from randomness, and the changes in vibrational entropy in the system.

In the following calculations, free energies, heats and entropies are divided by R, the gas constant. Thus ΔH and ΔG are expressed in kK (kilo-Kelvins) and the entropy is dimensionless. To convert those numbers into calories, or joules, one has to multiply with R (the gas constant).

LI-LIH SYSTEM

The phase diagram of the Li-LiH system is shown in a schematic fashion by Hansen [4b] Fig. 1. At high temperatures we have a single liquid which disproportionates into two liquids, L_1 and L_2 at lower temperatures and below that at the monotectic temperature we have a transformation into a two phase region the liquid L_1 phase in equilibrium with solid LiH. As our interest is mainly and practically only in the liquid region, we will consider only the measurements carried out in the liquid region.

Our approach is to calculate from the phase boundary of the two liquid region ($L_1 + L_2$) in Figure 1, the thermodynamic functions of the system in the liquid phase i.e., the activity of Li and LiH as a function of composition and temperature. Then from the H_2 (and D_2 and T_2) pressures in the plateau region, i.e., in the region of the two liquid phases, we can obtain the free energy of formation of stoichiometric LiH and combining this with the equations for the activity of Li and LiH we obtain the Sievert's law constant. The advantage of this method is that it is possible to obtain the properties for H_2 , D_2 and T_2 , and also the fact that a number of data are available in the temperature and composition range question.

Phase boundary

Phase boundaries of the ($L_1 + L_2$) region, in the Li-LiH system are given by Veleckis [20], Smith [9], Heumann [5], and Shpilrain [12]; in the Li-LiD system by Veleckis [8], Smith [9], Heumann [5], and in the Li-LiT system by Heumann [5]. Plateau pressures in the Li-LiH system are given by Veleckis [20], Smith [9], Heumann [5], and Shpilrain [12] in the Li-LiD system by Veleckis [8], Smith [9] and Heumann [5], and in the Li-LiT system by Heumann [5]. Veleckis [7] measured the plateau pressures in all three systems.

Heumann [5] used only an enriched T_2 gas for his measurements. Smith [9] noted that the phase boundaries in the Li-LiH and Li-LiD system are identical.

Veleckis (6) noted that the plateau pressures were in the ratio

$$\frac{P_{D_2}}{P_{H_2}} = \sqrt{2}, \frac{P_{T_2}}{P_{D_2}} = \sqrt{3},$$

below the monotectic temperature in the two phase region Li(l) + LiH(s).

Table 1 contains the phase boundaries and plateau pressures of Veleckis [8, 20], Smith [9], Heumann [5] and Shpilrain [12]. The first column is the temperature, second and third the phase boundary x_1 and x_2 in LiH (resp. LiD and LiT) atom fractions, the fourth and fifth the interaction parameter calculated from Li, resp. LiH activities, the ninth the plateau pressure. The pressure for D_2 and T_2 are connected in the next column to H_2 pressures by dividing them by $\sqrt{2}$ and $\sqrt{3}$ resp. As Smith [9] had the same phase boundaries in the Li-LiH and Li-LiD systems, the plateau pressures are next to each other.

Interaction parameter.

Fig. 1 shows an asymmetric miscibility gap indicating repulsion, and 3 atom complexes [1]. The heat of mixing of a system as this is given by [1]

$$\Delta H_m = 3x^2y\Omega_1 \left(1 - x^2y \frac{C}{T} \Omega_1\right) + 3xy^2\Omega_2 \left(1 - xy^2 \frac{C}{T} \Omega_2\right) \quad (1)$$

x atom fraction of LiH (LiD or LiT)
y atom fraction of Li

$$C = \frac{2 \cdot n(n-1)}{z}$$

n number of atoms in complex, z: neighbors in liquid; n = 3, z = 10

We have also shown [1] that $\Omega_1 = 2 \Omega_2$, for simplicity reason $\Omega_2 = \Omega_0$.

Thus one obtains

$$\frac{\Delta H_m}{3} = \Omega_0 xy (1 + x) - \Omega_0^2 \frac{C}{T} x^2 y^2 (3x^2 - 2xy + 1) \quad (2)$$

by differentiation [1] we obtain the partial excess free energy of the x component $\overline{\Delta G}_x^{\text{ex}}$ and of the y component $\overline{\Delta G}_y^{\text{ex}}$

$$\frac{\overline{\Delta G}_x^{\text{ex}}}{3y^2} = \Omega_0 \left(1 + 2x \right) \left(1 - \frac{1.5T}{H_V} \right) + \Omega_0^2 \frac{C}{T} x \left(25x^3 - 28x^2 + 9x - 2 \right) \left(.5 - \frac{1.5T}{H_V} \right) \quad (3)$$

$$\frac{\overline{\Delta G}_y^{\text{ex}}}{3x^2} = 2\Omega_0 x \left(1 - \frac{1.5T}{H_V} \right) + \Omega_0^2 \frac{C}{T} y \left(-25x^3 + 23x^2 - 7x + 1 \right) \left(.5 - \frac{1.5T}{H_V} \right) \quad (4)$$

The ΔH_V enters into the vibrational entropy correction, and the error is negligible when using ΔH_V of Li for LiH.

From Eq. (3) we obtain an expression for the activity of LiH, and from Eq. (4) for Li.

For every author, at every temperature, at the 2 phase boundaries x_1 , and x_2 , the Li and LiH activities must be equal. Stating that

$T \ln x + \overline{\Delta G}_x^{\text{ex}}$ must be equal at x_1 and x_2 and

$T \ln y + \overline{\Delta G}_y^{\text{ex}}$ must be equal at x_1 and x_2

we calculate one Ω_0 from the Li and one from the LiH activity. Those are given in column 4 and 5 of Table 1. The values calculated for LiH are very constant, from Li show a trend, because at x_2 the Li concentration is very small.

Averaging the Ω_0 from LiH and LiD of Veleckis, Smith and Heumann et al, in Table 1, giving each author equal weight we obtain $\Omega_0 = .602 \pm .011$ kK.

The phase boundaries x_1 and x_2 given in Table 1, for Li-LiH, Li-LiD and Li-LiT are plotted in Fig. 2. They coincide (the Li-LiT of Heumann [5] being an exception, his T_2 gas contained large amount of D_2 and H_2). The average values of x_1 and x_2 are given in Table 2.

Plateau pressures

The plateau pressures given in Table 1 P_{H_2} and the converted P_{D_2} and P_{T_2} are plotted in Fig. 3. The measurements of Veleckis [7] are plotted in Fig. 4. The reason that Veleckis [7] measurements are plotted separately is, that there are so many points, it would overshadow the other authors data. P_{H_2} and the converted P_{D_2} and P_{T_2} data fall on a common line in both figures, and the line is

$$\ln P_{atm} = 14.85 - \frac{17.60 \cdot 10^3}{T} + 1/2 \ln u \pm .06 \quad (5)$$

where $u = 1$ for H_2 , $u = 2$ for D_2 and $u = 3$ for T_2 .

Free energy of formation of LiH. (LiD and LiT)

For the reaction



$$\Delta G^{\circ f} = - T \ln a_{LiH} + T \ln a_{Li} + 1/2 T \ln P \quad (7)$$

Using Eq. 3 and 4 we have

$$\begin{aligned}
 -T \ln a_{\text{LiH}} + T \ln a_{\text{Li}} &= T \ln \frac{y}{x} + 3 \left[\Omega_0 (3x^2 - 1) \left(1 - \frac{1.5T}{19.125} \right) \right. \\
 &\quad \left. + \Omega_0^2 \frac{C}{T} (30x^5 - 60x^4 + 40x^3 - 12x^2 + 2x) \left(.5 - \frac{1.5T}{19.125} \right) \right] \quad (8)
 \end{aligned}$$

To use for $\ln P$ in Eq. (7) the plateau pressure given in Eq. (5), Eq. (8) must be evaluated at various temperatures with the phase boundary x_1 and Ω_0 as given in Table 2. Because of the uncertainty in x_1 and that in Ω_0 , at each temperature we obtain 9 points, the best fit through those points is

$$(-T \ln a_{\text{LiH}} + T \ln a_{\text{Li}})_{\text{at } T, x_1} = .340 - .565T \pm (.033T) \text{ [kK]} \quad (9)$$

Combining Eq. 7 and 9

$$\Delta G_{\text{fLiH}(1)}^0 = -8.46 + 6.86T + \frac{1}{4} T \ln u \pm (.045T) \text{ [kK]} \quad (10)$$

To obtain K, Sieverts law constant, Eq. (10) and (8) are substituted in Eq. (7), $y \approx 1$, and x corresponds to the atom fraction of H (or D or T) in Eq.(8), $x \approx 0$, gives

$$1/2 \ln P \approx -\frac{6654}{T} + 6.718 + \frac{1}{4} \ln u + \ln x \pm .045 \text{ [atm}^{1/2}] \quad (11)$$

and

$$\ln K_{\text{Li}} = \frac{6654}{T} - 6.718 - \frac{1}{4} \ln u \pm .045 \text{ [atom fraction atm}^{-1/2}] \quad (12)$$

Using Eq. (9) and Eq. (8), x_1 can be calculated and through Eq. (3) x_2 can be obtained. These are given in Table 2 under calculated values.

To check our calculations, P_{D_2} at 973K (700°C) is calculated at $x=10^{-6}$ and at 10^{-1} , using Eq. (7), (8) and (10). We obtain $\log P_{D_2}$ (torr) = -9.07 at $x = 10^{-6}$ and $\log P_{D_2}$ (torr) = .915 at $x=.1$. These values are plotted in Fig. 5, which is taken from Veleckis [6], where the data of Veleckis [6], Ihle and Wu [11], McCrackem et al [10] and Smith [9] are compared. The agreement is excellent.

Our free energy of formation ΔG_f^0 of LiH calculated from Eq. 10 is 0.26 kcal more negative than that given by Janaf [19] (in 1967).

PB-H SYSTEM

The Pb-H system has been reviewed by Hansen (4a) and no significant new results seem to be available. If we take the high value given by Opie et al [13] the Sievert's law constant is given by

$$\ln K_{Pb}^1 = -3.66 - \frac{5540}{T} - \frac{1}{4} \ln u \left[K_{Pb}^1 \text{ in atom fraction} \cdot \text{atom}^{-1/2} \right] \quad (13)$$

The D_2 and T_2 behavior is assumed to be similar to the LiH system. At 600°C, Hofmann et al [14] found a 25 times smaller solubility than Opie et al [13]. If we pass a parallel line to Eq. 13 through the point of Hofmann et al [14], we obtain

$$\ln K_{Pb}^1 = -6.88 - \frac{5540}{T} - \frac{1}{4} \ln u \left[K_{Pb}^1 \text{ in atom fraction} \cdot \text{atm}^{-1/2} \right] \quad (14)$$

We are using Eq. (14) in our calculations. However, even at very low Li content in the ternary alloy Pb-Li-H, $x \approx .01$, Eq. (14) has very little influence on the total Sievert's law constant.

PB-LI SYSTEM

The thermodynamics of this system was discussed in detail by Hoch, Arpschofen and Predel [2]. Summarizing the results we have EMF measurements of Saboungi et al [18] at 770, 812, 869 and 932 K, a total of 110 points; also EMF measurements by Demidov et al [16] at 800 degrees K (10 pts), heat of mixing measurements by Predel and Oehme [15] at 1000 K (46 pts), and mass spectrometry data of Ihle, Neubert and Wu [17] at 750, 800 and 850 K. The system can be described as having complexes of 4 atoms and one single interaction parameter $\Omega_0 = -1.23 \pm .04$ kK. The data above 75 atomic % Li scattered significantly as the activity of Li is close to its atom fraction and small measurement errors introduce large errors in Ω_0 .

The heat of mixing of 4 atom complexes is given by [1]

$$\Delta H_m = 4x^3y\Omega_1 \left(1 - x^3y\Omega_1 \frac{C}{T}\right) + 6x^2y^2\Omega_2 \left(1 - x^2y^2\Omega_2 \frac{C}{T}\right) + 4xy^3\Omega_3 \left(1 - xy^3\Omega_3 \frac{C}{T}\right) \quad (15)$$

In 4 atom complexes (1) $\Omega_1 = 3 \quad \Omega_2 = 2 \quad \Omega_3 = \Omega_0$ we have

$$\frac{\Delta H_m}{4xy} = \Omega_0(1 + x + x^2) + xy\Omega_0^2 \frac{C}{T} (-16x^4 + 16x^3 - 12x^2 + 4x - 1) \quad (16)$$

where x is the at fraction of Li, y that of Pb, $C = \frac{2 \cdot n(n-1)}{z}$

n is the number of atoms in the complex, $n = 4$ and z is the coordination number in the liquid $z = 10$. Differentiating we obtain the excess partial free energy of Li and Pb

$$\frac{\overline{\Delta G}_x^{ex}}{4y^2} = \Omega_0 \left(1 + 2x + 3x^2\right) \left(1 - \frac{1.5T}{H_{vap}}\right) + x \frac{C}{T} \Omega_0^2 \left(112x^5 - 192x^4 + 140x^3 - 64x^2 + 15x - 2\right) \left(\frac{1}{2} - \frac{1.5T}{H_{vap}}\right) \quad (17)$$

$$\frac{\overline{\Delta G}_y}{4x^2} = \Omega_0 (3x^2) \left(1 - \frac{1.5T}{H_{\text{vap}}} \right) + y \frac{C}{T} \Omega_0^2 \left(112x^5 - 176x^4 + 124x^3 - 52x^2 + 11x - 1 \right) \left(\frac{1}{2} - \frac{1.5T}{H_{\text{vap}}} \right) \quad (18)$$

where ΔH_v are the heat of vaporization, ΔH_v (Li) = 19.125 kK, ΔH_v (Pb) = 23.7 kK [19].

We have one more measurement to obtain Ω_0 in the Pb-Li system: Veleckis et al [16] measured the H_2 pressure in the Pb-Li-H system, where 3 solid phases are in equilibrium; LiH and two Pb-Li alloys. The plateau pressures correspond to the various univariant equilibria (in their Figure VI). The plateau pressures can be expressed as a function of temperature in the various systems. Inspecting the Li-Pb phase diagram, [4a], one finds that at one moment the monovariant equilibria reach an invariant equilibrium where a liquid, and 3 solid phases (LiH(s) plus 2 Li-Pb alloys) are present. Extrapolating the hydrogen pressure curve to the temperature of the invariant point we obtain from Eq. (7) and (10) the activity of Li, a_{Li} . The activity of LiH $a_{LiH}(1)$ can be calculated from the heat of fusion of LiH, 2.718 kK [19], and the monotectic (equals the melting) point, 694°C. Eq. (17) permits then to calculate Ω_0 in the Pb-Li system. The calculations are carried out in Table 3. The agreement with the direct measurements is very good except for $x_{Li} = .825$, which is above .75, where scatter is always present.

TERNARY PB-LI-H, PB-LI-D AND PB-LI-T SYSTEMS

The solubility of H_2 (and D_2 , T_2) in liquid Pb-Li alloys can be expressed by the equation

$$K = K_{Li} a_{Li} + K_{Pb} \cdot a_{Pb} \quad (19)$$

where K_{Li} is given by Eq. (12), K_{Pb} by Eq. (14) and a_{Li} is calculated from Eq. (17) and a_{Pb} from Eq. (18).

Eq. (19) assumes, that a certain amount of H_2 is dissolved due to Li, another amount due to Pb, and the two are independent. It is seen in Table 4, that $K_{Pb}a_{Pb}$ does not contribute significantly even when $x_{Li} = .01$, this assumption is justified. Table 4 gives $\log K$ (atm torr^{-1/2}) of D_2 at three temperatures 500, 1000 and 1500, K as a function of the Li concentration. At 3 small Li concentrations, $\log K'$ and $\log K_0$ is also given, to show that the lead effect is negligible. For $\log K'$ Eq. (13) is used, for $\log K_0$ $K_{Pb} = 0$ is assumed. At 500°K, the values are for a supercooled liquid, as in the Pb-Li phase diagram the liquid is only the stable form around $x_{Li} = .17$. The data are also plotted in Fig. 6. In Eq. (19), a_{Li} is multiplied by K_{Li} , which is constant at a certain temperature. The variation of K with composition follows that of a_{Li} : It is 1 at $x_{Li} = 1$, decreases sharply at $x = .75$, and continues a moderate decrease to $x_{Li} = .01$. The combination of $K_{Li}a_{Li}$ is such, that K is independent of temperature when $.01 < x_{Li} < .6$.

The error in $\ln K_{Li}$, $\pm .045$ gives a factor of 1.046 in K_{Li} ; the error of $\pm .04$ in Ω_0 , gives a factor of 1.56 in a_{Li} at 500K, 1.20 at 1000K and 1.01 at 1500K, making the total error in $\log K \pm .213$ at 500K, $\pm .099$ at 1000K, $\pm .023$ at 1500K.

Closer inspection of the values of Ω_0 in the Pb-Li system [2] shows a possible trend in Ω_0 with composition. Using this variable Ω_0 , $\log K$ is again calculated and given in Table 5 and plotted in Fig. 7. The error in this case, may be somewhat smaller than with a constant Ω_0 . The difference between the calculations is small.

Finally, as most of the interest is with the alloy containing 17 at % Li, $x_{Li} = .17$, Table 6 contains the interpolated values from Tables 4 and 5.

K is independent of Temperature when $0.05 < x < 0.6$. Table 7 contains the average value of K from table 4 and 5.

REFERENCES

1. Hoch, M. and Arpshofen, I., Über ein modifiziertes Assoziatmodell zur Berechnung der thermodynamischen Zustandsfunktionen flüssiger Legierungen, Z. Metallk., to be published.
2. Hoch, M. and Arpshofen, I., Predel, B., Anwendung eines modifizierten Assoziatmodells auf binäre und ternäre flüssige Legierungen, Z. Metallk., to be published.
3. Guggenheim, E.A., Mixtures, Oxford, Clarendon Press, 1952.
- 4a. Hansen, Max and Anderko, Kurt, Constitution of Binary Alloys. 2nd ed. McGraw-Hill Book Company, New York, 1958.
- 4b. Elliott, Rodney P., Constitution of Binary Alloys, First Supplement, McGraw-Hill Book Company, New York.
- 4c. Shunk, Francis A., Constitution of Binary Alloys, Second Supplement, McGraw-Hill Book Company, New York.
5. Heumann, F.K, Salmon, O.N., US. AEC, KAPL-1677 (1956).
6. Veleckis, E., Yonko, R.M. and Maroni, V.A., The Current Status of Fusion Reactor Blanket Thermodynamics, Proceedings of Thermodynamics of Nuclear Materials 1979, Vol. II, 3-25, International Atomic Energy Agency, Vienna, 1980.
7. Veleckis, E., Journal of Nuclear Materials, Vol. 79, 20-27 (1979).
8. Veleckis, E., Journal of Physical Chemistry, Vol. 81, 526-531 (1977).
9. Smith, F.J., Lan, J.F., Begun, G.M. and La Gamma de Batistoni, A.M., Journal Inorganic Chemistry, Vol. 41, 1001-1009 (1979).
10. McCracken, G.M., Goodall, D.H.J. and Long, G., The Extraction of Tritium from Liquid Lithium, IAEA Workshop on Fusion Reactor Design Problems, Culham, U.K. (1974).
11. Ihle, H.R. and Wu, C.H., Proc. 8th Symp. on Fusion Technology, Noordwijkerhout, The Netherlands, EUR-5182C, 787 (1974).
12. Shpilrain, E.E., Yakimovich and Sheresheskii, V.A., Teplofiz. Vys. Temp. 15, 661 (1977).
13. Opie, W.R. and Grant, N.J., Trans. AIME, 191, 244-245, (1951).
14. Hoffman, W. and Maatsch, J., Z. Metallkunde, 47, 89-95 (1956) correction on p. 528.

15. Predel, B. and Oehme, G., Z. Metallk. Vol. 70, 456, (1979).
16. Demidov, A.I, Mozachevskij and Lerasimenko, L.N., Electrochimija, Vol. 9, 848 (1973).
17. Ihle, H.R., Neubert, A. and Wu, C.H., "The activity of Lithium, and the Solubility of Deuterium in Lithium Lead Alloys", Proc. 10th Symp. Fusion Techn., Padova, Italy, 639 (1978).
18. Saboungi, M.L. and Blander, M., J. Chem. Phys. Vol. 68, 1375 (1978).
19. JANAF Thermochemical Tables, U.S. Dept. of Commerce, NSRDS-NBS37 (1971).
20. Veleckis, E., van Deventer, E.H. and Blander, M., J. Phys. Chem. Vol. 78, 1933-1940 (1974).

Table 1. Phase boundaries x_1 , x_2 and interaction parameter
in the liquid Li-LiH, Li-LiD and Li-LiT systems

System Li-LiH						
Reference	Veleckis (20)				Plateau pressures	
Temp. K	x_1	x_2	Ω_0 Li kK	Ω_0 LiH kK	P_{H_2} atm	P_{H_2} converted
983	.246	.984	.751	.617	.0506	
1032	.292	.971	.706	.616	.116	
1076	.332	.957	.679	.609	.225	
1120	.386	.923	.635	.600	.433	
1151	.418	.888	.616	.599	.658	
1176	.447	.855	.607	.597	.867	
System Li-LiD						
	Veleckis (8)				P_{D_2}	
978	.228	.980	.718	.634	.0645	.0456
1029	.280	.972	.706	.618	.152	.108
1078	.332	.953	.669	.609	.321	.227
1113	.377	.931	.644	.602	.527	.372
1144	.411	.905	.627	.601	.795	.562
System Li-LiH						
	Heumann, Salmon (5)				P_{H_2}	
973	.26	.96	.624	.594	.0349	
998					.0672	
1002					.0693	
1023	.30	.94	.609	.590		
1029					.116	
1047					.144	
1058					.173	
1073	.35	.92	.606	.587		
1077					.236	
1123	.405	.89	.602	.588		
1173	.47	.865	.610	.595		
1223	.55	.83	.619	.609		

					P_{D_2} atm	
973	.28	.94	.579	.573	.0592	.0419
1023	.325	.92	.578	.570	.118	.0837
1073	.38	.90	.583	.570	.333	.235
1123	.445	.875	.589	.574		
1173	.53	.825	.589	.581		
1223	.64	.735	.596	.595		

					P_{T_2} atm	
973	.31	.91	.541	.547	.0665	.0384
1001					.117	.0674
1023	.365	.88	.542	.544		
1028					.181	.105
1039					.196	.113
1044					.231	.133
1073	.43	.85	.549	.545		
1074					.345	.199
1123	.525	.80	.554	.550		

Smith (9)

					P_{H_2}	P_{D_2} atm	P_{H_2} atm converted
973	.24	.98	.713	.618	.0368	.0605	.0428
1023	.28	.97	.693	.613	.0974	.151	.107
1073	.33	.96	.689	.609	.217	.33	.236
1123	.46	.92	.633	.600	.447	.607	.429

Shpilrain (12)

1042	.32	.146
1015		.093
1088		.306
1160		.820
1196		1.281

Table 2. Summary of Data on the systems Li-LiH, Li-LiD and Li-LiT

T °K	$L_1 + L_2$ phase boundary			
	x_1	x_2	x_1 calc	x_2
973	.25 ± .015	.973 ± .015	.259	.955
1023	.292 ± .016	.958 ± .019		
1073	.345 ± .016	.942 ± .021	.339	.920
1123	.403 ± .017	.910 ± 0.18		
1173	.471 ± .022	.848 ± .016	.483	.860

Interaction parameter $\Omega_0 = .602 \pm .011$ kK

Free energy of formation ΔG_f^0 of LiH, LiD and LiT(l)

$$\Delta G_f^0 = -8.46 + 6.86 T + 1/4 T \ln u \pm (0.45T) \text{ in kK}$$

$u = 1$ for H, 2 for D, 3 for T

Sieverts law constant

$$\ln K = \frac{6654}{T} - 6.718 - \frac{1}{4} \ln u \pm .045 \text{ [}^{-K} \text{ in atom fraction}^{-1/2}]$$

Plateau pressure

$$\ln P_{(\text{atm})} = 14.85 - \frac{17.6 \cdot 10^3}{T} + \frac{1}{2} \ln u \pm .06$$

Table 3 Interaction parameter Ω_0 in the Li-Pb (l) system from Hydrogen pressure measurements in the 3 solid phase region of Veleckis et al [6]

<u>Systems</u>	$\ln p^{1/2}$ (atm ^{1/2})	Univariant Equilibrium			a_{LiH} (l)	a_{Li} (l)	Ω_0 kK
		Comp. liquid at fr. Li	Temp. K	$p^{1/2}$ atm			
LiH, Li ₄ Pb, Li ₇ Pb ₂	$8.91 - 8.65 \cdot 10^3 T^{-1}$.825	923	.630	1.14	.172	-2.07
LiH, Li ₇ Pb ₂ , Li ₃ Pb	$9.40 - 8.226 \cdot 10^3 T^{-1}$.715	931	1.76	1.11	.0652	-1.21
LiH, Li ₃ Pb, Li ₈ Pb ₃	$8.584 - 7.2618 \cdot 10^3 T^{-1}$.700	915	1.91	1.17	.0542	-1.17

Table 4 Solubility of D₂ in Pb-Li alloyslog K in (appm in alloy·torr^{-1/2}), $\Omega_0 = -1.23 \pm .04$ kK

x_{Li}	500K			1000K			1500K		
	K	K'	K°	K	K'	K°	K	K'	K°
0	-3.311	-1.912		-.907	0.491		-.105	1.293	
.01	1.012	1.012	1.012	.458	.764	.439	.389	1.324	.223
.05	1.210	1.193	1.193	1.025	1.127	1.020	.910	1.416	.874
.1	1.297	1.280	1.279	1.278	1.334	1.275	1.173	1.504	1.158
.15	1.45	1.433	1.432	1.456	1.492	1.454	1.347		
.2	1.595			1.601			1.483	1.658	1.48
.3	1.757			1.832			1.702		
.4	1.823			2.041			1.903		
.5	2.043			2.301			2.127		
.6	2.766			2.697			2.409		
.7	4.212			3.262			2.758		
.8	6.052			3.900			3.127		
.9	7.233			4.353			3.400		
1:0	7.346			4.457			3.493		

Error $\pm .213$ $\pm .099$ $\pm .023$ For H₂ all values of log K .075 more positiveFor T₂ all values of log K .044 more negative

Table 5 Solubility of Deuterium in Pb-Li alloys

K in (appm \cdot torr $^{-1/2}$)

x_{Li}	$-\Omega_0$ K	log K		
		500	1000	1500K
0		-3.310	-.907	-.105
.01	1.35	.567	.266	.306
.05	1.33	.736	.839	.813
.1	1.30	.934	1.141	1.101
.15	1.29	1.133	1.339	1.285
.2	1.27	1.374	1.522	1.443
.3	1.22	1.791	1.851	1.721
.4	1.17	2.137	2.158	1.975
.5	1.13	2.594	2.490	2.235
.6	1.14	3.217	2.843	2.490
.7	1.17	4.411	3.328	2.798
.8	1.20	6.075	3.913	3.141
.9	1.24	7.275	4.353	3.405
1		7.329	4.457	3.50

Error \pm .116 \pm .059 \pm .021

For H₂ add .075

For D₂ subtract .044

Table 6 Solubility of D₂, H₂ and T₂ in Li-Pb alloysat $x_{Li} = .17$ K in $\text{appm} \cdot \text{torr}^{-1/2}$

Ω_0 kK	500K	log K 1000K	1500K
$-1.23 \pm .04$	$1.49 \pm .213$	$1.514 \pm .099$	$1.406 \pm .023$
-1.28	$1.229 \pm .116$	$1.412 \pm .059$	$1.348 \pm .021$

For H₂ add .075For T₂ subtract .044

Table 7 Solubility of D_2 , H_2 and T_2 in Li-Pb alloys Average of Temperature (500, 1000, 1500 K) and Ω_0

x_{Li}	D_2	
	K in $\text{appm} \cdot \text{torr}^{-1/2}$	
	Log K	
.05	.922	$\pm .172$
.10	1.154	$\pm .132$
.15	1.335	$\pm .119$
.2	1.503	$\pm .070$
.3	1.776	$\pm .049$
.4	2.006	$\pm .132$
.5	2.298	$\pm .211$
.6	2.737	$\pm .205$

When $\alpha_{Li} > .6$, the curves at various temperatures diverge. The above given errors represent only the error in the calculated values. For the errors in measurements (or the $2 \Omega_0$'s) ± 116 at 500 K, ± 0.59 at 1000 K and $.021$ at 1500^0 K have to be added.

For H_2 add .075

For T_2 subtract .044

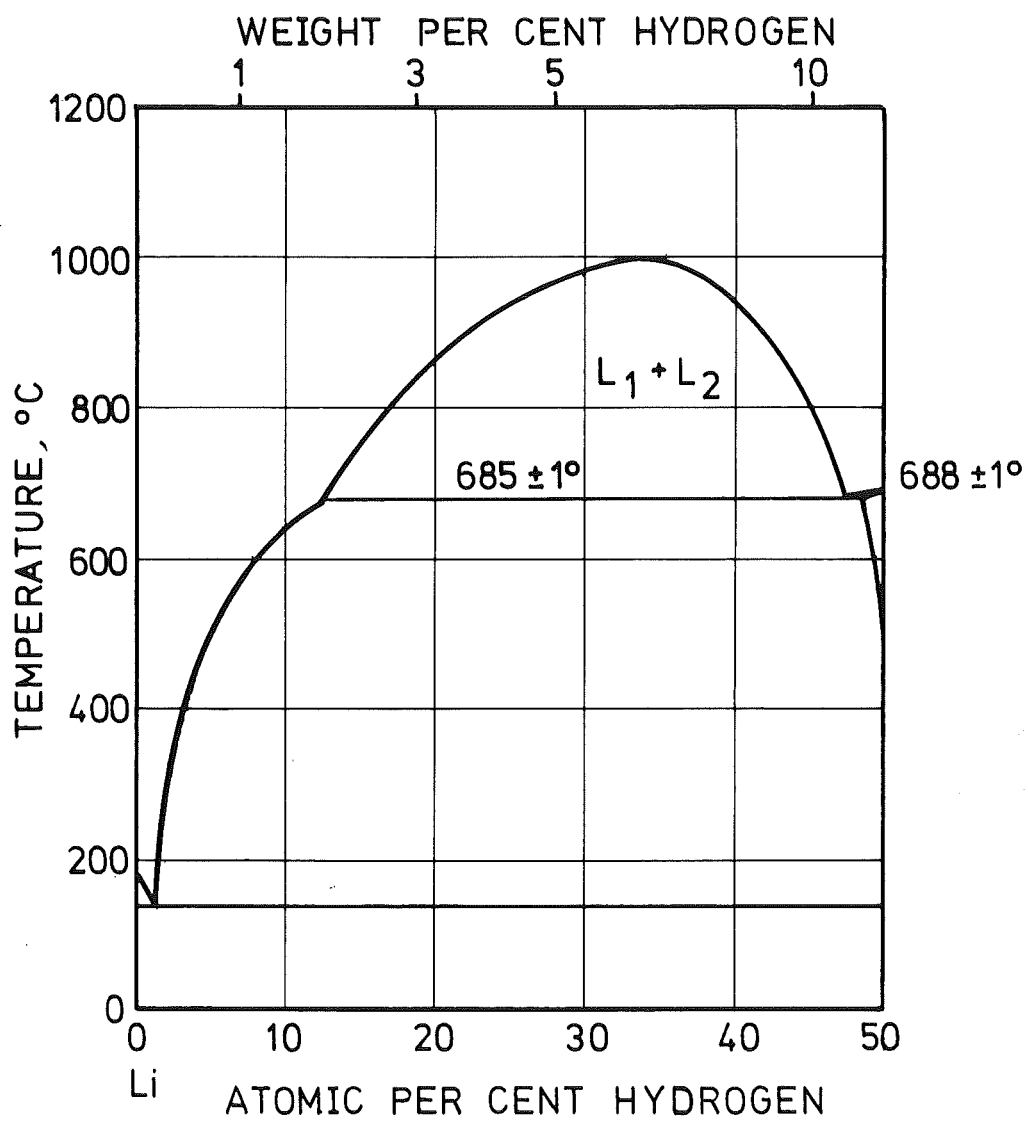


Fig. 1 Li - LiH system

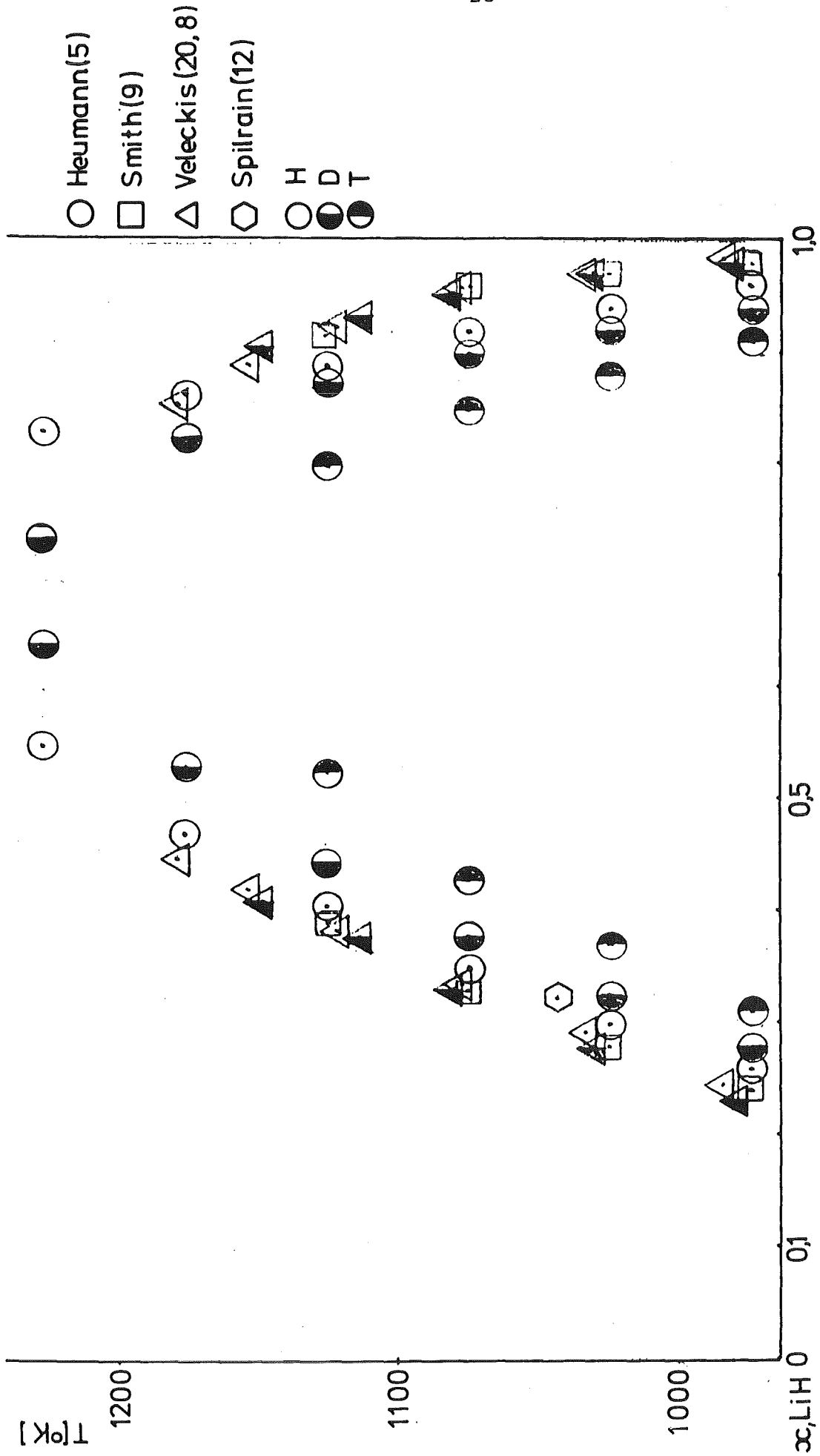


Fig.2 (L_1+L_2) phase boundaries

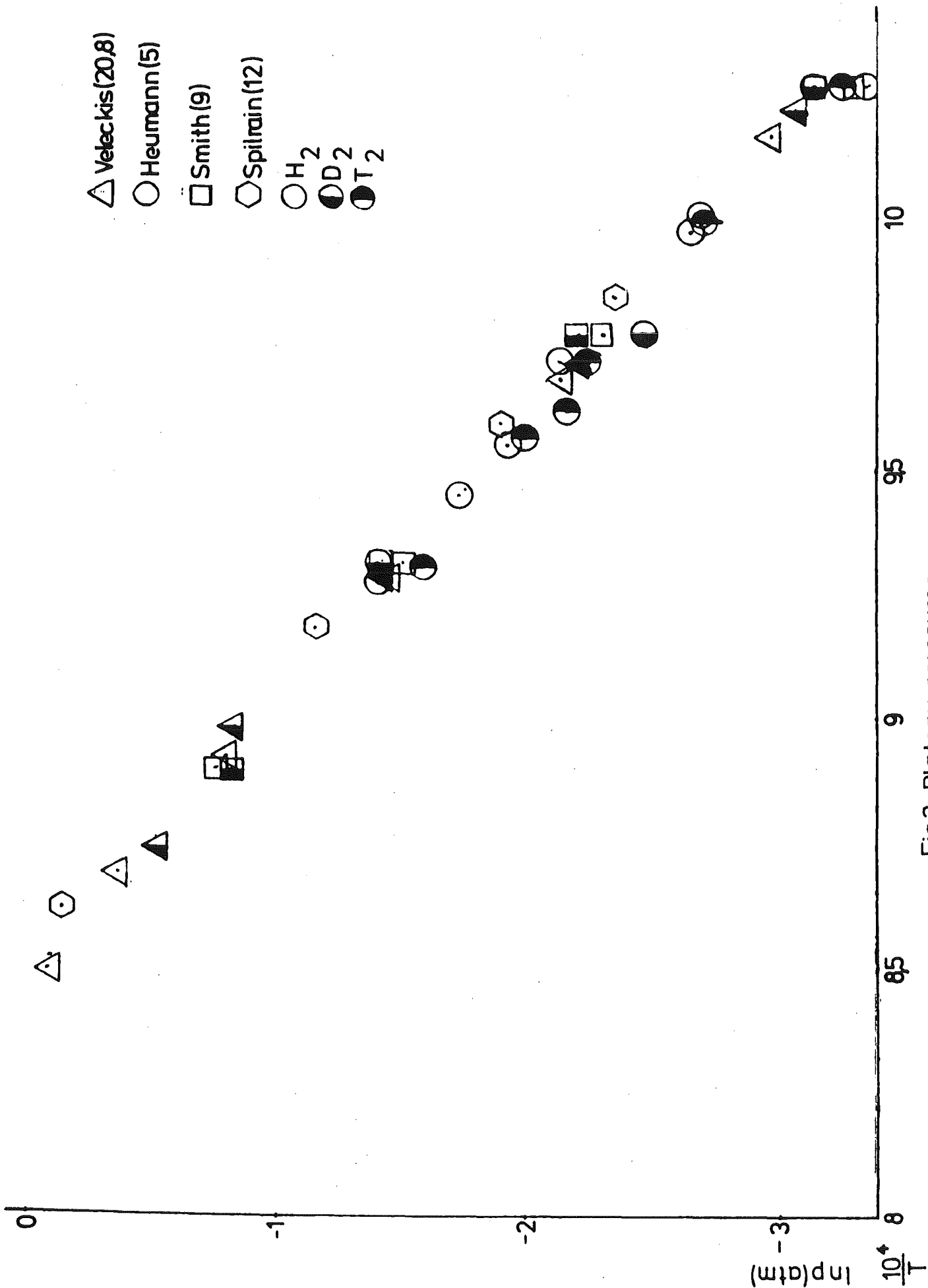


Fig.3 Plateau pressures

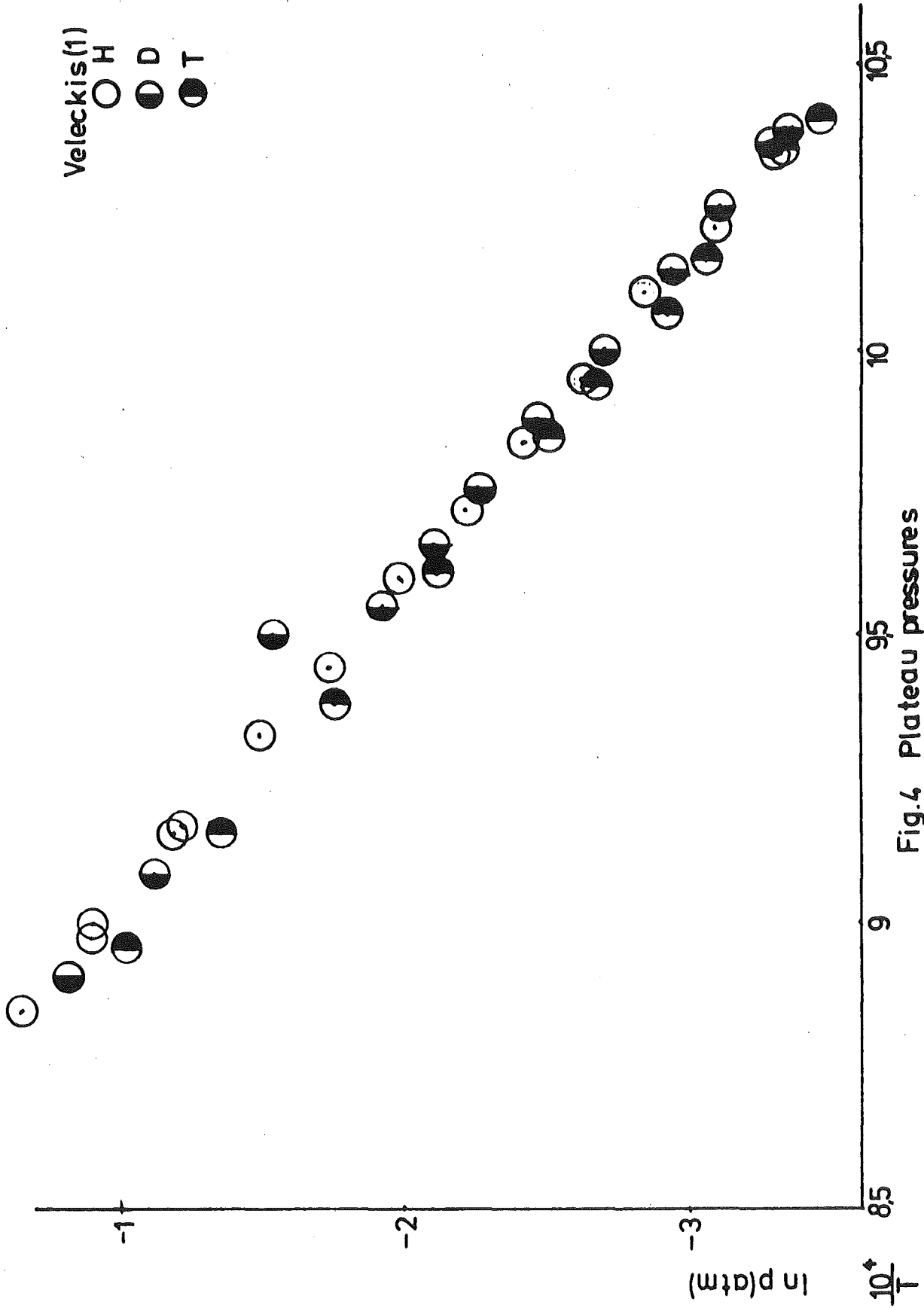


Fig.4 Plateau pressures

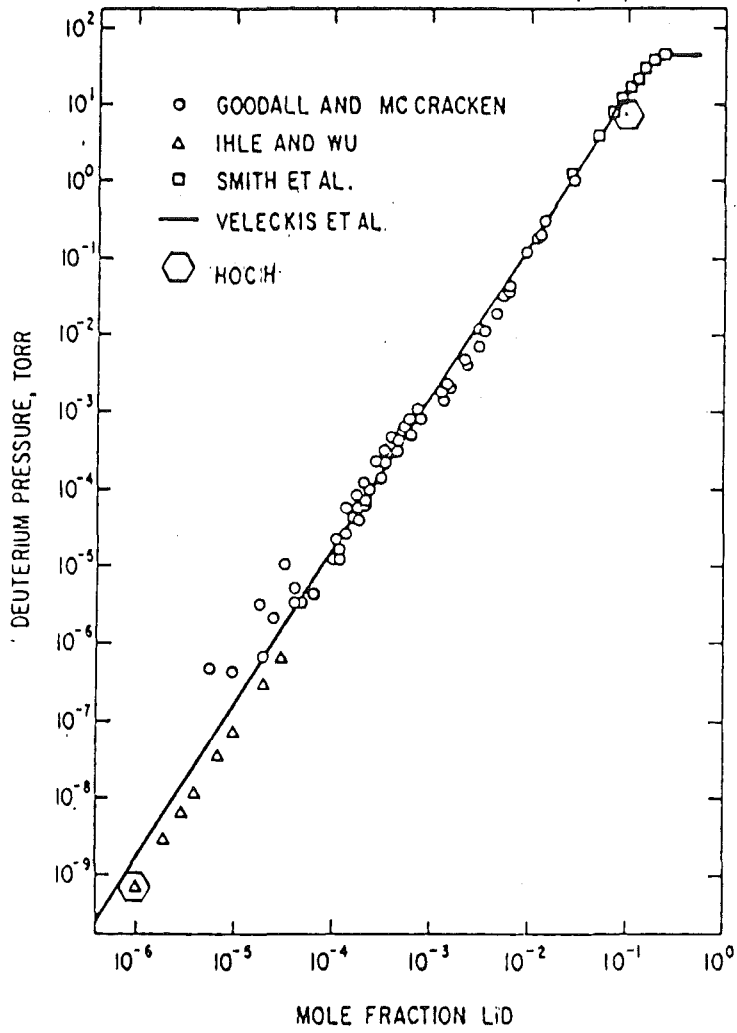


Fig.5 Comparison of the Calculated P vs. N Isotherm with the Literature Data at 700°C for the Li-LiD System.

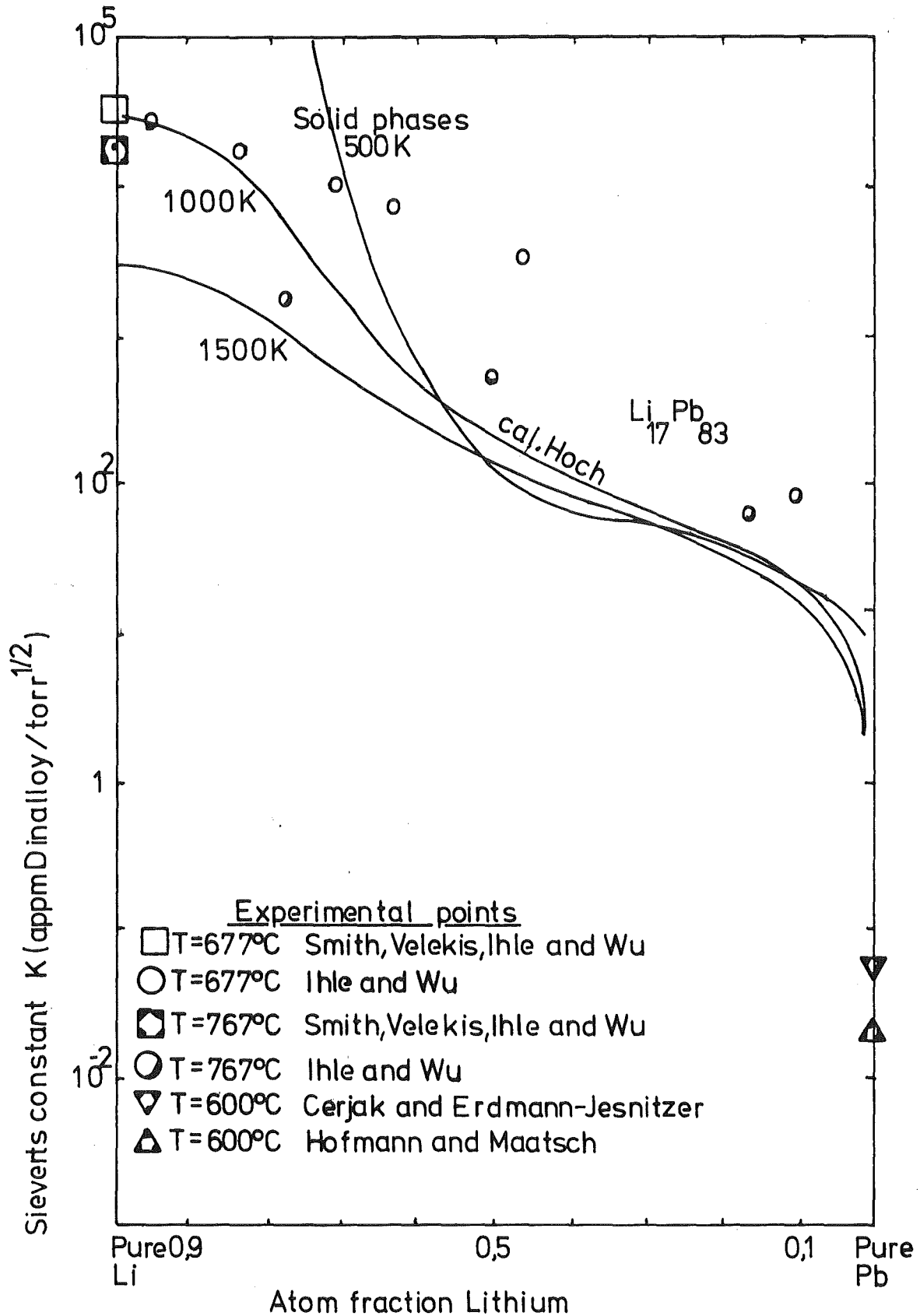


Fig.6 SOLUBILITY OF DEUTERIUM IN LIQUID Li-Pb ALLOYS FOR $\Omega = -1,23 \text{ kK}$

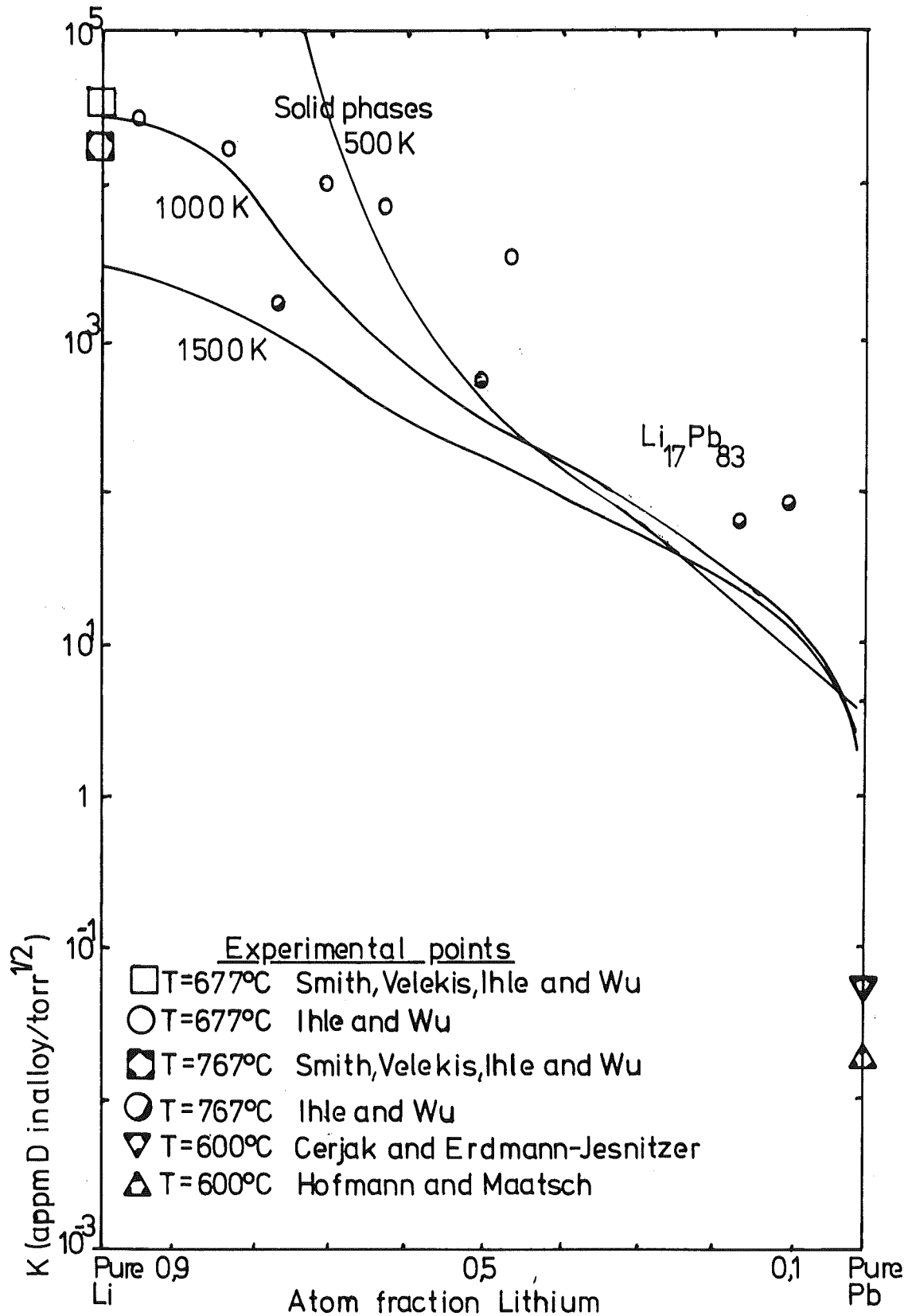


Fig.7 SOLUBILITY OF DEUTERIUM IN LIQUID LI-Pb ALLOYS FOR VARIABLE Ω_0