Table II. Vapor Pressures (Pascals) for Biphenyl, 4-Chlorobiphenyl, 2,2′,3,3′,5,5′,6,6′-Octachlorobiphenyl, and Decachlorobiphenyl at 25.0 °C[a]

compd	this work	lit. values
biphenyl	1.19 ± 0.03	1.03,[b] 1.29,[c] 0.579,[d] 0.969[e]
4-chlorobiphenyl	0.175 ± 0.006	0.61[f]
2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl	$(2.90 \pm 0.20) \times 10^{-5}$	
decachlorobiphenyl	$(5.30 \pm 0.31) \times 10^{-8}$	

[a] All values are extrapolated or interpolated from log vapor pressure vs. $1/T$ relationship. The uncertainty is the standard deviation determined from the average of the ratio of the standard deviation to the mean for each compound. [b] Reference *5*. [c] Reference *6*. [d] Reference *7*. [e] Reference *8*. [f] Reference *9*. This value was calculated by extrapolating from liquid vapor pressures and then making the melting point correction.

al. (*1*) using polyaromatic hydrocarbons. We have checked the validity of this method and of our experimental apparatus by using biphenyl as a test analyte. Vapor pressures and enthalpies of sublimation determined in this investigation for biphenyl are in good agreement with the published experimental values (Table II). Also, there is fair agreement between the experimental value from this investigation and the calculated vapor pressure for 4-chlorobiphenyl.

The total uncertainty in the measured vapor pressures (Table I) was estimated by performing a propagation of error analysis on the method of Thomson (*4*) with estimated maximum errors. The uncertainty was estimated to be less than 6.1%. The largest portions of the uncertainty were attributed to the actual quantification of the analyte (ca. 75%), to the estimation of the partial pressure of the water vapor in the inverted volumetric flask (ca. 22%), and to the temperature of the inverted volumetric flask (ca. 3%). The uncertainties attributed to the other temperatures and pressures were small.

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Registry No. Biphenyl, 92-52-4; 4-chlorobiphenyl, 2051-62-9; 2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl, 2136-99-4; decachlorobiphenyl, 2051-24-3.

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Solubility of Hydrogen in the Molten $Li_{17}Pb_{83}$ Alloy

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The equilibrium $H_2 \rightleftarrows 2H$ (dissolved) in a liquid $Li_{17}Pb_{83}$ alloy was studied at various temperatures in order to obtain the thermodynamic data required for the use of the alloy as a blanket material of fusion reactors. It is found that the system $Li_{17}Pb_{83}$/H is characterized by a very small value of $X_H/P_{H_2}^{1/2}$ ratio at infinite dilution and by strong deviations from the ideal behavior as the concentration of hydrogen rises in the alloy. An empirical equation, which correlates the activity coefficients and the concentration of hydrogen in the alloy, is proposed.

Introduction

During the last few years many studies have been carried out on the properties of the Li/Pb alloy, due to their increasing scientific interest.

It has been pointed out that these alloys belong to a particular class that exhibits unusual properties due to the partial electron transfer from one component to another producing an ionic species.

Many studies have confirmed the hypothesis that saltlike characteristics, which derive from the partial localizing of electrons on the Pb atoms to form lead anions, are particularly pronounced in the stoichiometric composition Li_4Pb. However, strong deviations from ideal behavior, short-range order in the liquid and solid states, and a preferred heterocoordination for nearest neighbors show themselves in alloys of all compositions (*1-4*).

Besides being of basic scientific interest, the study of these systems' behavior is of particular interest because they have been proposed as a potential alternative candidate for thermonuclear blanket material (*5*, *6*). This happened because some of their properties have advantages over other materials proposed: low tritium solubility, a good tritium breeding ratio, high blanket energy multiplication, and relatively good chemical stability at elevated temperatures.

In order to use these alloys as blanket material it is necessary therefore to study the behavior of the ternary system Li/Pb/hydrogen and its isotopes. This study can be particularly interesting because of the complex interactions which can develop in this system. Hydrogen, in fact, shows entirely different behavior with the two components of the alloy. lithium is a metal in which hydrogen presents the highest solubility value (*7-10*) and it forms one stable stoichiometric hybrid. On the

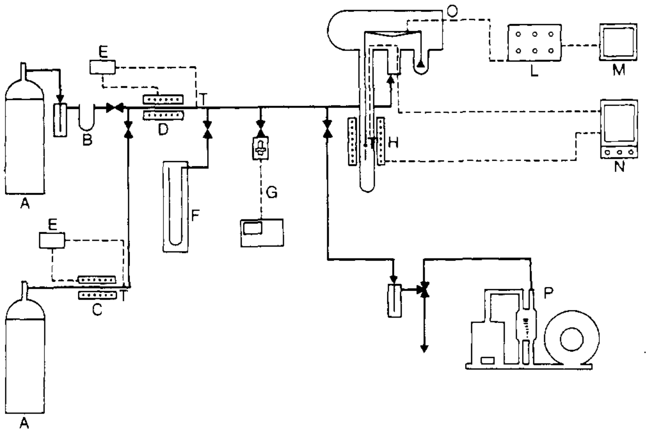

Figure 1. Experimental setup: (A) hydrogen and argon cylinder, (B) argon cleaning system, (C) hot titanium sponge, (D) preheater, (E) temperature control, (F) manometer, (G) Penning gauge, (H) furance, (I) sample, (L) controls for electrobalance, (M) weight recorder, (N) PDI temperature control, (O) electrobalance, (P) high-vacuum pump system, (T) thermocouples.

other hand, lead has only weak interactions with hydrogen (*11*, *12*).

Even though, recently, some studies have been published (*13*–*15*), there are still only limited data about hydrogen and its isotopes' solubility in Li/Pb alloys. For this reason we have carried out some experimental work to obtain hydrogen absorption isotherms over a wide pressure range in a Li/Pb alloy of eutectic composition.

Such an alloy was chosen because it is particularly attractive as a thermonuclear reactor blanket material because of its low melting point, which permits the alloy to be utilized in the liquid state at relatively low temperatures.

Experimental Section

Materials. The eutectic $Li_{17}Pb_{83}$ was prepared in the laboratory of the Material Division at the JRC of Ispra and its composition was determined by an analytical examination and by its melting point.

The hydrogen, pure at 99.9999%, was further purified by passing through a hot titanium sponge; the argon, pure at 99.999%, by bubbling in a liquid Na/K alloy.

Apparatus and Procedures. The eutectic samples, whose weights were about 300 mg, were put in a cylindrical stainless steel container of 0.5-cm diameter and depth. This operation was carried out under argon atmosphere in a drybox and the container with the sample inside was kept under inert gas and suspended from an electrobalance (CAHN RG Model with a sensibility of 10^{-7} g) by a Ni–Cr wire.

The pressure was reduced to 10^{-7} torr for 12 h before determining the zero position. The hydrogen was introduced until the desired pressure was obtained. The temperature was increased to a prefixed value. The run finished when the weight variation, which was continually recorded, was constant.

Before any determination, a preliminary run (without the sample) was carried out in order to correct the value of the final weight.

The experimental apparatus is shown in Figure 1.

At each pressure 10 runs were carried out and the average value was calculated. The values that we obtained are shown in Table I with the maximum deviation calculated for each series of runs.

Results and Discussion

The adsorption isotherms obtained for hydrogen in the $Li_{17}Pb_{83}$ alloy at temperatures of 350, 400, and 500 °C are shown in Figure 2. The isotherms do not show a plateau in the pressure range examined. This indicates that the adsorption of hydrogen by the examined alloy occurs in homogeneous phase, at least at pressures less than 1 atm. This observation is consistent with the one which emerges from Veleckis's (*16*) studies of the Li/Pb/H system. This author has pointed out that the large difference in reactivity of the two metal components of the alloys in regard to hydrogen could cause the separation of one phase constituted by pure Li/H when the Li/Pb alloys are subjected to the pressure of hydrogen. However, in order that this phase separation occurs in an alloy at small lithium concentration, very high pressures are necessary because of the strong decrease in lithium activity as the concentration of Pb rises in the alloy.

Table I. Experimental Average Values at Several Pressures and the Maximum Deviation

P_{H_2}, atm	10^2X_H, mol of H/mol of alloy	$10^2\epsilon^a$	P_{H_2}, atm	10^2X_H, mol of H/mol of alloy	$10^2\epsilon^a$
	T = 523 K				
0.178	0.62	0.02	0.640	2.40	0.04
0.202	0.81	0.02	0.788	3.10	0.03
0.270	1.32	0.04	0.919	3.40	0.03
0.300	1.66	0.05	0.998	3.20	0.05
0.311	1.83	0.04	1.00	3.54	0.02
0.350	2.04	0.05		T = 773 K	
0.591	2.95	0.05	0.298	0.60	0.02
0.788	3.67	0.04	0.389	0.96	0.02
0.920	4.09	0.03	0.511	1.38	0.02
	T = 673 K		0.780	1.65	0.01
0.260	0.62	0.02	0.850	2.10	0.01
0.343	1.10	0.03	0.920	2.59	0.03
0.403	1.32	0.04	1.00	2.89	0.02
0.490	1.93	0.03			

[a] Maximum deviation.

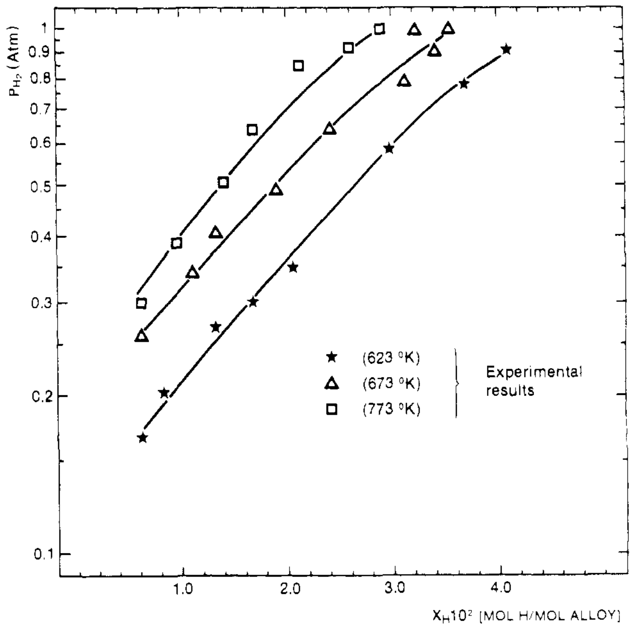

Figure 2. Absorption isotherms at three temperatures.

The equilibrium condition of the reaction

$$^1/_2H_2(gas) \rightleftharpoons H(alloy) \tag{1}$$

can be written as

$$P_{H_2}^{1/2} = a_H = N_H\gamma_H \tag{2}$$

where a_H is the activity, γ_H is the activity coefficient, and N_H is the atom fraction of the hydrogen dissolved in the alloy, if the biatomic pure gas at pressure of 1 atm is taken to be the

Table II. Values of the Constants of Eq 6

T, K	a_0	$10^{-3}a_1$	$10^{-2}b_1$	$10^{-3}\gamma_H^\circ$ ($Li_{17}Pb_{83}$), $atm^{1/2}/X_H$
623	8.29	1.27	4.39	4.0
673	8.40	1.53	4.94	4.4
773	8.19	1.26	3.99	3.6

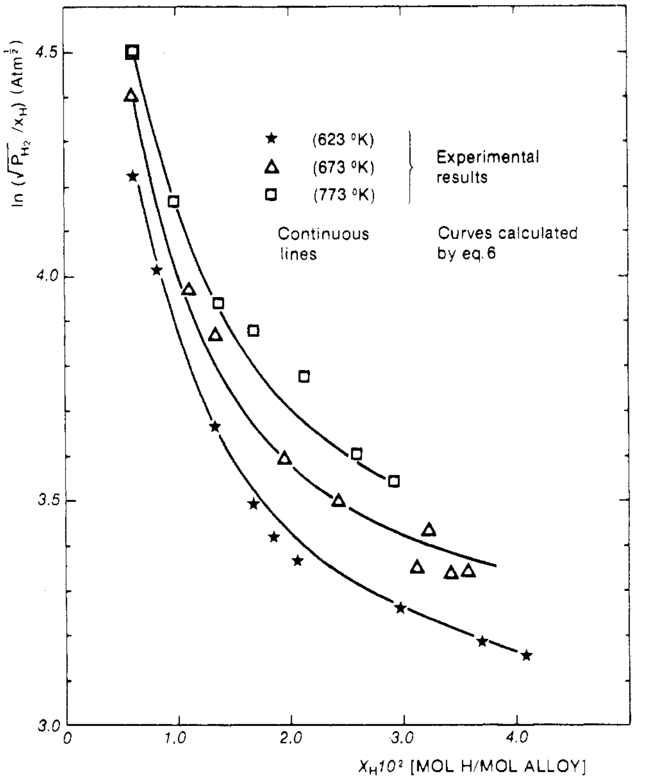

Figure 3. Experimental values and calculated behavior of ln ($P_{H_2}^{1/2}/X_H$) vs. hydrogen concentration at three temperatures.

reference state for the gaseous solute (*17*). A different reference state (i.e., ideal dilute solution) can also be chosen. In this case, the equilibrium conditions are given by the reaction

$$P_{H_2}^{1/2}/K_s = a_H = N_H\gamma_H \qquad (3)$$

where K_s represents Sievert's constant.

At the very low hydrogen concentrations used in this study, N_H becomes practically equal to the atomic ratio, X_H ($X_H = n_H/n_{Li_{17}Pb_{83}}$), and eq 2 can be written as

$$\gamma_H = P_{H_2}^{1/2}/X_H \qquad (4)$$

The curves of the experimental behavior of the ln ($P_{H_2}^{1/2}/X_H$) vs. X_H for the H/$Li_{17}Pb_{83}$ system were approximated for "best fit" by the ratio of the two polynomials (*18*).

$$\ln (P_{H_2}^{1/2}/X_H) = \sum_{i=0}^{n} a_i X_H^{\,i} / \sum_{j=0}^{m} b_j X_H^{\,j} \qquad (5)$$

The calculation of the constants a_i, b_j and the degree of polynomials m and n was performed with the aid of a computer minimizing the difference between the experimental data and those found by eq 5.

The best empirical equation was obtained for $m = n = 1$ and $b_0 = 1$; thus from eq 5 it follows that

$$\ln \frac{P_{H_2}^{1/2}}{X_H} = \frac{a_0 + a_1 X_H}{1 + b_1 X_H} \qquad (6)$$

The values of a_0, a_1, b_1 are shown in Table II and the behavior of ln ($P_{H_2}^{1/2}/X_H$) calculated by eq 6 is compared with experimental values in Figure 3.

Table III. Activity Coefficients of Hydrogen at Infinite Dilution in the $Li_{17}Pb_{83}$ Alloy Calculated by Using Some Theoretical Models

model	γ_H°, $atm^{1/2}/X_H$	ref
Wagner	23.4	*17*
Blander et al.	7.8×10^3	*27*
Jacob–Alcock	2.5×10^5	*25*
Gokcen	1.8×10^3	*28*

Table IV. Properties of the Binary Systems Calculated at 673 K

system	properties	value	ref
$Li_{17}Pb_{83}$	γ(Li)[a]	2.2×10^{-4}	*1*
	γ(Pb)[b]	0.96	*1*
	ΔH,[c] kJ/g-atom	-10	*2*
H-Pb	γ_H°(Pb),[d] $atm^{1/2}/X_H$	13.78×10^8	*7*
H-Li	γ_H°(Li),[e] $atm^{1/2}/X_H$	6.80×10^{-2}	*11*

[a] Activity coefficient of Li. [b] Activity coefficient of Pb. [c] Heat of formation. [d] Activity coefficient of hydrogen at infinite dilution. [e] Activity coefficient of hydrogen at infinite dilution.

The constant a_0 in eq 6 is the limiting value of ln (P_{H_2}/X_H) for $X_H \rightarrow 0$; it represents the ln γ_H° (with γ_H° the activity coefficient at infinite dilution) according to eq 2 or ln K_s (with K_s Sievert's constant) according to eq 3.

It is interesting to note that the values of K_s obtained by the constant a_0 do not differ appreciably from those experimentally determined by Veleckis, as reported by Sze (*13*) for the same system (5.8×10^3–9.5×10^3 $atm^{1/2}/X_H$), by Wu (*15*) for the deuterium/$Li_{17}Pb_{83}$ system (5×10^3 $atm^{1/2}/X_H$), and by Wu and Blair (*14*) for tritium/$Li_{17}Pb_{83}$ system (5.8×10^3 $atm^{1/2}/X_H$).

Besides, within the limits of uncertainty with which it is possible to determine the constant a_0 by means of eq 6, the values of γ_H° practically coincide at the three examined temperatures. A value of K_s of independent of temperature has also been found by these authors (*13*–*15*).

The thermodynamic behavior of the system H/$Li_{17}Pb_{83}$ characterized by a large value of γ_H° and a very strong variation of $P_{H_2}^{1/2}/X_H$ ratio indicative of considerable deviations from the ideal can be related to the interactions that can develop among the atoms of the system.

The value of γ_H° can be compared with the one calculated on the basis of many models and theories that have been recently developed in order to foresee the behavior of a minor constituent dissolved in a multicomponent system using the thermodynamic data of binary systems (*17*, *19*–*28*).

The values of γ_H° in the $Li_{17}Pb_{83}$ alloy at 400 °C obtained by using some models are shown in Table III and the ones of the parameters required for the calculation are reported in Table IV.

For an interstitial solute (i.e., hydrogen) in solvent alloys, such as Li/Pb, that deviates very much from the ideal behavior, the different models lead to strongly unlike values of γ_H° in relation to the fraction of bonds among metallic atoms which are thought to be influenced by the presence of the solute atom in the metallic lattice. This is particularly true for the activity coefficient value of hydrogen in the $Li_{17}Pb_{83}$ alloy which is small enough to be considered by the Wagner model (*17*), which assumes that the bonds among metallic atoms are not influenced by the solute (Table III).

Very elevated values of γ_H° are predicted by the quasi-chemical theory (*25*) in which the relative decrease in the strength of metal–metal bonds near the solute atom is considered, but the possibility that this effect may be accompanied by an increase of some types of bonding is not taken into account. All types of interatomic interaction are considered in the theory of Blander et al. (*27*) based on statistical-mechanical models that is much more preferable. Taken into account are the specific bond between the solute and solvent atoms, the interactions between solvent atoms which are disrupted or altered by the addition of an H atom and those between solvent atoms near the solute atom.

The $\gamma_H{}^\circ$ value calculated by the Blander model (7.8 × 10^3 atm$^{1/2}/X_H$ at 400 °C assuming that the fraction of the total interactions of Li or Pb atom influenced by an H atom is equal to 0.25) is consistent with the experimental results in this study (4.4 × 10^3 atm$^{1/2}/X_H$ at 400 °C). This value of $\gamma_H{}^\circ$ is sufficiently high to suggest a remarkable weakening of the bonds between the Li and Pb atoms near the hydrogen atom because of the setting of the preferred Li-H bonds.

Then the deviation from the ideal behavior in this system can be attributed to the onset of attractive forces between atoms absorbed in interstitial contiguous sites: these strengths are born in order to minimize the disturbance caused by the solute atom on the bonds between the alloy atoms and also on the short-range order existing in the molten state.

Concerning this, we wish to point out that in the Wu work (*14*) reported for the tritium/$Li_{17}Pb_{83}$ system, the values of $P_{T_2}{}^{1/2}/X_T$ decrease considerably when the tritium concentration increases in the alloy. This agrees perfectly with what we obtained for the H/$Li_{17}Pb_{83}$ system.

On the grounds of the hypothesis advanced a qualitative interpretation of the effect produced by the temperature on the global behavior of the system is also possible. The very small variation in the activity coefficient at infinite dilution of hydrogen in the alloy with increase of temperature could be due to the compensation of two opposite effects: the increase both in the activity coefficients of the two metallic components in the binary Li/Pb system (*1*) (the interactions that have to be partially reduced would then be minor) and in $\gamma_H{}^\circ$ in the binary H/Li system (*7*) (the interactions which can form would weaker themselves too). With a more elevated concentration of hydrogen, the differing of hydrogen activity coefficient values at the three temperatures examined (Figure 2) can be considered to be due to a minor deviation from ideal behavior at higher temperature when the interactions among solvent alloy atoms are minor.

Registry No. H_2, 1333-74-0; $Li_{17}Pb_{83}$ alloy, 73369-65-0.

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Some Thermodynamic Properties of Mellitic Acid

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The molar octanol-water partition coefficient of mellitic acid (benzenehexacarboxylic acid) at 22 °C is 0.036 if the mellitic acid dimerizes in the octanol phase with a constant of about 100 M^{-1}. The osmotic behavior of mellitic acid is independent of temperature between the freezing point and 25 °C and shows that the compound behaves much like a 1-1 electrolyte in aqueous solution, at concentrations between 0.01 and 1 *m*.

As part of a program to study the organic solvent-water partition coefficients of a series of diverse organic compounds, I have collected several thermodynamic data on mellitic acid (benzenehexacarboxylic acid).

This compound can be derived by oxidation of graphite; the aluminum salt occurs in oxidized coal humic acids as mellite [$Al_2C_6(COO)_6 \cdot 18H_2O$ (*1*)], an example of one of the relatively rare organometallic minerals (*2*).

Table I. Octanol-Water Partition Coefficient, K_{ow}, for Mellitic Acid (MA) at 22 °C

M_o, mol dm^{-3}	M_w, mol dm^{-3}	log K_{ow}	log $K_{ow}{}^a$	log $K_{ow}{}^b$
0.0001_1	0.008	−1.9 ± 0.1	−1.08	−1.08[c]
0.0018	0.073	−1.61 ± 0.05	−1.29	−1.40
0.014	0.34_2	−1.39 ± 0.05	−1.24	−1.49
0.038	0.55_0 (0.51 *m*)	−1.16 ± 0.05	−1.04	−1.44
				av = −1.45 ± 0.03

[a] Value after allowing for dissociation in the aqueous phase; $k_{i,1} = 10^{-1.40}$. [b] Value after also allowing for association in octanol phase according to reaction 2MA → $(MA)_2$, $k_a = 100\ M^{-1}$. [c] Value ignored in final average.