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A manometric method for the determination of hydrogen in Li-Al alloys

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Abstract

A method, based on the manometric measurements of hydrogen has been described for the determination of total hydrogen in the range 20-200 ppm in 4% Li-Al alloys which are used for the production of tritium. Because of the highly reactive nature of these alloys to O_2, N_2 and moisture, an *in situ* fabrication of the alloy was required for calibration purposes with proper precautions to prevent contamination. Hydrogen was extracted using a molten tin bath at 700° C and standard addition of hydrogen was done in the form of LiOH. Effect of exposure of this alloy to contact with atmosphere was evaluated and some thermodynamic considerations about the release of hydrogen included.

Key words: Manometric method, hydrogen, Al-Li alloys, effect of exposure.

1. Introduction

The determination of hydrogen in Li-Al alloys assumes importance because of the potential use in the production of tritium. A 4% Li-Al alloy is prepared for this purpose as this alloy, in comparison with soft lithium metal, has the desired mechanical strength to be machined. Further, the tritium produced during irradiation will be fixed as aluminium tritritide. However, the presence of hydrogen in these alloys will lead to the formation of HTO or HT, as the case may be, due to the presence of hydroxide or hydride. Hydrogen, present in these alloys, is preferentially associated with lithium because of its extremely high reactivity with oxygen and moisture of the atmosphere. The pick up of hydrogen is thought to be due either to the direct conversion of lithium to hydroxide by reaction with moisture or first by reaction with oxygen to form Li_2O, which being hygroscopic, picks up moisture. In comparison, aluminium hydride is unstable, decomposing at 100° C. As the alloy is fabricated at 900° C, at which temperature most hydrides are unstable, hydrogen is largely picked up at the fabrication and handling stages.

Several methods[1] have been employed for the determination of hydrogen in aluminium metal—some for solid metal and some for liquid metal. These include vacuum fusion[2], vacuum sublimation[3], hot extraction[4], first bubble[5], isotope dilution[6], etc. Similarly hydrogen in lithium metal has been analysed by several methods[1, 7, 8]. However, these methods cannot be readily adopted to the determination of hydrogen in Li–Al alloys due to the high volatility of lithium. Also hydrogen is present in these pure metals as hydride while in these alloys it is present mostly as lithium hydride. Hence a suitable method had to be devised and calibrated. The present paper describes a simple manometric method for the determination of total hydrogen in Li-Al alloys using a molten tin-bath. The method is based on the dissolution of the alloy in a molten tin-bath at 700° C and measurement of the released hydrogen using standard volumes and a differential oil manometer.

The primary requirements for the development of such a method are samples of the alloy which contain low amounts of hydrogen and a standard for hydrogen for addition and recovery of known amounts. Samples of the alloy, therefore, had to be fabricated *in situ* in order to minimise atmospheric contamination. Lithium hydroxide was used as the standard for the calibration purposes.

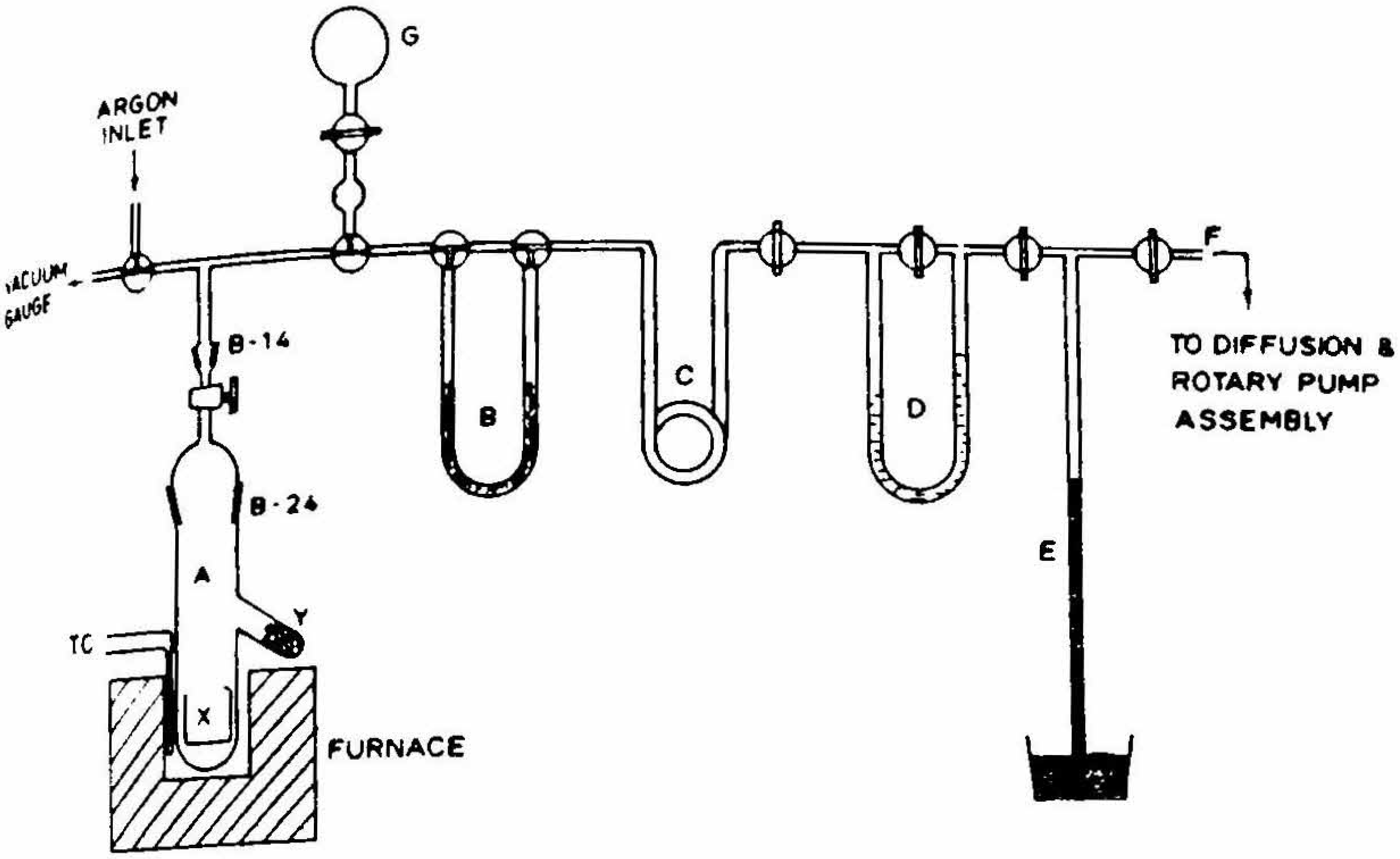
2. Experimental

The apparatus consists of a furnace section where hydrogen is extracted, a section for collection and measurement of evolved gases and a section for the analysis of the collected gas.

The apparatus manifold, as shown in fig. 1, consists of a quartz reaction tube (A) with a side arm for the addition of tin metal under the conditions of the experiment. *B*, also a quartz tube, contains heated copper oxide catalyst and serves to ascertain whether all the evolved gas is hydrogen or not. *C* is a glass moisture condensation coil to trap moisture, if any, in the evolved gas and to ascertain the presence of other gases in the evolved gas. *D* is a differential oil manometer containing Apiezon B oil, previously deaerated. A bulb (*G*) serves as a previously calibrated standard volume in order to calibrate the total volume of the apparatus. The rest of the figure is self-explanatory.

3. Fabrication of the alloy

In order to prepare samples of alloy containing low amounts of hydrogen, lithium has to be handled in an inert atmosphere in a glove box. Pieces of lithium metal were cut



A—Silica reaction tube; B—CuO tube; C—Moisture condensation trap; D—Oil manometer; E—Mercury manometer; G—Standard volumes; X—Stainless steel crucible; Y—side arm.

Fig. 1. Set-up for the alloy fabrication and analysis for hydrogen.

and surfaces cleaned with a sharp scalpel in a glove box filled with argon of high purity (99·99%). A small piece was taken and loaded in a vacuum tight bottle, previously weighed and kept inside the glove box. The weight of lithium metal was ascertained by weighing this bottle. Requisite amounts of pure aluminium metal (99·9%) in the form of foils were weighed out and transferred to a stainless steel crucible placed inside the main reaction tube *A*. This tube was then transferred to the glove box and the lithium metal was added to the stainless steel crucible. The side arm of the reaction tube was loaded with 20 gm of pure tin metal, previously melted to remove any hydrogen present. The closed reaction tube was then taken out of the glove box and connected to the manifold. The whole system was completely evacuated and argon let in to a pressure of 5–6 cm of Hg. The reaction tube was then heated using a resistance furnace for a period of 90 min at 900° C in order to homogenize the two metals. It was found that during this time the formation of the alloy was complete in the form of a grey button.

Heating was then stopped and the alloy was allowed to be cooled in the atmosphere of argon. The tube (*A*) was detached from the manifold and tilted in order to add the tin metal into the stainless steel crucible. Then the tube was re-attached to the manifold and the apparatus was evacuated to a high vacuum of 10^{-5} torr. The tube was heated, again at first slowly and then at higher rate to 700° C. The dissolution of the alloy in the tin-bath took place and a slow lowering of the oil manometer level on the pressure side resulted. The heating was continued until the level remained constant. It was found that all the hydrogen was evolved in an hour. The reaction tube was quenched to the room temperature. The reading on manometer was noted and the amount of hydrogen formed was computed. The copper oxide tube was then heated to 600° C and opened to the gas atmosphere. The absence of any other gas other than hydrogen was ascertained as the gas reacted with CuO to form water which condensed in the trap (*C*) and consequently brought the oil levels in the manometer equal.

For calibration purposes requisite amounts of standard lithium hydroxide solution were evaporated on small thin dishes made of quartz and these were loaded in the stainless steel crucible as described earlier. For the standard addition these dishes were loaded with the tin metal in the side arm of the main reaction tube (*A*).

In the case of samples, they were loaded inside the glove box and the analysis conducted in the same manner.

4. Results and discussion

Table I gives the recoveries of some typical fabrication experiments on the determination of hydrogen in lithium hydroxide. The results of this typical set reveal that the method can be successfully used for the recoveries of hydrogen in Li-Al alloys. Table II sets out the results on two typical alloys prepared in the laboratory using lithium metal from two different sources. The first sample contained a mean value of 46·1 ppm of hydrogen while the second sample was seen to contain 180 ppm. The results are a mean of direct determination as well as standard addition. Table III gives the results of a sample which has been badly contaminated, with most of the lithium already converted to lithium hydroxide.

Table I

Recoveries of hydrogen from standards in the form of lithium hydroxide

Sl. No.	Hydrogen taken μg	Hydrogen recovered μg	% recovery of hydrogen ($\mu g/100\,\mu g$)	S.D.	C.V.
1	78·5	79·7	101·5	4·3	4·2
2.	126·0	130·8	103·8		
3.	126·0	120·2	95·3		
4.	157·5	168·5	107·0		
5.	157·5	159·9	101·5		
		Mean	101·8		

Table II

Analysis of 4% Li-Al alloys prepared in the laboratory

S. No.	Wt. of alloy mg	H_2 added (as LiOH) μg	Total H_2 recovered μg	H_2 content in alloy μg	ppm of H_2 in alloy	S.D.	C.V.
Sample 1							
1	730	...	31·1	31·1	42·7	2·1	4·6
2	507	96·9	121·1	24·2	47·7		
3	629	129·2	157·0	28·8	45·8		
4	712	68·6	97·6	33·0	46·4		
5	580	129·2	157·0	27·8	48·0		
				Mean	46·1		
Sample 2							
1	100·0	96·9	114·2	17·3	173·0	12·4	6·9
2	737·5	...	145·3	145·3	197·0		
3	638·0	...	115·5	115·5	181·0		
4	803·0	64·6	200·3	135·7	169·0		
				Mean	180·0		

Table III

Analysis of a highly contaminated sample

Wt. of alloy taken mg	H_2 present μg	% H_2
38·0	207·6	0·55
50·0	224·9	0·45
47·0	200·7	0·43
56·0	259·5	0·46
	Mean	0·47

4.1. *Effect of exposure to atmosphere*

Sample 1 was exposed to a controlled atmosphere inside a desiccator using calcium chloride as the desiccant. The alloy picked up moisture from the atmosphere increasing the hydrogen content from a value of 46·1 ppm to nearly 450 ppm in about 10 days (Fig. 2). These values indicate that rigorous control of atmosphere, free from oxygen and moisture, is required for the fabrication, handling and storing of the alloy.

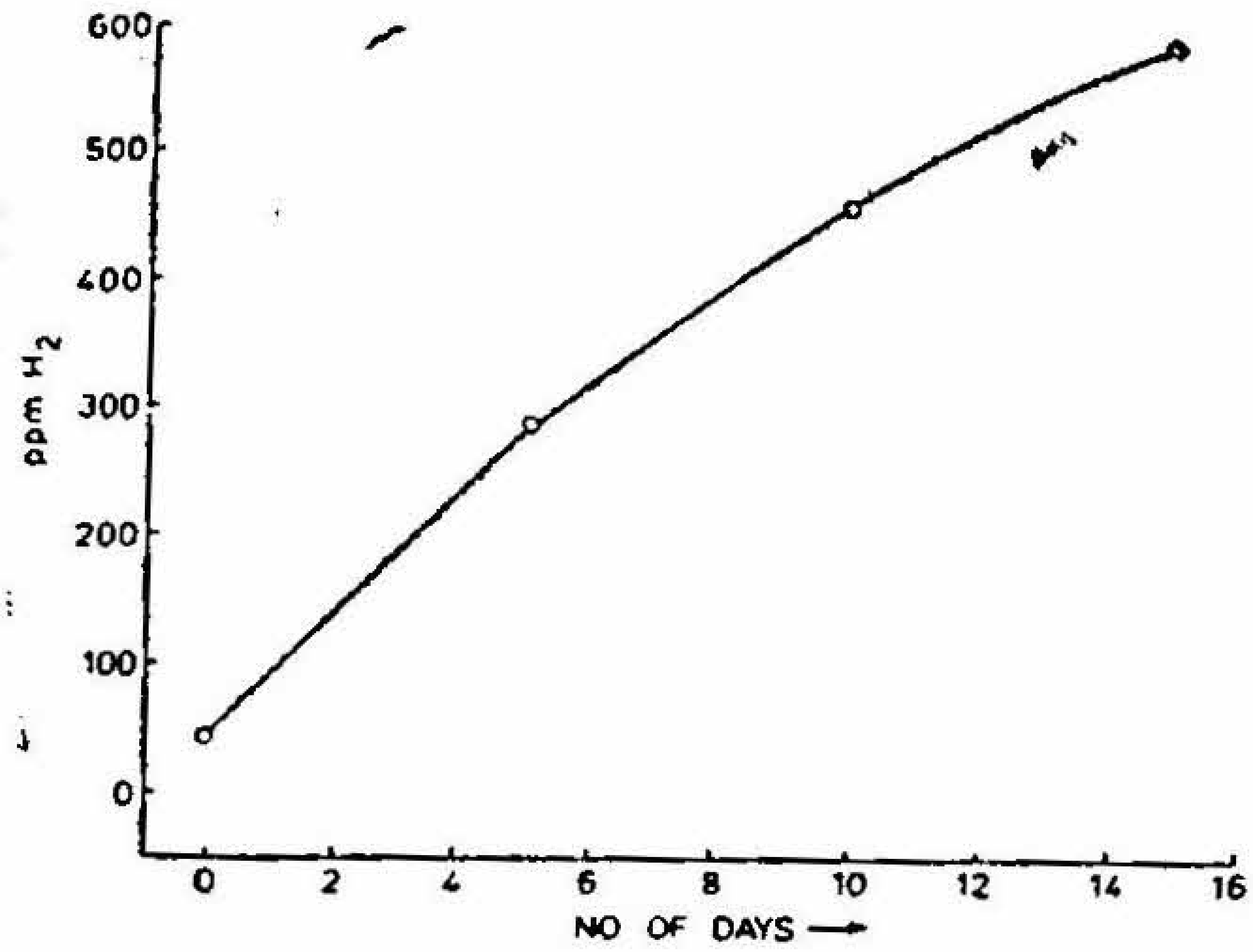


FIG. 2. Effect of exposure on hydrogen content in 4% Li-Al alloy.

The mechanism of liberation of hydrogen from the alloy can be visualized in different ways. LiOH can decompose at high temperature to form Li_2O and H_2O and Sn can decompose the latter to form H_2 and O_2 with O_2 being retained as a stable oxide of Sn or Al. The preponderance of Sn and the higher affinity to O_2 points out to a higher probability of Sn getting oxidised and retaining the O_2. It has been found that even in the absence of Sn, H_2 is liberated which may be due to the slow decomposition of LiOH and the consequent reaction of H_2O with Li metal. However, the kinetics of this reaction is too slow to be useful for analytical purposes. The earlier mechanism can be summed up in three probable reactions :

(*a*) $Sn + 4\,LiOH \rightarrow SnO_2 + 2Li_2O + 2H_2$

(*b*) $Sn + 2\,LiOH \rightarrow SnO + Li_2O + H_2$

(*c*) $2Al + 6\,LiOH \rightarrow Al_2O_3 + 3\,Li_2O + 3H_2$

Free energy values for these reactions in the range of 300 to 1100 K were calculated using literature values available and free energy functions[9]. It has been assumed that LiOH is free and inspite of the homogeneity of the alloy, moisture reacts preferentially with Li, breaking the bonds between Al and Li. Figure 3 shows the plot of the ΔG values for these reactions as a function of temperature. It is seen from the curves that the reactions (*c*) has the highest negative free energy. However, it is possible that mass law considerations deter this reaction being the most probable. For reactions (*a*) and (*b*) it is seen that between 500 and 600 K plateau regions are observed, while otherwise the values go on monotonously increasing. While the role of molten tin can be understood as a solvent, forming intermetallic compounds with both Al and Li, breaking the metallic bond between them and reducing their melting point, its role in the liberation of H_2 is not clearly understood. Reaction (*a*) seems to be more probable and Sn seems to play a role more important than a catalyst.