

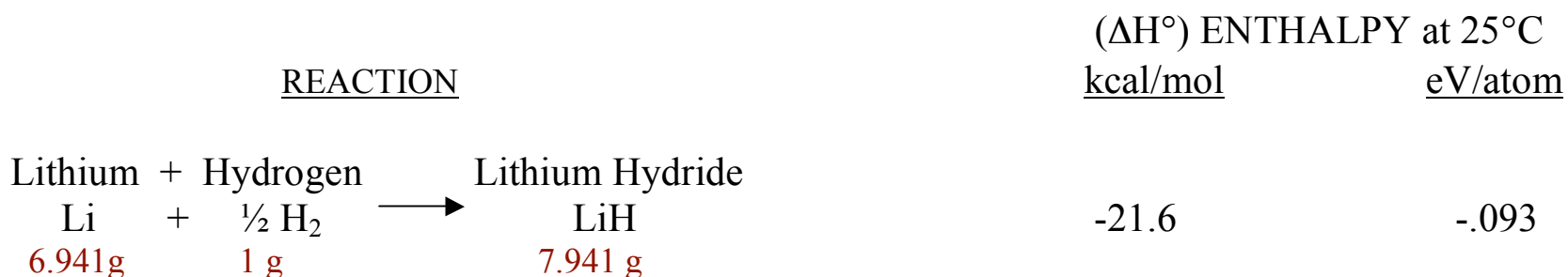
LITHIUM CHEMISTRY IN NSTX:  
PREDICTABLE – BUT DON'T COUNT ON IT

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- Lithium will encounter inert gases like helium and argon as well as non-inert materials such as protium and deuterium, water, nitrogen, oxygen, carbon dioxide, carbon monoxide, carbon, boron, molybdenum, stainless steel, methane and hydrocarbons. Beneficial and adverse effects can occur from interactions with these materials.
- Reactions of lithium with some of these materials can produce new materials such as lithium hydride and deuteride or the intense reaction of lithium, oxygen, and molybdenum producing lithium molybdate.
- Lithium is the least reactive of the alkali metals group of the Periodic Table.
- Hydrogen is technically a member of this group, but doesn't undergo reactions anything like the rest of the group and is therefore excluded.
- Properties of the group are sequential:

| Element             | Francium | Cesium | Rubidium | Potassium | Sodium | Lithium |
|---------------------|----------|--------|----------|-----------|--------|---------|
| Atomic No.          | 87       | 55     | 37       | 19        | 11     | 3       |
| Melting Point (K)   | 2300     | 301.59 | 312.46   | 336.53    | 370.87 | 453.69  |
| Boiling Point (K)   | 2950     | 944    | 961      | 1032      | 1156   | 1615    |
| (Symbol) Reactivity | (Fr)     | > (Cs) | > (Rb)   | > (K)     | > (Na) | > (Li)  |

- Chemical reactions are shown in terms of kcal/mol (converted to eV/atom) where a mol is a gram equivalent weight (e.g. hydrogen = 2 grams, deuterium = 4 grams, lithium = 6.941, oxygen = 32, nitrogen = 28, carbon = 12, molybdenum = 95.94, etc.)
- An exothermic reaction is noted with a minus sign and an endothermic reaction is shown as positive.
- An exothermic reaction may or may not proceed spontaneously (lithium has numerous examples). Likewise, an endothermic reaction may proceed spontaneously (e.g. instant cold packs with ammonium chloride dissolving in water - since there are no obvious lithium examples).
- A low to moderately intense reaction occurs between lithium and hydrogen (with deuterium having a nearly identical heat of reaction). This is the reaction affecting recycling:



**DOES THIS REACTION REALLY PREDICT WHAT WILL HAPPEN?**

- In the laboratory, Mansfield and Timberlake have been test firing sabots for use in the pellet injector to introduce lithium powder at velocities in the order of 5m/s into the plasma edge.

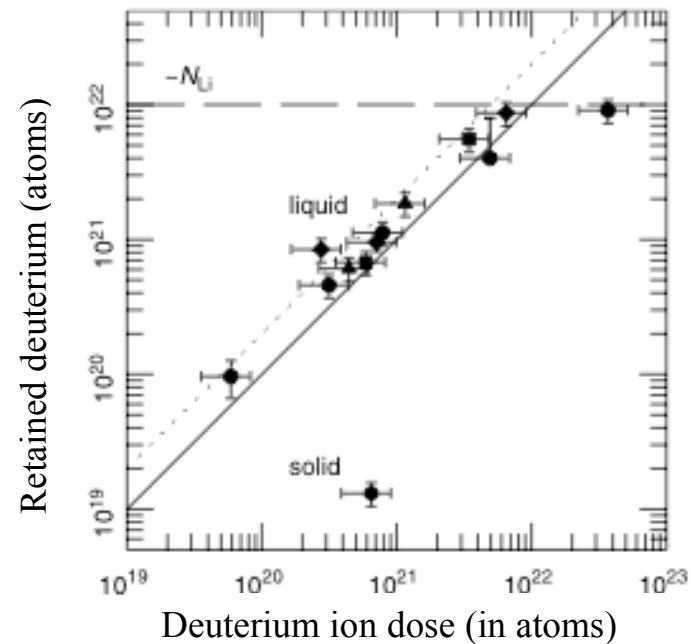
- The sabots are stainless steel tubes 5 inches long and about .080 inches inside diameter with a fill of ~15 mg of lithium powder and are fired with a deuterium gas pulse at 75 psi for no more than 100 ms. The test chamber pressure rises to  $\sim 10^{-2}$  Torr.
- For a sabot that didn't appear to unload its lithium, we observed a heat ring typical of stainless steel at a high temperature, and there was an internal blockage at the location of the ring:



**SOLID LITHIUM REACTING WITH DEUTERIUM GAS AT ROOM TEMPERATURE SUPPORTS THE PREDICTED LITHIUM WITH HYDROGEN REACTION.**

- Similar results have not been reported on NSTX for larger pellets used. Reasons may be smaller surface area, better natural protective coating, or just may be too subtle to be seen.

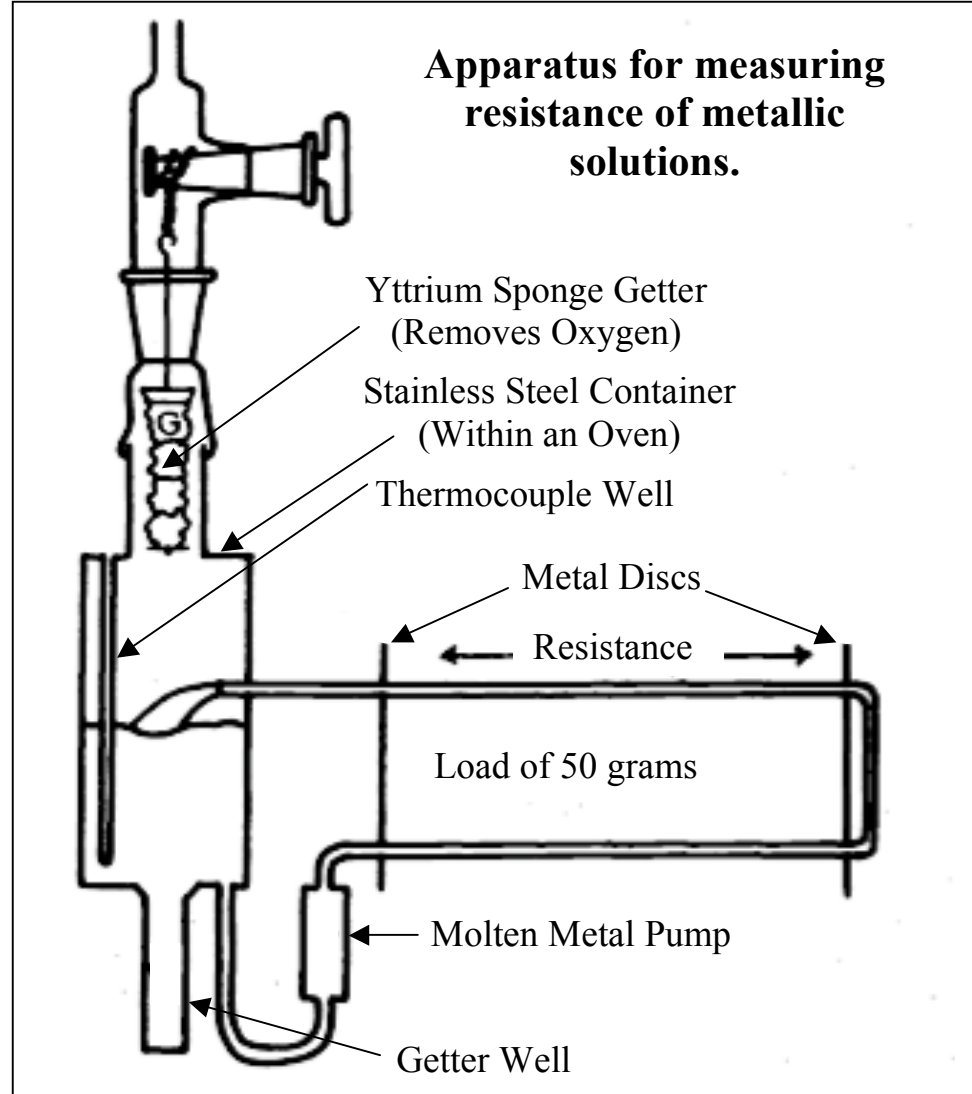
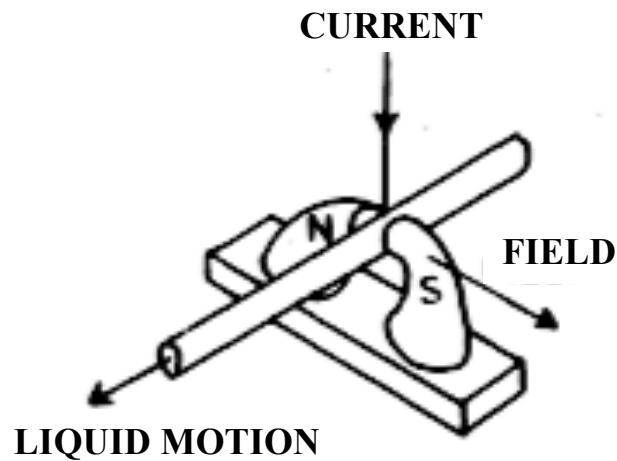
- On PISCES-B, Baldwin<sup>1</sup> et al used ~50 eV D ions with doses of  $10^{19} - 10^{23}$  atoms to bombard solid and heated (523 – 673K) lithium.
- Except for the solid lithium, they found the uptake to equal the ion fluence plus charge exchange neutral atom flux.
- They also note that after all available lithium atoms are taken up with deuterium, the lithium sample changes from a low recycling medium to a high recycling medium.
- In another test, they exposed clean liquid lithium (573K) to molecular deuterium at .75 Torr for > 8 minutes. No deuterium uptake was found.



**Figure 5.** Plot of deuterium atom retention against plasma ion fluence. Data points are TDS measurements for lithium samples (liquid and solid) exposed to deuterium plasma. The sample exposure temperatures were: (solid) 323 K, (liquid) ● 523 K, ■ 573 K, ◆ 623 K, ▲ 673 K. The solid line indicates full retention of ions. The upper dashed line is the number of lithium atoms in samples. The dotted line is an estimate of the total atom fluence received by samples: the sum of the measured ion fluence and calculated neutral atom fluence [34].

**FOR MOLTEN LITHIUM WITH ENERGETIC DEUTERIUM, THE REACTION IS SUPPORTED. IT IS NOT SUPPORTED FOR SOLID LITHIUM EITHER WITH ENERGETIC DEUTERIUM IONS OR ATOMIC DEUTERIUM. THE REACTION, WITH CONDITIONS, IS ALSO NOT SUPPORTED FOR MOLTEN LITHIUM AND MOLECULAR DEUTERIUM.**

- Ca. ~1977 the molten metal pump using no moving parts (below), honed resistivity measurements of molten alkali metals (right).
- Pulham made solubility measurements of nitrogen, protium, and deuterium in liquid lithium with some observations.



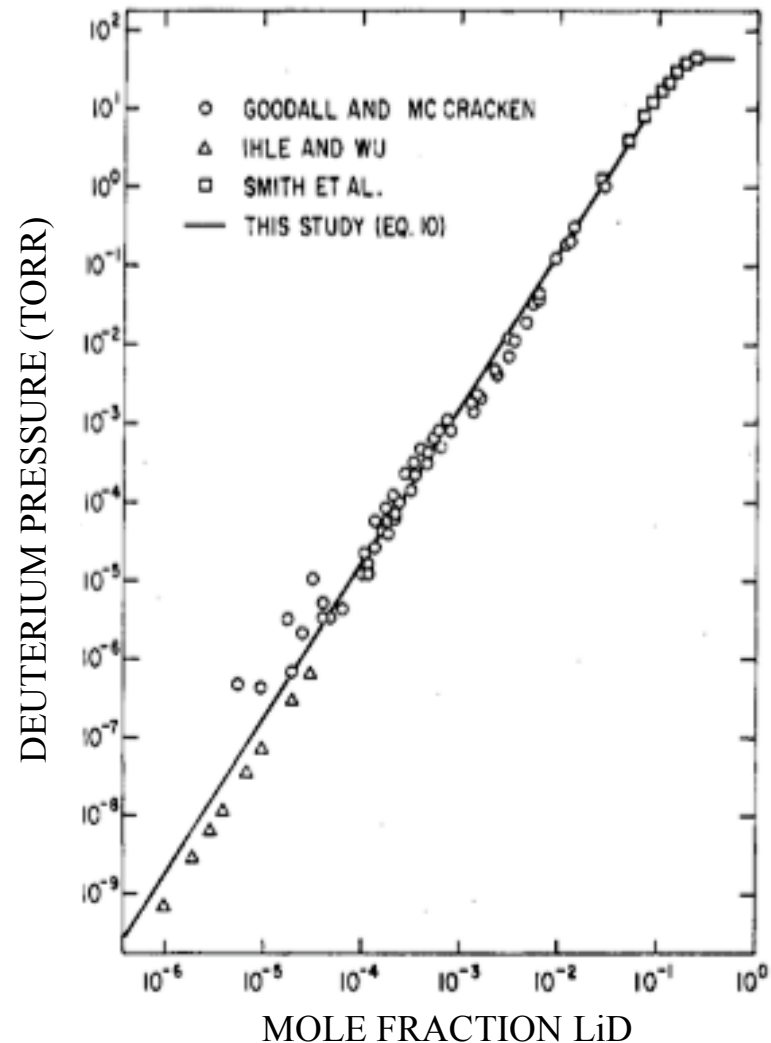
- Pulham observed that the salt ( $\text{Li}_3\text{N}$ ,  $\text{LiH}$ , or  $\text{LiD}$ ) formed at the interface between the gas and liquid. It did not impede flow of liquid metal. For deuterium, the solubility is described by:  $\log X_D = 2.321 - 2873/T$  where  $X_D$  = mole fraction of deuterium and  $549 < T < 724\text{K}$
- Pulham also noted that the gas will continue to react with the liquid metal until the metal is completely converted to salt, or there is no more gas.

At the deuterium – liquid lithium interface: 1) Deuterium gas dissolves in the liquid lithium. 2) Deuterium reacts with lithium forming lithium deuteride. This removes a lithium atom from the melt. 3) To keep the  $\text{Li} - \text{LiD}$  melt at a constant concentration, a  $\text{LiD}$  molecule precipitates out of solution. Once equilibrium is reached, the liquid concentration will only change with temperature

UNDER DIFFERENT CONDITIONS, THE REACTION BETWEEN MOLTEN LITHIUM AND MOLECULAR DEUTERIUM IS SUPPORTED, AND POINTS TO A REASON WHY THIS WAS NOT OBSERVED BY OTHER RESEARCHERS.

- Resistivity measurements could provide useful information on the  $\text{Li-LiD}$  monotectic phase diagram, but this has not been reported. Nevertheless, a distinction has been provided for the difference between the reactivity of immobile molten lithium and flowing molten lithium. Unless the molten material is refreshed, the formed  $\text{LiD}$  apparently prevents the reaction of molecular deuterium with lithium to form more  $\text{LiD}$ .
- The NSTX Liquid Lithium Divertor concept involves the use of immobile molten liquid lithium. LTX is planning to have molten liquid lithium walls that have been refreshed with material.

- Lithium hydride (deuteride) is more reactive than lithium and references note that “there is no known substance which can contain the molten material.” Fortunately this is not true at low pressures. Rather, the formed salt will decompose into its constituents.
- Unfortunately, decomposing into its constituents can produce a high background pressure as shown by Veleckis at 700° C from a compendium of data of other researchers (right). At this temperature, a very small mole fraction of LiD ( $10^{-4}$ ) can produce a background pressure of  $10^{-5}$  Torr. Lower temperatures are also a concern.
- Fortunately, raising the temperature might aid in the decomposition of LiD.
- Unfortunately, forcing the decomposition of LiD could lead to increased recycling.

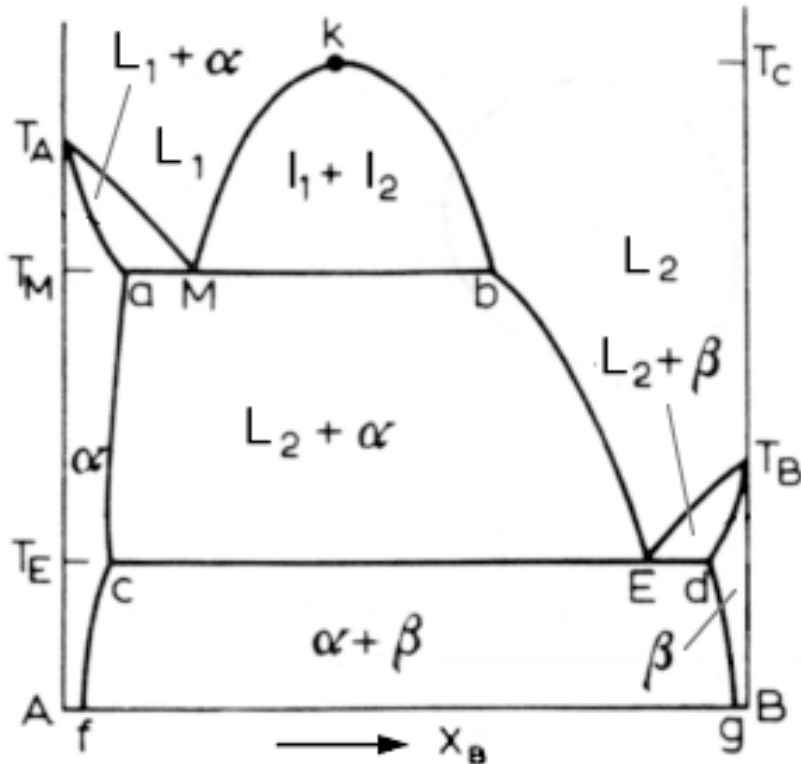


**Figure 2.** Comparison of the calculated  $P_{b_2}$  vs.  $N_{LiD}$  isotherm with the literature data at 700 °C.

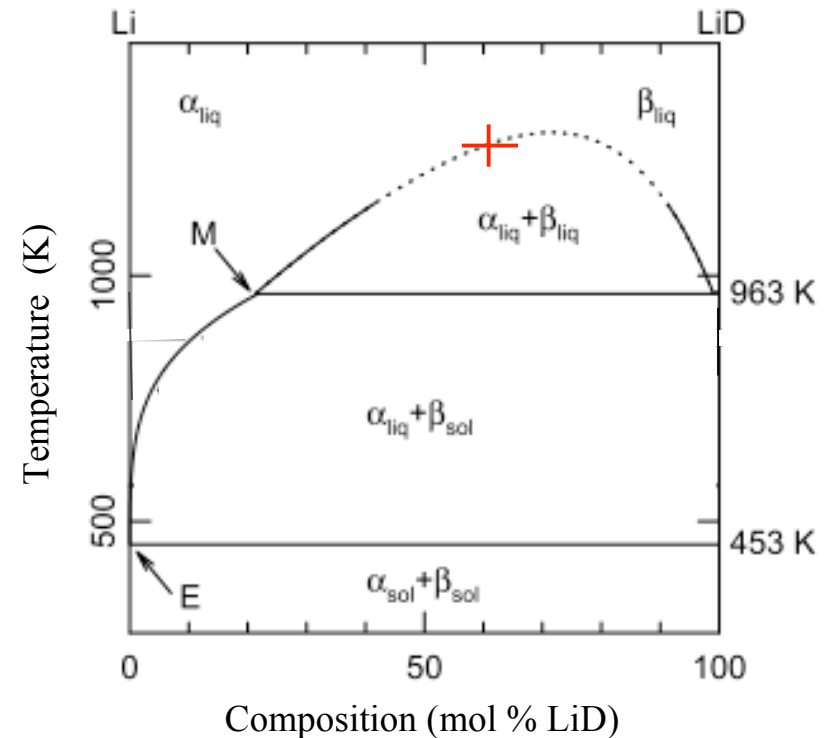


## monotectic reaction

The *reversible transition*, on cooling, of a liquid to a mixture of a second liquid and a solid:  $\text{liquid}_1 \rightleftharpoons \text{liquid}_2 + \text{solid}$ .



Generalized Monotectic phase diagram for a non-metal in a metal.  $T_M$  is the monotectic temperature. Under the top “dome”,  $I_1 + I_2$  are two immiscible liquids like oil and water.  $k$  is the consolute point.



Li-LiD phase diagram constructed from Pressure Concentration Temperature data from literature by Baldwin<sup>2</sup> et al. The dotted line for the predicted closure of  $\alpha_{\text{liq}} + \beta_{\text{liq}}$  remains unverified. Veleckis calculates the consolute at  $1273 \pm 10^\circ\text{K}$  and  $61 \pm 3 \text{ mol\% LiD}$ .

## OTHER MORE ENERGETIC LITHIUM REACTIONS

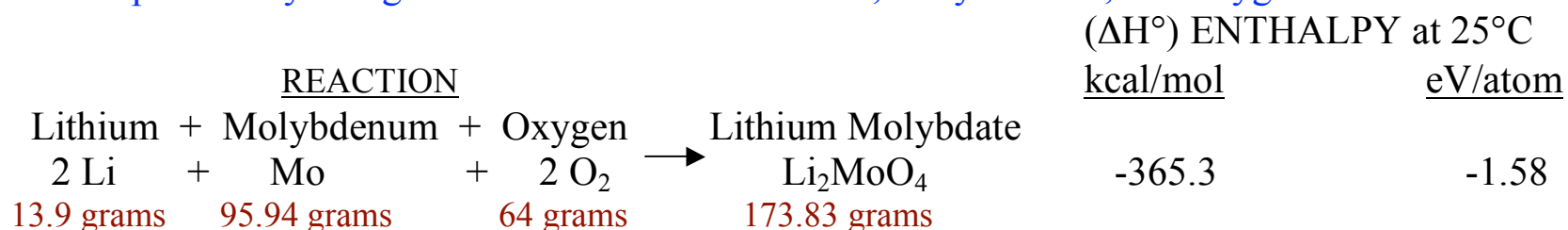
- It is a misconception that the whitening of lithium in air is from oxide formation. This is not true. The oxidation, or burning, of lithium is accompanied by dazzling white light and high temperatures. Burning is not easily started as some literature sources note temperatures  $>600^{\circ}\text{C}$  are needed. We hope to avoid this reaction:

| <u>REACTION</u>                   |   |                                | <u>(<math>\Delta H^{\circ}</math>) ENTHALPY at <math>25^{\circ}\text{C}</math></u> |
|-----------------------------------|---|--------------------------------|--|
|                                   |   |                                | <u>kcal/mol</u> <u>eV/atom</u>   |
| Lithium + Oxygen                  | → | Lithium Oxide                  |  |
| Li + $\frac{1}{2}$ O <sub>2</sub> |   | Li <sub>2</sub> O              |  |
| 6.941 g    16 g                   |   | 29.882 g                       | -142.7                      -.62   |
| Lithium + Oxygen                  | → | Lithium Peroxide               |  |
| Li + O <sub>2</sub>               |   | Li <sub>2</sub> O <sub>2</sub> |  |
| 6.941 g    32 g                   |   | 45.882 g                       | -151.9                      -.66   |

- When lithium burns, a small amount of lithium peroxide is formed. This is used on spacecraft and submarines for air purification.
- On CDX-U, the filled lithium tray was at  $300^{\circ}\text{C}$  and under intense argon glow when a large window broke. The glow was terminated without a hint of an aggressive reaction.
- Lithium can also garner oxygen less energetically by stealing it from other weaker molecules such as glass - silicon dioxide. When the oxygen is stripped, the constituent element, silicon, is left behind.
- An example of molten lithium on glass is where molten lithium spilled onto a bottom window of CDX-U. When the lithium and lithium salts are removed, a layer of silicon remains.

## LLD CHEMISTRY – A POTENTIALLY VERY ENERGETIC REACTION

- One potentially energetic reaction involves lithium, molybdenum, and oxygen as follows:

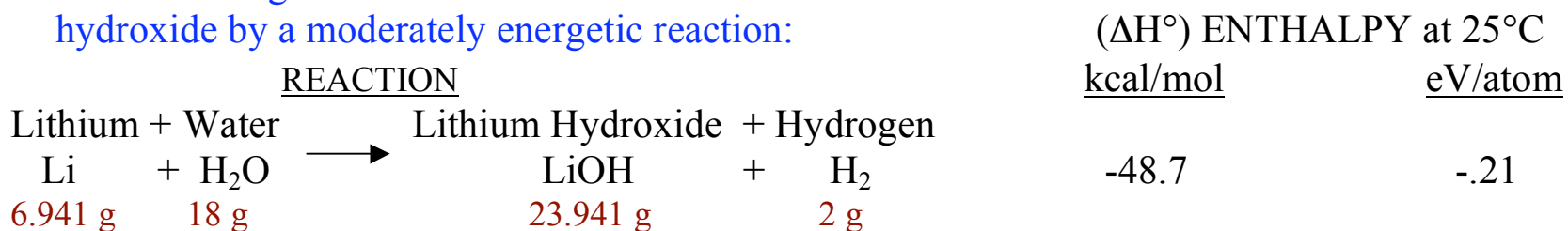


- Certainly there will be enough lithium and molybdenum for this reaction to go as written. 64 grams of oxygen is a large order. However, the primary impurity in lithium is oxygen and there is water in the machine which contributes oxygen. What about an air leak?

AS WITH OXYGEN AND LITHIUM CHEMISTRY, ENERGY IS NEEDED TO IGNITE THE REACTION. THIS REACTION LIKELY WILL NOT OCCUR, BUT THE POTENTIAL RESULT OF THIS REACTION REQUIRES DUE DILIGENCE.

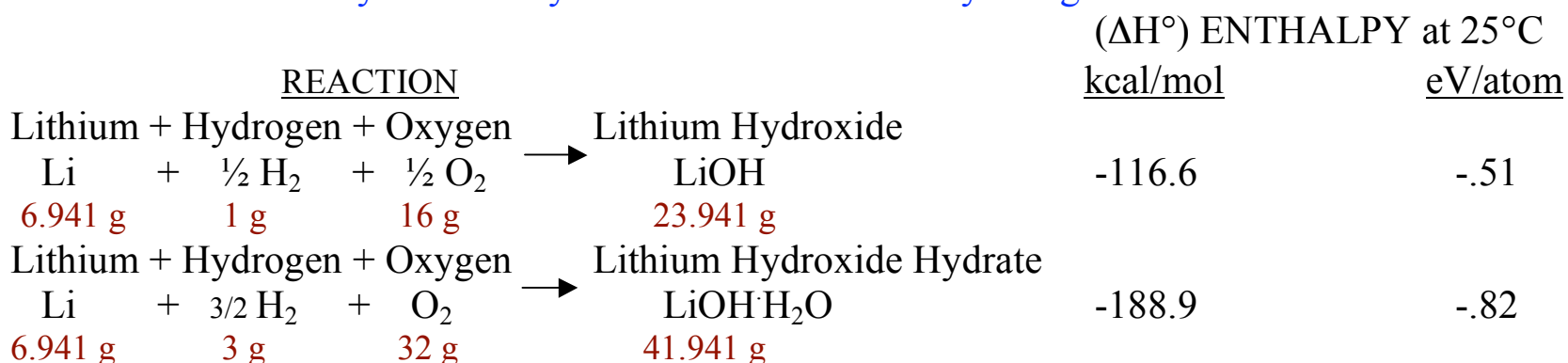
- Oxygen minimization can begin by not putting it into the divertor tray. Stay away from the battery grades of lithium. Use only the highest purity, and if in doubt have it analyzed again.
- There are materials that getter oxygen (e.g. yttrium or cerium Sponge) from molten lithium which could be incorporated into the design.
- Because LiD is an active material, tests of the tray including this with lithium would be wise.

- The whitening of lithium in air and in PPPL's machines is from the formation of lithium hydroxide by a moderately energetic reaction:



LITHIUM REACTS WITH WATER WITHOUT SELF IGNITING OR EXPLODING WHICH THE OTHER ALKALI METALS DO, **BUT** LITHIUM CAN CAUSE WET COMBUSTABLE MATERIAL TO IGNITE - LIKE CLEANING LITHIUM WITH A WET PAPER TOWEL.

- There are other ways lithium hydroxide can be formed by energetic reactions:



- While these reactions could occur because the ingredients are on hand, factors that make these reactions unlikely are insufficient quantities of oxygen and hydrogen at a single time and the temperature to jump start the reaction.

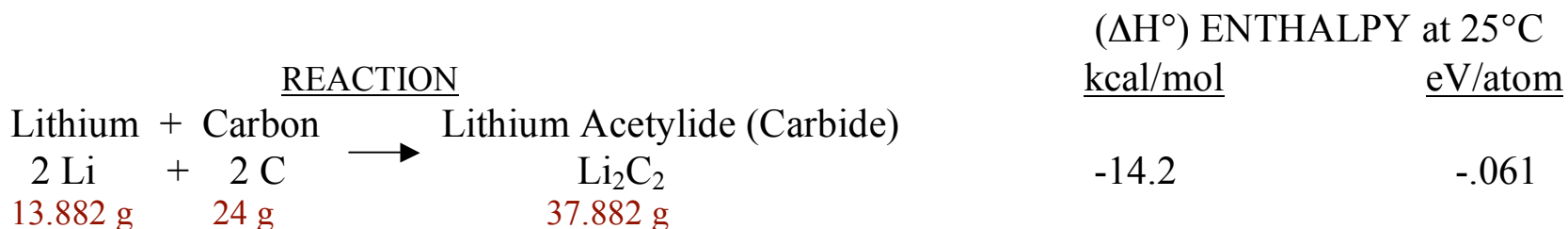
- By allowing carbon dioxide (from air) to react with lithium hydroxide coated metal, a quiescent reaction forms lithium carbonate ( $2 \text{LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}$ ). Lithium carbonate is unusual in that it is the only alkali carbonate that is non-soluble. With a coating of the carbonate, we have seen underlying lithium metal protected for years on CDX-U components.
- We do not want to see lithium carbonate formed by the following reactions:

| <u>REACTION</u>           |               |   | <u>(<math>\Delta H^\circ</math>) ENTHALPY at 25°C</u> |                |
|---------------------------|---------------|---|---|----------------|
|                           |               |   | <u>kcal/mol</u>                                       | <u>eV/atom</u> |
| Lithium + Carbon Monoxide | $\rightarrow$ | Lithium Carbonate + Carbon              |   |                |
| 2Li + 3 CO                |               | Li <sub>2</sub> CO <sub>3</sub> + 2 C   | -210.5  | -.91           |
| 13.882 g + 84 g           |               | 73.882 g + 24 g                         |   |                |
| Lithium + Carbon Dioxide  | $\rightarrow$ | Lithium Carbonate + Carbon              |   |                |
| 2Li + 3/2 CO <sub>2</sub> |               | Li <sub>2</sub> CO <sub>3</sub> + 1/2 C | -148.6  | -.64           |
| 13.882 g + 66 g           |               | 73.882 g + 6 g                          |   |                |

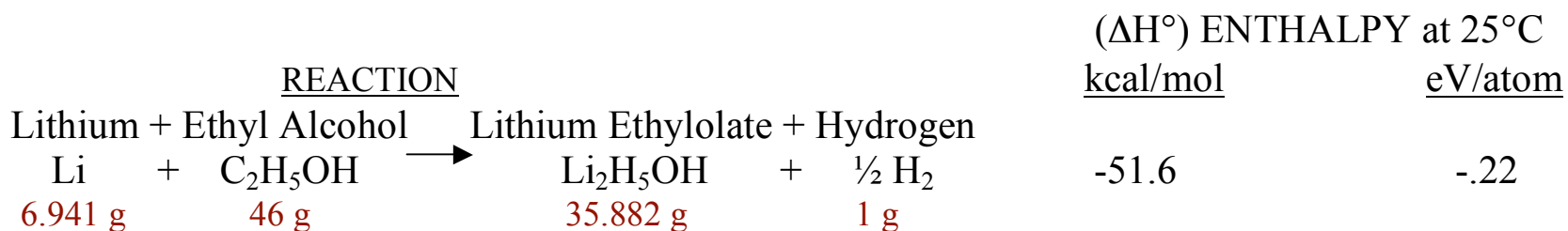
- Incendiary bombs using lithium were made so they could not be easily extinguished. A lithium fire cannot be put out with a carbon dioxide fire extinguisher.
- Carbon dioxide can also protect lithium from hydroxide formation.

THE LITHIUM POWDER BEING TESTED FOR USE IN THE PELLET INJECTOR IS PROTECTED BY A SURFACE COATING OF CARBON DIOXIDE. IF THIS POWDER IS HEATED TO THE M.P (180°C) OF LITHIUM, IT MAY BECOME PYROPHORIC.

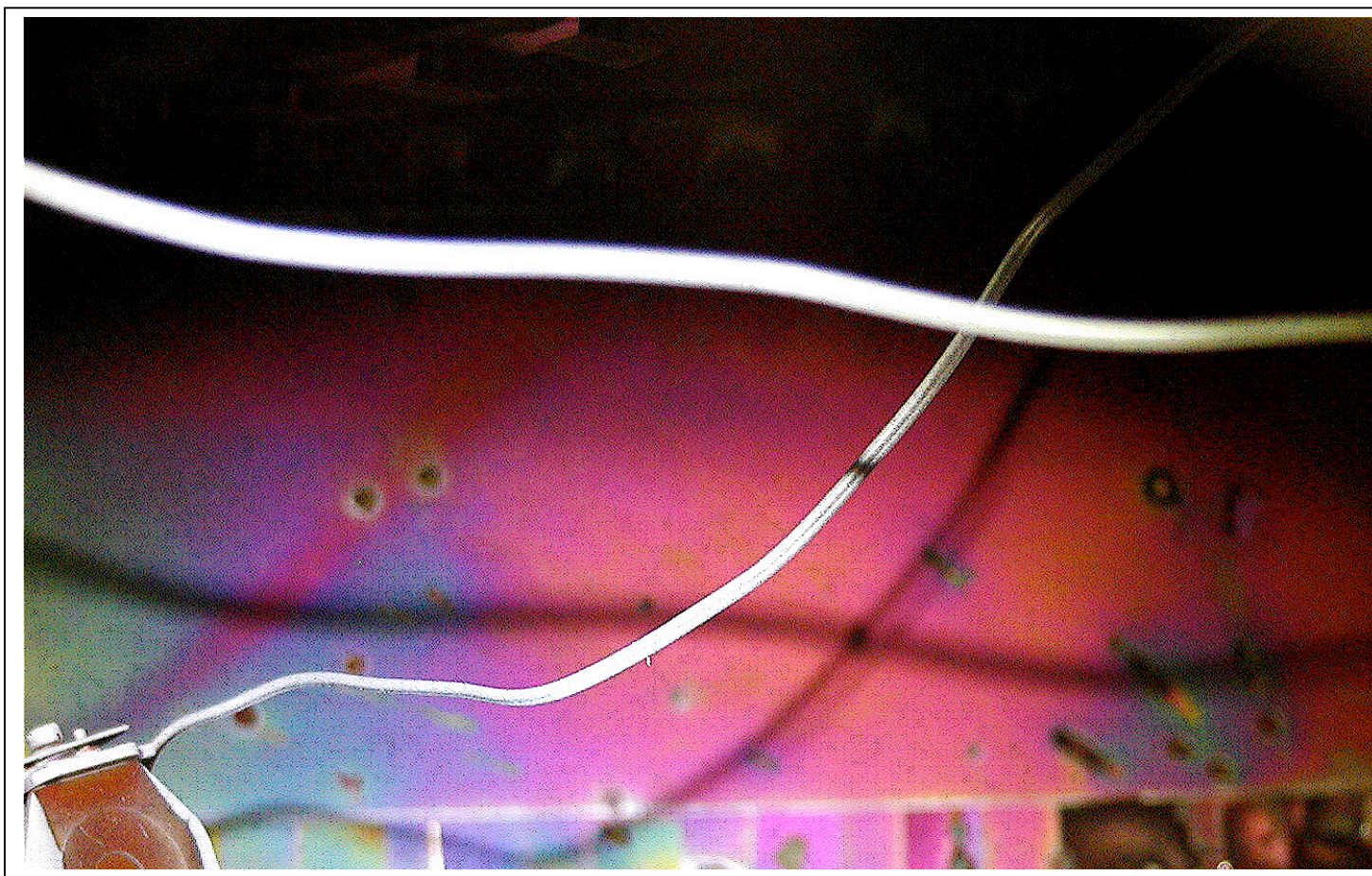
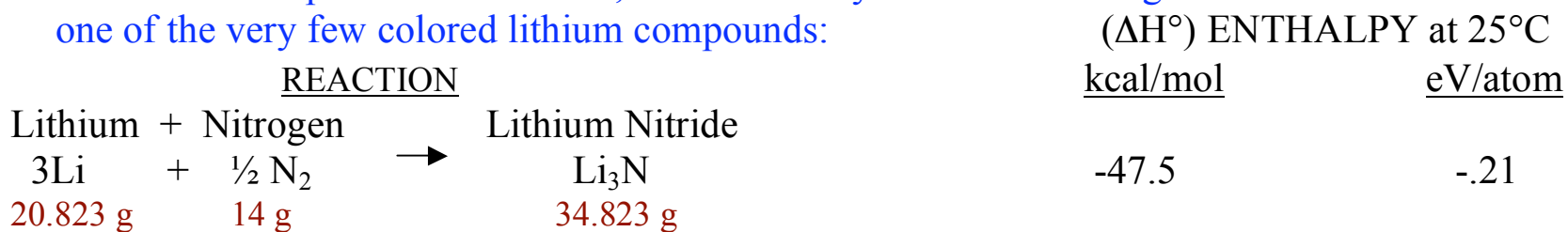
- Lithium reacts with carbon without any coxing:



- Lithium acetylide reacts with water (from air) to produce acetylene with its very characteristic odor ( $\text{Li}_2\text{C}_2 + 2 \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2 + 2 \text{LiOH}$ ) – identified by a few immediately after opening NSTX after the first round of lithium evaporation. This is an excellent confirmation that lithium acetylide was indeed formed. How deep the coating formed is a matter for analysis.
- Lithium also reacts with solvents used to clean the machine. Ethyl alcohol reacts more vigorously with lithium than does water.



- With a little help of some moisture, lithium readily reacts with nitrogen to form red lithium nitride one of the very few colored lithium compounds:



## CONCLUSION

- Undesired energetic reactions involving lithium can be controlled principally by eliminating the supply of non-lithium materials. While these reactions will generally not begin without a starting energy threshold, circumstances for excitation cannot be ruled out.
- Desired reaction with lithium ( $\text{Li} + \text{D} \rightarrow \text{LiD}$ ) has been shown to be more advantageous with molten rather than solid lithium. The formation of LiD in a stationary tray will also likely decrease the potential effectiveness of molten lithium.
- While freezing point curves have not been effective for evaluating the remaining lithium inventory after an evaporation, these curves in principal could serve to evaluate formation of LiD in a tray. Unfortunately, there is a lack of sufficient useful monotectic data.
- The formation of lithium acetylide (carbide) from lithium and carbon while being reversible at an elevated temperature ( $\sim 800^\circ\text{C}$ ), has consequences of structural integrity. Analysis of the depth to which lithium has penetrated into carbon tiles has more meaning if the depth of any tile damage is also evaluated by a simple test such as Vickers, Brinell, Rockwell, or Knoop hardness.
- At the present time, clean-up of lithium has been tested with Cotronics 300BL Insulating Paper. It is quite effective for lithium powder.



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