A STUDY OF THE KINETICS
OF LITHIUM-OXYGEN REACTIONS

by

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ABSTRACT

An experimental study was carried out to determine the reaction rate in forced convection lithium-oxygen reactions. Lithium, held in a small, stainless steel chamber, was heated above its melting point, and oxygen was run from a tank of high pressure, through the reaction chamber, into a tank of low pressure. The pressure loss indicated the amount of oxygen lost to the reaction; knowing the duration of the reaction and the surface area of the pool of molten lithium allowed the reaction rate to be calculated per unit area per unit time. The test was run at various temperatures between 325°C and 800°C and the results plotted to show the dependence of reaction rate on temperature.

Impure lithium led to erratic results ranging from refusal of the lithium to melt to vigorous reactions that melted the stainless steel temperature probe. Reactions involving lithium of greater purity caused melting of the probe and the reaction chamber.

A new reaction chamber made of tungsten was designed to withstand the heat produced in lithium-oxygen reactions.
CHAPTER 1 INTRODUCTION AND BACKGROUND

This chapter will discuss the need for the work done in this study and past work in this area. It will also introduce the reader to the properties of lithium that are relevant to this study.
1.1 BACKGROUND

Lithium has been proposed as a potential blanket material in conceptual fusion reactors. In addition to being a good tritium breeder, its high thermal conductivity makes it an ideal coolant. What has kept lithium from being the obvious blanket choice is the fact that it is flammable and highly corrosive in its liquid state and will experience severe temperature excursions in some chemical reactions. It is important, therefore, to have a good model of the reaction kinetics of lithium and the various reactants with which it could come in contact in the event of a containment rupture. With this model, the consequences of lithium fires can be weighed and the decision made on the suitability of lithium as the blanket material.

The purpose of the work presented here is to measure the reaction rate between lithium and oxygen at various temperatures to illustrate the relationship between reaction and temperature.

Before we discuss the work done in this experiment, some knowledge of the general properties of lithium will give good insight into the necessity of this work and serve as an explanation for our approach. We will cover first the physical and thermal properties.

As is true of all the alkali metals, lithium has a high thermal conductivity, which makes it a good coolant. Its melting point of 180°C allows its use in liquid form at relatively low temperatures. Lithium has the lowest density of any metals, which means that handling
machinery can be of a lighter construction and, therefore, less expen-
sive. Finally, at atmospheric pressure, lithium will not boil at
temperatures below 1350°C, allowing use of unpressurized systems,
again lowering costs and, additionally, increasing safety.

Of equal importance are the nuclear properties of lithium, which
make it a good choice for blanket material. The blanket, as breeder,
must promote the breeding of tritium, a necessary ingredient in pro-
posed thermonuclear reactor plasmas. Lithium-6, upon absorbing one of
these slow neutrons, yields a tritium ion plus an alpha particle. The
tritium is then used to fuel the fusion reaction.

1.2 INTRODUCTION

It is obvious then, that lithium has many advantages as a blanket
material. However, the disadvantages must also be taken into account.
At high temperatures, lithium will corrode glass, ceramics, carbon
steel, and some stainless steel. [D.W. Jeppson, 1978] It reacts
readily with air and concrete, and violently with water. In addition,
several runs of the experiment described in this thesis experienced
temperature excursions as notable as 1000°C in 10 seconds.

It is of utmost importance, then, to have a model that accurately
predicts these reactions. The experiment presented later is one of a
series of projects sponsored by EG&G to characterize the reaction
kinetics. A computer code, LITFIRE, was developed at MIT with the
intention of predicting the consequences of lithium air reactions, but
a lack of data in several areas forced the authors to make assumptions that were not always qualified by data. [M.S. Tillack and M.S. Kazimi, 1980] In 1978, researchers at Hanford Engineering Development Laboratory ran a series of experiments measuring pressures and temperatures experienced in contained lithium reactions. [D.W. Jeppson, 1979] LITFIRE was applied to the HEDL tests and was shown to overpredict both nitrogen and oxygen reaction rates. It was realized that, for LITFIRE to have credibility, more accurate data would have to be incorporated. Work has been underway at MIT for several years to produce the needed data. [W.J. Ijams and M.S. Kazimi, 1985]
CHAPTER 2 APPARATUS AND PROCEDURE

This chapter will briefly describe Ijams' work, present an overview of the present experiment, and describe the apparatus and procedures used.
2.1 BACKGROUND

Data needed to modify LITFIRE include, among others, rates for lithium-nitrogen, -oxygen, and -air reactions at various temperatures.

In 1984, William J. Ijams at MIT ran a series of tests measuring reaction rates with nitrogen. The apparatus and procedures used are essentially the same as those in this experiment. They will be covered in detail later in this chapter. A copy of the curve Ijams generated for nitrogen reaction rate vs. temperature has been included here for reference (Fig. 2-1). It can be seen that at low temperatures (300 - 600°C) the reaction rate is relatively small, less than 0.2 g Li/cm²/min. At around 650°C, the rate increases sharply, levels off at 0.8 g around 800°C, and drops rapidly at 1100°C.

2.2 OVERVIEW OF EXPERIMENT

To measure the reaction rate, the gas is run from a tank fitted with a pressure meter through a small chamber containing molten lithium, and into a second tank, also with a pressure meter. The pressure in the two tanks is read simultaneously and recorded. Using the known volumes of the tanks, the total pressure loss can be calculated. This pressure loss is fed into the ideal gas equation to find the number of moles of gas reacted. This number is then used in the reaction's molar balance equation to solve for the mass of lithium reacted. The mass is then divided by the area over which the reaction
takes place and the time interval between readings to yield the number of grams of lithium reacted per square centimeter per minute, which is plotted against the temperature of the lithium pool for that particular run. A complete run-through of the equations, including conversion factors, is presented in Section 2.3.
Fig. 2-1. Reaction rate for nitrogen as a function of temperature.
2.3 CALCULATIONS

\[ P_{1i} = \text{initial pressure of tank 1} \]
\[ P_{2i} = \text{initial pressure of tank 2} \]
\[ P_{1f} = \text{final pressure of tank 1} \]
\[ P_{2f} = \text{final pressure of tank 2} \]
\[ V_1 = \text{volume of tank 1} \]
\[ V_2 = \text{volume of tank 2} \]

\[ \Delta P_1 = \frac{V_1}{V_2} (P_{1i} - P_{1f}) = \frac{0.00416 \text{ m}^3}{0.01402 \text{ m}^3} (P_{1i} - P_{1f}) \]

\[ \Delta P_2 = (P_{2i} - P_{2f}) \]

\[ \Delta P_{\text{total}} = \Delta P_1 - \Delta P_2 \text{ (psi)} \]

\[ n = \text{number of moles of oxygen reacted} \]

\[ \frac{\Delta P_{\text{tot}} \cdot V_2}{R \cdot T} = \text{number of moles of oxygen reacted} \]

\[ R = \text{ideal gas constant} \]

\[ T = \text{temperature in } ^\circ \text{K} \]

\[ \Delta P_{\text{tot}} = \frac{(1 \text{b/in}^2) \cdot 101328 \text{ (Pa/atm)} \cdot 0.01402 \text{ (m}^3)}{8.314 \text{ (J/mol/}^\circ \text{K)} \cdot 14.696 \text{ (lb/in}^2\text{/atm)} \cdot T(}^\circ \text{K)} \]

\[ n = \text{n mol oxygen} \]

reaction rate = \( n \text{ mol} \div 7.5 \text{ s} \) (time between readings)

reaction rate (g Li/min) = \( \frac{n \text{ mol O}}{60 \text{ s}} \cdot \frac{60 \text{ s}}{\text{min}} \cdot \frac{6.942 \text{ g Li}}{\text{mol Li}} \cdot \frac{4 \text{ mol Li}}{1 \text{ mol O}} \)

reaction rate per unit area (g Li/min/cm\(^2\)) = \( rr \text{ (g Li/min)} \div 3.88 \text{ cm}^2 \)
2.4 APPARATUS

The experimental apparatus was designed and built by William Ijams of MIT for his study of nitrogen-lithium reactions. Fig. 2-2 is a schematic of the set-up. The gas flows in 1/4"OD copper tubing from the oxygen and nitrogen bottles, through a Linde Molecular Sieve, grade 4A, to remove humidity, and into tank 1. Tank 1, made of aluminum, has a volume of 0.00416 m$^3$; a pressure sensor transmits the pressure reading to the data acquisition system. The gas then runs through a flow meter made by Fischer Porter of Warminster, PA and into a stainless steel pipe, through the reaction chamber, and out another stainless steel pipe. The stainless steel pipe is connected to the copper tubing by compression fittings. The gas then flows through a heat exchanger and a filter (for removing particulate reaction products), and into tank 2. The heat exchanger consists of a length of the tubing situated under water. As the gas flows through this section it is cooled to approximately room temperature, which is the temperature of the gas before the reaction. In this manner, the two pressure readings are made at the same temperature, eliminating the need to correct for that in the ideal gas relation. The difference between the two tanks is less than 1°C.

The lithium used was purchased from Aldrich Chemical Co. of Milwaukee, WI. That used for the first nine runs of the experiment was in pebble form, with a purity of 99.5%. The surface was a dark brown-gray, with occasional specks of red or white. The white would indi-
cate oxide, the red, nitride, and the dark brown-gray, either nitride or hydroxide. For the last two runs, the lithium was bought in ribbon form, 0.38 mm thick, with a purity of 99.9%. This was a dull silver in the shipping bottle and would soon turn dark gray when exposed to the atmosphere. Both types were shipped and stored in argon-filled glass bottles.

Fig. 2-3 is a photo of the reaction chamber, gas lines, tanks, and the furnace. The furnace consists of heaters and insulating walls. The four heaters are a high temperature ceramic rated to 1200°C, and each delivers 700 W. The furnace walls are one foot square blocks of "Fiberfrax" insulation, 6" thick, made by Carborundum Corp. of Niagara Falls, NY. Fiberfrax is composed of aluminum oxide and silicon oxide. The floor of the furnace has a stainless steel sheet on top of the insulation to catch any spills. The furnace walls are attached to a framework of standard perforated angle-iron. The top and front panels of the furnace are not shown in Fig. 2-3.

The reaction chamber is shown in detail in Fig. 2-4. It is made of stainless steel 316. Its inner diameter is 2.22 cm, with walls 0.32 cm thick; its cross sectional area is 3.88 cm². The gas enters and exits the chamber via a 0.430"ID pipe, also of type 316 stainless steel. The chamber lid and bottom are bolted together with six 10-32 bolts, 1" long. The stainless steel bolts and nuts are treated to eliminate fusing at high temperatures. The treatment consists of painting on the hardware #1000 Lubelok, made by Electrofilm, Inc., of Cherry Hill, NJ. The painted nuts and bolts are baked in the oven at
550°C for 15-30 minutes. After cooling, they are painted with #2006 (somewhat darker than #1000). They are then baked at 275°C for 2 hours.

The thermocouple probe, made by Omega Engineering of Stamford, CT, extended through a hole in the chamber roof in Ijams' design but was later moved to the bottom the chamber, where it is welded into place. This makes for much work when the probe needs to be replaced due to melting or excessive corrosion. The probe was replaced twice during Ijams' nitrogen tests on account of corrosion and three times during the oxygen tests because of melting. A type K thermocouple is inserted into the probe and fixed in place with Omega CC High Temperature Cement. The thermocouple extends approximately 0.5 cm into the reaction chamber. It is important that the probe remain under the surface of the lithium pool, as it is the temperature of the pool we wish to measure. The reaction takes place just above the surface of the pool at a temperature much higher than that of the lithium pool. Initially, we had the probe enter the chamber from above, but this left it exposed to the reaction, which caused it to melt. The probe is also SS316 and has an outer diameter of 3/16". Type 304 stainless steel was found to be too susceptible to corrosion and melting. The 316, with a melting point of around 1400°C was not found to melt in the nitrogen runs. In the oxygen runs, which produce a greater amount of heat, there was a problem with the 316 melting.

The O-ring is made of Inconel X-750 by Advanced Products Co. of
North Haven, CT. It is coated on top and bottom with a thin layer of a silver-nickel compound to allow for a good seal. This compound is "Silver Goop," made by the Crawford Fitting Company of Solon, OH. The Goop used is from an old tube and partially dried out. New Silver Goop is too liquid. Inconel is able to withstand the high temperatures and corrosion well enough to be used repeatedly. However, the flattening experienced when compressed limits the O-ring usage to two runs.

Temperature readings are taken with thermocouples in tank 1, the reaction chamber, and tank 2; additionally, a reading is taken of room temperature. Pressure is measured in both tanks with sensors made by Setra Systems, Inc., of Acton, MA. In both cases, the data is sent to the "Remote Analog Multiplexing Processor" manufactured by Kaye Instruments of Bedford, MA. The RAMP receives the signal in millivolts and outputs degrees centigrade or psi. It can take input through 64 channels; we use 12. In addition to the six channels mentioned previously, 4 thermocouples take readings along the gas pipeline for monitoring purposes. We use both K and E type thermocouples, both of which require a reference data point; these account for the two remaining channels. The four gasoline and two reference thermocouples are not read during a run. The RAMP is equipped with a printer, so the experimenter need focus his attention only on the flow meter during a run. When the RAMP is set on "Autolog" mode, it reads and records the six channels in 7.5 seconds. This is the minimum time interval; it can not be reduced by recording fewer channels.
Ijams' original design used standard mechanical pressure meters on the two tanks. These required monitoring during the experiment, which meant that two people were needed to run the tests. With the addition of the digital meters, the pressure was read and recorded automatically, eliminating the need for the second person. This alteration was performed by T.K. Gil of MIT.
Fig. 2-2. Experimental Setup
Fig. 2-3. Photo of apparatus showing reaction chamber, gas lines, tanks, heat exchanger, and furnace.
Fig. 2-4. Reaction Chamber
2.5 PROCEDURE

2.5.1 Introduction

Oxygen from a 2000 psi bottle is bled through a chamber containing molten lithium, where some of the gas reacts, and then into tank 2. The pressure gain in tank 2 is compared with the pressure loss in tank 1. The difference is the gas that reacted.

2.5.2 Purging the Tanks and Filling Tank 1

Both tanks must be purged before each run to ensure there is no gas present that would alter the results. Tank 2 is purged by filling with argon to approximately 5 psi, allowing the gas to equilibrate, and then emptying the tank. This procedure is followed four or five times. Argon is used because it is inert and easy to work with. Argon is also used as the cover gas for the lithium.

Tank 1 is emptied of any gas remaining from the previous run and slowly filled to 50 psi with oxygen. The fill should be slow enough to allow the molecular sieve to remove any moisture in the gas flow. Again, there is a few minute wait for equilibration, and the tank is emptied. This procedure is followed four or five times. On the last two purges, some amount of the oxygen should be run through the flow meter and discarded to the atmosphere via valve 6. This removes any contaminants and leaves the section of tubing between the tank and valve 6 filled with oxygen. Tank 1 is then slowly filled to 52 psi and held. Some will leak out.
2.5.3 Lithium Loading and Heatup

The lithium is stored in a jar filled with argon and sealed against the atmosphere with tape. The transfer of lithium from the jar to the reaction chamber takes place inside a large plastic bag from which the air has been expelled with a steady stream of argon. The jar is opened and the rolled lithium ribbon removed. Rubber gloves are worn to avoid contamination of the lithium. Several inches are unrolled, torn off, re-rolled tightly, and placed in the chamber bottom. For the runs involving the lithium shot, the loading process involves simply pouring approximately 2 grams of pellets into the chamber. Enough lithium should be put in so that, once melted, the pool will cover the probe. The jar is then resealed, and the lithium-filled chamber removed from the plastic bag. While the lid is being bolted to the chamber, the lithium is protected from the atmosphere by a flow of argon from a rubber hose led into the chamber's outlet pipe. Before the lithium loading, while the tanks are being purged, the Inconel O-ring is coated on both sides with Silver Goop and placed in the slot on top of the reaction chamber bottom. It is important that the chamber bottom and lid be aligned perfectly, or a poor seal will result.

The reaction chamber is then placed in the oven and the connections to the copper tubing tightened. The left end is tightened first while the rubber hose from the argon tank remains in the right side. When the left side is tight, the hose is extracted from the pipe and
reattached on the left side to valve 6. Valves 6 and 7 are then opened, and the pipe exiting the reaction site is connected. At this point, valves 8 and 9 are opened to keep pressure from building up in the chamber before the Silver Goop has had a chance to melt and form a good seal. Valve 9 is adjusted to keep a constant pressure in tank 2. Valve 8 is opened all the way. The heaters are then turned on.

When the lithium is approaching the desired temperature, valves 6, 7, and 9 are closed, and the pressure in tank 2 is monitored. Decreasing pressure would indicate a leak along the pipeline. When it has been determined that the system is leak-free, valve 8 is closed and valve 9 opened. When the pressure in tank 2 has decreased to less than 0.03 psi, valve 9 is closed.

2.5.4 The Reaction

Once the desired lithium pool temperature is reached and maintained, the experiment can be run. Valve 8 is opened to decrease the pressure in the reaction site. Valve 9 is then closed. The RAMP is programmed to read channels 5 through 10 with zero time delay between readings. Autolog is started and valve 7 opened. The timing is important here, as the gas held in check behind valve 7 is the oxygen-argon mix. Before the RAMP has started the second set of readings, valve 5 is opened, allowing the gas from tank 1 to flow to the reaction site and then on to tank 2.

The gas flow is kept constant by adjusting valve 5. While monitoring the gas flow, the experimenter must also keep his eye on the
temperature reading from the reaction site. If the temperature starts climbing rapidly, the gas flow should be turned off to avoid melting the probe. After four or five readings (the pressure in tank 1 should be 42 to 44 psi), valve 5 is closed.

2.5.5 Cooldown and Cleanup

The oven is opened to allow the reaction chamber to cool. When it has cooled enough to handle, the pipes are disconnected from the copper tubing and the chamber is taken apart by removing the 6 bolts. The residue in the chamber bottom is inspected and observations recorded. The chamber is then soaked in water to loosen the reaction products. Any unreacted lithium remaining at this time will react with the water. The residue should come out easily after a few hours of soaking. The chamber is then dried, the O-ring pried out, and the inside cleaned with a fine grade emery cloth. The O-ring and O-ring slot are also cleaned with emery cloth.
CHAPTER 3 RESULTS OF OXYGEN RUNS

This chapter discusses the results of the lithium-oxygen tests.

Each run is discussed separately.
3.1 OVERVIEW

Eleven tests with oxygen were run at temperatures in the range 325°C to 800°C, meeting with very erratic results. Several runs experienced little or no melting of the lithium pellets, even at temperatures well above the melting point of lithium, 180°C. In others the lithium melted and there was a measurable reaction that left a questionable residue and produced an irregular reaction rate. And some runs resulted in a violent reaction that melted the stainless steel temperature probe and, in one case, the wall of the reaction chamber itself. The first runs used lithium pellets (as opposed to lithium ribbon), and had the thermocouple enter the chamber from the top.

3.2 RUN 1

The first oxygen run, made at a pool temperature of 385°C, yielded a reaction rate of 0.166 grams of lithium per square centimeter per minute. When compared with Ijams' result at that temperature for nitrogen (0.04 g/cm²/min), support was lent to HEDL's prediction of a reaction rate for oxygen four times that for nitrogen. [D.W. Jeppson, 1979] However, opening the chamber revealed that the pellets had not melted. There was some fusing together at the bottom of the chamber, but the majority of the pellets were unchanged in form.

3.3 RUN 2

A second test was made at 385°C to attempt to account for the
behavior of the lithium. Again, the lithium pellets remained intact, but this time, the reaction rate was found to be 0.082 g/cm³/min, half of the previous result.

3.4 RUN 3

It was decided to go to a moderately high temperature, 540°C, for the next run, to ensure melt. The lithium did melt and there was a very strong reaction that melted the stainless steel temperature probe. The magnitude of the increase in temperature is not known, as the data acquisition system overloaded on the channel reading the pool temperature. The first temperature reading, taken at the opening of the valve allowing gas into the chamber, was 537°C. 7.5 seconds later, at the second reading, the temperature was 557°C. The third and following readings were overloaded. Two possible causes of the overload reading are that damage sustained by the thermocouple wires caused a short or that the temperature change was too rapid for the system to process. Opening of the chamber revealed an impervious, severely irregular surface that was colored a dull gray. Soaking in water loosened the residue and exposed the bottom inch of the temperature probe, which had burned through at the surface of the lithium pool where the reaction took place. This can be seen in Fig. 3-1. The reaction rate of 0.40 g/cm³/min seemed plausible, but uncertainty over the effects of the melted stainless steel on the reaction make the results questionable.
3.5 RUN 4

The temperature probe was replaced and a new thermocouple installed. It was decided to heat the lithium to 530°C and then cool it to 330°C for the run. It was thought that the resistance to melting in the earlier runs was caused by the surface layer of oxide and nitride on the pellets. Once melted, the lithium would give up some of these impurities and remain in liquid state when lowered to a safe working temperature. This procedure was followed and the test was run. Inspection showed that, again, the pellets did not melt, even though they had been heated to 530°C. Considering the lithium was not molten during the reaction, the yielded rate of 0.38 g/cm²/min seemed abnormally high. Plotting showed this to be the case.

3.6 RUN 5

Hypothesizing that the lithium used in the first four runs was contaminated in some way, a new batch of pellets was purchased and a run made at 450°C. This time the lithium was heated to 610°C and cooled. The lithium experienced partial melt, and the rate obtained, 0.18g/cm²/min, looked good on the graph.
Fig. 3-1. Photo of probe melted in Run 3 (magnification approximately 2\(\frac{1}{4}\)X).
3.7 RUN 6

For the sixth run, the new lithium was heated to 800°C and cooled to 600°C. Lithium melt was complete, and the results (0.50g/cm²/min) looked good. However, the reaction product was dull black, whereas lithium oxide is white.

3.8 RUN 7

The heatup was to 800°C again and the run temperature was 410°C. Melt was again complete, but results looked bad. The rate was somewhat high, and the residue was orange, except where the probe entered the solidified pool, where it was black. The probable explanation for the coloration is that new Silver Goop was used which was much more liquid than the old and it appeared to have leaked into the chamber.

3.9 RUN 8

A new batch of lithium pellets was obtained, although it was of the same lot as the previous bottle. The run was made at 665°C after heating to 900°C. Residue was black, and the rate was low, actually falling below the nitrogen curve. When soaking the chamber during cleanup, it was noticed that the reaction with the water was less vigorous than in cases where the lithium-oxygen reaction appeared to be less complete (i.e., cases of incomplete melt). This was anomalous in that the reaction rate here was lower.
3.10 RUN 9

For the ninth run the newer lithium was again used, and the run temperature was 800°C. This run resulted in a temperature excursion and melted probe. On this occasion, the excursion was observed, as the thermocouple apparently remained intact until the gas flow was shut off and the reaction stopped. Temperature readings, taken every 7.5 seconds, were 800, 1030, 1254, 1359, 1142. The gas flow was stopped prior to the final reading. It's not certain at what location in the chamber these readings were taken. When a probe is mounted in the chamber, the thermocouple wires extend to the tip of the probe. At some point in this run the probe melted at or near the pool surface and fell away. Apparently the exposed thermocouple wires remained in contact near the melt. At any rate, the temperatures are almost certainly of the reaction site and not the pool. These readings are plotted against time in Fig. 3-3.

Inspection of the chamber produced some interesting observations. Black and red residue coated the inside of the lid and the portion of the walls above the pool. A relatively large amount of this residue was found in the inlet pipe in hard, jagged chunks. The pool surface was smooth, unlike that of run number three, the first excessive reaction. The surface was light gray with a slight green tint and flaked off easily. Just beneath was darker gray and very solid. Again, the reaction rate fell below the nitrogen curve.
3.11 RUN 10

It was decided that the 99.5% pure lithium would not yield valid results, as evidenced by the erratic reactions. New lithium was purchased in ribbon form with 99.9% purity. The experiment was run at 430°C and the probe melted at the pool surface. This time, only one reading was taken before the temperature overloaded, so there was no indication of the extent of the temperature rise. The residue was dull gray, as was the case with the other two runs in which the probe melted. The coloration is assumed to have come from the stainless steel. The reaction rate attained was ridiculously high, 3.48 g/cm²/min, due probably to the probe.

3.12 RUN 11

The chamber was redesigned with the probe entering from the bottom so it would be under the surface of the pool and not subjected to the high temperatures of the reaction site just above the surface. Lithium ribbon was loaded in and a run made, starting at 435°C. The temperature climb was observed and the run completed with pool temperatures remaining well below the 1400°C required to melt the probe. Readings were 435, 800, 1134, 1057. The gas flow was turned off prior to the last reading. When the oven was opened, it was discovered that the heat at the reaction site had been great enough to melt a hole in the side of the chamber (see Fig. 3-2). The reaction rate for that side was a bit high, but plausible at 1.08g/cm²/min. Fig. 3-3 is a
graph of the two observed temperature excursions.
Fig. 3-3. Time Record of Temperature Excursions in Runs 9 and 11.
3.13 CONCLUSIONS

The graph of reaction rate for the various runs (Fig. 3-4) shows how erratic the results were. Runs 1, 2, and 4 had essentially no melting of the lithium pellets. These points fall above the curve for nitrogen as HEDL and others had predicted, despite the decreased reactivity of solid lithium. The reason for this is that pellets provide a much larger surface area to support the reaction. These results would have to be discarded even if they were more homogeneous, as there is no way to gauge the reaction area unless the lithium melts. The runaway reaction in run 3 is somewhat puzzling as it involved the same lithium as the two runs before it and the one after. The cause was probably contamination other than the impurities in the lithium. Water, which acts as a catalyst in many lithium-gas reactions, had entered the experimental apparatus as a result of some other work related to this project. It is suspected that attempts to dry out the system prior to run 3 were not entirely successful. The next five runs saw incomplete melt at low temperatures, complete melt with strangely colored reaction products at medium temperatures, and a violent reaction at a moderately high temperature resulting in probe melt. Lithium of higher purity (99.9%) was used in runs 10 and 11. These low temperature runs resulted in runaway reactions that melted the probe and then the reaction chamber.
Fig. 3-4. Results of tests for reaction rate vs temperature in lithium-oxygen reactions.
Apparently the purity of the new lithium would be great enough to ensure accurate results if the apparatus could withstand the heat of the reaction. Inserting the temperature probe through the chamber bottom eliminated danger to it as long as the depth of the lithium pool is great enough to cover the probe. But the reaction chamber, which was subjected to the full heat of the reaction, had to be redesigned.
CHAPTER 4 DESIGN OF NEW CHAMBER

This chapter will discuss the work done in designing a new chamber. It presents the heat transfer calculations and design considerations. The design of the original chamber is discussed, and the decision-making process on the new design is described.
4.1 INTRODUCTION

In order to design a new chamber, it was necessary to calculate the amount of heat conducted to the chamber wall and the temperature drop across the wall. Different designs employing various materials could then be compared and a decision made on the best design. Since the chamber bottom is of simple construction and relatively small, cost of materials and manufacturing was considered of secondary importance. The limited choice of materials capable of withstanding the temperatures and corrosion inherent in this experiment forces the experimenter to neglect economics in his decision.

4.2 HEAT TRANSFER CALCULATIONS

The first step in the decision-making process is the heat transfer calculations. The HEDL report "Interactions of Liquid Lithium with Various Atmospheres, Concretes, and Insulating Materials; and Filtration of Lithium Aerosols" stated that the heat released by the complete reaction of lithium with oxygen is 142.7 kcal per gram-atom of oxygen. This corresponds to 142.7 kcal per 14 grams of lithium. We estimated the mass of lithium used in a run to be 2 grams. For an average run time of 25 seconds, this gives a heat transfer rate of 3.42E3 watts.

\[ Q = \frac{142.7 \text{kcal}}{14g} \cdot 2g \cdot \frac{1}{25 \text{s}} \cdot \frac{4.19E3 \text{J}}{\text{kcal}} = 3.42E3 \text{ W} \]

Now, for conduction in a cylinder (assuming steady state thermal
resistance can be used):

$$\Delta T = Q \cdot R$$

where

$$R = \frac{\ln (ro/ri)}{2 \pi L k}$$

ro = outer radius of chamber  
ri = inner radius of chamber  
L = height of reaction site, estimated here to be 0.5 cm  
k = thermal conductivity in W/m°K

Therefore, to find the temperature change across the wall, values must be inserted for the radii and the thermal conductivity. These values are the design considerations. It should be noted that the transient time for heat transfer across the 0.32cm chamber wall is much less than the 25 second reaction time.

When the calculation is done for the original design (ro = 0.0143 m, ri = 0.0111 m, L = 0.005 m, and k = 26 W/m°K (for lithium at 1000° C)) the temperature drop is found to be 1060°C. Lower thermal resistance would mean a smaller temperature difference, more heat convected from the outer wall of the chamber to the air in the oven, and therefore less risk of melting the chamber. There are two means of achieving this lower resistance: reduce the ratio of ro/ri, or increase k. (We assume L to be a constant over which we have no control.)

Reducing the radius ratio would have a very slight effect on the thermal resistance, since the term is logarithmic. Therefore the focus of our attention is on k, determined by the material from which the chamber is constructed.
4.3 ORIGINAL DESIGN

Stainless steel 316 was chosen for the original chamber because of its relatively high melting point (1375-1400°C) and its resistance to corrosion. In liquid form, lithium is highly corrosive to most materials, including many metals. Stainless steel 316 is resistant, as evidenced by the fact that Ijams lost only two temperature probes to corrosion during 50 tests, and the wall of the probes is 1/16 inch thick. The original design was sufficient to accommodate temperatures in the nitrogen tests but not the oxygen. The low thermal conductivity of SS316 caused heat to build up to the point where the temperature was above the melting point.

What was needed, then, was a material with a high melting point, high thermal conductivity, and resistance to corrosion by lithium.

4.4 MATERIALS CONSIDERED

4.4.1 Stainless Steel

Stainless steels were considered first due to their abundance and ease of machining. Those in the 304-316 series were discounted due to low thermal conductivity and low melting point. The 405-416 group was looked at because of a generally higher melting point and slightly higher k, around 30W/m·K. [Kirk-Othmer, 1984. NOTE: All values in this section are from same reference.] This would resist melting on a 1000°C run as long as the temperature of the reaction remained below 1460°C, which is not a big enough margin. In addition, this series is
not as resistant to corrosion.

4.4.2 Molybdenum

Molybdenum was considered because of its high melting point of 2600°C and thermal conductivity of 100 at 1000°C. However molybdenum is not resistant to lithium above 925°C.

4.4.3 Tantalum

Tantalum was the next choice with $k = 54 \text{ W/m}^\circ\text{K}$ (at 20°C), high melting point of 2996°C, and resistance to corrosion by liquid metals. Tantalum is very ductile and easy to work with, but reacts with air at temperatures above 260°C.

4.4.4 Tungsten

Tungsten was finally chosen as the correct material because of its high thermal conductivity of 118W/m°C at 1000°C and easily sufficient melting point of 3500°C. Tungsten resists lithium up to 1620°C, and above that, the attack is slow. Heat transfer calculations show the temperature drop to be 235°C.

4.5 DESIGN

There were two designs considered, a new chamber made entirely of the chosen material, tungsten, or a liner placed inside the existing stainless steel chamber. The liner, unlike the whole-chamber material, should have a low thermal conductivity to act as a shield and
maintain a large temperature difference between the reaction and the stainless steel. It must also have a very high melting point and be resistant to lithium. No available materials were found that fit these requirements.

The final design was a chamber of the same dimensions, made entirely of tungsten. It was decided there would be no benefit from altering the physical design, as that would cause other apparatus to be redesigned and make little difference in thermal behavior or cost. The temperature drop across the tungsten wall would be 235°C, ensuring the integrity of the chamber.
CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS
5.1 ORIGINAL INTENT OF PROJECT

This project was undertaken with the intent of measuring and recording the reaction rate in lithium-oxygen reactions at various temperatures. We took existing equipment, made minor alterations, and ran 11 tests.

5.2 RESULTS

The first 9 tests met with erratic results ranging from resistance of lithium to melt, even 400°C above the melting point, to violent reactions that melted the stainless steel temperature probe. Lithium of greater purity was acquired for the last two runs. The first reaction melted the probe, so we redesigned the chamber with the probe entering through the bottom to avoid the extreme temperatures at the pool surface. The last one melted a hole in the side of the chamber. A new chamber was designed of tungsten to withstand the high temperature and corrosion of the lithium-oxygen reaction.

5.3 RECOMMENDATIONS

Tungsten reacts with oxygen at very high temperatures. Therefore, a small amount of the metal should be placed in an oven and heated to 1600°C to test its viability as the material choice for the new chamber. An oven other than the one used in this project must be used, as it is rated only to 1200°C. Following successful completion
of this test, the new chamber can be built and the oxygen-lithium testing resumed.
REFERENCES


D.W. Jeppson, "Interactions of Liquid Lithium with Various Atmospheres, Concretes, and Insulating Materials; and Filtra-


### APPENDIX

<table>
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<tr>
<th>RUN #</th>
<th>TEMP(°C)</th>
<th>$P_{1i}$</th>
<th>$P_{2i}$</th>
<th>$P_{1f}$</th>
<th>$P_{2f}$ (psi)</th>
<th>REACTION RATE(g/cm²/min)</th>
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