NASA-CR-192771

GRANT
IN-25-CR
154178
P.58

THE PROPERTIES OF

AND

ANALYTICAL METHODS FOR

DETECTION OF

LiOH AND Li_2CO_3

DR. GUNA SELVADURAY
DEPARTMENT OF MATERIALS ENGINEERING
SAN JOSE STATE UNIVERSITY
SAN JOSE, CA 95192

February 8, 1991

This investigation was supported by NASA-Ames Research Center under Cooperative Agreement Number NCC2-640, Grants Officer for NASA-Ames: Barbara Hastings, Technical Monitor: Bernadette Luna. The findings and opinions reported here are those of the author, and do not necessarily reflect those of NASA-Ames.

(NASA-CR-192771) THE PROPERTIES OF AND ANALYTICAL METHODS FOR DETECTION OF LiOH AND Li2CO3 (San Jose State Univ.) 58 p

N93-25240

Unclas

G3/25 0154178

ACKNOWLEDGEMENTS

The author wishes to acknowledge the guidance and support of the following individuals, without which this study could not have been completed:

Bernadette Luna, NASA-Ames, Technical Monitor of this project.

Waley Sung, Department of Materials Engineering, San Jose State University, who devoted endless hours in the library, and on the computer.

Dr. Ernie Unwin, Industrial and Systems Engineering Department, San Jose State University, who was the Principal Investigator of this project.

Table of Contents

Page

Acknowledgements ii

Table of Contents iii

1. Background 1

2. Objective of Study 3

3. Properties of LiOH, $LiOH.H_2O$, and Li_2CO_3 3

4. Some Preliminary Considerations that will Affect Choice of Experimental Technique 4

5. Analytical Methodologies for Measurement of the Conversion of LiOH to Li_2CO_3 9

5.1 Direct Techniques 10

5.1.1 X-ray Diffraction 10

5.1.2 Infra-Red Spectroscopy 12

5.1.3 Gas Mass Spectrometry 13

5.1.4 Ion Chromatography 14

5.1.5 Auger Electron Spectroscopy 15

5.1.6 Electron Spectroscopy for Chemical Analysis 15

5.1.7 Wet Chemical Analysis 15

5.2 Indirect Techniques 16

5.2.1 Temperature/Thermocouples 16

5.2.2 Differential Scanning Calorimetry 18

5.2.3 Dissociation Method 19

5.2.4 Thermogravimetric Analysis 20

5.2.5 Phase Diagram Method 21

5.2.6 True Sample Density 22

Table of Contents (continued)

Page

5.3 Equipment Costs 23

6. Conclusion 23

7. References 25

Appendix A Computerized Literature Search of the American Chemical Society Database

Appendix B Computerized Literature Search of COMPENDEX

Appendix C Computerized Literature Search of HEILBRON

Appendix D Computerized Literature Search of STN International Database

Appendix E Calculation of Thermodynamic Data for LiOH - Li_2CO_3 Reactions

Appendix F Calculation of the Piling-Bedworth Ratio for LiOH/Li_2CO_3

Appendix G Stoichiometric Amount of CO_2 Reacting with LiOH

Appendix H X-ray Powder Diffraction for Quantitative Analysis of LiOH and Li_2CO_3

Appendix I Wet Chemical Quantitative Analysis for Lithium Compounds

Appendix J Listing of Thermodynamic Symbols used in this Study

1. Background

Lithium hydroxide (LiOH) is used as a CO_2 absorbent in the Shuttle Extravehicular Mobility Unit (EMU) Portable Life Support System (PLSS). The space suit exhaust gas, containing exhaled breathing gas, is passed through a canister containing the LiOH chemical before being replenished with oxygen, dehumidified, and cycled again through the breathing loop. The absorbent reaction proceeds in two steps as follows:

$$2LiOH\ (s) + 2H_2O\ (g) = 2LiOH.H_2O\ (s) \qquad (1)$$

$$2LiOH.H_2O\ (s) + CO_2\ (g) = Li_2CO_3\ (s) + 3H_2O\ (g) \qquad (2)$$

The net reaction may be represented more simply as:

$$2LiOH\ (s) + CO_2\ (g) = Li_2CO_3\ (s) + H_2O\ (g) \qquad (3)$$

LiOH is also used as an absorbent in diving breathing systems, and a great deal of research has been done on the efficiency of the chemical under varying conditions. The reaction is influenced by parameters such as flow composition, velocity, temperature, humidity, and canister geometry. The former properties may vary spatially throughout a given canister geometry, and so the extent of LiOH conversion will vary spatially throughout the canister. This may be the case with the Shuttle EMU Contaminant Control Cartridge (CCC). The canister geometry and inlet/outlet configuration suggest non-uniform flow within. If such non-uniform conditions result in non-uniform conversion, the canister cannot attain its true maximum theoretical CO_2 capacity. Characterizing the local conversion is the first step towards attainment of that theoretical capacity.

Very little work, if any, has been done to investigate the local chemical conversion within particular canister geometries, including the Shuttle EMU CCC. Canisters have been optimized for the mission of interest, operating conditions, and application specific design constraints (low volume, low weight, etc.). Canisters have been optimized from an "overall" viewpoint only, without regard to local areas of low or high conversion. If these areas of low conversion are significant, the opportunity exists for a significant increase in canister duration with no volume penalty and little or no weight penalty. Alternatively, one could use the knowledge of these areas of varying conversion to "program" the canister, so that the chemical was exhausted in a spatially sequential fashion. If such a "programmed" canister could be attained, and it was oversized for a typical mission (safety factor), one might be able to replace **only** the exhausted chemical after a mission, instead of the **entire** canister contents. On advanced, long duration space missions with substantial amounts of planned Extravehicular Activity (EVA), this translates directly to a savings in launch/resupply weight, and it may be significant.

It is desired at this time to devise a method of determining the local occurrence of the LiOH conversion reaction, and the extent of conversion, either in real-time during a test run, or at the completion of several test runs, each of increasing duration, so as to get a four dimensional "map" of the reaction, with time being the fourth dimension.

Reaction (3) is exothermic. Therefore, thermocouples have been used in the past to monitor the occurrence of the conversion reaction in real-time. A great number of thermocouples have never been used simultaneously, as the local conversion has not been of interest in the past. Such instrumentation would likely interfere with the flow and may alter true results. Alternatively, after a canister is expended, simple drying and weighing techniques have been used to quantify the extent of conversion of the LiOH. This conveniently gives the extent of conversion for the entire canister - an overall conversion. More spatially localized conversion rates can be obtained by subdividing the contents of a canister, e.g., by manually removing specific geometric portions of the granular chemical and analyzing each separately. This becomes increasing time consuming and labor intensive with higher degrees of localization.

2. Objective of Study

The first objective of this study was to survey parameters that may be used to indicate conversion of LiOH to Li_2CO_3, and compile a list of all possible properties, including physical, chemical, structural and electrical, that may serve to indicate the occurrence of reaction. These properties were compiled for the reactant (LiOH), the intermediate monohydrate compound ($LiOH.H_2O$), and the final product (Li_2CO_3).

The second objective of this study was to survey measurement and analytical techniques which may be used in conjunction with each of the properties identified above, to determine the extent of conversion of LiOH to Li_2CO_3. Both real-time and post-run techniques were of interest. The techniques were also evaluated in terms of complexity, technology readiness, materials/equipment availability, and cost, where possible.

3. Properties of LiOH, $LiOH.H_2O$, and Li_2CO_3

Tables 1 through 16 list the various properties of LiOH, $LiOH.H_2O$, and Li_2CO_3, to the extent they were determinable. For ease of reference, these have been categorized into the following groups: physical, thermodynamic, structural (crystallographic), and chemical.

The physical properties are listed in Tables 1 through 4. The thermodynamic properties are listed in Tables 5 through 13. The electrical properties are listed in Tables 14 and 15, and the structural (crystallographic) properties are listed in Table 16.

The data reported in these tables were obtained by both manual and computerized literature searches. The manual search for data was conducted by physically searching the multitude of references available at the Clark and Wahlquist Libraries, San Jose State University. References that provided relevant data are listed in the footnotes.

The computerized literature search covered the following databases: American Chemical Society, COMPENDEX, HEILBRON, and STN. The results of these searches are attached in Appendices A through D.

In order to render the data contained in Tables 1 through 16 more usable, the properties that differ significantly for LiOH and Li_2CO_3 have been extracted and are listed in Table 17. As can be seen from this table, several of these "property differences" could possibly be exploited for the purpose of this investigation.

4. Some Preliminary Considerations that will Affect Choice of Experimental Technique

There are a number of items that must first be considered, and discussed, before the experimental techniques, and their appropriateness can be discussed.

The thermodynamics, and mechanism, of the reactions between water and carbon dioxide with lithium hydroxide have been reviewed by Boryta and Maas.(1) Based on a review of previous papers pertaining to this subject, Boryta and Maas state that the reaction of water and carbon dioxide with lithium hydroxide can be represented by Equations (1) and (2), with the overall process being represented by Equation (3).

The Gibbs Free Energy changes for reactions (1) through (3), and the direct carbonation and hydration of Li_2O were calculated and are presented in Appendix E. The thermodynamic data indicates that LiOH will be carbonated by CO_2 since the Standard Gibbs Free Energy change for Reaction (3) is a negative quantity. Given this fact, the only plausible explanation for the requirement that the hydrated species be formed first is that the activation energy barrier for Reaction (3) is extremely high at the temperature(s) of interest. In which case, the formation of $LiOH.H_2O$ serves to lower the activation energy barrier, i.e., it functions as a catalyst.

The exact kinetic mechanism by which the carbonation reaction proceeds will also affect the extent of reaction. The LiOH used in the EMU CCC is in the form of white porous granules with high surface area, having an apparent density of 0.42 g/cc, with between 60 to 90 % of the granules having a particle size of -8 +14 mesh.(2,3) These particle sizes correspond to particles having diameters between 2.38 mm and 1.41 mm.

When CO_2 begins to react with LiOH (or $LiOH.H_2O$), the Li_2CO_3 will form on the surface of the LiOH granule. Further reaction will then be limited by the capability of CO_2 to diffuse through this layer to react with fresh LiOH. If the Li_2CO_3 forms a protective layer, the reaction will slow down, with the rate of reaction being inversely proportional to the thickness of the Li_2CO_3 layer.

In order to determine if the Li_2CO_3 will form a protective layer on LiOH, the Piling-Bedworth Ratio for the Li_2CO_3/LiOH couple was calculated and found to be 2.14. Appendix F contains the calculations of the Piling-Bedworth Ratio. This indicates that

Li_2CO_3 will not form a protective layer on top of LiOH. However, despite this, the total LiOH surface area available for the reaction will still decrease, and the reaction can be expected to slow down, though not quite as fast. Total (100%) conversion of the LiOH to Li_2CO_3 will therefore take an extremely long time, and may not be practical in any case.

The currently required chemical conversion (from LiOH to Li_2CO_3) is greater than 80%.(3) The guaranteed CO_2 absorption of 0.79 g/gLiOH(2) corresponds to a conversion ratio of approximately 86% based on a stoichiometric absorption amount of 0.92 g CO_2/g LiOH, as determined by the calculations shown in Appendix G.

A conversion ratio of 86%, for a gas-solid reaction, is quite reasonable. However, the factor that has thus far not been identified is the time taken to attain this conversion ratio. The problem, therefore, is twofold. The first issue is: is the LiOH contained in the canister being converted uniformly? Coupled to this issue is the second issue of the speed of overall conversion. If the conversion is occurring at preferential locations, then the overall conversion rate could slow down more than expected due to build-up of reaction products at selected locations, while other locations are insufficiently reacted.

It is therefore necessary to characterize the localized conversion rate(s), within the canister, if the overall conversion rate is to be pushed to its maximum.

To summarize, there are two major issues that must be addressed when the extent of conversion of the LiOH to Li_2CO_3 is to be considered. First, there is the problem of distribution of localized conversion ratios within the canister. This is a result of the flow pattern of the CO_2 containing gases. Second is the question of extent of conversion of the individual granules of LiOH. Formation of Li_2CO_3 on the surface of the LiOH reduces the surface area available for further reaction with CO_2. This second question is one of kinetics of gas-solid reactions, and is directly affected by the specific surface area of the granules; in general, the higher the specific surface area, i.e., the smaller the particles, the greater the extent of reaction. Unfortunately, it is not always possible to make the granules infinitely small in order to obtain near-total conversion - gas flow would be severely hindered.

However, the surface area available for reaction can still be increased by increasing the porosity of the particles. This approach enables one to utilize relatively larger particles, which would be easier to handle, while providing an increased surface area for the reaction to proceed.

The next section, on analytical methods for measuring the conversion ratio of LiOH to Li_2CO_3, will therefore address methodologies for measurement of not only overall conversion within localized areas, but also conversion of individual granules (or particles) of LiOH.

Emphasis in the discussion of experimental techniques has been placed on detection of LiOH and Li_2CO_3. In some cases the presence of moisture can complicate the results. Water can be present as either adsorbed water or chemically bound water, which is the case in $LiOH.H_2O$.

It is assumed that all adsorbed water will be driven off first before any analysis is done. This could either be necessary or unnecessary, depending upon the particular technique. In the case of any technique that depends upon sample weight or volume of dissociated gases the presence of adsorbed moisture can confuse the results, and care must be taken to drive off the adsorbed moisture first. In the case of techniques that measure crystallographic planes or interatomic bonding, the presence of adsorbed moisture will not affect the results. Adsorbed moisture is usually driven off by heating the sample to approximately 120°C.

Chemically bound water, on the other hand, will not be driven off at 120°C, but rather at temperatures between 250 to 300°C. However, it is important that this form of water be not driven off because it represents the formation of the intermediate product. Common techniques, such as X-ray Diffraction, are capable of distinguishing between LiOH and $LiOH.H_2O$.

As has been stated earlier, Section 5 focuses on the detection of LiOH and Li_2CO_3 primarily, because these two compounds represent the starting and ending points. It is the absorbance of CO_2 that is of critical importance, and this is represented by the formation of Li_2CO_3.

5. ANALYTICAL METHODOLOGIES FOR MEASUREMENT OF THE CONVERSION OF LiOH TO Li_2CO_3

This section discusses the various possible methods for detection of LiOH and Li_2CO_3 and how they can be used to determine the extent of conversion of LiOH to Li_2CO_3. The methods can be divided into two major categories: (1) Techniques that "fingerprint" each of the compounds and are also capable of providing quantitative information on the concentration of each, and (2) Techniques that are based on information and or assumptions about the conversion reaction; this information is then used to either calculate or deduce the extent of conversion. For the purposes of this report, the first category is referred to as **Direct Techniques**, and the second category is referred to as **Indirect Techniques**.

In this particular case, real-time measurement of the reaction, and conversion of LiOH to Li_2CO_3 poses a special difficulty. It would be impossible to measure this conversion without breaching the canister, which in turn could result in disturbances to the usual pattern of gas flow.

The question of computerized data collection and digitizing of the information is not addressed on a technique-by-technique basis. With the technology available today, it would be possible to computerize data collection for most of the techniques described in this section. The question that cannot be answered at this point is the cost involved in computerizing the data collection process. This can vary very widely from technique to technique, and involves significant effort. It is therefore recommended that the best technique(s) for the purpose of this project be first identified, followed by an investigation of the equipment and cost involved in computerizing and automating data collection and data analysis for this particular technique.

The estimated cost of the equipment required for each of the techniques discussed here is presented in Section 5.3

5.1 Direct Techniques

There are a variety of direct techniques that provide both a "fingerprint" of, and quantitative information, on LiOH and Li_2CO_3. These techniques are reviewed and assessed in this section.

5.1.1 X-ray (Powder) Diffraction (XRD)

One of the oldest, and very well established, techniques is X-ray Diffraction, which is based on the diffraction of incident x-rays by the crystal structure of the solid upon which the x-rays are incident, in accordance with Bragg's Law. Figures 1 and 2 show the crystal structures of LiOH and $LiOH.H_2O$ respectively. A similar crystallographic diagram for Li_2CO_3 could not be located. This technique can be used for both qualitative and quantitative determinations. Tables 18 and 19 contain X-ray diffraction data for LiOH and Li_2CO_3. This data identifies LiOH and Li_2CO_3 uniquely, and there will be no other compounds with the same data. Actual measurements will result in a chart. The location of the peaks, and their intensities, will be in accordance with the 2θ and I/I_0 data contained in Tables 18 and 19, thus providing charts that are totally unique for each compound.

The most common technique for utilization of X-ray Diffraction is the Powder Method, in which the sample must first be pulverized or powdered. This approach is widely taken to ensure that reliable bulk analysis is carried out. If the sample is not pulverized, and mixed properly, before analysis, XRD will characterize only the surface, up to a depth of approximately 1000 A. When utilizing XRD for the purposes of this investigation, the sample (granules) must be first powdered and mixed thoroughly before analysis. Otherwise, XRD will detect only the Li_2CO_3 formed on the surface, thus leading to the possibly erroneous conclusion that conversion is complete.

There are two general methods for quantitative determination of the concentration of the constituents - the External Standard Method, which is the most common method, and the Internal Standard Method. The principles behind these methods, and the methods of calculation are described in Appendix H. The intensity of the major diffraction peak (I_0 in Tables 18 and 19) represents the concentration of the constituent, and can be determined either graphically by measuring the area under the peak, or numerically by recording the number of counts per fixed period of time. A comparison of the intensities yields information on the concentration of the constituents.

For increased reliability, it is strongly recommended that controlled runs with known concentrations of the individual constituents be run, and their respective intensities measured. Concentrations in unknown samples can then be determined by interpolation.

Depending on the particular X-ray diffractometer, the sensitivity varies. Minimum detection limits are generally 0.1 wt. % concentration, though some diffractometers have minimum detection limits of 1 to 2 wt. %. Despite the technique being very well established, it is not a very common piece of equipment. In general, it is only the more sophisticated research laboratories and universities that tend to have diffractometers.

This technique does not lend itself well to real-time measurements for this particular project. However, it is capable of very accurate post-run analysis. Due to the extremely small sample size requirement, it will be able to detect conversion ratios not only for localized regions, but also individual granules of LiOH.

5.1.2 Infra-Red Spectroscopy (IRS)

This is a technique that is very similar to X-ray diffraction, with the exception that infra-red radiation is utilized. Most of the capabilities and limitations are also similar to XRD. The limit of detection is approximately 0.5 wt. % concentration in the sample being analyzed. Quantitative determinations are made by measuring the intensity of the major peak(s), and controlled runs with known concentrations of constituents are necessary for reliable quantitative analysis. This technique is particularly suited for identification of molecular species, but provides very little, if any, elemental information. For the purposes of this project, the lack of elemental information is not a limitation. The infra-red spectrum for Li_2CO_3 is shown in Figure 3. A similar spectrum, but with peaks (or troughs) at different wavenumbers and having different intensities (area within the troughs) will exist for LiOH.

IRS is a technique that can be used for real-time measurements. This would be possible in two ways - either by measuring the LiOH to Li_2CO_3 conversion directly, or by measuring the concentration of CO_2 in the inlet and outlet gases.

Direct measurement of LiOH to Li_2CO_3 conversion can be made by using IRS in the reflectance mode. In order to do this, the canister containing LiOH will have to be modified to provide a "transparent" window on one side. Two other limitations come along with this approach. The first limitation is due to the fact that the measurement will be made in a reflectance mode rather than a transmission mode. Results will be based on the surface of the particles, closest to the windows, and will not be representative of the conversion rate through the thickness of the canister. The second limitation is due to the fact that measurements cannot be made over the entire area of the window, but only in a very narrow area at any one given time. Special equipment will have to be designed and built to move the canister so that measurements can be made over the area of the window, over a period of time. While this approach permits real-time measurement of the conversion, it will lack in reliability since the measurements are made in one small spot at any given time, and will not be representative of the rest of the canister. Sampling will be less than 1% at one time. Also, the requirement to design special equipment that does not exist at this time can be expected to make this approach extremely expensive. Diffuse reflectance infrared spectroscopy, coupled with a Fourier Transform Infra-red Spectroscopy (FTIR) has been used to study the carbonation of LiOH.(4)

Measurement of the CO_2 content in the inlet and outlet gases permits real-time measurement of the overall rate of absorption of CO_2, but does not yield localized information. It is assumed here that the difference in CO_2 content between the inlet and outlet gases is due to the reaction of CO_2 with LiOH and the subsequent conversion of the latter to Li_2CO_3. This can still be a very useful technique for measuring the efficiency of the CO_2 scrubber system. Very minor equipment modifications will be necessary.

5.1.3 Gas Mass Spectrometry (GMS)

Gas analysis by mass spectrometry, or gas mass spectrometry, is a useful analytical tool for investigations performed in controlled atmospheres or in vacuum. A sample (the gas) is introduced into the ion source of the mass spectrometer for ionization. The resulting ions are separated according to their mass/atomic number ratio by a mass analyzer and collected by a detector. The resulting mass spectrum contains the information necessary to identify and quantify the components of the sample.

In this project, GMS can be used in a manner similar to IRS for measurement of the CO_2 concentration in the inlet and outlet gases, thus measuring the overall rate of absorption of CO_2 by the system. This can be done in real-time, using sample bottles attached to the gas flow tubing. The sampling bottles used must be not only cleaned properly, but also evacuated and purged of adsorbed gases, to ensure that residual contaminants adsorbed on the interior walls are removed. Samples should also be analyzed as soon as possible (within the same day) to avoid contamination due to diffusion and other leaks in the sample bottles.

This technique can be extremely sensitive, with detection capabilities in the parts per million range.

5.1.4 Ion Chromatography (IC)

Ion chromatography is usually employed for qualitative and quantitative analyses of a wide range of inorganic and organic anions, and certain cations, in aqueous solutions. Detection of cations is usually limited to alkali and alkaline earth metals. IC is a technique that has been in existence for a very long time, and is therefore very well established. It is generally capable of detecting ions at the parts per million level, and is therefore extremely sensitive.

The compounds to be analyzed must be water soluble. Both LiOH and Li_2CO_3 are soluble in water, though to different degrees, as shown in Table 1. By dissolving a LiOH-Li_2CO_3 mixture in water, at levels below the solubility limit of Li_2CO_3, and then measuring the concentration of Li^+ and CO_3^{2-}, the relative concentrations of LiOH and Li_2CO_3 can be determined.

Based on the sample preparation procedure utilized, this technique can be used not only for bulk analysis, but also localized analysis and analysis of individual grains.

This technique is obviously not capable of distinguishing between LiOH and $LiOH.H_2O$. If identification of the $LiOH.H_2O$

content is desired, other means will have to be employed, in conjunction with IC. One possible approach is to heat the sample at a temperature sufficiently high to drive off the H_2O from $LiOH.H_2O$, record the weight change, and then use this information to deduce the concentration of $LiOH.H_2O$.

IC cannot be used for real-time determinations, but only for post-run determinations, due to the fact that the material to be analyzed must be in the form of an aqueous solution.

5.1.5 Auger Electron Spectroscopy (AES)

Auger Electron Spectroscopy is basically a surface analytical technique, and is not thought to be suitable for the type of bulk analysis required in this project. It is also not capable of real-time measurements in this instance.

5.1.6 Electron Spectroscopy for Chemical Analysis (ESCA)

ESCA, similar to AES, is fundamentally a surface, and shallow sub-surface, analytical technique. It is not thought to be suitable for the bulk analysis required here. It is also not capable of real-time measurements in this instance.

5.1.7 Wet Chemical Analysis

The procedure recommended for determination of LiOH conversion to Li_2CO_3 by NASA is chemical titration.(3) The method(s) outlined in Appendix I is a minor variation of the method outlined by NASA.

Like most of the techniques described above, wet chemical analysis is not amenable to real-time determination of the conversion. It will yield reliable conversion rates, but is capable of only "bulk" analysis, even on a localized level. Information pertaining to the kinetics of carbonation, especially on a granule to granule basis will not be really possible with this technique.

The equipment and technology exists to computerize and/or automate this analysis, however. Computerized titrations, with automatic data collection directly on computers is possible with state-of-the art equipment. Since indicator solutions are used, it will still need to be supervised by humans to detect color changes for determination of end of titration runs. It would be possible to automate this aspect of the analysis as well, but the capital outlay could be quite significant.

5.2 Indirect Techniques

As mentioned at the beginning of this chapter, the term "indirect techniques" is used to refer to methods that lead to an inference that the conversion of LiOH to Li_2CO_3 is occurring, without providing direct information on either of the compounds.

5.2.1 Temperature/Thermocouples

Both Jaunsen(5) and Freebeck(6) describe the use of temperature, as measured by thermocouples, for detection of rate of conversion. This is based on the fact that the conversion reaction is exothermic, and therefore, if the reaction proceeds forward, then the temperature should rise.

Thermocouples can be used in two different ways to measure the conversion reaction's progress.

First, the temperature of the outlet gases can be measured, and this information can be used to interpret the progress of the conversion reaction. While this approach is easy to implement, and record data, it yields very little information that can be used to interpret conversion ratios - both overall and localized. At best, it gives very vague information on the progress of the reaction, and its cessation.

The second possible method of implementation is to plant a series of thermocouples into the canister, and measure the temperature at several locations. This approach yields more useful information about conversion profiles within the canister, which in turn can be used to interpret localized conversion ratios. However, the information acquired through this technique can at best be used to obtain information on relative conversion ratios; absolute conversion ratios cannot be determined. There is the further danger of the thermocouple implants actually disturbing the gas flow pattern within the canister. This could result in data that cannot be applied when the thermocouples are removed.

In either of the approaches outlined above, the temperature at any given time must be compared to the maximum temperature attained in order to make judgements about extent of conversion. It needs to be pointed out that the maximum temperature attained is also very strongly a function of the rate of the (exothermic) reaction. Temperature represents the "amount" of heat accumulated in a given location. Since the flowing gases will also be constantly removing heat, the rate at which a reaction proceeds will affect the maximum temperature attained. If the same total volume of gas is passed through the canister, but at a slower rate, then the maximum temperature attained in the chemical can be expected to be lower. This represents an inherent uncertainty in this approach.

Mostly importantly, the use of thermocouples, or other techniques, to measure the temperature of either the outlet gases, or localized regions within the canister, does not yield information that can be directly correlated to the extent of conversion of LiOH to Li_2CO_3.

5.2.2 Differential Scanning Calorimetry

Thermodynamic data for Li_2CO_3 shows that it goes through two solid-state phase transformations, at 623 K and 683 K, before melting at 993 K. LiOH, on the other hand, does not display similar solid-state phase transformations. This difference can be exploited for both qualitative and quantitative analysis of Li_2CO_3 content in a sample.

The equipment that would be used for such measurements is a Differential Scanning Calorimeter.

All phase transformations are accompanied by either heat absorption or heat release. The transition from a lower temperature structure to a higher temperature structure is usually endothermic, and the exact quantity of heat required is termed the "Enthalpy of Transformation". The most common example of such a transition is "Melting". A solid (the lower temperature structure) at its transformation temperature (in this case the melting point) absorbs a fixed amount of heat (Enthalpy of melting) and transforms to a liquid (the higher temperature structure) at the same temperature.

Figure 4 shows a typical scan from a DSC. The area under the peak marked A represents the amount of heat absorbed by the sample in transforming from one structure to another. The temperature at which this transformation occurs is also determined from the same graph. If the weight of the sample used is measured, then the enthalpy of transformation, on a per molar basis, or on a weight basis, can be determined.

For the purpose of this project, calibration runs with pure Li_2CO_3 should be run first, to determine the enthalpy of transformation for the two transformations at 623 K and 683 K. Once this data is established, by measuring the total weight of the sample, and the heat absorbed for each of the transformations, the content of Li_2CO_3 in the sample can be determined.

5.2.3 Dissociation Method - Measurement of H_2O and CO_2 Volume

The dissociation reactions for LiOH and Li_2CO_3 are as follows:

$$2LiOH\ (s) \rightarrow Li_2O\ (s) + H_2O\ (g)$$

$$Li_2CO_3\ (s) \rightarrow Li_2O\ (s) + CO_2\ (g)$$

If a sample consists of a mixture of LiOH and Li_2CO_3 only, and the sample is heated to cause it to dissociate, then the only source of H_2O is LiOH and the only source of CO_2 is Li_2CO_3. The presence of $LiOH.H_2O$ would also contribute to the release of H_2O, but not to the release of CO_2.

It is therefore possible to determine the Li_2CO_3 content in a sample by measuring the amount of CO_2 released when a sample is heated until dissociation. From the data contained in Table 10, it can be seen that Li_2CO_3 starts to decompose at 800°C, and decomposition is complete at 1270°C. These temperatures are easily attainable with laboratory-type or commercial furnaces.

The equipment necessary for such measurements can be quite easily assembled in a laboratory. A closed system consisting of a crucible, a heat source (electric or gas), and suitable temperature measuring system (thermocouples) is necessary to heat the sample. The sample would be heated until decomposition is complete. The gases released would first be passed through a dessicant such as silica gel, to absorb the water vapor content, before being collected in a suitable measuring cylinder. A vacuum pump is necessary for evacuating the measuring cylinder first before the gases from decomposition are collected.

The amount of dead volume in the system could be a major source of error. The dead volume is the volume of the system outside the measuring cylinder. If this volume is too large, then the amount of CO_2 trapped within it could be significant, thus leading to lower calculated conversion ratios. The design of the system is therefore extremely critical.

When one or more of either the products or reactants are gaseous, volumetric measurements generally yield more accurate results than gravimetric measurements. One mole of CO_2 at STP occupies 22,400 ml, and weighs 44 gm. 10 ml will therefore weigh 0.0196 gm. It is not only easier to measure 10 ml than 0.0196 gm, but the former can be measured with greater precision with relatively simple equipment than can 0.0196 gm. However, to-date, gravimetric measurements have tended to be more prevalent.

5.2.4 Thermogravimetric Analysis

Measurement of the change in weight of a sample, as it participates in a reaction, with or without a change in temperature is usually termed gravimetric analysis. When there is also a change in temperature, it is termed thermogravimetric analysis (TGA). A common type of TGA is the microbalance which is capable of measuring weight changes down to 1 μgm.

If a TGA were to be utilized for the purposes of this project, a sample would be heated, and its weight change measured. As can be deduced from Table 10, the sample must be heated to temperatures on the order of 1000°C. This temperature is easily attainable with laboratory furnaces, and such a furnace can be coupled to the TGA.

However, while the weight change measured is extremely accurate, no information on the cause of the weight change is available. The loss of weight would arise from loss of H_2O and CO_2 from the sample. The TGA by itself is not capable of distinguishing between these two causes of weight change; it provides information only on total weight loss, regardless of the cause.

Since the interest in this project is to determine the extent to which LiOH has been converted to $Li_{2CO}3$, it is necessary to distinguish between the two causes of weight loss. Therefore, by itself, the TGA would not be a suitable technique for the purposes of this project. However, in conjunction with the Dissociation Method described, it can be effectively used. By combining the two techniques the effect of the dead volume in the system can be minimized. Calibration runs with pure Li_2CO_3 can be utilized to first determine the exact amount of residual CO_2 within the system. Once the correlation between amount of CO_2 released, and amount of CO_2 collected is established, further analyses can be done quite accurately.

5.2.5 Phase Diagram Method

Another potential technique is to use the LiOH - Li_2CO_3 phase diagram to determine the Li_2CO_3 content in a sample. Typically, the liquidus temperature is measured, and the Li_2CO_3 content of the sample determined from this measurement. The technique itself is quite simple, and the equipment needed is quite modest - a good furnace, and temperature measurement equipment (thermocouples).

There are, however, some impediments to this technique. In the course of this investigation, a LiOH - Li_2CO_3 phase diagram was not found. It would, therefore, be necessary to first establish this phase diagram. Since the nature of the interaction between LiOH and Li_2CO_3 is not known at this time, establishment of the phase diagram could in itself be a major undertaking. One of the factors that could complicate this measurement is the extent of dissociation of both of these compounds as they approach the liquidus temperatures. If they decompose to any significant extent (beyond 1 or 2 %), then the data collected would no longer be representative of the initial sample.

In general, when phase diagrams are utilized to establish chemical composition, it should be borne in mind that the presence of impurities can significantly affect the results. Impurities, depending upon their interaction with either of the major components, can cause the liquidus temperature to change, thus leading the investigator to make erroneous conclusions.

The possible presence of $LiOH.H_2O$ in the case of this project makes the use of phase diagrams particularly unsuitable as an analytical technique for determination of Li_2CO_3 content in a mixed sample.

5.2.6 Calculation of True Sample Density

Another possible technique is to use the sample weight and density. It must be mentioned here that the density to be used is the true density of the individual compounds, and not the bulk density. Measurement of bulk density is difficult to reproduce. There are many factors that can affect the results, including particle size, particle size distribution, particle shape, and particle porosity. True density, on the other hand, is independent of such factors. The theoretical density of LiOH is 1.46 g/cc whereas that of Li_2CO_3 is 2.11 g/cc. There is a sufficient difference here to be able to measure the density of mixtures of the two compounds, and deduce therefrom the concentration of each.

The possible presence of $LiOH.H_2O$, however, poses a major problem. If the concentration of $LiOH.H_2O$ is not known a priori, then this technique will be ineffective for determining the concentration of Li_2CO_3.

One means of avoiding any difficulties that might arise from the presence of $LiOH.H_2O$ would be to actually heat the sample to drive off the H_2O. By recording the weight change, the H_2O content can be determined first. This information, in conjunction with information on the density of the mixture, can be used to calculate the LiOH, $LiOH.H_2O$, and Li_2CO_3 concentrations.

5.3 Equipment Costs

The cost of the equipment for the techniques discussed in Sections 5.1 and 5.2 is summarized in Table 20. The cost estimates presented in this table are not intended to be accurate costs, but rather indicative of the relative capital investment required. The exact cost of each of these pieces of equipment can vary considerably, depending on the specific features and capabilities selected.

6. CONCLUSIONS

For the nature of measurements required in this project, it would be extremely difficult to conduct conclusive real-time measurements that would yield results that are representative of the reactions actually going on inside the canister containing the LiOH, without disturbing the gas flows within the canister.

It is recommended that real-time measurements be used to monitor the overall conversion of the LiOH to Li_2CO_3. Post-run measurements should then be used to determine the conversion profile within the canister.

The most appropriate approach to monitor the overall conversion on a real-time basis is to measure the CO_2 content of the gases exiting the canister. Infrared Spectroscopy and Gas Mass Spectrometry appear to be the most suitable techniques for this purpose.

Post-run measurements for determination of localized conversion ratios are best done with techniques that can yield reliable quantitative data. The techniques most suitable for this purpose are X-ray Diffraction, Ion Chromatography and Wet Chemical Analysis. Thermogravimetric Analysis can also yield very accurate results if the experimental procedure is carefully planned.

In order for accurate determination of localized conversion ratios, the sampling procedure needs to be very carefully planned and executed. Depending upon the analytical method(s) chosen, the sampling procedure may actually vary, and vice versa. It will be very important to ensure that the contents of the canister are immobilized, and not "mixed up" in any way, before sampling. One means of achieving this would be to "freeze" the entire contents of the canister, using a resin that will flow in through the $LiOH/Li_2CO_3$ particles, and then harden upon setting. If a resin is used for immobilization, then TGA would not be a suitable technique. Wet chemical analysis could also face serious challenges in this case. This is an area that requires further detailed planning and analysis.

7. REFERENCES

1. Boryta, D.A., and A.J. Maas, "Factors Influencing Rate of Carbon Dioxide Reaction with Lithium Hydroxide", Ind. Eng. Chem. Process Des. Develop., Vol. 10, No. 4, 1971, pp 489-494.

2. CYPRUS Foote Mineral Company, "Lithium Hydroxide Anhydrous Premium Grade - (6 x 4 Mesh)", Nov. 1, 1989.

3. National Aeronautics and Space Administration, "General Specification NASA-JSC Requirements for Lithium Hydroxide used for CO_2 Removal in Closed Environments", SD-L-0024A, May 1985.

4. Smyrl, N.R., E.L. Fuller, Jr., and G.L. Powell, "Monitoring the Heterogeneous Reaction of LiH and LiOH with H_2O and CO_2 by Diffuse Reflectance Infrared Fourier Transform Spectroscopy", Applied Spectroscopy, Vol. 37, Nov 1983.

5. Jaunsen, J.R., "The Behavior and Capabilities of Lithium Hydroxide Carbon Dioxide Scrubbers in a Deep Sea Environment", Trident Scholar Project Report No. 157, United States Naval Academy, Annapolis, Maryland, July 7, 1989. p 11.

6. Freebeck, N.J., "The Effect of Extreme Cold Temperatures upon the Performance of Carbon Dioxide Absorbents", Naval Systems Engineering Department, U.S. Naval Academy, Annapolis, Maryland, May 2, 1990.

7. Atack, F.W., Handbook of Chemical Data, Reinhold Publishing Co., New York, 1957, pp230-231, 262-263.

8. Weast, R.C. Ed., CRC Handbook of Chemistry and Physics, 69th Edition, CRC Press, Inc., 1988, p B-101.

9. Oliver, R.E., Inorganic and Theoretical Chemistry, Volume II Supplement II, The Alkali Metals, Part 1, Longman Publishers, 1961, pp 159-171, 250-256.

10. Mellor, J.W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume II, Longmans Green and Co. Ltd., 1927, pp 500-511, 747-764.

11. "JANAF THERMOCHEMICAL TABLES", J. Phys. Chem. Ref. Data Vol. 14, Supplement 1, 1985, pp 609-611, 1228.

12. Ibid, p 1228.

13. Ibid, p 609.

14. Chang, Y.A., and N. Ahmad, Thermodynamic Data on Metal Carbonates and Related Oxides, 1982, pp 115 - 121.

15. Bailar, J.C. Jr., Comprehensive Inorganic Chemistry, Pergamon Press, pp 351 - 356.

16. Zemann, J., "Die Kristallstruktur von Li_2CO_3", Acta Crystallographica, Vol. 10, 1957, pp 664 - 666.

17. Mair, S. L., "The Electron Distribution of the Hydroxide Ion in Lithium Hydroxide", Acta Crystallographica, July 1978, pp 542-547.

18. Effenberger, H., and J. Zemann, "Verfeinerung der Kristallstruktur Lithiumkarbonates", Acta Crystallographica, 1967, pp 664 - 666.

19. Gemelins Handbuch der Anorganischen Chemie, Systemnummber 20, Verlag Chemie, GmbH, 1960, pp 262 - 273, 494 - 501.

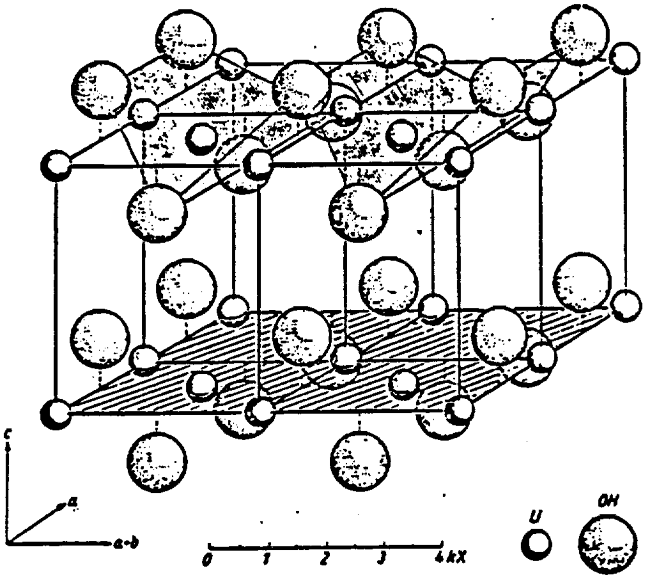


Figure 1: Lattice Structure of LiOH

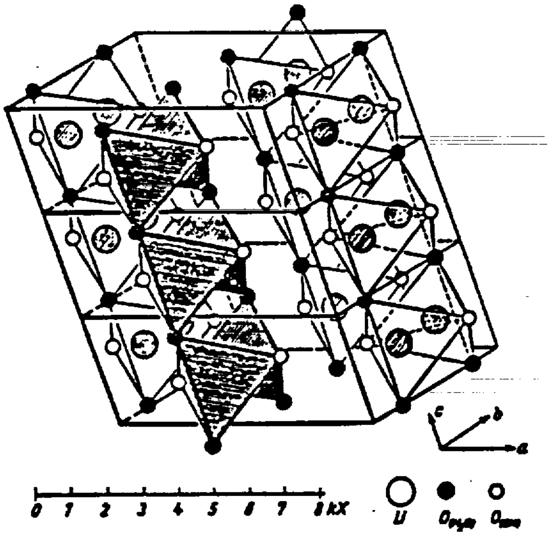


Figure 2: Lattice Structure of LiOH.H_2O

20362-9 *CAS [554-13-2]*
Lithium carbonate, 99.999%

FW 73.89
mp 618°C
d 2 110

Merck 10,5352

Figure 3: Infrared Spectroscopic Scan for Lithium Carbonate

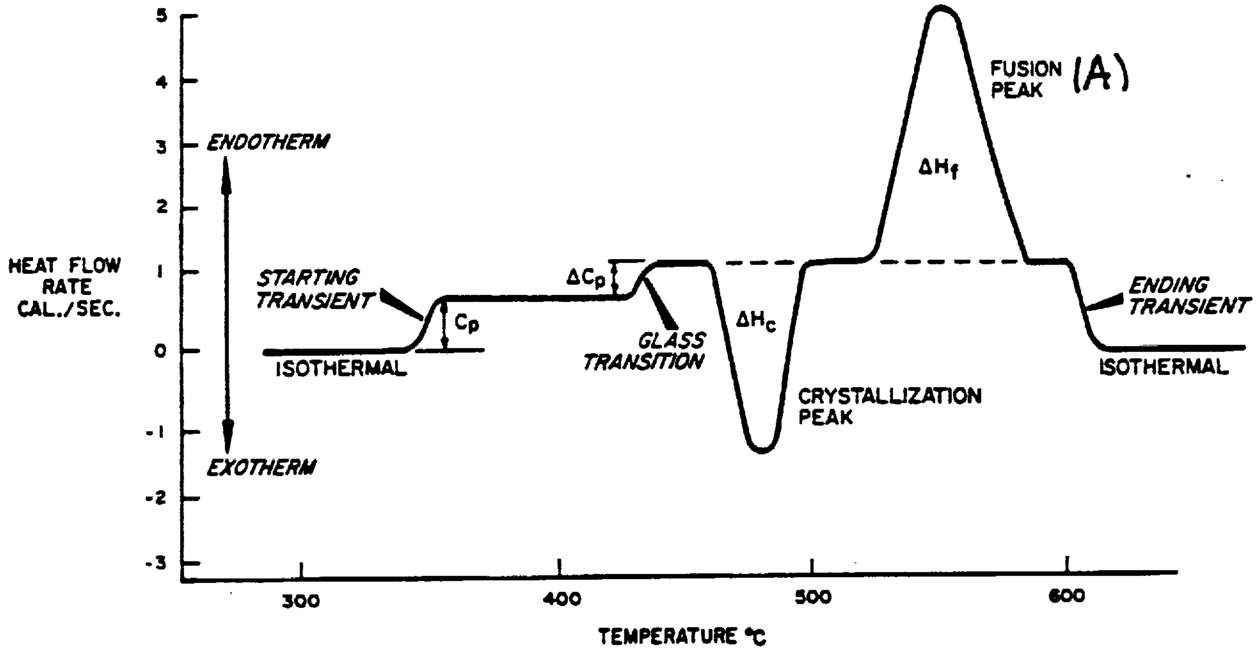


Figure 4: Typical Differential Scanning Calorimeter Scan

Table 1. **PHYSICAL PROPERTIES OF LIOH, LIOH.H_2O AND Li_2CO_3**

Physical Property	**Lithium Hydroxide LIOH** (Reactant)	**Monohydrate LIOH.H_2O** (Intermediate)	**Lithium Carbonate Li_2CO_3** (Product)
Formula Weight	23.95awu[7][8]	41.96awu[8]	73.88awu[7] 73.89[8]
Theoretical Density (g/cm^3)	1.46[8] or See Table 2. (aqueous sol'ns)	1.51[9] [8]	2.11[9] [8]
Melting Point (°C)	450[8] 471.3[9]		618[7] 723[8]
Boiling point (°C)	924[8]		1310[8]
Solubility (g/100 cc H_2O at 15°C)	12.8[8]	22.3[8]	1.37[7] 1.54[8]
Solubility (g/ 100 cc H_2O at 100°C)	17.5[8]	26.8[8]	0.72[7] [8]
Solubility (in Alcohol, acids or alkalies)	sli. soluble Alc[8]	sli. soluble Alc.[8]	insoluble Alc.[7] [8]
Surface Tension	See Table 3.[9]		152.5 dynes/cm[10]
Viscosity	See Table 4.[9]		

Table 1. PHYSICAL PROPERTIES OF LIOH, LIOH.H_2O AND Li_2CO_3 (continued)

Physical Property	Lithium Hydroxide LIOH (Reactant)	Monohydrate LIOH.H_2O (Intermediate)	Lithium Carbonate Li_2CO_3 (Product)
The ratio of cross sections for neutron capture σ_{Li}/σ_H	185[9]		
Collision diameter of excited atoms σ_{Li}^2 (cm^2)	$22x10^{-16}$ [9]		
Magnetic Susceptibility (esu)			$-29.3x10^{10}$.[9]
Spectra (frequencies for strong characteristic absorption bands) $(cm)^{-1}$			1096,870,860 741,740,711 [9]

Table 2. DENSITY OF AQUEOUS SOLUTIONS OF LIOH[9]
(g/cc)

Concentration	20°C	30°C	40°C
0.5N.	1.0113	1.0087	1.0053
1.0	1.0242	1.0212	1.0178
2.0	1.0483	1.0451	1.0415
3.0	1.0703	1.0671	1.0843
4.0	1.0914	1.0880	1.0843
5.0	1.1117	1.1082	1.1049

Table 3. **SURFACE TENSION OF AQUEOUS LIOH[9]**

Concentration	Surface Tension at 20°C (dynes/cm.)
4.089N.	77.9
3.22	77.4
2.09	75.8
1.018	74.2

Table 4. **VISCOSITY OF AQUEOUS SOLUTIONS OF LIOH IN CENTIPOISES**[9]

Concentration	20°C	30°C	40°C
0.5N.	1.139	0.907	0.743
1.0	1.294	1.028	0.841
2.0	1.686	1.325	1.069
3.0	2.223	1.720	1.368
4.0	2.990	2.255	1.758
5.0	4.084	3.008	2.305

Table 5. THERMODYNAMIC PROPERTIES OF LIOH, LIOH.H_2O AND Li_2CO_3

Thermodyn. Property	Lithium Hydroxide LIOH (Reactant)	Monohydrate LIOH.H_2O (Intermediate)	Lithium Carbonate Li_2CO_3 (Product)
Thermodynamic data (Cp°, S°, -[G°-H°(Tr)]/T, H°-H°(Tr),$\Delta H°_f$, $\Delta G°_f$, Log K_f)	See Table 6.		See Table 7.
Specific heat of solution(g mol.LiOH/ 100 g mol. H_2O) (J/mol.K)	0.9813[9]		
Molar Heat capacity ϕ_c (J/mol. K)	$-19.98+12.53\ m^{1/2}$ (m = 2.5)[9] m = molarity of the solution		
Partial molar Heat capacity C_{p2} (J/mol.K)	$-19.98+\ 18.8\ m^{1/2}$ (m = 2.5)[9] m = molarity of the solution		
Heat capacity for molar entropy value (298.16K) (E.U.)	10.23 ± 0.05 [9]	17.07±0.05 [9]	
Heat content Data	See Table 9.		
$H_T - H_{298.15}$ (crystal)	See Table 13.		See Table 13.
$S_T - S_{298.15}$ (crystal)	See Table 13.		

Table 5. THERMODYNAMIC PROPERTIES OF LiOH, LiOH.H_2O AND Li_2CO_3
(continued)

Thermodyn. Property	**Lithium Hydroxide LiOH** (Reactant)	**Monohydrate LiOH.H_2O** (Intermediate)	**Lithium Carbonate Li_2CO_3** (Product)
Heat of Fusion ΔH°_{fus} (KJ/mol.)	20.942 [9] (at 744.3°K) 20.862 [15]		44.769±0.4 [11] (at 993±1°K)
Thermal dissociation pressure	See Table 10.		See Table 10.
Vapor pressure	See Table 11. and 12.		

NOTE: The thermodynamic symbols are explained in Appendix J.

Table 6. THERMODYNAMIC DATA FOR CRYSTALLINE LIOH.[12]

T_r = 298.15°K; P = 0.1 MPa

Temp. (K)	C_p° (J/mol•K)	S° (J/mol•K)	-[G°-H°(T_r)]/T (J/mol•K)	H°-H°(T_r) (KJ/mol)	ΔH°$_f$ (KJ/mol)	ΔG°$_f$ (KJ/mol)	Log K_f
0.	0.	0.	infinite	-7.416	-479.144	-479.144	infinite
100	14.644	8.561	77.138	-6.858	-482.033	-468.453	244.695
200	35.977	25.632	46.892	-4.270	-484.08	-453.960	118.562
298.15	49.591	42.821	42.821	0.	-484.926	-438.958	76.904
300	49.761	43.128	42.822	0.092	-484.933	-438.672	76.380
400	58.530	58.678	44.886	5.517	-485.047	-423.222	55.267
500	63.647	72.260	49.032	11.614	-487.874	-407.475	42.569
600	68.208	84.277	53.924	18.212	-487.303	-391.441	34.078
700	72.279	95.101	59.045	25.239	-486.298	-375.538	28.023
744.30	73.970	99.588	61.326	28.479	--- CRYSTAL <--> LIQUID ---		

The Log K_f data are determined by the reaction as follows:

$$\frac{1}{2}\ Li_2O + \frac{1}{2}\ H_2O \dashrightarrow LiOH$$

NOTE: The thermodynamic symbols are explained in Appendix J.

Table 7. **THERMODYNAMIC DATA FOR CRYSTALLINE Li_2CO_3.**[13] Tr = 298.15 °K; P = 0.1 MPa

Temp. (K)	C_p ° (J/mol•K)	S° (J/mol•K)	-[G°-H°(T_r)]/T (J/mol•K)	H°-H°(T_r) (KJ/mol)	ΔH°$_f$ (KJ/mol)	ΔG°$_f$ (KJ/mol)	Log K_f
0	0.	0.	infinite	-15.174	-1207.891	-1207.891	infinite
100	34.811	20.048	158.357	-13.831	-1211.955	-1186.400	619.172
200	72.425	56.513	98.271	-8.352	-1214.852	-1159.562	302.847
298.150	96.23	90.171	90.171	0.	-1216.038	-1132.120	198.343
300	96.567	90.767	90.172	0.178	-1216.048	-1131.600	197.029
400	112.173	120.752	94.156	10.638	-1216.269	-1103.403	144.090
500	128.951	147.525	102.190	22.668	-1222.020	-1074.589	112.262
600	149.369	172.780	111.863	36.550	-1220.241	-1045.224	90.995
623.150	154.643	178.533	114.233	40.069	TRANSITION --- I <--> II ---		
683.150	170.212	194.286	120.612	50.331	TRANSITION --- II <--> III ---		
700	140.875	200.969	122.505	54.925	-1214.552	-1016.396	75.844
800	158.992	220.962	133.565	69.917	-1212.279	-988.225	64.524
900	177.025	240.727	144.376	86.716	-1208.404	-960.434	55.742
993.150	194.096	258.989	154.270	104.001	TRANSITION --- III <--> LIQUID ---		

The Log K_f data are determined by the reaction as follows:

$$2\,LiOH + CO_2 \dashrightarrow Li_2CO_3 + H_2O$$

NOTE: The thermodynamic symbols are explained in Appendix J.

Table 8. **THE HEAT OF DILUTION OF LIOH SOLUTIONS** [9]

LiOH solution (moles)	Quantity of water added (moles)	Heat of dilution (cal.)
$LiOH+25H_2O$	$+25H_2O$	+133
$LiOH+25H_2O$	$+75H_2O$	+223
$LiOH+25H_2O$	$+175H_2O$	+288
$LiOH+25H_2O$	$+375H_2O$	+338
$LiOH+25H_2O$	to infinite dilution	+390

Table 9. **HEAT CONTENT DATA FOR AQUEOUS SOLUTIONS OF LIOH** [9]

Moles solute (per 1000 grams water)	$\Phi_h - \Phi_h^\circ$ (g.-cal. per mole solute)	$H_2 - H_2^\circ$ (g.-cal. per mole solute)
0	0	0
0.01	42.	63.
0.04	82.	119
0.09	118	168
0.16	150	212
0.25	180	252
0.36	208	286
0.64	258	360
1.00	310	440
1.44	362	525
1.96	418	615

where, $\Phi h - \Phi h^\circ$ = the relative apparent heat content of the solute.
$H2 - H2^\circ$ = the relative partial molal heat content of the solute.

Table 10. **DISSOCIATION PRESSURE OF LIOH AND Li_2CO_3** [9] [10]

Temperature (°C)	P_{H2O} (mm. Hg) dissociation of LiOH [$2LiOH \rightarrow H_2O + Li_2O$]	P_{CO2} (mm. Hg) dissociation of Li_2CO_3 [$Li_2CO_3 \rightarrow CO_2 + Li_2O$]
561.	9.2	-----
700.	92.0	-----
750.	-----	0.000
782.	234	-----
800.	-----	3.100
850.	-----	8.100
875.	526	-----
900.	-----	17.40
924.	760	-----
950.	-----	32.70
1000	-----	56.20
1100	-----	134.4
1200	-----	300.0
1270	-----	760.0

Table 11. **VAPOR PRESSURE OF AQUEOUS LIOH** [9]

Concentration (moles water per mole solute)	Vapour Pressure (mm. Hg) 0°C.	 10°C.
10.83	3.85	7.44
13.30	3.99	8.02
17.10	4.12	8.29
22.37	4.24	8.54
44.52	4.40	8.86
∞	4.57	9.20

Table 12. VAPOR PRESSURE OF LiOH (crystal) [9]

Temp. (°K)	Pressure (atm. x 10^7)
533	7.030
557	35.40
589	135.0
598	231.0
619	505.0
620	531.0
621	648.0

Table 13. Heat Content and Entropy of LIOH and LI_2CO_3 (crys.)[9,14]

	Compound	Expression	Temperature Range
Heat Content	LiOH	$H_T - H_{298.15} = 11.988\ T + 0.00412\ T^2 + 226{,}700\ T^{-1} - 4701$ g.-cal.	400-744.3°K
	Li_2CO_3	$H_T - H_{298.15} = 156.430\ E\text{-}3\ T + 16.059\ E\text{-}6\ T^2 + 82.788\ E{+}2\ T^{-1} - 75.737\ (\pm\ 2.276\%)$	298-993.15°K
Entropy	LiOH	$S_T - S_{298.15} = 27.603\ \log T + 0.00824\ T + 113{,}350\ T^{-2} - 72.035$ E.U.	400-744.3°K

NOTE: The thermodynamic symbols are explained in Appendix J.

Table 14. ELECTRICAL PROPERTIES OF LIOH, LIOH.H_2O AND Li_2CO_3

Electrical Properties	**Lithium Hydroxide** LIOH (Reactant)	**Monohydrate** LIOH.H_2O (Intermediate)	**Lithium Carbonate** Li_2CO_3 (Product)
Conductance $(M\Omega\text{-cm})^{-1}$	223.1 (0.02703 mol./kg. of H_2O)[9] 232.5 (0.001394mol./kg.of H_2O) [9] 237.2 (Limit value) [9] See table 15.		See table 15.

Table 15. **ELECTRICAL CONDUCTIVITY OF LIOH and Li_2CO_3 SOLUTIONS**[9]

Concentration (g/100ml.H2O at 18°C)	LiOH $(M\Omega\text{-cm})^{-1}$	Li_2CO_3 $(M\Omega\text{-cm})^{-1}$
0.20	80.00	63.5
0.50	105.4	-----
0.63	-----	51.9

Table 16. STRUCTURAL PROPERTIES OF LIOH, $LIOH.H_2O$ AND LI_2CO_3

Structural Property	**Lithium Hydroxide** $LiOH$ (Reactant)	**Monohydrate** $LiOH.H_2O$ (Intermediate)	**Lithium Carbonate** Li_2CO_3 (Product)
Crystal system	Tetragonal[9]	Monoclinic[9]	Monoclinic [15]
Crystal parameters	a =b= 3.55 A[9] c = 4.34 A[9]	a = 7.37 A[9] b = 8.26 A[9] c = 3.19 A[9]	a = 8.39 A [16] b = 5.00 A [16] c = 6.21 A [16]
Axial ratios a:b:c	1:1:1.223	0.892:1:0.386[15]	1.67:1:1.24 [15]
β angle	90°	110° 18' [9]	114° 25' [15]
Unit Cell	Li^+ at 000 and $\frac{1}{2}\frac{1}{2}0$ [9], [8] OH^- at $0\frac{1}{2}u$ and $\frac{1}{2}0u$ [9], [8] See Fig. 1 [8]	See Fig. 2 [8]	
Lattice volume, A^3	54.588 [17]		237.06 [16] ,[18]
Crys. space group	P4/NMMS; 129 [17]		C12/C1; 15 [16]
Laue class	4/MMM [17]		2/M [16]

Table16. STRUCTURAL PROPERTIES OF LIOH, LIOH.H_2O AND Li_2CO_3 (continued)

Structural Property	**Lithium Hydroxide** **LIOH** (Reactant)	**Monohydrate** **LIOH.H_2O** (Intermediate)	**Lithium Carbonate** **Li_2CO_3** (Product)
Pearson symbol	TP6 [17]		MC24[16]
Crystal class	4/MMM; D4HM [17]		2/M; C2H[16]
Formula type	AX [17]		AB2X3[16]
Lattice energy	856.9 KJ/mol.[9]		

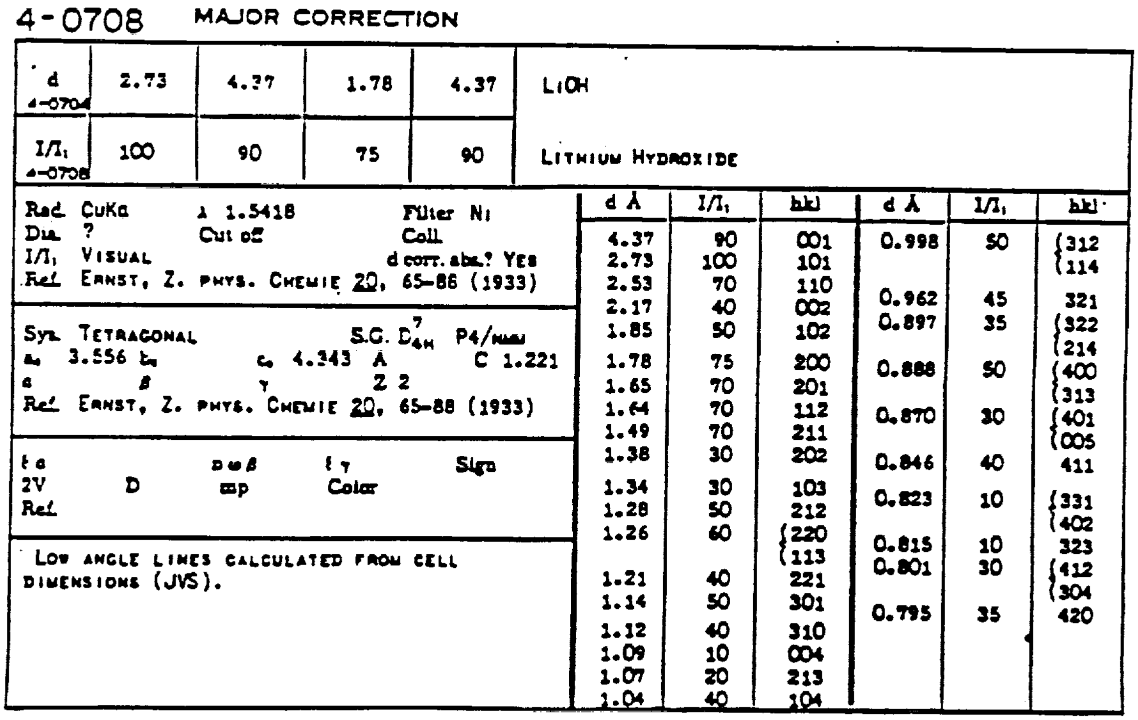
Table 17. **THE SIGNIFICANTLY DIFFERENT PROPERTITIES OF LIOH AND Li_2CO_3**

Properties	**Lithium Hydroxide** LiOH	**Lithium Carbonate** Li_2CO_3
<u>Physical</u>		
Formula weight	23.95 [8]	73.89 [8]
Theoretical Density	1.46 [8]	2.11 [8]
Melting point	450°C [8]	723°C [8]
Boiling point	924°C [8]	1310°C [8]
Solubility(g/100cc)		
H_2O at 15°C	12.8 [8]	1.54 [8]
H_2O at 100°C	17.5 [8]	0.72 [8]
Other solvents	slightly sol. alcohol [8]	insol. alcohol [8]
<u>Thermodynamic</u>		
Cp° (298.15K) (J/mol.•K)	49.591[12]	96.232 [13]
S° (298.15K) (J/mol.•K)	42.821[12]	90.171 [13]
$\Delta H°_f$ (298.15K) (KJ/mol.)	-484.926[12]	-1216.038 [13]
$\Delta G°_f$ (298.15K) (KJ/mol)	-438.958 [12]	-1132.120 [13]
Gibbs Energy funct.(298.15K) (J/mol•K)	42.821 [12]	90.171 [13]
Log K_f (298.15K)	76.904 [12]	198.343 [13]

Table 17. THE SIGNIFICANTLY DIFFERENT PROPERTITIES OF LIOH AND LI_2CO_3
(Continued)

Properties	**Lithium Hydroxide** LiOH	**Lithium Carbonate** Li_2CO_3
Transtion temp.(K)	744.300(crys.->liq.)[12]	623.150(I->II)[13] 683.150(II->III)[13] 993.150(III->liq.)[13]
Heat of fusion	20.882 KJ/mol[15] (at 744.300K)	44.769 KJ/mol[13] (at 933.15K)
Dissociation Press.	P_{H2O} =760 mm Hg[15] (at 924°C for 2LiOH->H_2O + Li_2O)	P_{CO2} =760 mm Hg[15] (at 1270°C for Li_2CO_3-> CO_2 + Li_2O)
Structural		
Crystal system	Tetragonal[17]	Monoclinic[16]
Crys. space group	P4/NMMS; 129[17]	C12/C1; 15[16]
R-value	0.042[17]	0.104[16]
Laue class	4/MMM[17]	2/M[16]
Pearson symbol	TP6[17]	MC24[16]
Crystal class	4/MMM;D4HM[17]	2/M;C2H[16]
Formula type	AX[17]	AB2X3[16]

Table 18. LiOH POWDER DIFFRACTION PATTERN:



4-0708 MAJOR CORRECTION

d 4-0704	2.73	4.37	1.78	4.37	LiOH
I/I₁ 4-0708	100	90	75	90	LITHIUM HYDROXIDE

Rad. CuKα λ 1.5418 Filter Ni
Dia. ? Cut off Coll.
I/I₁ VISUAL d corr. abs.? YES
Ref. ERNST, Z. PHYS. CHEMIE 20, 65-86 (1933)

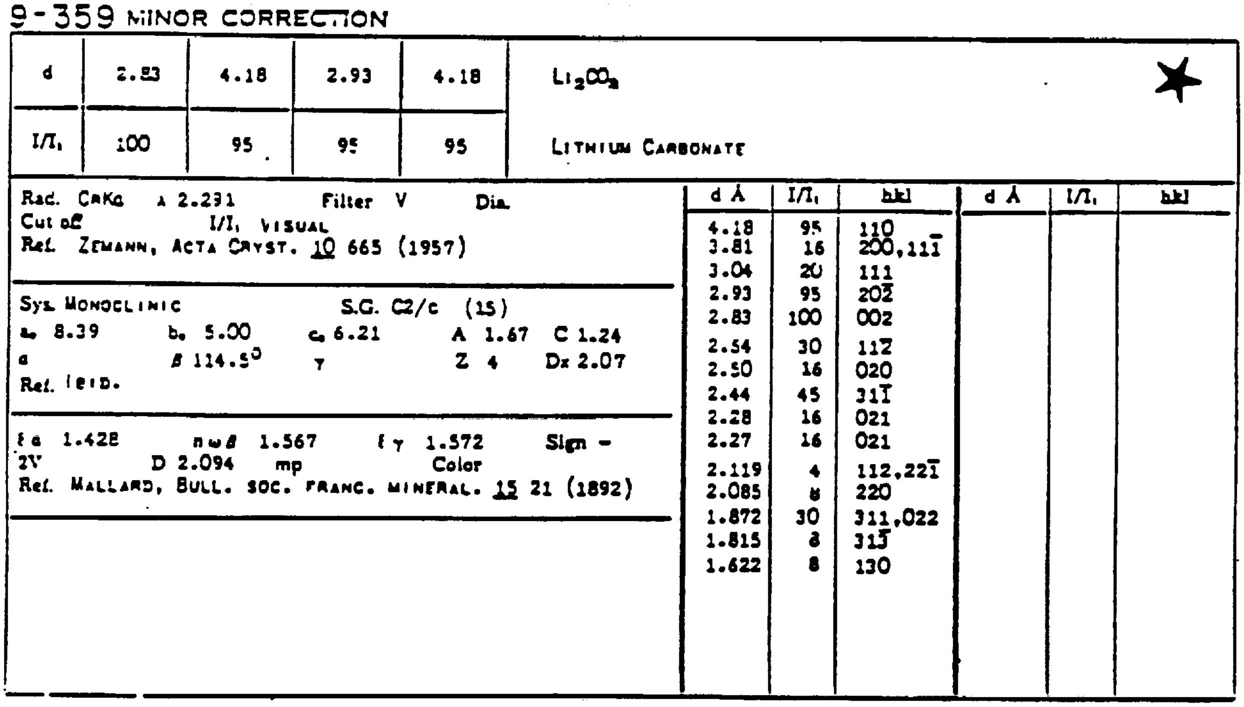
Sys. TETRAGONAL S.G. D_{4H}^{7} P4/nmm
a₀ 3.556 b₀ c₀ 4.343 A C 1.221
α β γ Z 2
Ref. ERNST, Z. PHYS. CHEMIE 20, 65-88 (1933)

εα nωβ εγ Sign
2V D mp Color
Ref.

LOW ANGLE LINES CALCULATED FROM CELL DIMENSIONS (JVS).

d Å	I/I₁	hkl	d Å	I/I₁	hkl
4.37	90	001	0.998	50	312 114
2.73	100	101	0.962	45	321
2.53	70	110	0.897	35	322 214
2.17	40	002	0.888	50	400 313
1.85	50	102	0.870	30	401 005
1.78	75	200	0.846	40	411
1.65	70	201	0.823	10	331 402
1.64	70	112	0.815	10	323
1.49	70	211	0.801	30	412 304
1.38	30	202	0.795	35	420
1.34	30	103			
1.28	50	212			
1.26	60	220 113			
1.21	40	221			
1.14	50	301			
1.12	40	310			
1.09	10	004			
1.07	20	213			
1.04	40	104			

Table 19. Li_2CO_3 POWDER DIFFRACTION PATTERN:



9-359 MINOR CORRECTION

d	2.83	4.18	2.93	4.18	Li_2CO_3 ★
I/I_1	100	95	95	95	LITHIUM CARBONATE

Rad. CrKα λ 2.291 Filter V Dia.
Cut off I/I_1 VISUAL
Ref. ZEMANN, ACTA CRYST. 10 665 (1957)

Sys. MONOCLINIC S.G. C2/c (15)
a_0 8.39 b_0 5.00 c_0 6.21 A 1.67 C 1.24
α β 114.5° γ Z 4 Dx 2.07
Ref. IBID.

εα 1.428 nωβ 1.567 εγ 1.572 Sign −
2V D 2.094 mp Color
Ref. MALLARD, BULL. SOC. FRANC. MINERAL. 15 21 (1892)

d Å	I/I_1	hkl	d Å	I/I_1	hkl
4.18	95	110			
3.81	16	$200, 11\bar{1}$			
3.04	20	111			
2.93	95	$20\bar{2}$			
2.83	100	002			
2.54	30	$11\bar{2}$			
2.50	16	020			
2.44	45	$31\bar{1}$			
2.28	16	021			
2.27	16	021			
2.119	4	$112, 22\bar{1}$			
2.085	8	220			
1.872	30	$311, 022$			
1.815	8	$31\bar{3}$			
1.622	8	130			

Table 20. **ESTIMATED CAPITAL COSTS FOR EXPERIMENTAL TECHNIQUES**

Technique	Text Reference (Section)	Estimated Cost ($1000)
X-ray Diffraction	5.1.1	100
Infra-red Spectroscopy	5.1.2	50~100
Gas Mass Spectroscopy	5.1.3	40~80
Ion Chromatography	5.1.4	40
Auger Electron Spectroscopy	5.1.5	300~600
Electron Spectroscopy for Chemical Analysis	5.1.6	300~600
Differential Scanning Calorimetry	5.2.2	40~60
Dissociation Method	5.2.3	20~40
Thermogravimetric Analyzer	5.2.4	50
Phase Diagram Method	5.2.5	60~100