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PROGRESS REPORT

ALLOY DEVELOPMENT PROJECT

THE ORGANIC AMALGAM SYSTEM

Progress through December 31, 1951

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PROGRESS REPORT

ALLOY DEVELOPMENT PROJECT

THE ORGANIC AMALGAM SYSTEM

Progress through December 31, 1951

February 15, 1952

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MATERIALS CHEMISTRY DIVISION

G. H. Clewett, Division Director

OAK RIDGE NATIONAL LABORATORY

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CARBIDE AND CARBON CHEMICALS COMPANY
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FOREWORD

Through fiscal 1951, the progress of the work on the separation of lithium isotopes was reported in the quarterly progress reports of both the ANP Project and of the Materials Chemistry Division. At the request of the Oak Ridge Operations Office, reports on this work will now appear as separate documents under the title of Alloy Development Project. The present report describes one phase of the work carried out from its inception on September 24, 1951, through December 31, 1951.

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THE ORGANIC-AMALGAM SYSTEM FOR SEPARATION OF LITHIUM ISOTOPES

Progress through December 31, 1951

INTRODUCTION

G. H. Clewett

In the initial survey by this division of chemical methods of separating lithium isotopes it was recognized that a stable system composed of lithium amalgam and organic solvent would satisfy the requirements for a suitable system. This conclusion was based upon the moderate success achieved by Lewis and McDonald[1] using lithium amalgam versus solutions of a lithium salt in alcohol and dioxane. The side reactions and emulsion troubles encountered by Lewis and McDonald prevent exploitation of their system for large scale production. The inherent possibilities, however, were recognized as being great enough to warrant a determined search for a solvent free of reaction or emulsion effects in contact with amalgam. Such a search was conducted many months ago in this division but it only served to firmly establish the conclusion (disproved by the present work) that all organics either reacted or emulsified with lithium amalgam. This approach to the lithium isotope problem then lay dormant until recently as the electroexchange method underwent development.

The Amalgam-Diamine Process

Some recent studies by H. H. Garretson* in this laboratory on electrolysis in ethylenediamine indicated that this solvent exhibits unusual stability with lithium amalgam. Extensive tests were initiated on ethylenediamine in contact with lithium amalgam and neither reaction nor emulsification could be made to take place. It was then recalled that J. W. Kennedy** had suggested ethylenediamine some months earlier to this writer but the suggestion had not been pursued because of the uniformly negative results in the early work. Plans were made then for a further study of the suitability of this system.

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**Washington University, St. Louis, Missouri

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Besides the initial requirement of system stability, several other requirements must be met if a feasible separation process is to emerge. Two such requirements are: very rapid isotopic exchange must take place between lithium in the two phases, and the equilibrium constant for the isotopic exchange reaction must differ from unity. These requirements have set the pattern for preliminary examination of this system as with any system.

One of the major advantages of the amalgam-diamine system over the electroexchange system is the absence of any tendency for net transfer between phases which allows the organic and amalgam phases to be contacted in normal liquid-liquid contacting equipment such as pulse columns which have been shown to give short height equivalents of theoretical stages. Pulse column equipment was therefore selected for pilot plant study of the process.

Since all chemical exchange plants for separating isotopes require large ratios of interstage flow to product and waste flow, some method of reflux at the top and bottom of the cascade must be devised. If this is difficult or costly, as is usually the case, then the variation of the separation factor with temperature can be utilized in a "Dual Temperature" process which obviates the need for reflux.

Although no clear cut apriori preference is possible between a reflux plant or dual temperature plant, a brief examination of the problems to be solved in establishing the technical feasibility of each method as applied to the amalgam-amine system will serve to clarify the program underway at present which emphasizes the dual temperature system.

Reflux Process (Schematically represented in Figure 1)

Electrolysis of Lithium Chloride Brine to Produce Dry Amalgam. This is so similar to the well established commercial methods of making pure sodium hydroxide by electrolysis of sodium chloride brine in a mercury cell that it does not appear to be a major problem. However, since lithium amalgam decomposition is much more sensitive to catalysis by brine impurities, it is felt that some work must be done to establish the large scale feasibility of this step. A research contract under ORNL is now being negotiated with Mathieson Chemical Corporation to study lithium chloride electrolysis. There is reasonable assurance of dry amalgam emerging from this electrolysis by virtue of the freedom

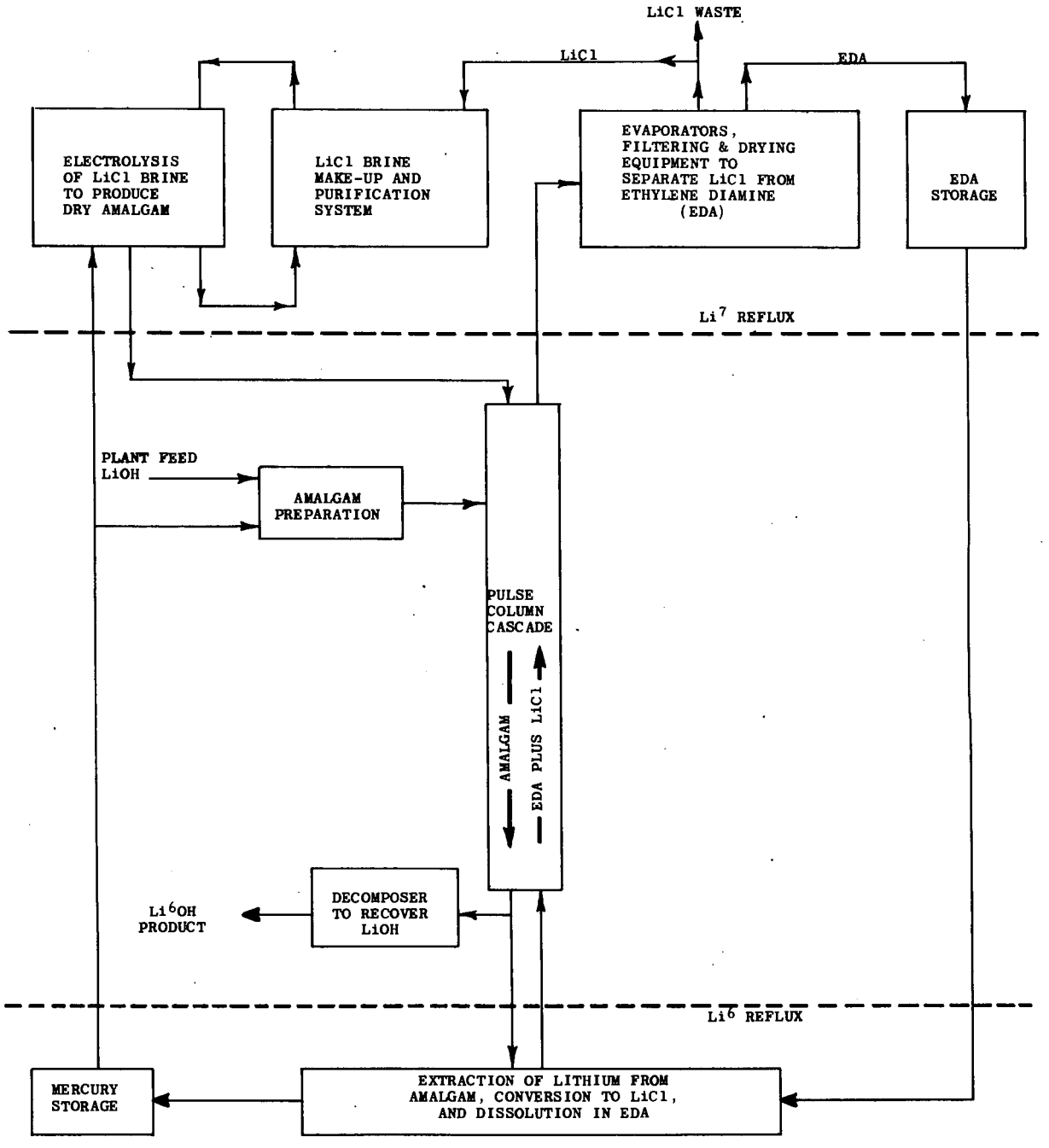

FIGURE 1: AMALGAM-AMINE-REFLUX SYSTEM

from chloride of the sodium hydroxide made in a Mathieson cell since the chloride content is a direct measure of the moisture carry-over in the sodium amalgam. This will be checked in the lithium electrolysis.

Lithium Chloride Brine Make-up and Purification System. The Mathieson contract should supply design data for this step also.

Evaporation, Filtering, and Drying Equipment to Separate LiCl from Ethylene Diamine. This appears to be the most difficult problem in the Li^7 reflux steps. Because of the large reflux ratio required in any process such as this, the amount of amine which must be handled daily at this point is very large and the equipment must be of such design as to effect complete recovery of the solvent or operating costs will be unreasonably high. The EDA must also be kept absolutely dry through these operations or a drying operation must follow. The LiCl salt which is recovered at this point should be relatively free of nitrogen compounds or additional purification steps in the brine cycle must be installed to prevent the introduction of nitrogen compounds in the electrolysis cells. Complete confidence in the technical feasibility in this combination of operations would seem to be difficult to establish without extensive large scale tests.

Plant Feed This is a straightforward operation which is small scale and has been demonstrated in the electro-exchange development program. It also appears in the dual-temperature plant.

Pulse Column Operation. This step is common to both the reflux system and the dual temperature process. Some development work for optimum amalgam-amine contacting is necessary for either system.

Extraction of Lithium from Amalgam, Conversion to LiCl, and Dissolution in EDA. This is not now believed to be as difficult as it first appears. The alkali metal exchange between lithium amalgam and solid sodium chloride in the presence of dry EDA to give a solution of LiCl in EDA has been briefly examined and is reported elsewhere in this document. Although this exchange looks useful there remains the necessity for developing suitable equipment for performing this operation continuously and completely quantitatively since losses here mean losses in product.

Decomposer to Recover LiOH Product. This is a straightforward operation which is small scale and has been demonstrated both in the electroexchange program and in the operation of commercial amalgam cells.

Dual Temperature Process (Schematically represented in Figure 2)

Temperature Coefficient of the Separation Factor. Since this process is based upon the decrease in separation factor with rise in temperature an accurate measure of this effect is necessary. The separation factors at 26°C and 99°C have been measured and are included in another section. Measurements at other temperatures are planned.

Amalgam Preparation of Feed. This appears in the reflux process as well and presents no problem.

Decomposers for Waste and Product. These appear in the reflux process as well and present no problem.

Design of Columns. Although columns appear in both systems they must be insulated against temperature change in the dual temperature system. It is also necessary to achieve extremely efficient contacting in this system since only part of the maximum separative effect is utilized which leads to much greater column requirements than in the reflux system.

Heat Exchangers, Heaters, and Coolers. These present no unusual design problem.

Column Pulsers. (Not indicated in Figure 2) Since much larger column flows are required in the dual temperature system the column pulsers must be much larger and might be considered to be a development problem.

Initial Development Program

Although detailed cost estimates have not been made and cannot be made with confidence as yet, it appears that the initial cost of a reflux plant might be less than a dual temperature plant. However, the time and effort which must be expended in development work on reflux devices to clearly establish their complete and unquestioned large scale feasibility looms rather large. In contrast, the dual temperature process consists of heat exchangers, similar

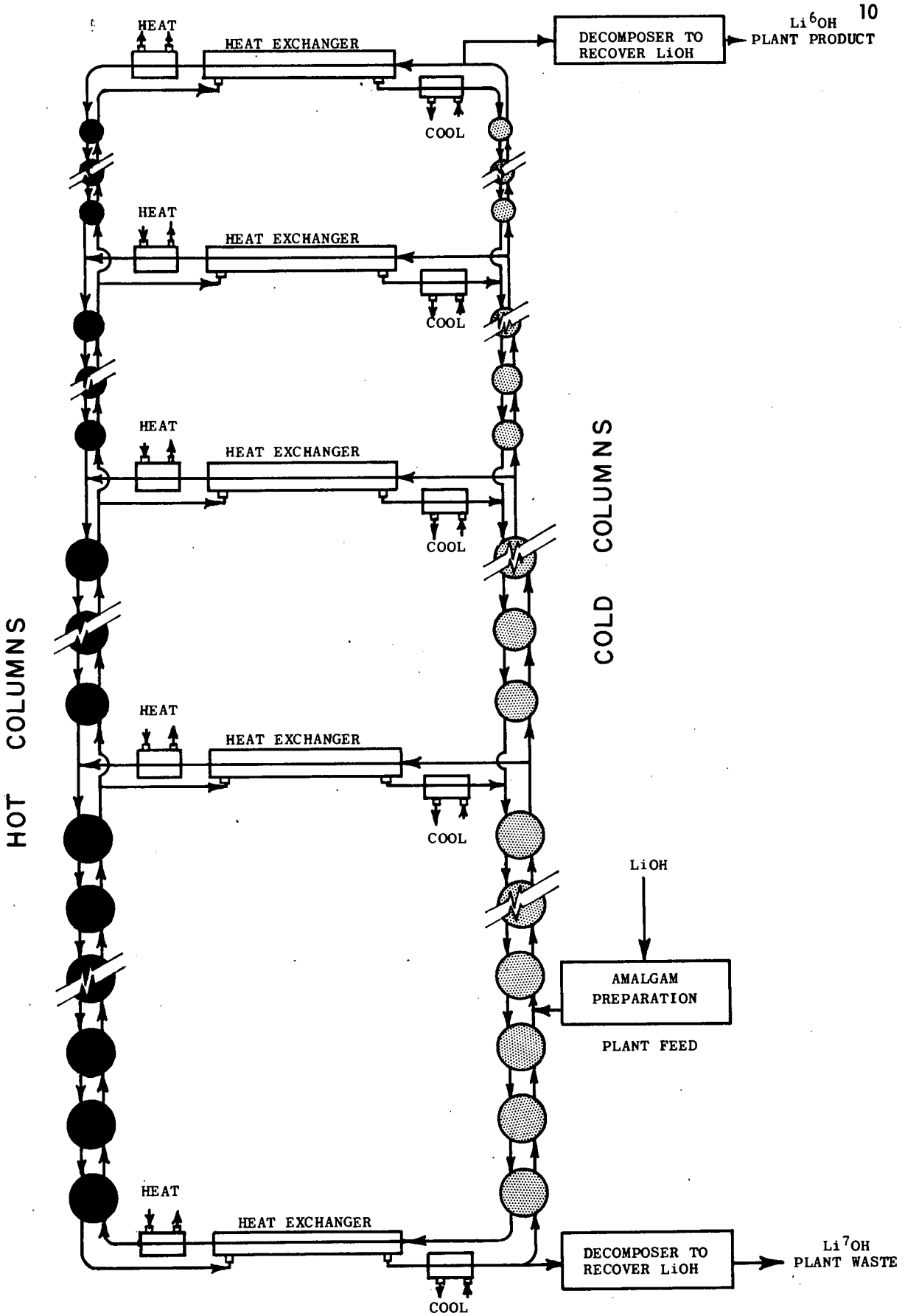

FIGURE 2: AMALGAM-AMINE DUAL TEMPERATURE SYSTEM

common equipment, and pulse columns. It is believed that pulse columns for the amalgam-amine system can be rapidly developed since all the variables affecting column performance with certain other liquids have been extensively studied by ORNL, Hanford, and Y-12 engineering groups. It appears, therefore, that the feasibility of the dual temperature system might be demonstrated at an earlier date while expending less effort on development work. The extreme simplicity of this type of system should lead to much lower operating costs which provides further justification for favoring it in this early program. If for any reason the dual temperature method proves to be inoperable, then the data obtained on flow rates, stage heights, perforated plate design, materials of construction, and considerable practical experience with pumps and flow control devices will be applicable to the reflux system.

In actuality, the two systems must be studied simultaneously since it may be necessary to operate single columns by reflux to obtain data for proper design of a dual temperature system.

It is obvious that three of the most important factors which influence plant cost for the dual temperature method are (a) separation factor, (b) stage height, and (c) throughput. The separation factor must be maximized by achieving the greatest possible temperature span between hot and cold towers. The stage height must be minimized by developing the best plate design and by optimizing pulse characteristics and other column variables. The throughput must be maximized not only by column design and operation but also by obtaining the maximum concentration of lithium in each phase. The development work is proceeding along all of these important lines.

The design groups at K-25 have been requested to develop all the necessary cascade equations for the dual temperature process.

Plans are also underway to obtain as a consultant, Dr. J. S. Spevack, the originator of the dual temperature method.

LABORATORY STUDIES

H. H. Garretson and J. S. Drury

Choice of the System

In undertaking an investigation of the thermodynamic properties of lithium amalgam, a solvent inert toward the amalgam and yet capable of dissolving moderate amounts of lithium salts was sought. The work of Putnam and Kobe[2], Isbin and Kobe[3], and Kennedy[4] had shown that anhydrous ethylenediamine would meet these requirements.

A 200 ml sample of the amine was available in the laboratory. This sample was very dark colored from contact with a black rubber stopper and was purified by distillation, reflux over solid sodium hydroxide and drying with chips of lithium metal. It was found that, when anhydrous, lithium was appreciably soluble in the amine forming brown, blue, or purple solutions depending upon temperature and concentration. Further lithium reacted slowly and continuously with the anhydrous amine with the evaluation of a gas, presumably hydrogen. This reaction was exothermic and proceeded very rapidly in the warm solvent. After drying with lithium metal, a water white liquid was distilled over boiling at 116-117°C.

Anhydrous lithium iodide and chloride both reacted with the anhydrous ethylenediamine with considerable heat of solvation, and then dissolved very slowly to produce solution about two-tenths molar

An electrolysis cell using a pool of lithium amalgam as an anode and a platinum wire cathode and a lithium iodide solution of ethylenediamine was arranged with a dry hydrogen atmosphere. On electrolysis lithium was deposited at the platinum cathode as was evidenced by the characteristic blue color of a solution of lithium metal in the region of the cathode. An adhering deposit on the platinum was not achieved apparently because of the solubility of the lithium in the solvent An appreciable amount of metallic lithium was then added to the electrolyte in an attempt to effect saturation, but in an electrolysis under these conditions no definite adhering deposit was achieved. On prolonged standing following this electrolysis, the solution turned from blue to brown and finally a metallic gray color. The electrolyte was then carefully decanted from the amalgam and distilled. A water white product was obtained but a

surprisingly large globule of mercury was found to have distilled over with the amine.

Since agitation of the electrolysis vessel indicated no tendency toward emulsification, a small sample of one-half molar lithium amalgam was shaken vigorously by hand with anhydrous ethylenediamine. The amalgam could be broken up into fine globules but these coalesced slowly on standing. This was repeated with amine first containing dissolved lithium iodide and again with amine containing dissolved lithium chloride. In neither instance could any tendency toward stable emulsification be observed. Later observations show that salt solutions of ethylenediamine have the same property of wetting a lithium amalgam surface with a distinct sheath of solution that is so characteristic of the amalgam with water and alcohol solutions.

Some further preliminary electrolysis and e.m.f. studies have been made in this system. A lithium chloride solution in ethylenediamine was electrolyzed using mercury pools both as anode and cathode. Lithium amalgam was formed at the cathode and a cream colored insoluble mercury salt was formed on the anode. In a similar experiment with lithium iodide, solution of the anode occurred. On prolonged electrolysis in this case a visible transport of mercury from anode to cathode occurred. A trace of an insoluble red precipitate was observed in the cathode compartment. In these experiments the electrolyte path from anode to cathode surfaces was approximately twelve centimeters and the two compartments were separated by a sintered glass disk. At twenty to thirty volts and electrode surface area of three square centimeters, currents of two to eight milliamperes were obtained. All these experiments were performed at room temperature under dry hydrogen atmospheres.

E.M.F. studies demonstrated that lithium amalgam electrodes established definite steady and reproducible potential against ethylenediamine solutions of lithium salts. Further, it was found that mercury overlayed with the chloride anode deposit produced an electrode with a stable potential. These observations indicate a direct and simple electrometric means of following the concentrations of lithium amalgam and of lithium ion in ethylenediamine solutions.

It has been observed that water solutions of ethylenediamine react with lithium amalgam to form an alkyl ammonium amalgam. This amalgam shows the same inflation characteristics that typify an ammonium amalgam. It was observed in

the experiments for the determination of the isotopic separation factor that after the lithium amalgam was apparently completely leached of its lithium that a small residual activity still remained which would only respond to concentrated hydrochloric acid. This was attributed to traces of the alkyl ammonium amalgam resulting from traces of moisture unavoidably absorbed during the manipulation and agitation of the system. In making this observation it was noticed that the concentrated hydrochloric acid would occassionally develop a clear green color which could be attributed to base metal impurities in small traces in the mercury.

Preparation of EDA For The Determination of The Isotopic Separation Factor Experiments

The ethylenediamine used in the mass transfer, equilibrium time studies and in the determination of the isotopic separation factor experiments was obtained as an Eastman Organic Chemical labelled as ninety-five percent. Purification was made by a reflux over solid sodium hydroxide in excess for several hours followed by a careful decantation of the warm supernatant liquid and a reflux with sodium metal in excess until a deep blue color persisted in the boiling solution. The ethylenediamine was then distilled directly in an atmosphere of dry helium into a liter flask receiving vessel which was glass sealed to the condenser. A mercury trap outlet was used on the bottom of the receiver so that the ethylenediamine was stored and could be handled without contact with stopcock lubricants. The product taken boiled from 115°-$117.5^{o}C$ and approximately eighty percent recovery was obtained. Amine which had been used in the experiments and was still essentially anhydrous was reprocessed in the same way except that the sodium hydroxide reflux was omitted.

The Preparation of Amalgam For The Determination of The Isotopic Separation Factor Experiments

The amalgam used in these experiments was prepared in batches of seven hundred and fifty milliliters each. The mercury was purified by agitation with air and five percent nitric acid for several days and then thoroughly washed and dried. A four molar lithium hydroxide solution which had been

allowed to clarify for several weeks or longer was used as an electrolyte. Electrolysis was performed with a platinum anode and with slow stirring of the mercury cathode but no agitation of the aqueous electrolyte. From seventy to ninety percent of the lithium was deposited and amalgams five to six-tenths molar were prepared. The amalgam was filtered through a refractory funnel provided with a copper tube outlet to retain moisture. The amalgam was allowed to settle under hydrogen and then transferred by gravity under hydrogen to a storage vessel that had been warmed and thoroughly flushed with dry hydrogen. The hydrogen used in these experiments was purified by passage through a heated copper catalyst, concentrated sulfuric acid and then through a chamber packed with copper wool and wet with fresh lithium amalgam. The lithium amalgam stored under these conditions developed only a very thin gray surface film on long standing and no changes in concentration on storage could be detected. More dilute amalgams were prepared from this stock by dilution with pure dry mercury.

Mass Transfer

The lithium chloride used was B and A Reagent grade and was dried in a tube furnace for one hour at 400°C in an atmosphere of anhydrous hydrogen chloride. After flushing with dried helium and cooling, the dried lithium chloride was removed from the furnace and placed in an erlenmyer flask previously dried and filled with dry helium. Dried EDA was added in amount calculated to produce a saturated solution. After dissolution of the chloride, five mls of the solution were added to a centrifuge tube fitted with a ground glass stopper. Approximately five mls of 0.5 M lithium amalgam were added and the contents of the tube agitated by hand for 20 seconds. At the end of this period the phases were separated and gravimetrically analyzed for lithium by weighing Li_2SO_4. The volume of amalgam originally taken was determined by weighing the dried mercury after extraction of the lithium with dilute HCl. The small error introduced by the partial molar volume of the lithium dissolved in the mercury was ignored. The results of this experiment are tabulated in Table 1.

Table I

	Sample of Amalgam Before Equil	Sample of EDA Before Equil.	Sample of Amalgam After Equil.	Sample of EDA After Equil.
Vol.(mls)	9.86	5 0	4.98	5.0
gms Li_2SO_4 found	0 2896	0.0722	0.1347	0.0738
gms Li/ml	0.0037	0.0018	0.0034	0.0019

Equilibrium Time

After establishing that no significant amount of lithium transfer occurs, even with a large concentration difference between the phases, two experiments were undertaken to determine the rate of exchange of the lithium species between the phases. In the first experiment, amalgam containing normal lithium was equilibrated with EDA containing lithium chloride enriched in Li^7 Samples of each phase were taken at 30, 60, and 120 second intervals The lithium content of these samples was analyzed gravimetrically as before, and isotopically with a mass spectrometer to determine the extent of exchange The results of this experiment are given in Table 2 Essentially complete exchange was found to occur within 60 seconds. It also was found possible to obtain an approximation of the single stage fractionation factor (α) from the ratio of the isotopic concentrations in each phase. The values of α = 1.04 and α = 1 05 proved to be in good agreement with values obtained in later work.

A second experiment was performed similar to the first but differing in that lithium chloride enriched in Li^6 was used in the EDA This was equilibrated with lithium amalgam of normal abundance for 120 seconds Since Li^6 is preferentially concentrated in the amalgam an overlapping of the isotopic assays in each phase is to be expected if exchange is complete within this time interval. Reference to Table 3 shows that this expected overlapping does occur. On the basis of the evidence from these experiments, the isotopic exchange between the lithium species in the system was considered to be rapid

Table 2

Exchange Run No. I

	Amalgam Before Exchange	EDA Before Exchange	Amalgam After 30 sec.	EDA After 30 sec.	Amalgam After 60 sec.	EDA After 60 sec.	Amalgam After 120 sec.	EDA After 120 sec.
Total grams Li present	0.0207	0.0011	0.0094	0.0020	0.0086	0.0028	0.0096	0.0021
Vol. each phase (mls)	9.71	5.0	4.86	5.0	4.83	5.0	4.98	5.0
gms Li/ml	0.0021	0.0002	0.0019	0.0004	0.0018	0.0006	0.0019	0.0004
Ratio Li^6/Li^7 ($\pm$ 0.001)	0.678	0.032	0.078	0.071	0.077	0.074	0.076	0.072

Table 3

Exchange Run No. 2

	Amalgam Before Exchange	EDA Before Exchange	Amalgam After 120 sec.	EDA After 120 sec.
Total gms Li present	0.0103	0.0114	0.0111	0.116
Vol. each phase (mls)	4.75	5.0	5.09	5.0
Gms Li/ml	0.0022	0.0023	0.0022	0.0023
Ratio Li^6/Li^7 ($\pm$ 0.001)	0.079	0.114	0.097	0.095

and essentially complete within 60 seconds under the conditions observed.

Separation Factor

After determining that rapid exchange occurs between the lithium species in the system, a batch run was begun to establish the single stage fractionation factor, α. The scheme used is diagrammed in Figure 3. The equipment used consisted of five round bottom flasks of suitable size fitted with a mercury-sealed stirrer and an inlet and outlet for sweeping the flask with inert gas. There was a capillary stopcock at the bottom of each flask. This arrangement effectively prevented any reaction of the lithium species with oxygen nitrogen, carbon dioxide, and moisture. However, this equipment did not prove to be a very efficient device for contacting the two phases and in spite of the rapid exchange of this system it was later necessary to lengthen the agitation time in order to attain isotopic equilibrium.

To begin the batch run, twelve hundred mls of amalgam 0.25M in normal lithium were prepared as described earlier. Six hundred mls of this solution were agitated with 600 mls of anhydrous EDA, 0.25M in LiCl under an atmosphere of dried helium. The LiCl in the EDA was prepared from lithium extracted

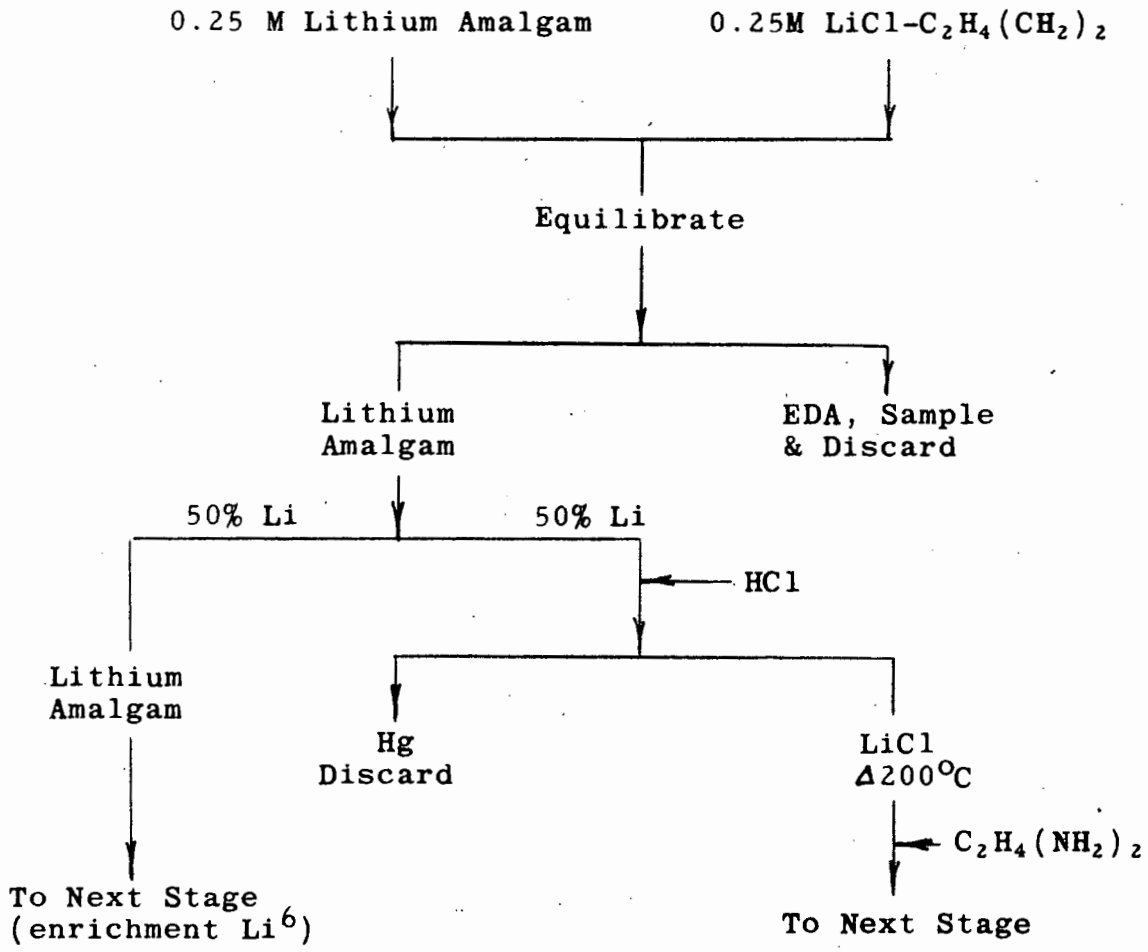

FIGURE 3 FLOW DIAGRAM OF ONE STAGE OF A LITHIUM AMALGAM-LITHIUM CHLORIDE-ETHYLENE DIAMINE BATCH RUN

from the other 600 mls of amalgam. After a suitable time, samples were taken from each phase and the amalgam phase was split into two equal volumes. One volume was preserved under dried helium for use in the next pass and the other part was leached with dilute HCl. The aqueous LiCl solution was evaporated to dryness, then heated to 200°C under a stream of dry helium until anhydrous LiCl was obtained. Sufficient dried EDA was then added to this salt to produce a 0.25M solution. This phase was then agitated with the amalgam solution. This recycling was repeated five times. The temperature was regulated to prevent thermal effects from entering into the measurements. The samples obtained were converted to Li I and submitted for analysis by the Mass Spectrographic Laboratory. Table 4 lists the isotopic concentrations of these samples.

Table 4

Batch Run No I 26° ± 1°C

Sampled After Pass No.	Equilibration Time per Pass (min)	Ratio Li^6/Li^7 ± 0.001	
		Amalgam	Amalgam Reassayed
0			0.0797
1	150	0 0809	0.0811
2	90	0.0841	0.0842
3	90	0.0871	0.0852
4	65	0.0858	0.0876 0.0856 0.0862
5	30	0.0873	0.0865

Different mass spectrometers were used in the initial analysis of these samples and, as can be seen from Figure 4, the precision of the results was too poor to permit conclusions to be drawn from the data. The samples were reassayed using the same mass spectrometer for each sample. Better precision resulted and it was possible to conclude that isotopic equilibrium had not been achieved during the latter passes of this run.

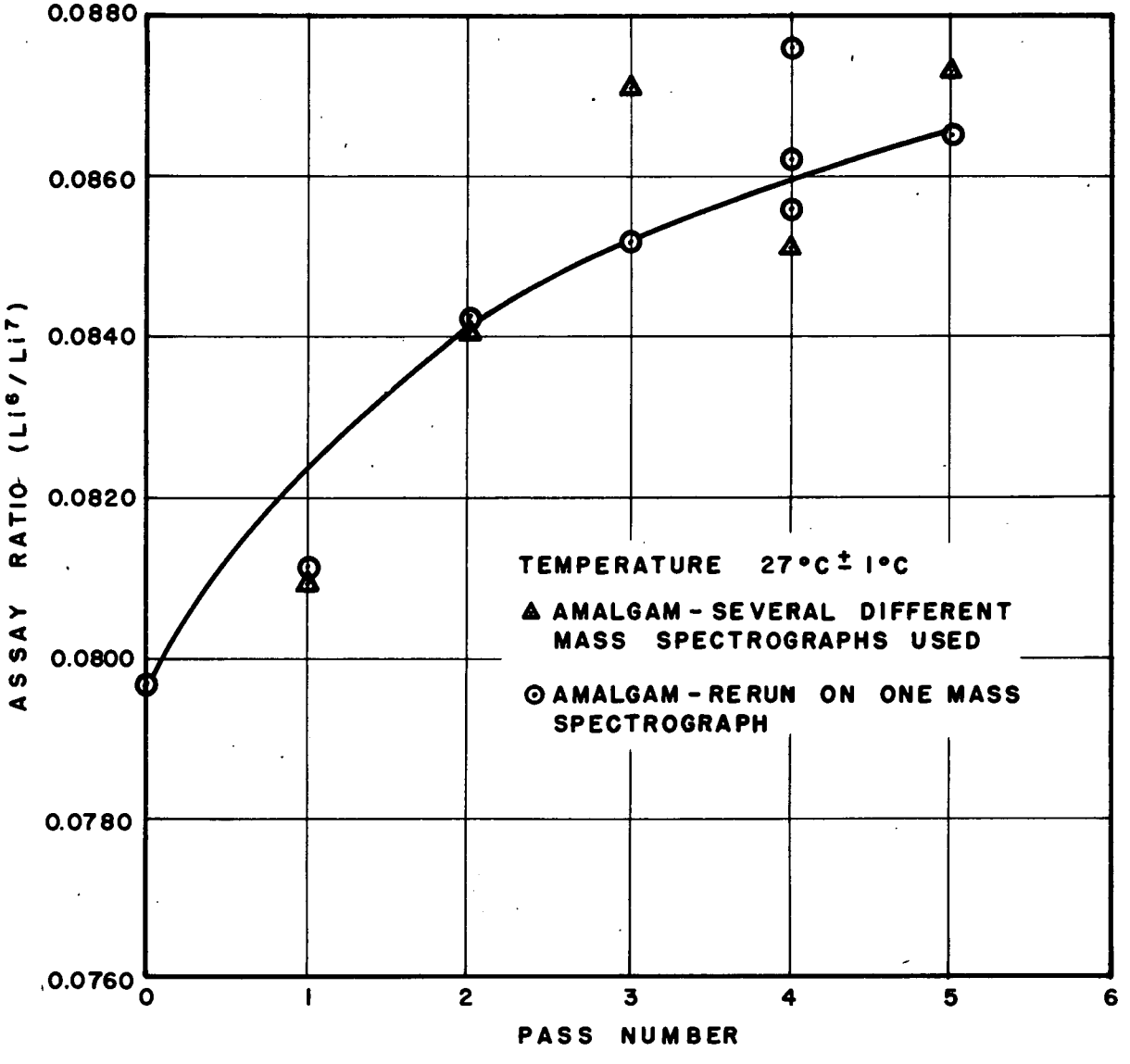

FIGURE 4. LITHIUM AMALGAM - ETHYLENE DIAMINE LITHIUM CHLORIDE BATCH RUN NO. 1

To verify this conclusion, a second run was made under similar conditions except that the time of agitation was achieved in this run evidenced by the linear relationship of the data obtained. These results are tabulated in Table 5. Figure 5 shows the isotopic concentration of these samples plotted versus the number of passes. From the average slopes of these lines, α, the single stage fractionation factor at this temperature may be calculated to be 1.051. The 95% confidence interval of α from the amalgam samples is (1.046, 1.050). This value from the EDA samples is (1.041, 1.067).

Table 5

Batch Run No 2 $27^{o} \pm 1^{o}C$

After Pass No.	Equilibration Time per Pass (min.)	Ratio $Li^6/Li^7 \pm 0.001$	
		Amalgam	EDA
0		0.0788	
1	240	0.0797	0.0759
2	240	0.0820	0.0780
3	240	0.0842	0.0810
4	240	0.0863	0.0818
5	240	0.0880	0.0845

In order to determine the temperature dependancy of the fractionation factor, a third batch run was made in which the temperature was maintained at $99^{o} \pm 1^{o}C$. Other conditions were similar to those which prevailed in the previous run. Four passes were made. A complete analytical evaluation of the samples taken is not yet available but Table 6 tabulates best values for the amalgam samples. These data are plotted in Figure 6 and give a separation factor of 1.028. From this curve the 95% confidence interval for α at $99^{o}C$ is (1.018, 1.039).

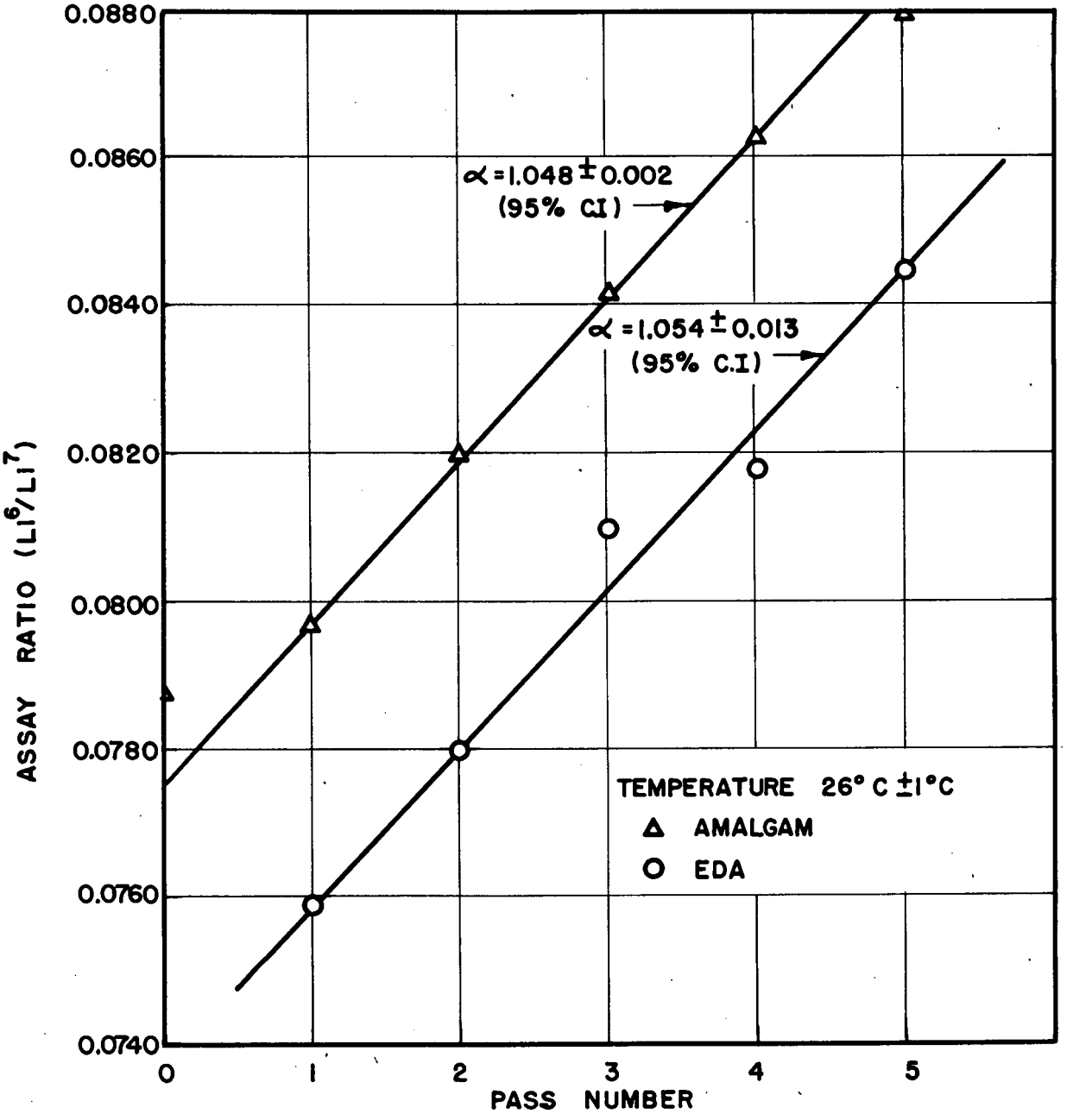

FIGURE 5. LITHIUM AMALGAM – ETHYLENE DIAMINE – LITHIUM CHLORIDE BATCH RUN NO. 2

Table 6

Batch Run No. 3 99 ± 1°C

After Pass No.	Equilibration Time per Pass (min)	Ratio $Li^6/Li^7 \pm 0.001$ Amalgam
0		0.0783
1	240	0.0785
2	270	0.0802
3	300	0.0810
4	300	0.0827

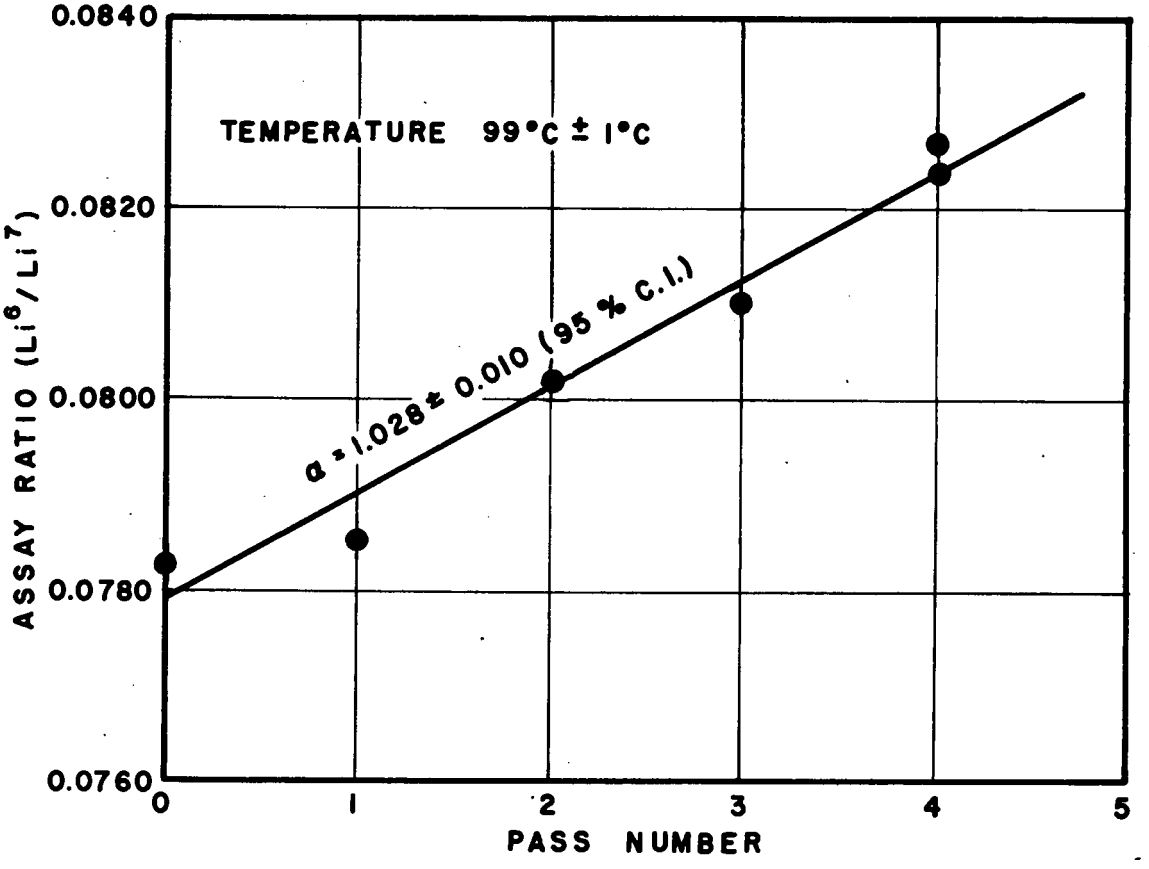

FIGURE 6. LITHIUM AMALGAN – ETHYLENE DIAMINE: LITHIUM CHLORIDE. BATCH RUN 3

PILOT PLANT STUDIES

J. Ramsey

Introduction

Time for construction of a pilot plant based on dual temperature pulse columns was extremely limited. Engineering and construction of the pilot plant began in the middle of November, 1951, the first construction requiring about six weeks. A run was attempted with moderate success on December 30, 1951.

Because of the need for haste, most of the engineering was done in the field and simplified construction was used wherever possible. It was necessary to use material on hand in the stores for all construction, and special materials which were ordered were added to the system as they were received later. Fortunately, many of the pipe fittings were on hand in the stores so that shop work and emergency purchases were held to a minimum amount.

Construction of Pulse Column

Columns. Tests of metals showed that stainless steel could be used for column construction. Glass pipe was another possibility but it was ruled out because of the difficulty involved in jacketing glass pipe for heating and cooling. One-inch outside diameter S.S. 316 tubing, with 16 gauge walls, was selected for column construction. Columns were constructed of four sections, each six feet long, jacketed with 1-1/2 inch iron pipe. Thus twenty-four feet of column length is provided for each of the hot and cold columns. The hot column was jacketed for steam heating, and the cold column was jacketed for cooling water.

Pumps. Milton Roy pumps were found to be available for construction of the pulse column unit. A duplex Milton Roy pump with capacity of 8 gph per side was found for pumping amalgam, and a duplex Milton Roy pump of 12 gph capacity per side was found for pumping amine. Two simplex Milton Roy pumps (7/8-inch diameter pistons) with variable speed drives were found for use as pulsers. The latter pumps, while having stuffing boxes with their inherent disadvantages, were available, and it was not possible to order and obtain diaphragm type pumps in the time which was available.

Plates. The early work with mercury in pulse columns had shown that moderate rates of flow could be obtained with both mercury and lithium amalgam on plates as fine as 70-mesh size. Since screens were available in stores in the 60-mesh size, this size was selected to start tests. Orders were placed for an assortment of various sizes of screens and perforated plates for future tests. Stainless steel was selected as screen material for first tests since its resistance has been fairly well established. Nickel screens and plates may also be used and may offer advantage of preferential wetting with consequent effect on stage height in the pulse column.

Filters. Sintered stainless steel filters of a convenient size were found in Y-12 and were obtained for testing in the pilot plant. These are manufactured by the Micro Metallic Corporation of Glen Cover, New York. Each filter offers an effective filter area of 3-1/2 square feet with passage size of 20 microns in a self-contained unit 4-1/2" diameter and 14" long. Filters were installed for amalgam and amine streams feeding the cold pulse column.

Packing and Gasket Materials. Packing and gasket materials which were tested included Tygon rubber, Silicone rubber, Teflon, Koroseal, polyethylene, and asbestos. These materials were tested with both 76% ethylenediamine and 1 molar lithium amalgam with the assistance of the Analytical Division. Tests showed that lithium amalgam reacts to some extent with all of these materials except asbestos. Ethylenediamine reacts with all materials except Teflon and asbestos. Garlock No. 7735 sheet packing material which was found to be available at Y-12 appears to be fairly resistant to both ethylenediamine and amalgam. This material is reported by the Garlock Company to be composed of asbestos fiber filled with GRS rubber. First construction was made with gaskets cut from asbestos sheet material, and replacement was later made with factory-punched Garlock 7735 gaskets. Milton Roy pumps are packed with chevron-type blue African asbestos packing which appears satisfactory.

Pipe Joints. A limited number of pipe joint cement materials were found to be available at Y-12. Fortunately, one of these was found to be resistant to both ethylenediamine and amalgam, a product known as Cyl-seal (West Chester Chemical Company, West Chester, Pennsylvania). The composition of this material is not specified at present. Although Cyl-seal pipe joint compound is fairly satisfactory, pipe joints and stainless steel fittings are prone to leak under service in ethylenediamine unless very carefully made. All-union construction or welded construction is desired wherever possible. It is believed that best construction for the pilot

plant would have been tubing and tubing fittings, with right angles made of tubing bends. Since tubing fittings for the job were not available, 1/4-inch stainless steel pipe with threaded joints was used.

Greases. Several greases were on hand in the Y-12 stores and several other greases were ordered. The greases available at Y-12 were several grades of Keystone greases (Keystone Lubrication Company, Philadelphia, Pa.) and several automotive lubricants distributed by the Gulf Oil Company of Pittsburgh, Pa. Five different greases which were recommended by the Rockwell Manufacturing Company of Pittsburgh, Pa., for use in alkaline systems were ordered and tested with ethylenediamine and lithium amalgam. All greases tested have at least a limited solubility in the process materials. The grease which appears to have the most resistance and the best characteristics is Keystone "Nevastane" heavy. This grease is being used to lubricate packing of plungers in Milton Roy pumps.

Preparation of Feed Materials

Amalgam. Procedures for making lithium amalgam from lithium hydroxide and mercury in electrolectic cells have been very well developed. An amalgam cell from the Electro-exchange Bench scale work was available for the dual temperature pulse column project. This employs a carbon electrode in a plexiglass trough with multistage agitators coated with Unichrome. A nickel electrode in the same cell is also to be tested as a means of eliminating fine particles of carbon which are formed with the graphite electrode.

The amalgam is separated from lithium hydroxide by double decantation.

Ethylenediamine. Preparation of ethylenediamine solutions for initial pulse column tests was carried out in the laboratory as is described elsewhere in this report. About 12 liters of solution are required to charge the pulse column system.

Pulse Column Trial Run

A trial run of the pulse column was made December 30, 1951, using 60-mesh screen. One of the most successful aspects of the run was satisfactory operation of Milton Roy pumps in pumping lithium amalgam to a height of 30 feet. The heat exchangers and column jacket operated fairly satisfactorily in controlling temperature although better controls were indicated to be desirable. Operation of the gravity leg, head tanks, and filters seemed satisfactory although certain

improvements were indicated, such as installation of check valves after the pumps and location of traps at critical points in the system. First operation was not completely successful inasmuch as it was not possible to obtain flow rates of greater than 50 cc/min through 60-mesh screen. It is indicated that flow rates of from 300 cc/min to 500 cc/min of each liquid phase should be practical with a more optimum screen size. The first run was not carried to equilibrium and no samples were submitted to the laboratory to determine isotopic separation because of an early gasket failure which limited the run length to four hours.

Temperature and Pressure Control

Temperature and pressure control of the pulse column system are both highly important. The pulse column is connected to a closed system in which the pressure is controlled to prevent boiling of the liquid in the hot column. Present construction is of such strength as to allow about 50 pounds pressure in the system if desired. Construction to allow greater pressures is feasible with only slight modification in the direction of heavier fittings. Pressure in the system is controlled by pressure regulation of a helium supply tank.

Hot and cold temperatures are both important. Temperature of the hot column must be high enough to give minimum separation coefficient (maximum difference between cold and hot coefficients) and not hot enough to cause vapor formation which obstructs the pulse. Temperature in the cold column must be low enough to give a good separation factor and not low enough to cause crystallization of the lithium chloride from the amine.

High temperature is controlled by flow of steam into the jackets of heat exchangers for the two liquids and for the column jacket. Steam flow is controlled by a steam pressure regulator and by needle valves on steam lines going into the jackets.

A method of controlling upper temperatures is used in which steam is bled from low pressure lines through needle valves at a low rate in order to keep the temperature at a point below 100°C. It is believed that temperatures in the range 120°C to 140°C may be reached as operating experience is obtained. In this event, construction will be made to provide pressure regulator valves to give control of jacket temperature by equilibrium temperature at the steam pressure furnished by the regulator. This method of control of temperatures above 100°C should be practical and should be more economical than temperature regulation systems employing

temperature controlling valves or motorized steam valves.

Flow of cooling water to the coolers is controlled by a water pressure regulator and globe valves on the lines to jackets. In first tests cold water to the jacket was cut off so that room temperature controlled the low temperature column.

Experimental Program

It is first desired to obtain a good evaluation of overall separation in a reasonable efficient pulse column using a fixed plate size and pulse rate. During the evaluation work it is expected that it will also be possible to bring forward any special operational difficulties, and to eliminate mechanical troubles from the system. Then it is planned to make a series of tests of the system to find the best combination of flow rates, plate sizes, and pulse rates to give the most efficient exchange, and the most efficient plant design. Also it is planned to develop amalgam and amine preparation systems for efficient handling of materials on a pilot plant scale.

First tests are to be made at total reflux, so first construction does not include feed lines or take-off lines for product. Pumps have been located to provide feed to columns and a preliminary design has been made. These lines will be connected as time permits and it is expected that the equipment will be ready by the time it is desired to obtain separation data at various ratios of feed to throughput.

PREPARATION OF ANHYDROUS ETHYLENEDIAMINE

D. W. Kuhn, D. A. Lee, A. A. Palko, A. D. Ryon

Introduction

In order to successfully employ a separation process using the system lithium chloride in ethylenediamine-lithium amalgam, the attainment and maintenance of an anhydrous system must be achieved. To illustrate the limitations imposed by this requirement, consider a system containing 0.3 molar lithium amalgam and an equal volume of ethylenediamine. If the ethylenediamine were 99.4% pure and contained only 0.6% water, there would be sufficient water present to strip the amalgam of all of its lithium by the formation of lithium hydroxide. Hence water cannot be allowed even in small amounts. The problem first of all is to prepare dry ethylenediamine and dry amalgam, and then introduce these into a dry column system and prevent any moisture pick-up in subsequent operation.

Ethylenediamine is usually prepared by reacting ethylene dichloride and aqueous ammonia.[5] This, of course, gives a product containing water which must be separated to obtain anhydrous ethylenediamine. Ethylenediamine and water form a maximum boiling mixture.[6] This maximum boiling point is 118.5°C (the boiling point of anhydrous ethylenediamine is 116.2°C) and at this temperature the mixture contains approximately 83% ethylenediamine and 17% water. Therefore, ethylenediamine cannot be readily separated from water by fractional distillation.

The usual procedure[2,3] for preparing anhydrous ethylenediamine in the laboratory has been to reflux ethylenediamine monohydrate with hot concentrated NaOH. This salts out the ethylenediamine and two phases separate, an amine phase and an aqueous NaOH phase. The amine phase which is 95% ethylenediamine is distilled from sodium yeilding anhydrous ethylenediamine.

Cornish, et al[7] have separated ethylenediamine from water by fractionating over 75% NaOH in a 6.09 meter column. Density measurements were used to determine the purity of the product.

Bailar[8] prepared anhydrous ethylenediamine in small amounts by preparing the zinc ethylenediamine oxalate complex salt and decomposing it at 200°C in a vacuum. The ethylenediamine collected was redistilled over sodium.

Pyridine, which is similar to ethylenediamine in some respects, has been successfully separated from water by azetropic distillation.[9] This seemed to be a good method of dehydrating amines and experiments which will be discussed later were inaugurated. There was no information found in the literature on the preparation of anhydrous ethylenediamine by azeotropic drying.

The present procedure for preparing anhydrous ethylenediamine is, briefly, to treat ethylenediamine monohydrate with sodium hydroxide, then reflux with calcium carbide, and finally distill from the calcium carbide.

In the sodium hydroxide "salting out" step, the amount of drying is a function of the NaOH concentration. Since the solubility of NaOH in water increases sharply with temperature, the ethylenediamine monohydrate is heated and solid NaOH added. Twenty liters of ethylenediamine monohydrate are heated in a monel vessel to 80°C, then 20 pounds of solid NaOH are added slowly with rapid stirring until all the NaOH is in solution. The amine and aqueous NaOH phases are separated.

The 95% amine obtained from this treatment is refluxed for 15-20 hours over calcium carbide. The reaction is complete when no more acetylene is given off. The amine is then distilled from over the CaC_2 into a dry flask. Since ethylenediamine is extremely hygroscopic, the reflux and distillation apparatus is vented through activated alumina dry tubes.

Ethylenediamine dried by this method does not produce hydrogen with sodium metal. A reliably quantitative analytical procedure to determine the amount of water in the product was not available during these experiments. The Analytical Division is working on this problem. However, the sodium test is very sensitive and shows whether or not the amine is dry.

Azeotropic Distillation

The separation of water from pyridine by the addition of a third component which forms an azeotrope with water has been described in the literature.[9] Any one of a list of ten organic liquids has been used satisfactorily as the third component or "entrainer" for the dehydration of pyridine. Among these entrainers are included benzene, toluene, diisobutyl ether, and methyl butyrate. A similar procedure was tried with wet ethylenediamine and a number of organic liquids including benzene, xylene, toluene, diphenyl ether, phenol, and aniline. Of these, benzene and xylene both showed promise of performing satisfactorily. A fractionating column

2" in diameter and 6' tall, packed with 1/2" Raschig rings, was used in these experiments. Results are not yet available as to how dry the product from such an azeotropic distillation can be obtained. However, experimental work will be continued.

Upon heating a mixture of benzene with 95% ethylenediamine, the distillate began coming over at a temperature of about 69°C, and shortly thereafter increased to 76-79°C. During this time a two-phase distillate was collected, the composition of which was approximately 98% benzene, 1% ethylenediamine, and 1% water. The aqueous amine layer was withdrawn and the benzene returned to the distilling flask. After the aqueous phase ceased to distill over, the temperature rose to 80°C and bezene was collected. Having separated all of the bezene, the temperature in the head of the column again rose abruptly to 115-116°C and ethylenediamine was collected. By this method, ethylenediamine of a purity of 98.5% has been prepared as determined by titration with standard hydrochloric acid. A modified Karl Fischer electrometric titration for determination of water in these samples has now been developed, and in future experiments the water content of the ethylenediamine will be known with greater accuracy.

A similar azeotropic distillation process was carried out using xylene as th entrainer. In this case, the first portion of distillate was collected at 111-112°C and was again a two-phase mixture which separated into a xylene layer and a water-ethylenediamine layer. The composition of this azeotropic mixture was approximately 13% xylene, 64% ethylenediamine, and 23% water. The next fraction to distill over was a clear, single phase liquid containing 64% by weight ethylenediamine and 36% xylene, which is exactly 3 moles of ethylenediamine per mole of xylene. This fraction was collected at 112-1/2 to 113°C. Then the temperature gradually increased to 116°C, by which time the xylene had been removed and the remainder of the distillate supposedly should have been anhydrous ethylenediamine. One sample of ethylenediamine prepared by the xylene distillation method was found to contain 3.3% water. It is hoped that either xylene or benzene can be made to produce at least 99% ethylenediamine after further work with this method.

Other Methods

Besides calcium carbide, other solid drying agents were studied. Barium oxide completely dried the amine. When the amine became dry it turned a brilliamt green. Barium oxide in lump form was a very suitable reagent, but it was not as available as calcium carbide and it is more expensive.

Activated alumina was also tried as a drying agent. It was slightly less efficient than CaC_2 or BaO.

Silica gel was the least suitable of the drying agents tested. This is probably due to the acidic nature of SiO_2.

Tests were attempted with calcium oxide, but no results were obtained because of the violent bumping of the flask. Powdered calcium oxide was all that was available. Lump calcium oxide may be suitable.

Another method which seemed feasible for drying the amine was to add an ester which could be hydrolyzed by the water in the amine to give an alcohol and an acid, the acid of course reacting with the amine to form a salt. However, esters also react with amines to form an alcohol and an amide. One preliminary test with methyl acetate was run and partial drying was obtained, but the product contained 2 to 3% water.

For our present needs, the present process is quite adequate. However, for a large plant a continuous process would be desirable. Therefore an azeotropic distillation process with a complete recycle of all processing chemicals would be extremely advantageous. Research on this type process will be continued.

SOLUBILITY STUDIES

G. M. Begun, A. C. Rutenberg, A. A. Palko

In considering the lithium chloride-ethylene diamine lithium amalgam system for the separation of lithium isotopes, it was desirable to obtain solubility data on lithium salts in ethylenediamine. If the solubility of the lithium salt in the amine could be increased above the 0.30M figure possible with LiCl at 25°C the size and cost of a possible plant could be reduced. The literature contains only one reference to such solubility work. Isbin and Kobe[3] list the solubilities of LiCl and LiBr in EDA at 25°C as 0.32 and 0.28 molar, respectively.

Preparation of Materials

Dry Ethylenediamine. The starting material was Carbide and Carbon Chemical Company 76% EDA. It was heated for several hours with an excess of sodium hydroxide pellets. Two phases appeared and the aqueous phase was removed and discarded while the solution was above 60°C. The EDA phase (now containing about 5% water) was refluxed over metallic sodium until the EDA turned blue. The blue color presumably indicates sodium metal is dissolving in, and or, reacting with the amine. This does not occur until all the water has reacted. The amine was distilled from the sodium under an atmosphere of dry helium. The dried amine was then redistilled from sodium as needed into the flasks containing the dry lithium salts.

Lithium Salts. The following lithium salts were tested for their solubility in EDA: formate, acetate, propionate, oxalate, heptafluobutyrate, sulfate, nitrate, perchlorate, fluoride, and iodide. The lithium salts of the organic acids were prepared by the action of the organic acid upon lithium carbonate. They were recrystallized from aqueous solution. In the case of the heptafluobutyrate, ether was used since the recrystallization from water was rather difficult as syrups were formed.

The lithium iodide sample used was prepared by the Stable Isotopes Division. The lithium perchlorate was prepared from perchloric acid and lithium hydroxide, and was recrystallized from aqueous solution. The lithium sulfate was prepared from the carbonate and was initially dried in a muffle furnace. Analytical grade lithium nitrate and fluoride were used without further purification.

All the above salts were given a final drying under vacuo while being heated below their decomposition temperatures. At the completion of the drying dry helium gas was admitted to the flasks. The amine was distilled directly over sodium metal into these flasks.

Solubility of Lithium Chloride

The solubility of lithium chloride (anhydrous) was determined in EDA (anhydrous) in a thermostated bath under a continuous blanket of dry helium. The solution was in contact with the solid phase at all times and was stirred continuously except when samples were taken. The samples were analyzed for chloride using a modified Volhard method. The results are given in Table 7.

Table 7

Temperature (°C)	Sol. (moles/liter measured at the sampling temp.)
12.5	0.1486
20	0.2020
29	0.3113
45	0.6570
60	1.369
77	2.584
96	4.741

These results are plotted in Figure 7. It can be seen that an increase in temperature would be well worth while in terms of additional lithium chloride solubility in EDA.

Other Lithium Salts

The salts were equilibrated with dry EDA at room temperature (25-27°C) by vigorously shaking the flasks containing the mixture for three to six hours in a mechanical shaker. The excess salt was allowed to settle and the supernatant liquid was quickly filtered and samples were pipetted into beakers. These samples were analyzed for their lithium content by one of two different methods.

In the gravimetric method, the lithium salt solutions were first evaporated to dryness to remove most of the EDA. The residues were then treated with nitric acid and in some

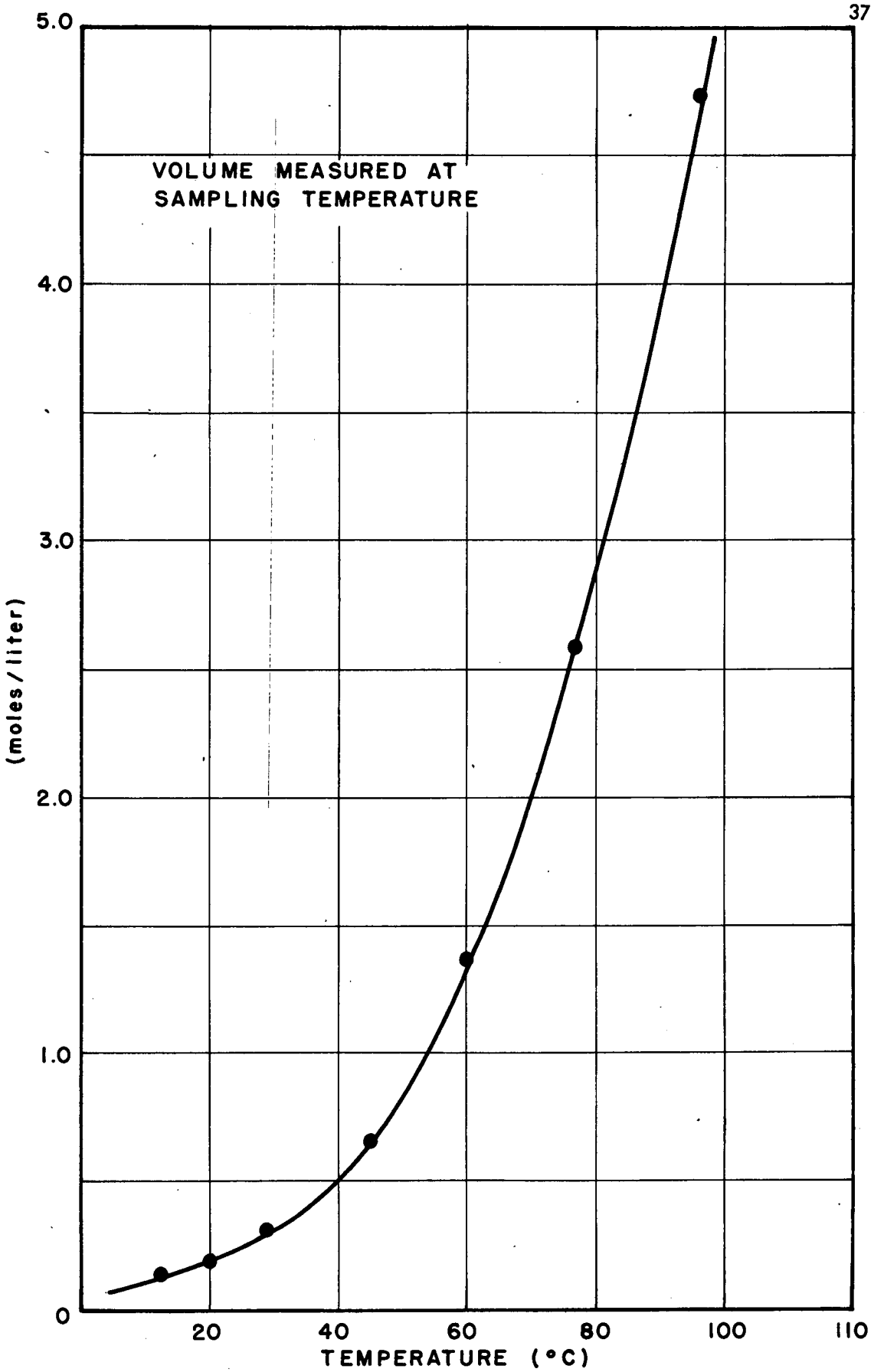

FIGURE 7. SOLUBILITY OF LiCl IN EDA

cases perchloric acid to destroy any residual organic matter. They were then fumed down to dryness several times with small quantities of sulfuric acid to convert the lithium salts to the sulfate. The lithium sulfate samples were transferred to tared platinum crucibles and ignited at 500°C. After cooling the samples were weighed as Li_2SO_4.

In the volumetric method the samples were evaporated to dryness as before. They were then treated with nitric acid to destroy organic material and finally evaporated down three to four times with hydrochloric acid to convert the lithium to the chloride. The last traces of HCl were removed by baking in an oven at 400°C. The lithium chloride samples thus prepared were titrated with silver nitrate and potassium thiocyanate for chloride content using the Volhard method with ferric ammonium sulfate indicator. The iodid samples were titrated directly as the iodide after neutralizing the excess amine. Results are given in Table 8.

Table 8

Solubility of a Number of Lithium Salts in Anhydrous EDA at 25-27°C

Salt	Conc. (M/l)
lithium chloride	0.32*
lithium bromide	0.28*
lithium iodide	0.37
lithium fluoride	<0.001
lithium sulfate	<0.001
lithium nitrate	0.75
lithium perchlorate	3.8
lithium formate	1.9
lithium acetate	0.34
lithium propionate	0.29
lithium oxalate	<0.001
lithium heptafluobutyrate	3.2

*Isbin and Kobe, JACS 67, 464-5 (1945)

The lithium salts whose solubilities were determined were chosen because of (a) possibilities of high solubility in EDA based on known solubilities in other solvents and (b) some promise of stability on intimate and prolonged contact with lithium amalgam.

Stability with Amalgam

The second phase of the work was to test the stabilities of the salt solutions in EDA vs lithium amalgam. Only salts appreciably more soluble than lithium chloride were tested for their stability in contact with amalgam. The following salts were tested and the results are given below.

Lithium Nitrate. Immediate reaction with lithium amalgam-EDA turned deep yellow.

Lithium Heptafluobutyrate. No immediate reaction at room temperature. On heating to 100°C in a water bath for several hours the solution turned yellow and a white precipitate appeared. A check on the amalgam showed appreciable lithium remained. It is possible that the reaction occurred only with the amine, as the heptafluobutyrate in amine turned yellow on heating to 100°C without amalgam present.

Lithium Perchlorate and Formate. Experiments are in progress.

ALTERNATE SOLVENTS

G. M. Begun, A. C. Rutenberg

The possibility of using another solvent in place of EDA has been given consideration. A possible solvent must meet a number of requirements: (a) it must dissolve an appreciable amount of a stable lithium salt; (b) it must be unaffected by prolonged and intimate contact with litium amalgam, and (c) it must not form an emulsion when shaken with lithium amalgam.

Based on the assumption that solvents of high dielectric constant would dissolve ionic substances such as LiCl, several non nitrogen containing solvents were carefully dried and the solubility of LiCl was determined in them. Ethylene dichloride and 1,2,3 trichloro propane were tried and found to dissolve no LiCl. It appears that the solubility of LiCl in organic solvents is a more specific effect possible involving coordination with specific functional groups. The high solubility of LiCl in nitrogen containing solvents may be due to coordination with the nitrogen atoms. LiCl is quite soluble in pyridine ($\sim$3.0 M at 25°C). In addition, if the pyridine phase is saturated with LiCl no emulsification with lithium amalgam occurs. However, on prolonged shaking with lithium amalgam, a reaction occurs with the pyridine phase becoming dark blue or brown and becoming viscous. The addition of pyridine to EDA was found to decrease the solubility of LiCl in EDA.

Diethylene triamine was investigated in some detail as a possible substitute for EDA. Due to its higher boiling point (207°C), it might better lend itself to a dual temperature operation. Preliminary tests gave indications of dissolving more LiCl than EDA.

The amine was very difficult to dry. An initial heating with NaOH pellets at around 140°C for a day did little if any drying. Drying with sodium took many days at 150° even for small amounts of amine. The slow drying appeared to be due to gaseous hydrogen surrounding the sodium globules due to the high viscosity of the liquid. Reducing the pressure aided the hydrogen evolution from the solution. The optimum conditions for most rapid drying were a temperature of about 120°C and 4-5 cm of mercury pressure. When the pressure was too low the boiling point of the solution was low and the reaction with sodium slowed down, while at higher pressures the hydrogen is not readily evolved from the solution.

Continued purification of the amine gave lower solubilities for LiCl. The lithium chloride concentration in a saturated solution of amine distilled over sodium was 0.26 M. The amine decomposes when heated for prolonged periods near its boiling point, but can be heated at 150° for several days with only slight coloring.

The pure amine emulsified on shaking with lithium amalgam as did the amine solution saturated with LiCl. The wet amine and the very dry amine did not emulsify with the amalgam nearly as badly as the almost dry amine which emulsified after a few seconds shaking. It is possible that a distillation method for drying diethylene triamine might be successful due to its high boiling point, but the ease of emulsification, moderate thermal stability and comparable solubility of LiCl to EDA do not make it a promising solvent.

Alpha methyl benzylamine was tried without drying and seemed to dissolve only a small amount of LiCl. No further work was done on this compound.

REFLUX OF AMINE-AMALGAM SYSTEM

G. M. Begun, A. C. Rutenberg

In order to operate a single temperature isotopic separation column based on the amine-amalgam system it is necessary that the materials be refluxed quantitatively at both ends of the system; i.e., that at the bottom of the column the lithium metal be quantitatively removed from the amalgam and dissolved in EDA as dry lithium chloride and that at the top of the column the lithium chloride be removed from the amine phase and be quantitatively converted into dry amalgam. It is particularly important that the stripping be quantitative since both the EDA and the mercury are reused and any lithium not removed will result in isotope dilution and reduce the over-all efficiency of the process.

Reflux at the Amalgam End

The most obvious type of reflux for this end would involve leaching the lithium out of the amalgam with dilute HCl and then drying the resulting chloride and dissolving it in EDA. There are several possible objections to this method. In the first place a drying step is introduced by adding water to the system and secondly, lithium chloride dissolves slowly in EDA.

One type of system which does not require adding water to the amalgam is the replacement of lithium in the amalgam by some other metal whose salt is dissolved in EDA. This requires that the presence of this additional metallic halide does not interfere with the operation of the system. Since any suitable metal will presumably form a more stable amalgam than lithium, the stripping of the amalgam will then be more difficult. Among the chlorides considered for possible use in such a reflux method were mercurous, mercuric, zinc and sodium. The mercury salts were tried first since they would introduce no extraneous metal ions into the amalgam. Mercurous chloride reacted immediately with EDA producing a dark precipitate. Mercuric chloride reacted with EDA when heated but seemed stable at room temperature. It was no sufficiently soluble in EDA, and gave a dark color on shaking with amalgam and was therefore discarded. Zinc chloride was practically insoluble in EDA and formed a voluminous precipitate, evidently an addtion compound with EDA.

The only salt of the group which showed promise was sodium chloride. Its solubility in EDA (ca 0.05M) was

sufficient so that a fairly rapid substitution might be expected to take place if a solution containing excess solid salt were used. The moderate solubility insured that the concentration of sodium ion in the amine portion of the solution would not rise above 0.05M. The sodium amalgam formed could be readily stripped by commercial apparatus.

Two preliminary experiments were tried using sodium chloride. In the first experiment a saturated solution of sodium chloride in EDA (containing less sodium than there was lithium in the amalgam phase) was placed over lithium amalgam and stirred at a moderate rate for 1.5 hours. At the end of this period the amine was sampled and a flame photometer analysis showed a Li/Na ratio of 350/1. In the second experiment an excess of sodium chloride (only partly in solution) was shaken vigorously with amalgam for four hours. An analysis of the amalgam layer gave a Li/Na ratio of 1/5000. These experiments indicate that almost complete replacement of Li by Na occurs in a reasonable period of time.

A kinetic run was made to get a better estimate of the rate of replacement of lithium in the amalgam phase by sodium from sodium chloride in the amine phase. The data for this run are given in Table 9. An excess of sodium chloride was used (undissolved solid present) in the amine phase. The amalgam phase contained only lithium at the start of the experiment. The two phases were stirred rapidly in a round bottom flask under an atmosphere of helium and periodically the stirring was interrupted and a sample of the amalgam was taken. The amalgam samples were leached with dilute HCl and analyses by flame photometer. Though the rate of substitution is a function of the efficiency of agitation, this study gives an indication of what might be expected for moderate agitation.

Reflux at the Amine End

One of the methods considered for reflux at this end was evaporation of the amine solution of LiCl and preparation of the amalgam from the aqueous chloride. A commercial electrolysis cell could be used for the latter portion. Drying would have to be done with quantitative removal of the amine from the LiCl and with recovery of most of the amine.

Table 9

Kinetics of the Reaction Li(Hg) + Na^+(EDA) $\longrightarrow$ Na(Hg) + Li^+(EDA) at 26°C

t_{min}	Li/Na(amalgam)
0	149
1	2.79
3	9.9×10^{-1}
7	1.03×10^{-1}
15	6.5×10^{-3}
30	3.2×10^{-4}
60	2.2×10^{-4}

Starting material: 126 ml 0.5M Li(Hg) and 275 ml saturated NaCl in EDA + undissolved solid.

To avoid decomposition of the amine into high molecular weight residues and for quickest drying, vacuum drying seemed desirable. One method attempted was distilling the amine off under vacuum using a water bath to heat the distillation flask. After all the visible amine was driven off, the flask was heated an additional hour to remove the residual amine. The LiCl was dissolved in water and titrated with acid. Approximately 1/3 molecule of EDA remained per molecule of LiCl. It appears that the EDA is held as a LiCl solvate and more vigorous conditions are necessary for its removal.

A reduced pressure spray drying technique proved more successful. An EDA solution of LiCl was dropped slowly into a long-necked, round-bottom flask. The flask was heated and the system was evacuated with a water aspirator while a small amount of dry helium was allowed to bleed in. The EDA removed was collected in a trap cooled with acetone-dry ice. LiCl produced by this method showed on titration no amine present, and no decomposition products appeared on prolonged heating on a hot plate. This experiment suggests the possibility of adapting commercial spray drying apparatus for us in such a process.

The possibility of some sort of electrochemical reflux was considered. One problem involved in a method which depends upon preparing the amalgam directly by electrolysis from the lithium salt dissolved in EDA is the low conductivity of the EDA solution when it is depleted in LiCl. Since it is essential that all the lithium be removed from the amine it would be necessary to add a conducting salt which would not form an amalgam at the EMF required to form lithium amalgam. Tetramethyl ammonium ion was suggested and the solubility of some of its halides in EDA was determined. The chloride was soluble to the extent of 0.0088M (Volhard titration). The bromide and iodide were even less soluble.

STATIC CORROSION STUDIES

G. M. Begun, A. C. Rutenberg

The ability of a number of materials of construction to stand up under prolonged contact with the EDA-amalgam system was tested under static conditions at room temperature. The materials which would not stand up under this mild test would certainly deteriorate rapidly under operating conditions.

The samples were placed in a vessel containing a mixture of 0.3M lithium amalgam and 0.25M LiCl in anhydrous EDA under dry helium. The samples floated on the interface and were completely covered with amine. The metal samples were cleaned and polished with emery cloth before testing. The samples were shaken briefly every few days. The following metals were tested:

Cold rolled steel
Hot rolled steel
Hastelloy-C
Stainless steel, 304, 316, and 321

After three to four weeks the metals showed no visible signs of having reacted and the amine was clear and colorless.

Tygon and asbestos gasket material were also tested. After one day the amine in contact with the tygon was light brown and the amine in contact with the asbestos was brown and cloudy.

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