

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Separation of Lithium Isotopes

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Except in the case of hydrogen the separation of isotopes will always be a laborious and expensive undertaking. However, even a partial separation will in many cases permit an answer to important questions relating to the difference between isotopes in chemical behavior, in spectra, and in nuclear transformations. The methods leading to effective separation will also be interesting in themselves; for even a casual inspection of the literature shows how unsystematic has been the exploration of the methods of separating similar substances.

Most chemical separations have depended upon a difference in the solubility of solids or in the vapor pressure of liquids. Fractionation by selective distribution between two liquid phases is only now being developed in some important industrial processes. The method which we have chosen for the separation of lithium isotopes involves a system of two liquids, but it is not a simple case of selective distribution. In principle it depends, as the first separation of hydrogen isotopes chiefly depended, upon the difference in electrode potentials between the two isotopes.

If a solution of a lithium salt is shaken with an amalgam of lithium, the ratio of Li^7 to Li^6 will not in general be the same in the two phases. The quotient of the two ratios, α , is the fractionating factor. If we use such a system in a continuously operating column of n cells, and equilibrium is established in each cell, then the maximum fractionating effect which can ultimately be obtained from the column is α^n . However, as in the similar case of distillation, when only small quantities of material are employed it is simplest to use a column without definite separation into cells, so that the number of theoretical cells or "plates" depends upon the conditions of operation and can only be determined experimentally.

In our column in which small drops of lithium amalgam fell through a long column containing a solution of lithium salt, we were never able to determine the actual plate efficiency, but several preliminary experiments indicated that the efficiency would be high. For example, when the fine drops of lithium amalgam such as we have used in our experiments fell through one meter of

aqueous sodium chloride, analysis of the amalgam which had passed through showed that 96% of the alkali metal in the amalgam was sodium and only 4% lithium. We may assume that this rapid interchange between lithium and sodium indicates a similar rapid interchange between lithium and lithium in our actual column.

The stocks of lithium amalgam, containing from 0.5 to 0.7 mole per liter, were prepared by electrolyzing a saturated aqueous solution of lithium carbonate, in the presence of excess solid carbonate, between platinum and mercury electrodes. The mercury was placed in flat crystallizing dishes, covered with about 2 cm. of water containing powdered lithium carbonate. Horizontal disks of platinum served as anodes. Four such cells were operated in series and these were placed in a trough of ice water to diminish the reaction between the water and the lithium amalgam already formed. Using a cathode current density of about 0.1 amp./sq. cm., the amalgams reached the desired concentration in six or eight hours, provided that reasonable care was taken to exclude such impurities as catalyze the reaction between water and amalgam. The process required little attention, but nevertheless was one of the more onerous parts of the investigation, during which over half a ton of the lithium amalgam was prepared.

The Column

The fractionating column consisted of a vertical glass tube 18 meters high and 4 mm. in internal diameter, which was filled with a solution of lithium salt. Through this solution a fine spray of lithium amalgam fell. It might be thought that the falling drops of mercury would cause serious mixing of the solution at top and bottom, but, on the contrary, when the stream of droplets is properly regulated they actually prevent such mixing. If the drops are of the right size and number they produce a condition of complete turbulence. Each drop of amalgam, as it passes down through the electrolyte, which is itself rising through the tube, assumes a zig-zag course, so that it takes four or five minutes to fall through the length of the column. This condition of turbulence, while causing intimate local mixing, prevents the mixing of the solution in one section of the column with that in another.

A state of turbulence is always very sensitive to slight changes in conditions and if the number of falling drops is increased much above that required for turbulence, the

drops begin to pile up, with or without coalescence, thus ruining the whole experiment. In order to avoid dangerous spots it was necessary that the sections of glass tubing used in building the column be welded together with care to prevent any constriction or irregularity.

The top of the column, as shown in Fig. 1, is a continuation and enlargement of the main column, L. The shape of the funnel between L and M is important, since any discontinuity in the stream line causes too great an accumulation of amalgam drops. There is always some accumulation of these drops from the bottom of the funnel to a point which varies with the rate of production of drops at the source M. If the accumulation rises as high as M, or in any case if the droplets remain long enough in the top to coalesce into larger drops, the result is fatal and the whole experiment must be begun anew.

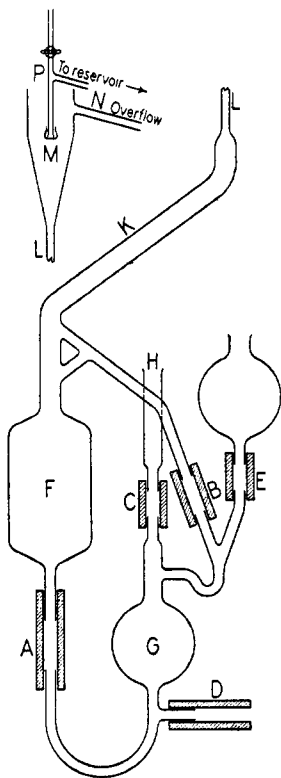


Fig. 1.

tained which gave drops of the necessary size and uniformity. As the amalgam falls through the column it displaces an equal volume of the solution which leaves by the overflow at N.

The lower end of the column is also shown in Fig. 1. In this part of the apparatus there are five cocks, A, B, C, D and E. The pressure at the bottom is about 2 atmospheres when the whole column is filled with the solution of lithium salt, and this pressure is approximately doubled when the amalgam is streaming down. Pressure stopcocks of glass were tried but it was found that the best cock for our purposes was afforded by a heavy walled rubber tube reinforced on the outside with adhesive tape and closed by a simple screw clamp (not shown in the diagram). The rubber tubing used in the cocks was boiled first with alkali and then with the solution which was to be used in the system. The cocks so prepared

caused no appreciable contamination of the mercury and showed no evidence of any rapid deterioration.

At the beginning of the experiment the solution of lithium salt fills the whole column, the bulbs F and G, and connecting tubes as far as the cocks C, E and D. Then, all cocks being closed, the amalgam spray is started at the top of the column. The droplets fall without coalescence as far as the diagonal tube K, which is sealed to, and is larger than, the main column L. Here the coalescence begins and continues as the mercury accumulates in F so that under satisfactory working conditions the amalgam in F becomes a single mass except for a small layer of individual drops at the top. A great deal of time was spent in finding the proper conditions for the coalescence. In one experiment with a solution of lithium chloride in amyl alcohol which was supposed to be ready for a complete run, the drops formed an emulsion in F and no simple method was found which would make the drops coalesce. On the other hand, in some solutions there is danger of too rapid coalescence, for if it begins in the vertical column the experiment is also ruined.

Our present system has one valuable characteristic which is unique. Ordinarily if a material is distributed between two liquid phases the concentration is different in the two, and if a fractionating column is set up it requires a complicated feeding device to ensure that the amount of material rising through the column is just equal to that which is descending. In our present case the concentrations of lithium in the amalgam and in the other phase are independent. We therefore make the concentration of lithium the same in the two phases, and since the falling amalgam displaces an equal volume of the other phase, there is exact equality in the amount of lithium ascending and descending.

The remaining problem is to withdraw a certain volume of amalgam from the bottom of the column, extract its lithium in the form of a salt, dissolve this salt in the same volume of the other solvent, and return this solution to the column without disturbing its operation.

Starting with all the stopcocks closed, the amalgam is allowed to accumulate in the bulb F until it exceeds 100 cc. Stopcocks A and B are then opened until 100 cc. of amalgam flows into the bulb G, being replaced by an equal volume of the solution rising through B. The cocks A and B are now closed, and the cock C is opened to the air, the standpipe H serving to catch any liquid which may be carried up by hydrogen that has been evolved. The cock D is then opened until the amalgam is withdrawn from G. The lithium must now be extracted rapidly from the amalgam, converted into the salt which is being used, and this salt dissolved in 100 cc. of the solvent. The resulting solution is introduced into the system through the cock E, after which, closing E and C, the system is in its original state. This whole maneuver must be executed before the next 100 cc. of the amalgam is collected in the bulb F. This took in our various experiments from thirteen to fifteen minutes.

Attempts were made to find some automatic method of effecting, at the bottom of the column, the exchange from lithium amalgam to a solution of lithium salt. One method which seemed promising was to allow the amalgam drops to fall through a saturated solution of the corresponding

salt of a heavy metal such as zinc. In such experiments, however, the zinc, instead of entering the amalgam, often formed a precipitate in the solution itself. Such methods were finally abandoned and we returned to the laborious but reliable methods of hand control.

If we are using, for example, a solution of lithium chloride in one of the alcohols, the simplest plan would be to treat the amalgam with an equivalent amount of an alcoholic solution of hydrochloric acid, but this process proved to be too slow. The reaction is rapid as long as the concentration either of lithium in the amalgam or free acid in the solution is high, especially when the system is kept at the boiling point of the solvent. However, even with amyl alcohol boiling at 130° it was found impossible to remove all the lithium from the amalgam by an equivalent amount of the acid solution during the fourteen or fifteen minutes available. Even a slight excess of acid could not be tolerated as it caused a violent evolution of hydrogen from the stream of amalgam drops. This evolution of hydrogen occurred to some extent in all of our experiments, but every effort had to be taken to keep it at a minimum.

The method finally employed is illustrated in Fig. 2. Two vessels A and B, operating on the counter current plan, are provided with small centrifugal stirrers which draw in amalgam at the bottom and spray it violently into the acid solution through a number of small openings. The burets C and D permit the introduction of measured volumes of a molal acid solution in the chosen solvent. In the vessel B, amalgam, from which most of the lithium has been removed in the vessel A, comes in contact with fresh acid until the last trace of lithium is removed. Through the stopcock F the mercury is withdrawn and discarded while the still acid solution is transferred to vessel A. Here 100 cc. of fresh amalgam enters directly from the column through the tube G.

The stirrer is then set in motion and a certain volume of acid introduced from the buret C. After a few minutes this acid is used up, as shown by an indicator, more acid is added, and the process repeated as long as time permits. The indicators used were phenolphthalein and chlorphenol red. Both are destroyed by violent agitation with lithium amalgam, so that they must be added near the end-point. At one of these end-points the stirrer is stopped, the nearly spent amalgam is transferred to vessel B, and the neutral solution is made up to 100 cc. and introduced into the column. The whole operation with both stirrers operating simultaneously took about ten minutes, leaving three or four minutes for the handling of the material at the bottom of the column.

All these operations had to be continued on schedule time and without the slightest departure from routine throughout the twenty-four hour run. At the end of each run, when the whole 10 liters of original amalgam had passed through the column, the two last samples of amalgam were withdrawn for analysis, as well as the solution which remained in the bottom of the apparatus and the lower end of the column.

The Isotopic Analysis

After the method of fractionating lithium isotopes had been developed it became an equally difficult task to ascertain the degree of enrichment of the light lithium isotope in the samples obtained from the column, for it is

necessary to determine the atomic weight in a sample which contains originally only about 0.4 g. of lithium even before the processes of purification are begun.

Formerly, in an entirely different attempt to separate the isotopes of lithium, we had met the problem of determining the atomic weight in a sample containing less than a milligram of lithium, and we used a simple method which would only be able to show a large change in the isotopic ratio. In that method the sample was purified as lithium fluoride and the fluoride was fused on a platinum foil in an inert atmosphere. The drop of fluoride, on freezing, was usually transparent in the center with some opacity at the edges. By breaking the crystal into small pieces and selecting the transparent ones, it was possible to determine their density by a flotation method, using a mixture of a heavier and a lighter organic liquid. The reproducibility thus obtained was about 0.1%. With the larger samples available in the present research a higher degree of accuracy was sought by some more conventional method of atomic weight determination.

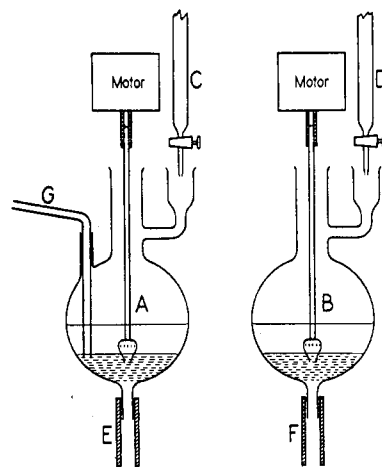


Fig. 2.

The method chosen consisted in titrating a weighed quantity of pure dry lithium carbonate against a solution of hydrochloric acid about 1.8 *N*. Since it was desired to obtain results reproducible to 0.01% it was necessary to take special precautions in the purification, the drying and the titration.

In order to test the method three samples of ordinary lithium carbonate containing 3 or 4 g. each were independently purified in the following manner. Each sample was dissolved in the requisite amount of pure water in a quartz flask. The solution was filtered through a small fine hardened filter paper, fastened by a clean rubber band to the end of a quartz tube. The filtrate was placed in a platinum flask of 900-cc. capacity and was then boiled until only 10 cc. of liquid remained. Most of the lithium carbonate was now in the form of a granular solid or a coherent layer on or near the bottom of the flask. The liquid was poured off and the remaining solid was rinsed with 10 cc. of pure water. The flask was next refilled with water to dissolve the carbonate and again boiled down for a second recrystallization. Each sample was crystallized three or four times. After two or three crystallizations the material gave every evidence of purity. It showed no flame

test for sodium and in certain other experiments in which Br^- and SO_4^{--} were originally present, these ions could no longer be detected. All of the water used in these recrystallizations was prepared in a still of block tin and was free from non-volatile impurities.

The purified sample consisting of 1 or 2 g. of lithium carbonate was dried in a platinum crucible at 200° . It was then transferred to a weighed crucible and heated in an electric furnace for thirty minutes at a temperature about 50° below the melting point. The drying and heating were both carried out in an atmosphere of pure carbon dioxide. Previous experiments had shown that without this precaution some of the carbonate is converted into oxide and causes etching of the crucible. If the carbonate is heated to fusion the crucible is always slightly etched, even in an atmosphere of carbon dioxide. Our method proved to be the only one leading to strictly reproducible weighings.

After the carbonate was so prepared and weighed it was titrated against the standard solution of hydrochloric acid. Aside from the ordinary difficulties inherent in such a titration, the chief source of error lies in the carrying away of carbonate or acid by the spray resulting from the evolution of carbon dioxide. This danger was avoided by allowing the reaction to occur in a closed vessel. The crucible containing lithium carbonate was lowered until it stood upright at the bottom of a 1-liter quartz flask. A small excess of the standard acid was then introduced from a weight buret so as to flow around the crucible without meeting its contents. The flask was then closed with a rubber stopper through which passed a glass tube fitted with a rubber tube and a pinchcock. The flask was exhausted until the first bubbles of air began to rise from the acid. The cock was then closed, the crucible overturned, and the flask gently agitated until the carbonate was dissolved entirely. The cock was now opened and the stopper removed and tested for traces of acid or alkali. This test was always negative if the flask was so tilted during the neutralization that there was no direct path from the effervescing liquid to the stopper. The drops adhering to the sides of the flask were washed down and the small excess of acid remaining was now titrated with no more than ordinary precautions, the carbon dioxide being boiled off from the acid solution and phenolphthalein being used as indicator. Dilute solutions of barium hydroxide and hydrochloric acid, standardized with respect to the standard solution of concentrated hydrochloric acid, were used.

The titration of the three samples gave as the ratio of the weight of the standard acid solution to the weight of the lithium carbonate the three values 13.129, 13.127 and 13.128. In later experiments the standard acid was checked against ordinary lithium carbonate prepared from ordinary lithium amalgam, in order to follow the exact procedure used in preparing the samples of lithium carbonate of unknown isotopic composition from the amalgam taken at the bottom of the column. The procedure was as follows. The lithium amalgam was treated with pure distilled water in a wax bottle. After a day or two the reaction was complete and the solution of lithium hydroxide was filtered into a quartz flask through fine hardened filter paper attached to the end of a quartz tube. This treatment will remove any impurity of magnesium,

which is the hardest element to separate from lithium. The filtrate was then immediately transferred to the platinum flask, converted into carbonate by a stream of carbon dioxide, and recrystallized by the method that we have already described.

The Three Operations of the Column

The First Run.—We first operated with half normal lithium amalgam and the same concentration of lithium chloride in ethyl alcohol. The method of transferring lithium from the amalgam to the electrolytic solution was in an experimental stage and broke down early in the run. In consequence a very crude and laborious method was necessary. The amalgam was treated with an excess of concentrated hydrochloric acid in a casserole which was heated until the excess acid had been driven off and the alcohol was added while the material was still hot and then brought to the proper concentration. About half way through the run one of the amalgam samples was lost completely. In addition to these difficulties the alcohol was not entirely free from water and there was therefore a large evolution of hydrogen in the column. This evolution of hydrogen does not seriously disturb the lower part of the column, for here the gas is under pressure and rises as small bubbles with the ascending solution, but as the bubbles rise they not only expand, but coalesce to form larger bubbles which produce much irregularity in the falling of the amalgam drops. In spite of these vexations the experiment was continued until the whole 10 liters of amalgam had passed through the column and the final amalgam at the bottom was analyzed. This analysis showed that Li^6 was being carried preferentially by the amalgam and that the ratio of Li^6 to Li^7 had approximately doubled. We were therefore encouraged to continue the experiments, avoiding as far as possible the difficulties of this run.

The Second Run.—Many experiments were now made with a variety of solvents and lithium salts, chiefly with the purpose of limiting the evolution of hydrogen. It was found in general that a solution which could be kept for hours in contact with lithium amalgam without appreciable reaction would react rapidly with the amalgam in the form of a fine spray. The rate of this reaction proved to be nearly independent of temperature, but depended markedly upon the presence of water and other impurities in the solvent, and was greatly increased by even a slight acidity.

Pure dioxane, which we prepared by a method similar to that of Kraus,¹ gives no reaction with lithium amalgam, but it is too poor a solvent to give the desired concentration of lithium salt. The system which seemed to suit our purpose best was a solution of lithium bromide in a mixture of four parts dioxane to one of ethyl alcohol, and our second run was started with this solution. However, the amalgam drops would not coalesce at the bottom of the column and it was necessary to begin anew with a solvent composed of two parts of dioxane and one of ethyl alcohol. This caused a somewhat greater evolution of hydrogen but not enough to cause serious trouble. One reason for using dioxane was that it seemed likely, on theoretical grounds that it would enhance the separation of the two isotopes

(1) Kraus, *THIS JOURNAL*, 55, 21 (1933).

We shall see, however, that this proved not to be the case.

At the bottom of the column the lithium was transferred from the amalgam to the electrolytic solution by the new method which we have already described. The stock acid solution was made by passing dry gaseous hydrogen bromide into absolute alcohol at -40° and this solution was then mixed with dioxane and kept at 0° , since at higher temperatures the hydrogen bromide reacts rapidly with both dioxane and alcohol. The run was satisfactory in every respect and two samples of amalgam were obtained at the end. These were purified carefully.

The pure lithium carbonate obtained in this experiment was titrated against our standard acid and its weight was compared with the weight of lithium carbonate of ordinary isotopic composition neutralizing the same amount of standard acid. For the ratio of the equivalent weight of the latter to the equivalent weight of the former we found in the first sample 1.0015, and in the second sample 1.0014. The calculation of the isotopic composition from these figures will be made presently.

The Third Run.—Since we found that contrary to our expectations the dioxane-alcohol mixture gave less fractionation than pure alcohol, it was decided to make one more run with lithium chloride in absolute ethyl alcohol, although the evolution of hydrogen is greater in this solvent. In the third run ten liters of 0.6 *N* amalgam were passed through the column in twenty-three hours. At the end, two 100-cc. samples of amalgam were obtained, and also a third sample containing the alcohol solution remaining in the bottom, together with some from the column itself.

The lithium carbonate from the first sample of amalgam was purified and at the end of the recrystallization 1.37 g. was left. The ratio of the weight of ordinary lithium carbonate to the equivalent weight of this sample was 1.0022. With the second sample of amalgam the process of recrystallization was carried further than we intended, leaving only 0.69 g., which gave 1.0026 as the ratio of equivalent weights.

On account of the small amount of the second sample a new determination seemed desirable. Therefore the material left from the titration of these two samples, containing chiefly lithium chloride and barium chloride, was treated with sulfuric acid and evaporated nearly to dryness. To the residue, water and an excess of barium carbonate were added, and carbon dioxide was bubbled through overnight. The solution was boiled, filtered and subjected to the usual recrystallizations. The resulting carbonate gave the lower ratio 1.0016. It is to be noted that every impurity that can be imagined to be present will diminish the value of the ratio. It seems probable that this sample, which was obtained by a different procedure from the others, still contained some impurity.

Finally, the lithium chloride which was present in the electrolytic solution at the bottom of the column was purified by the following method. An aqueous solution of the lithium chloride was treated with an excess of silver oxide, and carbon dioxide was bubbled through for many hours. The solution was then filtered, boiled and re-filtered. To remove the last traces of silver carbonate 2 cc. of 0.01 *N* hydrobromic acid was added. After filtration

the treatment was continued as in previous cases through four recrystallizations, during which all traces of Br^- disappeared. This carbonate gave, for the ratio of equivalent weights, 1.0019. Since this sample contained some liquid from the column where there would be less separation of the isotopes, this experiment tends to confirm the higher ratio obtained in the first two analyses.

Unfortunately at this point it was necessary to discontinue the experiments owing to the departure of one of the authors, but it seems that we can make no great error in taking as our final ratio for this run the weighted mean of the first two ratios, namely, 1.0023.

Interpretation of the Results

The ratio of Li^7 to Li^6 in ordinary lithium is 11.6, according to the most recent work of Brewer.² This identical value is also obtained by comparing the accepted atomic weight of lithium, 6.940, with the values 7.0182 for Li^7 and 6.0170 for Li^6 , obtained from mass spectra and nuclear disintegrations.³

In our third run, in which the highest concentration of Li^6 was obtained, we found the value 1.0023 as the ratio between the equivalent weights of ordinary lithium carbonate and of that from the column. Using the latest International atomic weights, we thus find that in our experiment the atomic weight of lithium was brought from 6.940 to 6.855. This means that the concentration of Li^6 has been raised from 8% in the original lithium to 16.3% in our new material. In other words, the ratio of Li^7 to Li^6 in our sample has been reduced to 5.1.

In our second run, using lithium bromide in a solvent containing one part of ethyl alcohol to two parts of dioxane, the ratio of Li^7 to Li^6 was brought to the value 6.6. Whether the smaller fractionation in this case was due to a smaller fractionating factor or to a lower efficiency in the column we cannot state.

Concerning the theory of the fractionation in our column, there is little to be said. In some experiments on the separation of the nitrogen isotopes, which will shortly be published by Lewis and Schutz, it was found possible to make in advance a rough calculation of the sign and the magnitude of the fractionating effect. In the present case there was no sure way even of predicting whether Li^6 would be concentrated at the top or bottom of the column. Since the fractionation must depend chiefly upon differences in zero-point energy, the zero-point energy always being greater in a substance containing a heavier isotope,

(2) Brewer, *Phys. Rev.*, **49**, 635 (1936).

(3) See, for example, Bonner and Brubaker, *ibid.*, **50**, 308 (1936).

our experiments indicate that lithium is held more tightly to oxygen in the electrolytic solution than it is to mercury in the amalgam. Since, presumably, in alcohol the lithium is held between two or more atoms of oxygen and attached ordinarily to only one oxygen in dioxane, it seemed likely that the fractionating effect would be higher with dioxane than with alcohol; but, as we have seen, this proved not to be the case.

Our experiments did not proceed far enough to enable us to determine either the exact fractionating factor or the number of theoretical plates in our column. We can, however, obtain a minimum value for the fractionating factor, as follows. We estimate that in our last run 0.012 equivalent of Li^6 accumulated at the bottom of the column in excess of the amount present in ordinary lithium. This figure is to be compared with the total of 0.48 equivalent of Li^6 which was present in the original ten liters of amalgam. If the column is assumed to have an infinite number of theoretical plates, the fractionating factor is then 1.025. If, on the other hand, the column was less efficient, and some of the excess Li^6 found its way to the overflow at the top of the column, then the fractionating factor is larger. Corresponding to a fractionating factor of 1.025, the electrode potential between lithium amalgam and a solution of lithium chloride in alcohol would, at room temperature, and under equivalent conditions, be 0.0006 volt higher for Li^7 than for Li^6 . Hence we may conclude that the difference in potential is at least as great as this.

The material obtained in this investigation will be used in several experiments to determine the difference in physical and chemical properties of the two lithium isotopes. Recently Mr. Brewer,² studying positive rays, has obtained indications of

the existence in ordinary lithium of the isotope Li^6 . If we attribute the concentration of Li^6 in our experiments mainly to differences in zero-point energy, a simple calculation shows that if Li^6 exists in the original lithium, it would be concentrated five-fold by our fractionation. We have, therefore, sent a sample of material from our third run to Mr. Brewer, who has been kind enough to examine it. He writes that in his first experiment conditions were unfavorable for observing Li^6 , but it is interesting that he finds in this sample exactly the same ratio of Li^7 to Li^6 which we found by the atomic weight method, namely, 5.1.

Summary

From the ordinary mixture of lithium isotopes, Li^6 has been enriched in an 18-meter column, where fine drops of lithium amalgam fall through a solution of lithium chloride in absolute ethyl alcohol or of lithium bromide in a mixture of alcohol and dioxane. At the bottom of the column, the lithium is extracted from the amalgam and added as lithium salt to the ascending electrolytic solution. After the passage of 10 liters of amalgam through the solution, the material at the bottom of the column is removed for the analysis, which consists in determining the atomic weight of this lithium relative to that of ordinary lithium. This was accomplished by the exact titration of dry lithium carbonate against a solution of hydrochloric acid. In the final experiment, the isotopic ratio Li^7 to Li^6 was changed from 11.6 in ordinary lithium to 5.1 in our material. The results show that, under equivalent conditions, the electrode potential between amalgam and alcohol solution is greater for Li^7 than for Li^6 by at least 0.0006 volt.

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