

## On the Electrolytic and Chemical Exchange Methods for the Separation of the Lithium Isotopes

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## LETTERS TO THE EDITOR

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### On the Electrolytic and Chemical Exchange Methods for the Separation of the Lithium Isotopes

A number of methods have been used in attempts to separate the lithium isotopes of mass 6 and 7. Early attempts by means of the mass spectrograph gave only minute quantities. However, Rumbaugh and Hafstad<sup>1</sup> have recently obtained sufficient quantities of the two isotopes by this method for a study of some of their nuclear properties. Kendall and Crittenden<sup>2</sup> attempted a separation by means of electrical mobility without success. Encouraged by the successful separation of the hydrogen isotopes by electrolysis, a number of investigators have started work on similar methods using a flowing mercury cathode. Eucken and Bratzler<sup>3</sup> have reported some experiments on the electrolysis of a lithium sulphate solution. The experimental error in the atomic weight determinations used to estimate the change in isotope ratio was practically as large as the effect observed. The value reported for the fractionation factor is therefore of doubtful accuracy.

Lewis and Macdonald<sup>4</sup> have secured a striking increase in the concentration of  $\text{Li}^6$  by using a counter-current extraction process which depended upon a difference in the distribution coefficients of the lithium isotopes between an ethyl alcohol solution of lithium chloride and a lithium amalgam. During the past year we have investigated two possible methods of effecting partial separations of the lithium isotopes, one depending upon a possible electrolytic separation, and the other a difference in distribution of the lithium isotopes between a solid material and a liquid solution.

In investigating the feasibility of the electrolytic method for separating lithium isotopes, we have used the electrolysis of a large quantity of lithium hydroxide down to a small residue. The object of this experiment was to determine the simple process fractionation factor, a knowledge of which is essential for the use of the method. The electrolytic cell consisted of a fluted nickel anode placed about 1 cm above a mercury cathode. This nickel anode was made by spot welding together strips of nickel bent such that the finished anode was a honey-cone shape. The mercury was stirred rapidly with a glass stirring device to give a uniform surface. The electrolysis vessel was surrounded by a water-cooling jacket to enable us to keep the temperature approximately controlled in the neighborhood of 25°C. Mercury from a separatory funnel was allowed to flow continuously

into the cell and out through a gooseneck tube in order to maintain the level of the mercury constant and to remove the lithium amalgam as it was produced. The lithium was removed from the amalgam with the formation of lithium hydroxide by allowing it to flow in a counter-current fashion with water over nickel rings under which condition hydrogen was generated due to formation of local couples. The cell was operated with a current density of 0.62 amperes per square centimeter of mercury surface. The procedure was to fill the cell with 800 cc of a 10 percent lithium hydroxide solution and electrolyze until about one gram of lithium hydroxide was left in the cell. When 20 such runs were completed, the residual solutions were united, concentrated, and electrolyzed further. From titrations of the original and final solutions against standard acid, the ratio of the initial to the residual lithium was found to be approximately 600.

The isotopic composition of the initial material and the final residue were determined by A. Keith Brewer, using his mass spectrometer. The ratio of  $\text{Li}^6$  to  $\text{Li}^7$  in ordinary lithium is 1 to 11.6, according to his determination. However, the lithium hydroxide used in these experiments was found to have an isotopic ratio of 1 to 12.5, though a sample of lithium from a commercial lithium bromide showed the normal abundance. The isotopic ratio of the final solution remaining in the electrolytic cell was 1 to 14.2, showing that  $\text{Li}^6$  is electrolyzed preferentially with respect to  $\text{Li}^7$ . Using the Rayleigh distillation formula

$$\left( \frac{1-N_0}{1-N} \right)^{1/\alpha-1} \left( \frac{N}{N_0} \right)^{\alpha/\alpha-1} = \frac{W_0}{W},$$

which applies to such processes, we find that the simple process fractionation factor,  $\alpha$ , is 1.020. This is very small compared to the values of 3 to 10 for the fractionation factor of hydrogen and deuterium. Lewis and Macdonald estimated that the fractionation factor from their results was approximately 1.025. This factor, of course, applies to the distribution between ethyl alcohol as a solvent and the mercury amalgam. This should check our result only if the relative solubilities of the  $\text{Li}^6$  and  $\text{Li}^7$  isotopes are the same in water and in ethyl alcohol.

We attempted a concentration of the lithium isotopes by extracting a water solution of lithium bromide with methylamyl alcohol and reduced the concentration in the water solution by a factor of 20 to 1. The residue showed no difference in isotopic ratio to the original material. Also, we extracted a solution of lithium bromide in methyl-

amyl alcohol with water and reduced the concentration by a factor of 1000 to 1, and likewise found no change in the isotopic ratio between the original material and the residue. This shows that the relative solubilities of the isotopes of lithium are very nearly the same in methylamyl alcohol and water. It seems probable that the solubilities of the lithium isotopes in ethyl alcohol and water are likewise nearly the same, and if this is true our enrichment factor in the electrolysis may be regarded as a check on the results of Lewis and Macdonald. The slight discrepancy between the two figures is probably within the experimental limits of error of either work, and indicates that we secured in our electrolysis only the equilibrium increased concentrations with no evidence for a kinetic effect as is found in the case of the separation of hydrogen and deuterium. Of course, it may be that kinetic effects will be important at high current densities and correspondingly increase the fractionation factor.

It is an interesting fact that the two samples of commercial lithium compounds should have markedly different isotopic ratios. It would appear that somewhere in the process of manufacture an appreciable separation of the isotopes of lithium occurred. It is difficult to see how this could occur in the usual commercial process since commercial methods usually produce a fairly high percentage of the element present in the crude material in the form of the final product, and, if this is done no fractionation could be expected. One method commonly used to extract lithium from some of its complex aluminum silicate ores is to heat the ore with potassium sulphate. A zeolite type reaction takes place in which the potassium replaces the lithium. This replacement may possibly be preferential with respect to one isotope. For this reason we thought that it would be of interest to investigate the exchange of the lithium isotopes between Permutite and solutions of alkali metal salts. For this purpose the Permutit Company kindly furnished some of their Permutite which is a complex sodium aluminum silicate of the zeolite type and has a comparatively high percentage of replaceable sodium.

In order to determine the approximate value of the simple process fractionation factor, a batch containing 300 g of lithium chloride in a twenty percent solution was extracted with a large number of successive 30 g portions of the zeolite. After each addition the mixture was shaken vigorously for 20 minutes before filtration in order to allow equilibrium to be established. At various intervals the sodium chloride resulting from the replacement of the sodium ion from the Permutite was separated. When the lithium chloride had been reduced by a factor of 70, the lithium chloride was converted to the carbonate and analyzed by A. Keith Brewer. The ratio of the two isotopes had changed from 11.6 to 12.7. Using the Rayleigh formula for an approximation, one gets 1.022 for the fractionation factor. It is difficult to estimate the accuracy of this value or its exact meaning because of the variable concentration of the sodium ion and the lithium ion in the solution being extracted. Rate processes may also be important. However, similar conditions will occur in the operation of a column so one may consider the above value as a fair approximation. This is small and one cannot expect appreciable

separation unless counter-current methods are employed. These fractionation factors are very close to one calculated by Urey and Greiff<sup>5</sup> for another reaction showing that their estimate of these fractionation factors is approximately correct.

A number of experiments were run in which a dilute lithium chloride solution was run slowly through a 35-foot column of the zeolite contained in a 3/4-inch stainless steel pipe. In one such experiment the first lithium chloride through the column gave the ratio 13.3 or a change of about 15 percent. From these experiments it seems that the lighter isotope is preferentially held by the zeolite. Similar experiments were made using a solution of ammonium chloride. The first ammonium chloride through the column was converted to nitrogen and analyzed with the mass spectrometer by Marvin Fox in this laboratory. The ratio of  $N_{14}N_{14}$  to  $N_{14}N_{15}$  in ordinary nitrogen was 124 to 1 while the ratio in the product obtained was 137 to 1 or a change of about 10 percent. It is to be noted that in the case of the ammonium ions, the one containing the heavier isotope seemed to be preferentially held by the zeolite while the lighter isotope of lithium is more strongly held. It is difficult to say what may account for this difference in behavior. The difference, however, may aid in determining the mechanism which is responsible for the separation of the isotopes. It is hoped that an appreciable fractionation of a number of isotopes may be achieved using zeolite or other suitable adsorbing substances much as is done in the separation of closely related organic compounds by the recently developed methods of chromatographic analysis.

The authors express their thanks to Dr. A. Keith Brewer of the Nitrogen Fixation Laboratory for the analyses which he has so kindly made, to the Permutit Company for supplying the Permutite for these experiments, and to Dr. John G. Dean of the Permutit Research Laboratories for his useful discussions and suggestions.

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June 14, 1937.

<sup>1</sup> Rumbaugh and Hafstad, *Phys. Rev.* **50**, 681 (1936).

<sup>2</sup> Kendall and Crittenden, *Proc. Nat. Acad. Sci.* **9**, 75 (1923).

<sup>3</sup> Eucken and Bratzler, *Zeit. f. physik. Chemie* **174A**, 269 (1935).

<sup>4</sup> Lewis and Macdonald, *J. Am. Chem. Soc.* **58**, 2519 (1936).

<sup>5</sup> Urey and Greiff, *J. Am. Chem. Soc.* **57**, 321 (1935).

### Corrections to: The Properties of Paraffins II

(*J. Chem. Phys.* **5**, 264 (1937))

Formula (1):  $Q = Q_0(1 - T/T_c)0.4$  should read:

$$Q = Q_0(1 - T/T_c)^{0.4}.$$

In the heading of column 6, Table VII,  $Q_b$  from gas should read:  $Q_b$  from  $Q_m$ . Page 266, right column, line 30: the power of  $U$  should read: the power of  $n$ . Formula (7):  $Q_B/T_B = 8.97 \times n^{0.25} + n^{8.99/0.17}$  should read:

$$Q_B/T_B = 8.97 \times n^{0.25} + 8.99/n^{0.17}.$$

A. H. W. ATEN, JR.

Hilversum, Netherland,  
June 4, 1937.