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frequency to solid frequency is 0.98 for both H_2S and D_2S . A splitting of this type has been observed in other solids²³ and is usually attributed to the effect of electric fields in the crystal lattice.

The single remaining frequency cannot be associated with ν_2 since this deformation frequency is usually much lower than the other two. Taking the gas frequencies for H_2S and D_2S from the work of Nielsen^{6,8} as 2685 and 2000 cm^{-1} for ν_3 , $\Delta\nu = 164 \text{ cm}^{-1}$ or 6.1 percent for H_2S and 167.5 cm^{-1} or 8.4 percent for D_2S . The ratio of gas to solid frequency is 0.74, for both H_2S and D_2S .

From x-ray data, Vegard²⁴ has concluded that H_2S is linear in the solid state. This conclusion conflicts with the fact that ν_1 and ν_3 appear in the Raman spectrum of the solid. Further, this interpretation of the data has been disputed by Sirkar and Gupta²⁵ who concluded from their

own Raman data and the x-ray results of Vegard that the molecule is bent, the angle being about 108° . However, their arguments are based upon erroneous conclusions of Dadiou and Kohlrausch²⁶ who obtained an angle of 90° from the spectroscopic data. While the angle is not known definitely, it is almost certainly not 90° . Both Dadiou-Kohlrausch and Sirkar-Gupta have used a simplified valence-force potential energy curve for the molecule. As shown above and in many other places, this sort of potential energy function may not be used except as a rough approximation for actual molecules. Moreover, the angle is very sensitive to slight changes in the frequency and for the latter, the actual mechanical frequency corrected for anharmonic terms must be used and not the observed frequency. All questions regarding angle, force constants and isotope effect can only be settled with more and better experimental data.

²³ A. A. Sidorova, *Acta Physicochim.* 7, 193 (1937).

²⁴ L. Vegard, *Nature* 126, 916 (1930).

²⁵ S. C. Sirkar and J. Gupta, *Ind. J. Phys.* 11, 119 (1937).

²⁶ A. Dadiou and K. W. F. Kohlrausch, *Physik. Zeits.* 38, 165 (1932).

Fractionation of the Lithium and Potassium Isotopes by Chemical Exchange with Zeolites*

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A study has been made of the fractionation of the lithium isotopes by electrolysis and of the lithium, potassium, and nitrogen isotopes by chemical exchange with zeolites. The fractionation factor obtained by a "batch" electrolysis of lithium chloride solution was 1.039. The normal abundance ratio of the lithium and potassium isotopes was determined and found to be 11.71 ± 0.14 for $\text{Li}^7 : \text{Li}^6$ and 14.10 ± 0.09 for $\text{K}^{39} : \text{K}^{41}$. The fractionation factor for the lithium isotopes in exchange with sodium zeolite was found to be 1.022. A partial separation of the lithium, potassium and nitrogen isotopes has been affected using long columns filled with zeolites. Both an increase and a decrease of about 25 percent from the normal abundance ratio has been obtained for the lithium isotopes and a change of about 10 percent for the potassium and nitrogen isotopes. Some of the factors involved in the mechanism of the process are discussed.

INTRODUCTION

RECOURSE may be had to a number of different methods in attempts to separate the isotopes of an element. One may choose a

method more or less directly dependent on physical properties related to the masses of the isotopes such as diffusion, distillation, or deflection in an electric and magnetic field using large capacity mass spectrographs. Electrolysis or reaction velocity may also lead to some fraction

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ation. Chemical exchange methods¹ have been used with success by Urey and his co-workers for the fractionation of a number of isotopes as, for example, oxygen,² carbon,³ nitrogen,^{4, 5} and more recently sulfur,⁶ lithium and potassium.

The use of large capacity mass spectographs has led to the separation of only minute quantities of the lithium⁷ and potassium⁸ isotopes. Lewis and Macdonald⁹ have obtained a marked increase in the concentration of Li⁶ by counter-current extraction of a lithium amalgam with an ethyl alcohol solution of lithium chloride. They estimated a lower limit of 1.025 for the fractionation factor of the process.

Encouraged by the successful separation of the hydrogen isotopes by electrolysis, a number of investigators started work on the separation of the lithium isotopes using a flowing mercury cathode. Of these may be cited the work of Eucken and Bratzler¹⁰ on lithium sulphate; Taylor and Urey¹¹ on lithium hydroxide; and Holleck¹² and Hutchison¹³ on lithium chloride. The fractionation factors obtained were respectively 1.07 (upper limit), 1.02, 1.07 and 1.062.

Heavesy and Logstrup¹⁴ have used a non-equilibrium distillation method and achieved some fractionation of the potassium isotopes. Nier and Hustrulid¹⁵ also obtained a small fractionation by a similar method during some studies on the radioactivity of potassium. Brewer¹⁶ has found that small changes in the isotope ratio occur in certain natural processes.

Some further experiments on the fractionation

factor for the electrolysis of the lithium isotopes have been made by the present authors. A 38 percent lithium chloride solution was electrolyzed in the same cell with the same current density as that used in the electrolysis of lithium hydroxide except that a graphite anode was used and the average temperature was 36°C. The mercury was stirred rapidly and the gases evolved at the anode stirred the solution. After electrolysis of 450 g of lithium chloride to 5 g, the ratio of the isotopes in the solution remaining in the cell was changed to 13.8 which gives a fractionation factor of 1.039. The lower fractionation factor may arise either from the higher current efficiency resulting from stirring the mercury or an effect due to dilution. The other investigators have electrolyzed in several stages taking the first part of the lithium electrolyzed for the next stage such that they were always electrolyzing from a concentrated solution. In the "batch" method as we have used there is a continual decrease in concentration.

In the course of the experiments on the electrolysis of lithium hydroxide, a sample was found in which the ratio of Li⁷ to Li⁶ was 12.5 instead of the normal ratio 11.6. It appeared that somewhere in the manufacture appreciable fractionation had occurred. Upon tracing the original source of the material, the manufacturer was hesitant in giving any information regarding its manufacture. One of the most general methods used to obtain lithium is to heat the silicate base ore, such as lepidolite, with potassium sulphate.¹⁷ A zeolite type reaction takes place in which potassium is exchanged for lithium. Such replacement may be preferential with respect to one of the isotopes. This led to an investigation of the possibility of fractionation of the isotopes of the alkali elements by the so-called base exchange reactions with zeolites. A preliminary report was made by Taylor and Urey¹¹ in which small changes in the ratio of the lithium and the nitrogen isotopes from ammonium ion were described. Further experiments were made on potassium isotopes and reported by Taylor, Brewer and Urey.¹⁸ The results have also been

¹ Urey and Greif, *J. Am. Chem. Soc.* **57**, 321 (1935).

² Huffman and Urey, *J. Ind. Eng. Chem.* **29**, 531 (1937).

³ Urey, Aten and Keston, *J. Chem. Phys.* **4**, 622 (1936).

⁴ Urey and Aten, *Phys. Rev.* **50**, 575 (1936).

⁵ Urey, Huffman, Thode and Fox, *J. Chem. Phys.* **5**, 856 (1937).

⁶ Thode, Gorham and Urey, *J. Chem. Phys.* **6**, 296 (1938).

⁷ Rumbaugh and Hofstad, *Phys. Rev.* **50**, 681 (1936).

⁸ Smythe and Hemmendinger, *Phys. Rev.* **51**, 128 (1937).

⁹ Lewis and Macdonald, *J. Am. Chem. Soc.* **58**, 2519 (1936).

¹⁰ Eucken and Bratzler, *Zeits. f. physik. Chemie* **174**, 269 (1935).

¹¹ Taylor and Urey, *J. Chem. Phys.* **5**, 597 (1937).

¹² Holleck, *Zeits. f. Elektrochem.* **44**, 111 (1938). See also *Zeits. f. angew. Chemie* **49**, 33 (1936).

¹³ Hutchison, Dissertation, Ohio State University (1938).

¹⁴ Heavesy and Logstrup, *Zeits. f. anorg. allgem. Chemie* **161**, 1 (1928).

¹⁵ Nier and Hustrulid, Private communication.

¹⁶ Brewer, *J. Am. Chem. Soc.* **58**, 365 (1936); *ibid.* **59**, 869 (1937).

¹⁷ Osborg, *Lithium* (The Electrochemical Society, New York City, 1935).

¹⁸ Taylor, Brewer and Urey, Rochester Meeting Am. Chem. Soc.

confirmed by Brewer and Reed¹⁹ in their laboratory using "greensand." A more complete discussion of the process and the results obtained on lithium and potassium will follow.

MASS SPECTROMETER FOR ANALYSIS OF ISOTOPIC ABUNDANCE RATIOS

One of the most difficult problems in studies on the separation of isotopes is the analysis of the results. One may make direct determinations on a mass spectrometer or make determinations of the atomic weight, density, or other properties associated with the mass of the atoms. During the first part of the investigation, methods of analysis were tried which depended upon a difference in the density of compounds containing the isotopic atoms in different ratios. One was an isopiestic density method and another the flotation of lithium fluoride crystals in an organic liquid mixture by variation of temperature and pressure. Both were comparative methods and required a long time for purification so a mass spectrometer of the Dempster type, as modified by Bainbridge²⁰ and Brewer¹⁶ was built to analyze the samples.

The apparatus was constructed and operated in most respects as described by Brewer.¹⁶ The positive ions produced by heating a platinum disk previously impregnated with the sample were drawn through the slit by applying 270 volts for potassium and 810 volts for lithium. The resolving chamber had a radius of 5 cm and was evacuated to a pressure of 1 to 5×10^{-6} mm Hg. The positive ion current was carried to a DuBridge²¹ balanced circuit amplifying system and the amplified current was read from the galvanometer scale. In making a determination the accelerating voltage was held constant and the magnetic field was varied until the galvanometer deflection was a maximum. This current was taken as a measure of the abundance of the isotope. The magnetic field was then changed until another isotope was brought to the collecting plate. If the amplification was linear, the ratio of the galvanometer deflections could be taken as the ratio of the abundances of the

isotopes. However, this was not always the case and the potentiometric method described by Cohn and Urey²² was used to get the exact ratios.

The principal source of error in the determinations was in reading the height of the smaller peak which is from one-tenth to one-fifteenth the larger one (25 to 40 cm). If the zero point drifts owing to unsteadiness of the amplifier, or if the positive ion beam is not constant, as is often the case, then there are further errors involved in reading the deflections. In general the readings are probably not better than 0.3 to 0.4 mm which means a possible error of 2 to 2.5 percent in a single determination. Averages for different filaments of the same material sometimes varied as much as 2 to 3 percent, especially if solid material remained on the disk or a gas was given off during heating. Also if the pressure was not kept sufficiently low the resulting poor resolution decreased the accuracy. However, there was generally no background between the lithium peaks and seldom as much as 0.1 to 0.2 mm between the potassium peaks. In general, it is considered that the ratios reported are not better than ± 0.1 to ± 0.2 from the true ratio, that is, about 1.5 to 2 percent.

Determinations of the normal ratio of the lithium isotopes made by different investigators¹² show wide variations. While our purpose was not the accurate determination of the abundance ratio, it is of interest to report our results in confirmation of the accepted values. The average value of the ratio $\text{Li}^7 : \text{Li}^6$ taken from determinations made at different times during the research is 11.71 ± 0.14 which is in fair agreement with those of Bainbridge²⁰ and Brewer,²³ 11.51 ± 0.31 and 11.60 ± 0.06 , respectively. Using 6.940 for the atomic weight of lithium and Bainbridge's²⁴ values for the masses of the atoms (6.0145 ± 0.0003 and 7.0145 ± 0.0007), a value of 11.84 is obtained calculated on the basis of Aston's²⁵ new value for He (4.00391). This is in good agreement with the mass-spectrographic measurements.

Potassium is known to have three isotopes with mass numbers 39, 40 and 41. The ratio of K^{39} to

¹⁹ Brewer and Reed, Nitrogen Fixation Laboratory. Private communication.

²⁰ Bainbridge, J. Frank. Inst. **212**, 3176 (1931).

²¹ DuBridge and Brown, Rev. Sci. Inst. **4**, 532 (1933).

²² Cohn and Urey, J. Am. Chem. Soc. **60**, 679 (1938).

²³ Brewer, Phys. Rev. **47**, 571 (1935).

²⁴ Bainbridge, Phys. Rev. **46**, 56 (1933).

²⁵ Aston, Nature **137**, 357 (1936).

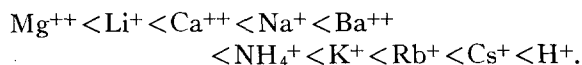
K^{41} is given by Nier²⁶ as 13.96 ± 0.1 and Brewer²⁷ as 14.25 ± 0.03 . Manley²⁸ using the ratio of the heights of the peaks in nuclear magnetic moment studies obtains the value 13.4 ± 0.5 . The isotope of mass 40 is radioactive and is present to the extent of only one part in 8000.²⁹ The ratio of K^{39} to K^{41} obtained from the average of a number of determinations made during this research is 14.10 ± 0.09 which is in good agreement with the above values.

THE NATURE OF ZEOLITIC SUBSTANCES

Many substances, particularly those which tend to form negative ionic micelles in the sense used by McBain,³⁰ possess the property commonly referred to as base exchange. That is, they exchange a positive ion held by the substance for one in solution. The most widely studied and well-known of these substances are the complex hydrated aluminosilicates known as zeolites. A review of the voluminous literature on these substances is given by Randall and Cann,³¹ Wiegner³² and Jenny.³³ Many naturally occurring zeolites such as the glauconites (greensands), the ultramarines, sodalite, nephilite, and the clays such as bentonite, all show a greater or less tendency to exchange their bases depending on their composition and structure. Artificial zeolites have been made by many different methods as, for example, the reaction of a solution of sodium aluminate and sodium silicate in such proportions that the product has an approximate composition represented by the empirical formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot x\text{H}_2\text{O}$. The sodium is replaceable by other positive ions, a divalent ion replacing two monovalent ones.

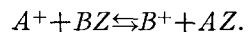
It has been known for a long time that the alkali and alkaline earth elements exhibit specific ion effects and may be arranged in a lyotrope or Hofmeister series according to their effectiveness in replacing one another from the zeolite. For an artificial zeolite, the ions of the alkali and

alkaline earth elements give the following series:



That is, lithium is the least strongly held while cesium is the most strongly held of the alkali elements. The order of the alkali elements is that of the decreasing size of the hydrated ion.³³ A change in the conditions affecting the solvation of the ions such as a change in the nature of the solvent³² or temperature³⁴ will change the behavior of the ions. Such change in behavior with change of conditions may prove important in the fractionation of isotopes.

If one shakes a quantity of zeolite with a solution of another positive ion, equilibrium is established in ten to twenty minutes and partial replacement takes place according to the reaction



Addition of more ion A^+ replaces more B^+ approximately in conformity to the mass law up to a certain maximum, beyond which only a small increase in exchange will take place with increased addition of A^+ . The amount of exchange is essentially independent of dilution³⁵ but depends principally on the ratio of the total quantities of the two electrolytes and zeolites present. Concentrations may be used only when reference is made to a fixed total volume. Specific properties of the zeolites and ions make it impossible to give equations applicable to all systems. Of the many proposed, one of the most generally applicable equations used to express the amount of base exchange at equilibrium is one of the type given by Rothmund and Kornfeld:³⁶

$$K = \frac{AZ}{BZ} \cdot \left[\frac{(B^+)}{(A^+)} \right]^\beta, \quad (1)$$

where K is an equilibrium constant, (A^+) and (B^+) are the concentrations of the two ions in the given volume of solution, and AZ and BZ are the equivalents of the two forms of zeolites present. The constant β varies from 0.5 to 1.0 for different

²⁶ Nier, *Phys. Rev.* **48**, 283 (1935).

²⁷ Brewer, *Phys. Rev.* **48**, 640 (1935).

²⁸ Manley, *Phys. Rev.* **48**, 921 (1936).

²⁹ Nier, *Phys. Rev.* **48**, 283 (1935). Brewer, *Phys. Rev.* **48**, 640 (1935).

³⁰ McBain, *Trans. Faraday Soc.* **9**, 99 (1913); *Kolloid Zeits.* **40**, 1 (1926).

³¹ Randall and Cann, *Chem. Rev.* **7**, 369 (1930).

³² Wiegner, *J. Soc. Chem. Ind.* **50**, 65T (1931).

³³ Jenny, *J. Phys. Chem.* **36**, 2217 (1931).

³⁴ Jaeger, *Trans. Faraday Soc.* **25**, 320 (1939).

³⁵ Wiegner and Muller, *Zeits. Pflanz. Dung.* **14A**, 321 (1929).

³⁶ Rothmund and Kornfeld, *Zeits. f. anorg. allgem. Chemie* **103**, 129 (1918).

systems and expresses the fact that the ratio of the two forms of zeolite are not necessarily the same as the ratio of the ions in solution.

According to the scheme used by Austerweil³⁷ the zeolite is considered to be a solid solvent nonmiscible with the solution of the cation which exchanges. The laws of extraction should apply and there should be a distribution of the two cations depending on the "solubility" or concentration ratio of the two zeolites. To extract a total fraction E of a cation from solution there would be required n extractions as given by $(1-\alpha')^n = 1-E$ where α' is the exchange or distribution coefficient.

Starting with the properties and behavior of zeolites as outlined above and the assumption that one isotope is taken up more readily than the other, a method must be devised to multiply the single stage effect many times. Any of the batch or batch-counter current methods of extraction³⁸ may be followed. A continuous counter current method as used in the separation of the nitrogen isotopes⁵ by exchange of NH_3 and NH_4^+ would be more effective but the difficulties of counter current motion are much greater for a solid and liquid than for a liquid and gas. The use of a long column packed with zeolite seems to be the most favorable scheme. A number of different procedures may be followed. A solution of lithium may be passed through a column containing a sodium zeolite. All the way down the column one isotope should be held back more than the other and the first lithium coming through should have a changed isotope ratio. This first sample will be called the "leading sample." After the column is converted to a lithium zeolite a solution of sodium chloride may be passed through the column. One isotope is replaced more readily than the other by the sodium and the last lithium coming through the column should have the isotope ratio changed in the opposite direction to that of the leading sample. This last sample will be called the "tailing sample."

Another procedure is one similar to that used in the separation of closely related organic substances by the recently developed methods of

chromatographic analysis.^{39, 40} According to this method a tube is filled with a suitable absorbing substance. The mixture to be separated is added at the top of the column where all the substances are absorbed. A solvent is passed through the column and the substances most strongly held remain in a layer near the top while those less strongly absorbed form successive layers down the column. By continued washing, the substances may be made to descend one by one through the bottom of the column. This method has been studied by Schwab and Jockers⁴¹ for the separation of inorganic cations on adsorbents like aluminum oxide. Analogous procedures can be used with zeolites as adsorbents and solutions of ions as the solvent.

A counter current system similar to that of a counter flow column with total reflux at both ends can be simulated as follows. The column can be filled with a zeolite having an easily replaceable cation compared to the isotopic ions. A quantity of a salt containing the isotopic ions is then added at the top of the column. Following this is a solution containing a cation very strongly held to the zeolite such that practically all the isotopic ions are replaced and descend down the column. The net result will be that effectively the quantity of zeolite containing the isotopic ions moves down the column with reflux at the leading and tailing end.

EXPERIMENTS ON THE FRACTIONATION OF THE LITHIUM ISOTOPES

Determination of the fractionation factor

In order to determine the possible effectiveness of the base exchange reactions in separation of the isotopes, a determination of the fractionation factor was made. It is given by the ratio $\text{Li}^6\text{Z} : \text{Li}^7\text{Z} / \text{Li}^{6+} : \text{Li}^{7+} = \alpha$, that is, the distribution of the isotopes between the two phases. If α were large enough, a single stage equilibrium could be used for its determination. However, it is small in most isotopic exchange reactions and thus the single stage must be multiplied many times. The method chosen was to extract a large quantity of

³⁷ Austerweil, Bull. Soc. Chem. France **51**, 732 (1932).

³⁸ Hunter and Nash, J. Ind. Eng. Chem. **27**, 836 (1935).

³⁹ Zechmeister and Cholnoky, *The Chromatographic Adsorption Method* (Springer, Austria, 1937).

⁴⁰ Lederer, Chemie und Industrie **33**, 1072 (1932).

⁴¹ Schwab and Jockers, Angew. Chemie **50**, 546 (1937).

lithium chloride solution with successive small quantities of sodium zeolite so that α is approximately given by the Rayleigh distillation formula,

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

where N_0 is the mole fraction of the heavy isotope in the initial amount of material W_0 , and N the mole fraction in the final amount of material W . A batch containing 300 g of lithium chloride in a 20 percent solution was extracted with a large number of successive 30 g portions of sodium zeolites. The zeolite was a synthetic one called "Decalco" and kindly furnished by the Permutit Company for this research. It had a calculated exchange capacity of about 0.32 equivalents per 100 grams and was graded by Tyler screens from 40 to 60 mesh. After each addition the mixture was shaken vigorously for twenty minutes before filtration. At various intervals the sodium chloride resulting from the replacement of the sodium ion from the zeolite was separated from the remaining lithium. When the amount of lithium had been reduced by a factor of 70, the ratio of the isotopes in the remaining solution was determined. These experiments were made before our mass spectrometer was constructed and the samples were kindly analyzed by A. Keith Brewer and later checked. The ratio of $\text{Li}^7 : \text{Li}^6$ had changed from 11.6 to 12.7. Substitution in the Rayleigh formula gives 1.022 for the fractionation factor. It is difficult to estimate the accuracy or exact meaning of this value because of the variable concentration of lithium and sodium ions, and because the Rayleigh formula does not apply very closely towards the end of the extraction where the quantities of zeolite added were comparable to the amount of lithium remaining. However, the value does give us a fair approximation to what one can expect in a column since somewhat similar conditions occur.

The reverse procedure was also tried in which 2 kg of lithium zeolite were extracted with 36 successive liters of 2 percent chloride solution. The lithium extracted by the last batches of solution showed a ratio of the isotopes of 10.7

which gives a fractionation factor of 1.023 calculated as above.

Experiments on zeolite columns

As pointed out previously, one of the most convenient ways of multiplying the single stage effect is the use of a column of zeolite. A number of preliminary experiments were made to determine if possible the best procedure and conditions for a fractionation. It was not known, for example, whether dilute or concentrated solutions would be more advantageous. One form of the zeolite may be more effective than another. Thus, the use of a more stable zeolite like potassium or barium in place of a sodium zeolite may possibly be better since this would afford more competition for the two isotopes. The possible significance of the rate of diffusion or reaction during exchange was not known. The operation of the column would be different if the rate of extraction or adsorption rather than some equilibrium process were the controlling mechanism. The answers to all these questions have not yet been determined, but the following experiments do give us some ideas as to the nature of the fractionation process.

The first column constructed was a three-quarter inch stainless steel pipe thirty-five feet long packed with about 2 kg of sodium zeolite. The second column was made of a one and one-quarter inch hard rubber pipe thirty feet long containing about 4 kg of sodium zeolite. A third column of one and one-quarter inch hard rubber pipe one hundred feet long was constructed in one of the stairwells of the Chandler Chemical Laboratory. This was filled with about 13 kg of sodium zeolite furnished by the Permutit Company. These columns will be referred to as *A*, *B*, and *C*, respectively. In all cases care had to be taken to make sure that no air bubbles or pockets were left in the column. The most convenient way to fill the column was to fill each ten-foot section as it was added. The section was filled with water and the wet zeolite poured in, the water displaced being drawn off by suction. Tees fitted with one-quarter inch outlets were placed between each section so that samples could be taken. The velocity of the liquid flow was regulated by pinch clamps on heavy pressure tubing at the bottom. The solutions were fed by

TABLE I. *Result on fractionation of lithium isotopes.*

EXPERIMENT	COLUMN	FORM OF ZEOLITE	SOLUTION AND PROCEDURE	SAMPLE OF Li THROUGH COLUMN	RATIO Li^7/Li^6 NORMAL RATIO 11.7
1	A	NaZ	3% LiCl passed through	Leading	13.3 ± 0.3
2	A	NaZ	1% LiCl passed through	Leading	12.5
3	A	NaZ	1% LiCl passed through	Leading	12.3
4	B	NaZ	15 g LiCl washed down with 0.5% NaCl	Leading Tailing	12.6 8.9
5	C	NaZ	15 g LiCl washed down with 3.0% NaCl	Leading Tailing	14.1 8.8

inverting a large bottle over the top of the column. When the liquid ran below the level of the outlet tube in the bottle, air entered the bottle and more liquid ran out, thus maintaining a fairly constant level.

The samples used for analysis of the isotope ratio were evaporated just to dryness and extracted with amyl alcohol. A little P_2O_5 was added to the lithium chloride and put on a platinum disk in the form of a paste. After heating to redness on a tungsten filament for ten to fifteen minutes under vacuum, the disk was cleaned and spot welded to the filament of the mass spectrometer and the ratio of the isotopes determined as previously described. The results reported are the average taken from eight to fifteen determinations.

The results for a number of experiments with lithium are given in Table I.

In experiments 1, 2, and 3 the column was initially full of distilled water and sodium zeolite. The lithium chloride was allowed to run in at the top at a rate of about 2 to 3 cc per minute. Tests were made at intervals on a spectroscope to determine when the first lithium came through the bottom of the column. The first lithium through was taken as the leading sample and was analyzed on the mass spectrometer as described above. About one-half the replaceable sodium in the column was exchanged before the first lithium appeared. Experiments 2 and 3 were made to test the effect of concentration, but the very first lithium coming through was missed in both of these and therefore the results do not necessarily show the influence of dilution. A

receiver system was used thereafter which allowed the effluent to successively fill 200 cc bottles. Between each experiment the zeolite had to be completely regenerated by passing sodium chloride solution through the column.

Experiments 4 and 5 were carried out according to the methods of chromatographic analysis. The columns were initially filled with sodium zeolite and with the same solution which was to be used for washing down the lithium chloride. The charge of lithium chloride was added at the top of the column in a fairly concentrated solution (10 percent) and the sodium chloride solution was allowed to run in at the rate of about 2–3 cc per minute. The first lithium appearing was taken as the leading sample and the last to come through as the tailing sample. In experiment 4 about 70 g of sodium chloride in a 0.5 percent solution were required before the first lithium came through the column. Experiment 5 was made with the 100 foot column during an experiment on potassium. We had expected much more change than was obtained. The 3 percent sodium chloride washed the lithium through the column rather rapidly. A more dilute solution would probably have given better results. Further experiments are being made to test this point. All of the solution coming through the column was saved and samples were analyzed to determine the isotope ratio and the total amount of lithium coming through up to the time of the sample. The amount of lithium was determined by the spectroscopic method.⁴² While this method of analysis does not give results to better than 5 percent to 10 percent, this accuracy is sufficient to show the variation in isotope ratio as the lithium comes through the column. Such a curve will give us an estimate of the quantities of changed material which can be expected by this procedure. A curve for experiment 5 is given in Fig. 1.

In all the experiments on lithium, the leading sample had a lower concentration of Li^6 while the tailing sample had a higher concentration. This means that Li^{6+} is preferentially taken up by the zeolite and is not so readily removed as Li^{7+} .

⁴² Skinner and Collins, U. S. Dept. of Agri. Bull. Chem. 153.

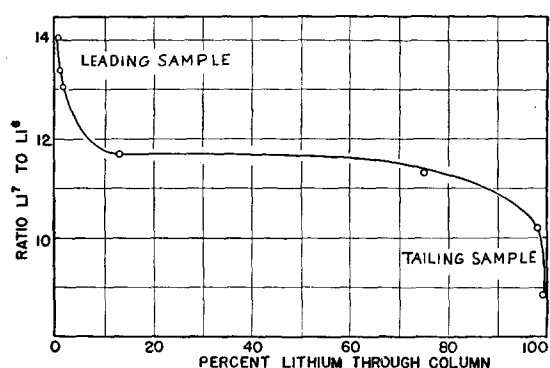


FIG. 1. Distribution of lithium isotopes coming through column in experiment 5.

EXPERIMENTS ON THE FRACTIONATION OF THE POTASSIUM ISOTOPES

The same general procedures as those used for the lithium isotopes were tried for potassium and for the nitrogen isotopes in NH_4^+ . A fractionation of the potassium isotopes with sodium zeolite was found to be more difficult especially in regards to the leading sample. This may possibly be due to the great difference in the binding of the lithium and potassium to the zeolite. Most of the preliminary experiments were made to see whether or not a change could be made on the leading sample.

The solution coming through the column was tested for potassium with sodium cobaltinitrite. When its presence was shown by this test, a quantity of the liquid was evaporated and the potassium precipitated as the cobaltinitrite. This was, decomposed by heating, and after filtering off the cobalt oxide, the sodium and potassium nitrites were converted to the chlorides. A little P_2O_5 was added and the ratio of the isotopes determined as described for lithium. The presence of sodium did not interfere with the analysis.

Table II shows the results of a number of the experiments.

In experiment 1 the 1 percent KCl solution was passed through the column of sodium zeolite at the rate of about 2 to 3 cc per minute. About three-fourths of the calculated replaceable sodium was exchanged before potassium came through in sufficient quantities to give a test with cobaltinitrite. No change was found in the leading sample, but after washing the potassium from the column with about forty liters of 5 percent

sodium chloride solution, the ratio of K^{39} to K^{41} was found to be 13.4. For experiment 2, the column was converted to calcium zeolite, filled with water, and a 3 percent potassium chloride solution started through as before. When sufficient potassium had come through to give a test with cobaltinitrite the ratio was 14.2 showing no significant change. However, about five liters of the first solution through the column was saved and later evaporated to recover any potassium. The small amount obtained (about 20 mg of $K_2NaCo(NO_2)_6$) was analyzed and found to have increased in ratio to 14.8.

Experiment 3, using 0.5 percent KCl instead of 3 percent KCl, showed no marked advantage in using more dilute solutions. However, under conditions where an appreciable fractionation is obtained, the more dilute solutions may yet prove to be more effective. The equilibrium constants as given by Eq. (1), or the constants from other equations,³ are generally about twice as large for replacement of ions from a zeolite by K^+ as for Na^+ . It was thought that a mixture containing two equivalents of sodium chloride to one of potassium chloride when passed down the column may give a better fractionation. Accordingly for experiment 4, the column was filled with sodium zeolite and 0.30 *N* NaCl solution. A mixture of 0.15 *N* KCl and 0.30 *N* NaCl was then started through. The leading sample again showed no significant change in isotope ratio. Experiments made in this manner using sodium or calcium zeolites apparently will not give large changes in the ratio of the potassium isotopes in the leading sample.

Experiment 5, carried out according to the methods of chromatographic analysis, gave no significant change in the leading sample, but the tailing sample was changed to a ratio of 12.9. The same experiment was tried on the 100 foot column but the potassium spread throughout the whole column so much during the passage of the 3 percent sodium chloride solution that the experiment was finally stopped when the ratio of the potassium isotopes in a sample taken from the top section of the column was 13.2. The use of larger quantities of potassium chloride and higher concentration of sodium chloride may have been better. Further experiments will be made later. The experiment using a column of sodium zeolite

and a solution of barium chloride to follow the potassium down shows some promise since a change was observed in both the leading and tailing samples. The use of ammonium zeolite and ammonium ion which is similar to potassium in replacing power may also prove more effective than the sodium zeolite.

In all those experiments in which a change in the ratio of the potassium isotopes was obtained, K^{41} was decreased in the leading sample and increased in the tailing sample. It seems, therefore, that the heavier isotope is taken up more readily by the zeolite and is more difficult to replace. This is the opposite of the effect observed for lithium.

Experiments on the exchange of ammonium ion with a sodium zeolite and a carbonaceous zeolite given to us by the Permutit Company showed a small change in the isotope ratio in the same direction as observed for potassium, i.e. the heavier isotope was more readily taken up by the zeolites. The analyses were made on a mass spectrometer by Marvin Fox in this laboratory.

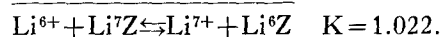
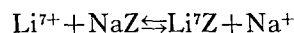
TABLE II. *Experiments on fractionation of potassium and nitrogen isotopes.*

EXPERIMENT	COLUMN	FORM OF ZEOLITE	SOLUTION PASSED THROUGH COLUMN	SAMPLE OF K THROUGH COLUMN	ANALYSIS $K^{39} : K^{41}$ 14.10
Potassium 1	A	NaZ	1% KCl passed through	Leading	14.1 ± 0.2
1a	A	KZ	5% NaCl passed through	Tailing	13.4
2	A	CaZ ₂	3% KCl passed through	Leading (a) Leading (b)	14.8 14.2
3	A	CaZ ₂	0.5% KCl passed through	Leading	14.2
4	A	NaZ	0.15 NKCl + 0.30N NaCl	Leading	14.1
5	B	NaZ	100 g KCl washed down with 5% NaCl	Leading Tailing	14.3 12.9
6	C	NaZ	100 g KCl washed down with 3% then 5% KCl	—	13.20
7	B	NaZ	15 g KCl washed down with 1 M BaCl ₂	Leading Tailing	14.6 13.5
Nitrogen 1	(NH ₄ ⁺) A	NaZ	2% NH ₄ Cl passed through	Normal Leading	$N^{14}N^{14} : N^{14}N^{15}$ 124.3 136.8
2	8 ft.	HZc	1% NH ₄ Cl passed through	Normal Leading	127.4 130.8

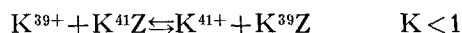
DISCUSSION

The fractionation of the isotopes by this method depends upon a difference in binding of the two isotopic ions with water and with the zeolite. The differences are due to a difference in the zero point energies and the vibrational and rotational frequencies of the two isotopic combinations in much the same way as those calculated for gaseous systems by Urey and Greif¹ and demonstrated experimentally for the liquid-gas chemical exchange systems previously referred to. Solvation of the ions and the specific nature of the zeolite are, therefore, important considerations. Any change in the system affecting the nature of the solvent medium will affect the binding of the two isotopic ions, and if this is not in the same ratio for the solvation and binding of the ions to the zeolite, there will be a change in the effectiveness of the fractionation. We cannot predict whether it would improve or decrease the desired fractionation, nor can calculations be made for such a complicated system. Thus far we have studied the fractionation with only one or two forms of the same zeolite and have not markedly changed the nature of the solvent medium. Other types of zeolites such as the bentonite clays, the natural "greensands" or the newly developed organic exchange resins are to be studied. Addition of alcohol or other solvent may also influence the fractionation obtained.

If the process by which the isotopes are fractionated is an equilibrium one, we may write the following equations:



Similarly



The lighter lithium isotope is preferentially taken up by the zeolite while the reverse is true for the potassium and ammonium ions. The process responsible for the fractionation is essentially an equilibrium one rather than one due to differences in the rate of diffusion or reaction,

since otherwise the lighter isotopes would all diffuse faster resulting in changes of the isotope ratio in the same direction. In those experiments in which lithium chloride solutions were passed through the column filled with sodium zeolite, differences in the rate of diffusion of the two isotopic ions would tend to decrease the concentration of Li^6 and therefore increase the fractionation in the leading sample. If diffusion or rate of reaction were the important process, the tailing sample produced by passing sodium chloride solution through a column of lithium zeolite should also give a solution containing a higher concentration of Li^7 since Li^6 should diffuse out of the zeolite faster. This is not the case. In those experiments made according to the procedures of chromatographic analysis, the decrease of Li^6 in the leading sample is approximately the same as the increase of Li^6 in the tailing sample.

The experiments are not yet extensive enough to draw definite conclusions as to which method is the most effective procedure. The procedure according to the methods of chromatographic analysis will give samples with both higher and lower amounts of Li^6 . However, if a change is desired in one direction, it seems that the first procedure should be better. That is, to obtain a higher concentration of Li^6 , the column should be converted to lithium zeolite and sodium chloride solution slowly passed in at the top so as to displace the lithium from the zeolite. The sodium ion replaces Li^{7+} more readily than the Li^{6+} such that the last lithium replaced from the column has a higher concentration of Li^{6+} . Since there is a distribution of the lithium between the two phases following the laws previously described, one may obtain the number of stages by methods similar to those used in extraction problems. By assuming the number of effective isotopic ex-

changes is the same as the number of stages thus determined, it is possible to calculate the separation which can be expected once the fractionation factor is known.

Acknowledgments and thanks are due Dr. A. Keith Brewer for his suggestions and advice in construction of the mass spectrometer and for some of the analyses during the first part of the investigation. Thanks are also due Dr. John G. Dean and the Permutit Company for the zeolites used in the research.

SUMMARY

1. The methods used in fractionation of the lithium and potassium isotopes have been discussed and some additional results on the electrolysis of lithium chloride reported.

2. The properties of zeolitic substances significant in studies on the separation of isotopes by chemical exchange are described.

3. The natural abundance ratio of the lithium and potassium isotopes have been determined by analysis on the mass spectrometer and compared to the values reported in the literature. The average value obtained for the ratio $\text{Li}^7 : \text{Li}^6$ was 11.71 ± 0.14 and for $\text{K}^{39} : \text{K}^{41}$ was $14.10 \pm .09$.

4. The fractionation factor for the lithium isotopes in the exchange with sodium zeolite was found to be 1.022.

5. A fractionation of the lithium, potassium and nitrogen isotopes using long columns filled with zeolites has been effected. Both an increase and decrease of about 25 percent from the normal abundance ratio of the lithium isotopes has been obtained. A change of about 10 percent has been obtained for the potassium and nitrogen isotopes.

6. Some of the factors involved in the mechanism of the process are discussed.