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Natural Abundance of the Lithium Isotopes

DWIGHT A. HUTCHISON
Chemistry Division, Argonne National Laboratory, Lemont, Illinois

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The natural abundance ratio of the lithium isotope of mass 7 to the isotope of mass 6 has been determined from the density and x-ray data for certain crystals. Consideration of the maximum limits of variation of this ratio in nature and the error assignments of the data used in this calculation have resulted in the value 11.53 ± 0.29. This value disagrees with the mass spectrometric and optical determinations. Some of the possible errors in the mass spectrometric work are considered.

I. INTRODUCTION

EXPERIMENTAL determinations of the natural abundance of the lithium isotopes have yielded a great variation in the ratio Li^7/Li^6. The values of this ratio vary from approximately 11.5 to 13.0. Apparently, the best determinations rest upon mass spectrometric methods applied by Brewer,[1] Lu,[2] White and Cameron,[3] and Hintenberger.[4] From the description of these experimental determinations of the abundance ratio, it seems plausible to conclude that the observed variation does not represent the natural variation of the ratio; rather, the observed variation represents an incomplete knowledge of the isotopic fractionation effects in the experimental preparation of samples for analysis, in evaporation or ionization processes, and in numerous instrumental factors.

From a review of previous work it is apparent that a determination of the lithium isotopic abundance by a method which is independent of the mass spectrometric or optical methods[5] would be highly desirable both to give a reliable value to the abundance ratio, and to serve as a guide in perfecting the various analytical techniques that may be of use in studies of isotopic reactions and separation processes. Such a method fulfilling these requirements exists and has been presented by Hutchison[6] and by the writer[6] in connection with a determination of the atomic weights of calcium and fluorine. In essence, the method consists of a comparison of the molecular weights of two crystalline substances for which there are accurate x-ray and density data available.

The purpose of this paper is to present the application of the x-ray density method to the determination of the natural isotopic abundance of lithium, and to evaluate the reliability of the value thus determined.

II. THE LITHIUM ISOTOPIC RATIO FROM X-RAY AND DENSITY DATA

In the present calculation we wish to compare the molecular weight of lithium fluoride with the molecular weights of calcite, diamond, sodium chloride, and potassium chloride for all of which accurate x-ray and density data exist. By use of the mass values for fluorine and the two lithium isotopes we can arrive at the isotopic composition of the lithium in a highly purified sample of lithium fluoride which was purified by a method shown not to alter its isotopic composition.

The comparison of molecular weights is given by the relation,

$$M_1=M_2(\rho_1/\rho_2)FR_g^3, \qquad (1)$$

where subscripts 1 refer to data for LiF and subscripts 2 refer to data on the other four crystals; M is an isotopic, atomic, or molecular weight based on the physical mass scale; ρ is a density in units of g-cm^{-3}; R_g is the ratio of the x-ray grating space of lithium fluoride to that of one of the other four crystals; F is a factor depending on the crystal geometries, and the arrangements and number of ion pairs or molecules in the unit cells.

The R_g is expressed in terms of the observed reflection angles, ϑ_i, by the relation,

$$R_g=\frac{n_1\lambda_1\sin\vartheta_2(1-\delta_2/\sin^2\vartheta_2)\xi}{n_2\lambda_2\sin\vartheta_1(1-\delta_1/\sin^2\vartheta_1)}, \qquad (2)$$

which utilizes the Bragg law together with the appropriate refraction corrections. The ξ is a factor which corrects for the fact that x-ray reflection angles are not from corresponding planes in the two crystals; λ is the wavelength of the radiation employed in the determination of the x-ray reflection angles and was computed from the reflection angles for the Cu $K\alpha_1$ and Mo $K\alpha_1$ lines from calcite as obtained by Bearden and Shaw,[7] and Larsson[8]; ϑ is the Bragg reflection angle; n is the order of the reflection; and δ, the unit decrement of the index of refraction of the crystal, is defined by the relation, $\delta=1-\mu$, where μ is the index of refraction. The δ's were computed from the relation, $\delta=(ke^2\lambda^2/2\pi mc^2)$ which assumes the wavelengths used to be much shorter than any critical absorption wavelength of the

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[1] A. K. Brewer, J. Chem. Phys. **4**, 350 (1936).

[2] H. Lu, Phys. Rev. **53**, 845 (1938).

[3] J. R. White and A. E. Cameron, Phys. Rev. **74**, 991 (1948).

[4] H. Hintenberger, Naturwiss. **34**, 52 (1947).

[5] Ornstein, Vreeswijk, and Wolfsohn, Physica **53**, 1 (1934); G. Nakamura, Nature **128**, 759 (1931); W. R. v. Wijk and A. J. v. Koeveringe, Proc. Roy. Soc. (London) **A132**, 98 (1931).

[6] C. A. Hutchison, J. Chem. Phys. **10**, 489 (1942); D. A. Hutchison, J. Chem. Phys. **13**, 383 (1945).

[7] J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935).

[8] A. Larsson, Phil. Mag. [7] **3**, 1136 (1927).

TABLE I. Data for the calculation of the natural isotopic abundance of lithium, with estimated maximum errors for various factors expressed in parts per million (ppm).

Substance	Calcite	Diamond	Lithium fluoride	Sodium chloride	Potassium chloride
$\rho_{20°\mathrm{C}}$ (g-cm^{-3})	2.71030[a] ±22 ppm	3.51540[b] ±20 ppm	2.64030[c] ±53 ppm	2.16360[d] ±18 ppm	1.98827[e] ±20 ppm
ϑ (radians)	0.117106[f,g] ±12 ppm 0.486229[a] ±30 ppm	0.409016[f] ±5.9 ppm	1.463790[h] ±1.7 ppm	0.276656[i] ±14 ppm	0.112989[f] ±17 ppm
Reflecting plane	Natural cleavage	100	111	100	100
Reflection order	1 4	1	3	1	1
$\delta \times 10^6$	1.85 $\pm 5 \times 10^4$ ppm	2.39 $\pm 5 \times 10^4$ ppm	7.91 $\pm 5 \times 10^4$ ppm	1.41 $\pm 5 \times 10^4$ ppm	1.32 $\pm 5 \times 10^4$ ppm
ξ	1	1	$\sqrt{3}/2$	1	1
F	0.912459 ±9.1 ppm	0.250000 ±0.0 ppm	1.000000 ±0.0 ppm	1.000000 ±0.0 ppm	1.000000 ±0.0 ppm
$\alpha \times 10^5$ (°C^{-1}) (linear)	1.04[j] $\pm 2.0 \times 10^4$ ppm	0.118[k] $\pm 2.0 \times 10^4$ ppm	3.41[l] $\pm 2.0 \times 10^4$ ppm	4.05[m] $\pm 2.0 \times 10^4$ ppm	3.77[n] $\pm 2.0 \times 10^4$ ppm
B	0.151539 ±45 ppm	0.151541 ±37 ppm		0.151540 ±42 ppm	0.151540 ±59 ppm

[a] J. A. Bearden, Phys. Rev. **38**, 2089 (1931).
[b] J. A. Bearden, Phys. Rev. **54**, 698 (1938).
[c] C. A. Hutchison and H. L. Johnston, J. Am. Chem. Soc. **62**, 3165 (1940).
[d] H. L. Johnston and D. A. Hutchison, Phys. Rev. **62**, 32 (1942).
[e] D. A. Hutchison, Phys. Rev. **66**, 144 (1944).
[f] Y. Tu, Phys. Rev. **40**, 622 (1932).
[g] A. Larrsson, Phil. Mag. [7] **3**, 1136 (1927).
[h] Straumanis, Ievins, and Karlsons, Z. physik. Chem. **B42**, 143 (1939).
[i] M. Siegbahn, Ann. Physik **59**, 56 (1919).
[j] A. Larsson, Inaugural-Dissertation, Uppsala, 1929 (unpublished).
[k] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1927), **3**, p. 21.
[l] H. Adenstedt, Ann. Physik **26**, 69 (1936).
[m] M. Straumanis and A. Ievins, Z. Physik **102**, 353 (1936); Straumanis, Ievins, and Karlsons, Z. anorg. u. allgem. Chem. **238**, 175 (1938).
[n] Klemm, Tilk, and Mullenheim, Z. anorg. u. allgem. Chem. **176**, 1 (1928).

crystals. In the latter expression k is the number of electrons per cubic centimeter and other symbols have their usual significance.

By substitution of Eq. (2) in (1) and solving for the atom fraction, $\chi(\mathrm{Li}^6)$, of the mass-6 lithium isotope, we obtain the following expressions used in this calculation:

$$\chi(\mathrm{Li}^6) = C - AB, \tag{3}$$

where

$$C = \frac{M_{\mathrm{Li}^7} + M_{\mathrm{F}}}{M_{\mathrm{Li}^7} - M_{\mathrm{Li}^6}}, \tag{4}$$

$$A = \rho_1 \left[\frac{n_1 \lambda_1 \xi_1}{\sin\vartheta_1 (1 - \delta_1 / \sin^2\vartheta_1)} \right]^3, \tag{5}$$

$$B = \frac{F M_2}{\rho_2} \left[\frac{\sin\vartheta_2 (1 - \delta_2 / \sin\vartheta_2)}{n_2 \lambda_2} \right]^3. \tag{6}$$

It will be observed that the calculation summarized in Eq. (3) is independent of the Avogadro number and of λ_g/λ_s, the ratio of wavelengths on the grating or Ångstrom scale to the wavelengths on the Siegbahn scale. The quantities which are temperature-dependent, i.e., the ρ's and ϑ's, have been reduced to the common temperature of 20°C. The densities were temperature-corrected by use of the appropriate thermal expansion coefficients, and the x-ray reflection angles by means of the relation,

$$\log \sin\vartheta_{20°\mathrm{C}} = \log \sin\vartheta_T - \alpha(20 - T)/2.303, \tag{7}$$

where T is the centigrade temperature at which the reflection angles were determined.

The atomic, isotopic, or molecular mass values are based on chemical atomic weight determinations except for M_{Li^6}, M_{Li^7}, and M_{F} which have been derived from nuclear reaction data. It is this very accurate mass value for fluorine that makes possible the application of the x-ray-density method of the calculation of the natural isotopic abundance of lithium.

The value employed to convert from the chemical to the physical mass scale is 1.000272. The values of the quantities used in this calculation together with references to their literature sources are summarized in Tables I and II. With each quantity there is listed in parentheses the estimated maximum error expressed in parts per million (ppm).

The first step of the calculation was to obtain the value of B by Eq. (6) in which the x-ray and density data of all the crystals except lithium fluoride were employed. The individual B values and their errors, propagated from the error assignments of the primary data, are listed in Table I. The value for calcite is a

TABLE II. Atomic masses employed in calculations, with estimated maximum errors expressed in parts per million (ppm).

Element	Mass (physical mass scale)
C	12.0137[a] (±18 ppm)
Ca	40.0959[b] (±130 ppm)
Cl	35.4666[c] (±15 ppm)
K	39.1066[d] (±14 ppm)
Na	23.0033[c] (±23 ppm)
F	19.004456[e] (±0.79 ppm)
Li^7	7.018223[e] (±3.7 ppm)
Li^6	6.017021[e] (±3.7 ppm)

[a] G. P. Baxter and A. H. Hale, J. Am. Chem. Soc. **59**, 506 (1937); A. F. Scott and F. H. Hurley, J. Am. Chem. Soc. **59**, 1905 (1937).

[b] O. Hönigschmid and K. Kempter, Z. anorg. u. allgem. Chem. **163**, 315 (1927); **195**, 1 (1931).

[c] T. W. Richards and R. C. Wells, "A Revision of the Atomic Weights of Sodium and Chlorine," Carnegie Institution of Washington, Publication No. 28 (1905); W. A. Noyes and H. C. P. Weber, J. Am. Chem. Soc. **30**, 13 (1908); E. Zintl and A. Meuwsen, Z. anorg. u. allgem. Chem. **136**, 223 (1924); Hönigschmid, Chan, and Birckenbach, Z. anorg. u. allgem. Chem. **163**, 315 (1927); O. Hönigschmid and R. Sachtleben, Z. anorg. u. allgem. Chem. **178**, 1 (1929); A. F. Scott and C. R. Johnson, J. Phys. Chem. **33**, 1975 (1929); O. Hönigschmid, J. Am. Chem. Soc. **53**, 3012 (1931).

[d] T. W. Richards and A. Stahler, J. Am. Chem. Soc. **29**, 623 (1907); T. W. Richards and E. Mueller, J. Am. Chem. Soc. **29**, 639 (1907); G. P. Baxter and W. M. MacNevin, J. Am. Chem. Soc. **55**, 3185 (1933); O. Hönigschmid and R. Sachtleben, Z. anorg. u. allgem. Chem. **213**, 365 (1933); R. K. McAlpine and E. J. Bird, J. Am. Chem. Soc. **63**, 2960 (1941).

[e] Li, Whaling, Fowler, and Lauritsen, Phys. Rev. **83**, 512 (1951).

weighted average[9] of the two B values from the two reflection angles listed. From the first-order reflection one obtains $B(n=1)=0.151540$ (±69 ppm) and from the fourth-order reflection, $B(n=4)=0.151538$ (±60 ppm). A weighted average[9] of the B values obtained from the four values listed in Table I gives

$$B_{\text{wt'd Av}}=0.151540\ (\pm 22\ \text{ppm}).$$

The value obtained for A from Eq. (5) is

$$A_{\text{LiF}}=170.9885\ (\pm 66\ \text{ppm}).$$

The value obtained for C from Eq. (4) is

$$C=25.99144\ (\pm 34\ \text{ppm}).$$

Finally, combination of B, A, and C according to Eq. (3) yields

$$\begin{aligned}\chi(\text{Li}^6)&=0.0798\ (\pm 2.5\ \text{percent})\\&=0.0798\pm 0.0020,\end{aligned}$$

and the abundance ratio of mass-7 to mass-6 lithium isotopes becomes

$$\begin{aligned}R(7/6)&=11.53\ (\pm 2.5\ \text{percent})\\&=11.53\pm 0.29.\end{aligned}$$

The errors stated are obtained by a least-squares propagation of the maximum error assignments given for the quantities in Tables I and II. The relatively large errors of the calculated quantities, $\chi(\text{Li}^6)$ and $R(7/6)$, when compared with the small error of the quantities given in Tables I and II, are due to the fact that in Eq. (3) a small difference is obtained from two accurately determined quantities, i.e., C and AB.

III. THE NATURAL ABUNDANCE OF LITHIUM ISOTOPES

The value calculated for the abundance of the mass-7 and mass-6 lithium isotopes represents the abundance for crystals prepared from a particular batch of carefully purified lithium fluoride[10] in which the lithium isotopic composition was not altered within the stated limits of accuracy for its density determination. It is felt reasonable to assume that the $R(7/6)$ determined here represents the best average natural ratio, and that the only question remaining is that concerning the natural variation in the ratio.

There appear to be at least two types of processes that would cause natural variation in the lithium isotopic abundance, that due to chemical reactions and, to a smaller degree, that due to thermal neutron absorption. From Urey's[11] computations of the partition functions for the lithium isotopes, their hydrides and deuterides, the differences predicted in the thermodynamic quantities of the isotopic lithium compounds suggest that some isotopic exchange may occur in nature which would give a small separation of the lithium isotopes. A rough estimate of a maximum figure for the variation in the abundance ratio may be about 0.5 percent. Evidence for thermal neutron capture is to be found in the work of Aldrich and Nier[12] who observed He^3 concentrations in the lithium-containing mineral, spodumene, which were greater than that of other minerals. This fact may be attributed to the $Li^6(n,\alpha)H^3$ reaction. Thode and co-workers[13] have found the ratio of the boron isotopes, $R(11/10)$, to vary from 4.27 to 4.42, or a 3.5 percent variation, depending on the natural source. On the assumption that all of this variation is due to neutron capture by B^{10}, then taking into account the isotopic composition of boron and lithium, the $R(7/6)$ for lithium should vary as the ratio of the thermal neutron absorption cross sections for Li^6 and B^{10}. This would mean that the lithium abundance ratio should vary by only 0.36 percent. However, neutron intensities in the earth's atmosphere, especially in the earth's crust, due to cosmic and other sources would seem too low to account for the observed variation in boron such that the variation expected in the lithium ratio would be less than the 0.36 percent figure.

From the qualitative considerations above concerning the maximum variation of the lithium abundance ratio in nature, we may conclude that the 2.5 percent

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[9] The fractional error obtained for the final weighted B value was obtained from internal consistency. The ratio of errors obtained from external consistency to that from internal consistency is 0.138 indicating that too great allowances have been made for systematic errors in the primary data used in the calculations. For a discussion describing the method of taking the weighted averages, see R. T. Birge, Phys. Rev. **40**, 207 (1932).

[10] C. A. Hutchison and H. L. Johnston, J. Am. Chem. Soc. **62**, 3165 (1940); H. L. Johnston and C. A. Hutchison, J. Chem. Phys. **8**, 869 (1940).

[11] H. C. Urey, J. Chem. Soc. 562 (1947).

[12] L. T. Aldrich and A. O. Nier, Phys. Rev. **74**, 1590 (1948).

[13] Thode, Macnamara, Lossing, and Collins, J. Am. Chem. Soc. **70**, 3008 (1948).

error of the $R(7/6)$ value obtained in this calculation well includes the expected natural variation.

IV. DISCUSSION AND CONCLUSIONS

In the mass spectrometric determinations[1–4] of $R(7/6)$, the workers mentioned in the introduction have employed thermal emission of ions or electron bombardment of vapor from lithium containing compounds placed on a platinum or tungsten substrate which was heated to about 600–900°C. Apparently, in none of these determinations has anyone given consideration to the effect of the process of solution of the lithium compound in the substrate on the possible alteration of $R(7/6)$ in the compound from which the lithium vapor or ions were obtained. For example, Brewer[1] dissolved lithium salt in a platinum disk at red heat, scraped the salt from the platinum, and washed with water. In his theoretical considerations no attention was given to the process of solution of the lithium in the platinum. An isotopic separation certainly must have existed due to different isotopic rates of diffusion. Further, he assumed perfect mixing of Li^7 and Li^6 in the platinum substrate, which seems untenable as his data show. It becomes evident that further experimental and theoretical consideration should be given to the processes of diffusion of lithium into and out from the metal substrate.

Probably more important than the solution processes in the mass spectrometric measurement of ion current ratios of light mass ions are the many instrumental effects. A typical property of instruments employing two parallel plates with slits in the ion source for acceleration of ions without previous ion focusing is the so-called "voltage effect." The observed effect is that the collected ion current increases with ion accelerating voltage until a voltage is reached at which the ion current may remain essentially constant with further increase in voltage. In the case of the molecular ion species of the various isotopic hydrogen molecules, distinct maxima[14] exist in the curves of peak height *versus* accelerating voltage such that, at a given accelerating voltage, measured current ratios may deviate by more than 50 percent from their correct values. For the usual magnetic field intensities employed in mass spectrometers, the ion accelerating voltages for collection of lithium ions will vary from 1000 v to 4000 v over which range the observed "voltage effect" occurs and must have existed in the determinations of $R(7/6)$. This effect in itself could account for the wide range of values found for $R(7/6)$. It becomes apparent that a thorough study of the preparation and handling of lithium-containing samples and of instrumental effects on the collected ion currents is necessary before the mass spectrometric determinations can be considered reasonably trustworthy.

Bainbridge and Nier[15] have adopted Lu's value of 12.29 ± 0.20 for $R(7/6)$, with supporting evidence from a value computed from the chemical atomic weight and the physical isotopic weights. Inherent in the present x-ray density determination of $R(7/6)$ is the result that the atomic weight[16] of lithium is somewhat lower than the value adopted by the Committee on Atomic Weights of the International Union of Chemistry. Hence, a smaller value of $R(7/6)$ is obtained.

The x-ray density determination presented here gives a relatively precise determination of $R(7/6)$ which is independent of mass spectrometric or optical work. Qualitative considerations of the natural variation to be expected in $R(7/6)$ give a variation within the stated probable error of $R(7/6)$ from this calculation. The result obtained here disagrees with the mass spectrometric determinations. However, consideration of the mass spectrometric techniques shows that sample handling and instrumental effects raise many debatable questions concerning the validity of these determinations. The results obtained in the present work are based upon a highly consistent set of data as evidenced by the consistent results obtained through its use by Birge[17] in his determination of the Avogadro number and by the writer[6] in his determination of the atomic weights for calcium and fluorine. Birge has concluded that these crystals must be geometrically perfect to better than 1 part in 10 000 as judged from the consistency of his values of the Avogadro numbers obtained from the data on each of these crystals. In the present calculation the consistency of the quantity B rules out any noticeable effect of crystal imperfections on the stated results. The mass spectrometric and optical determinations of $R(7/6)$ varying from 11.5 to 13.0, however, do not appear to form a consistent set of results. The great consistency of the x-ray and density data collected from many measurements by different observers should lend credence to the present calculation of $R(7/6)$.

The writer wishes to thank Dr. O. C. Simpson for his suggestion of this problem.

Note Added in Proof.—It may be of interest to consider the effect on the present calculations of the changes of the atomic weights of sodium and carbon as adopted by the International Commission on Atomic Weights and given in the American Chemical Society report by E. Wichers [J. Am. Chem. Soc. **76**, 2033 (1954)]. When the new values are employed, there results the weighted average B value, 0.1515400, in exact agreement with the result of this paper. Therefore, the value of $R(7/6)$ remains unchanged.

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[14] From unpublished data taken by the writer. The data were taken without the usual magnetic field across the ion source for alignment of the electron beam.

[15] K. T. Bainbridge and A. O. Nier, Prelim. Rep. No. 9, Nuclear Science Series, Div. of Math. and Phys. Sci., Natl. Research Council, December, 1950 (unpublished).

[16] D. A. Hutchison, J. Am. Chem. Soc. **76**, 967 (1954).

[17] R. T. Birge, Am. J. Phys. **13**, 63 (1945).