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The Atomic Weight of Lithium from Density and X-Ray Data

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The atomic weight of lithium has been calculated from density and X-ray data to be: $M_{\mathrm{Li}} = 6.9364 \pm 0.0018$. This is less than the commonly accepted value of 6.940. A critical evaluation of previous work on the atomic weight of lithium does not preclude the present value.

Introduction

In the course of recent work[1] on the determination of the natural abundance of the lithium isotopes from X-ray and density data, it became apparent that the atomic weight of lithium would have to be 0.06% lower than the commonly accepted value of 6.940 in order to be consistent with the well-established X-ray, density and atomic weight data for the crystals involved. The purpose of this paper is to present the calculation of the atomic weight of lithium and to critically evaluate the result obtained.

The method and the data, with minor changes, which are employed in the present determination have been presented previously[2] but they will be reviewed briefly here for the sake of clarity. The data are those for the crystals: calcite, diamond, lithium fluoride, sodium chloride and potassium chloride. For the comparison of the molecular weights of any two of these crystals, there must be known the ratio of the absolute densities, the ratio of the X-ray grating spaces, and the geometrical arrangements of the ion pairs or molecules in the unit cell of each substance. The relation of the molecular weights of two of the above crystals to one another may be expressed as

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

where M is a molecular or atomic weight on the chemical mass scale; ρ is a density; F is a factor depending on the crystal geometrics, and the arrangements and number of ion pairs or molecules in the unit cells; R_g is the ratio of the X-ray grating spaces of the crystals; and the subscripts refer to the two crystals, the data of which are employed. If M_1 in eq. 1 is the molecular weight of lithium fluoride, then we may obtain

$$M_{\mathrm{Li}} = \left(M_2 \frac{\rho_{\mathrm{LiF}}}{\rho_2} F R_g^3\right) - M_{\mathrm{F}} \qquad (2)$$

where the subscript 2 refers to the remaining four crystals. Thus, four solutions for the atomic weight of lithium result from which a weighted average may be obtained. From eq. 2 it is seen that a precise value for the atomic weight of fluorine is required. In fact, it is the addition of this precise value (see Table II) obtainable from nuclear reaction data that makes the present calculations possible.

TABLE I

X-RAY AND DENSITY DATA FOR CRYSTALS USED IN THE DETERMINATION OF THE ATOMIC WEIGHT OF LITHIUM

Chemical formula of crystal	$\vartheta_{20^\circ\mathrm{C.}}$ (degrees)	$\rho_{20^\circ\mathrm{C.}}$ (g./cm.^{3})
$CaCO_3$	6°42′34.9″ ± 0.3″[a,b]	2.71030[e] ±0.00005
NaCl	15°15′4.4″ ± 0.8″[c]	2.16360[f] ±0.00004
C	23°26′5.8″ ± 0.5″[a]	3.51540[g] ±0.00006
LiF	83°51′15.7″ ± 0.5″[d]	2.64030[h] ±0.00014
KCl	6°28′25.8″ ± 0.4″[a]	1.98827[i] ±0.00004

[a] Y. Tu, *Phys. Rev.*, **40**, 662 (1932). [b] A. Larsson, *Phil. Mag.*, [7] **3**, 1136 (1927). [c] M. Siegbahn, *Ann. Physik*, **59**, 56 (1919). [d] M. Straumanis, A. Ievens and K. Karlsons, *Z. physik. Chem.*, **B42**, 143 (1939). [e] J. A. Bearden, *Phys. Rev.*, **38**, 2089 (1931). [f] H. L. Johnston and D. A. Hutchison, *ibid.*, **62**, 32 (1942). [g] J. A. Bearden, *ibid.*, **54**, 698 (1938). [h] C. A. Hutchison and H. L. Johnston, THIS JOURNAL, **62**, 3165 (1940). [i] D. A. Hutchison, *Phys. Rev.*, **66**, 144 (1944).

Data for the Atomic Weight Determination.—The X-ray and density data employed in these calculations are summarized in Table I. The X-ray reflection angles, ϑ's, have been corrected to 20° from their most probable literature values by means of the relation

$$\log \sin \vartheta_{20^\circ\mathrm{C.}} = \log \sin \vartheta_{\mathrm{T}} - \frac{\alpha(20 - T)}{2.303} \qquad (3)$$

where α is the linear coefficient of expansion of the crystal and T is the centigrade temperature at which the reflection angle is reported in the literature. Also, the densities have been corrected to 20° by use of their linear temperature-expansion coefficients which are listed elsewhere[2] together with the appropriate literature references to the original data. The computed δ's which were used in making the refraction corrections to the ϑ's are listed in a previous paper.[2] The reflection orders of the X-ray angles are equal to one for all crystals except that for lithium fluoride which is equal to three. For diamond, sodium chloride and potassium chloride, the reflection angles are from the (100) plane, and for lithium fluoride and calcite, they are from the (111) and the natural cleavage planes, respectively.

The value of the atomic weight of lithium depends, as seen in eq. 2, upon the values of the atomic masses of the elements composing the crystals. Chemical atomic weights were used for all elements except fluorine. For fluorine the atomic mass computed from nuclear reaction data was employed. The conversion factor, 1.000272, was used to convert from the physical to chemical mass scale. The atomic masses based on the chemical

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[1] D. A. Hutchison, to be published elsewhere.

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

mass scale which were employed, and the references to the original data are summarized in Table II.

TABLE II

ATOMIC WEIGHTS EMPLOYED IN THE CALCULATIONS

Chemical symbol	Value (chem. mass scale)
C	12.0104[a] ± 0.0002
Cl	35.4570[b] ± 0.0005
F	18.999280[c] ± 0.000096
K	39.0960[d] ± 0.0005
Na	22.9970[b] ± 0.0005
Ca	40.085[e] ± 0.005

[a] G. P. Baxter and A. H. Hale, THIS JOURNAL, **59**, 506 (1937); A. F. Scott and F. H. Hurley, Jr., *ibid.*, **59**, 1905 (1937). [b] 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, THIS JOURNAL, **30**, 13 (1908); E. Zintl and A. Meuwsen, *Z. anorg. allgem. Chem.*, **136**, 223 (1924); O. Hönigschmid, S. B. Chan and L. Birckenbach, *ibid.*, **163**, 315 (1927); O. Hönigschmid and R. Sachtleben, *ibid.*, **178**, 1 (1929); A. F. Scott and C. R. Johnson, *J. Phys. Chem.*, **33**, 1975 (1929); O. Hönigschmid, THIS JOURNAL, **53**, 3012 (1931). [c] C. W. Li, W. Whaling, W. A. Fowler and C. C. Lauritsen, *Phys. Rev.*, **83**, 512 (1951). [d] T. W. Richards and A. Staehler, THIS JOURNAL, **29**, 623 (1907); T. W. Richards and E. Mueller, *ibid.*, **29**, 639 (1907); G. P. Baxter and W. M. MacNevin, *ibid.*, **55**, 3185 (1933); O. Hönigschmid and R. Sachtleben, *Z. anorg. allgem. Chem.*, **213**, 365 (1933); R. K. McAlpine and E. J. Bird, THIS JOURNAL, **63**, 2960 (1941). [e] O. Hönigschmid and K. Kempter, *Z. anorg. allgem. Chem.*, **163**, 315 (1927); **195**, 1 (1931).

Calculations and Results for the Atomic Weight of Lithium.—According to eq. 2 the atomic weight of lithium is dependent on the ratio, R_g, of the grating spaces of lithium fluoride and one of the other four crystals. The ratio has been computed by means of the expression,

$$R_g = \frac{n_{\text{LiF}} R_\lambda \sin \vartheta_2 (1 - \delta_2/\sin^2\vartheta_2)\xi}{n_2 \sin \vartheta_{\text{LiF}} \, (1 - \delta_{\text{LiF}}/\sin^2 \vartheta_{\text{LiF}})} \tag{4}$$

where ξ is a factor which corrects for the fact that the X-ray reflection angles are not from corresponding planes in the two crystals, and since the X-ray reflection angle for lithium fluoride was measured from its (111) plane while for diamond, sodium chloride and potassium chloride from their (100) planes, and for calcite from its natural cleavage plane, it follows that in each calculation the factor ξ is equal to $\sqrt{3}/2$. R_λ is the ratio of the wave lengths employed in the determination of X-ray reflection angles and was calculated from the reflection angles for the Cu$K\alpha_1$ and Mo$K\alpha_1$ lines from calcite as obtained by Bearden and Shaw,[3] and Larsson[4]; n is the order of the X-ray reflection; and δ, the unit decrement of the index of refraction[2] of a crystal, is defined by the expression, $\delta = 1 - \mu$, where μ is the index of refraction.

The results of the four solutions for the atomic weight of lithium are summarized in Table III. For the first three calculations F is unity since the crystals involved belong to the cubic system. For calcite, however, the unit cell is a rhombohedron of volume ϕd^3 where d is the Bragg spacing and ϕ is a function of the obtuse angle[5] between the crystal edges. The F-factor in calculation (4) thus becomes the reciprocal of ϕ. The R_λ is equal to 2.17199 (±1) in calculations (1), (3) and (4), and equal to 1.00000 (±2) in calculation (2). Although the numerical values obtained are equal, the probable errors are not. Hence, a most probable error for the weighted average of the four values has been obtained based on the most probable errors of the individual results. However, one cannot obtain the probable error of the final value directly from the probable errors of the individual results in Table III. The errors of the primary data (ϑ's, ρ's, etc.) for lithium fluoride were combined with the most probable average of the errors for the remaining four crystals. Thus, the final adopted value becomes

$$M_{\text{Li}} = 6.9364 \pm 0.0018$$

TABLE III

THE ATOMIC WEIGHT OF LITHIUM

Calculation no.	Mol. wt. compared	Rg	Calcd. atomic wt.
1	$M_{\text{LiF}}/M_{\text{KCl}}$	0.639860 ±0.000023	6.9364 ±0.0023
2	$M_{\text{LiF}}/M_{\text{NaCl}}$	0.713733 ±0.000012	6.9364 ±0.0020
3	$M_{\text{LiF}}/M_{\text{C}}$	1.128610 ±0.000047	6.9364 ±0.0020
4	$M_{\text{LiF}}/M_{\text{CaCO}_3}$	0.663048 ±0.000015	6.9364 ±0.0028
The most probable value and error:			6.9364 ±0.0018

Discussion and Conclusions

Apparently, the basis of adoption of the value 6.940, by the committee on Atomic Weights of the International Union of Chemistry must rest largely upon the work of Richards and Willard.[6] These workers made very precise measurements of the weight ratios, LiCl/AgCl, LiCl/Ag and LiCl/LiClO$_4$. From the LiCl/AgCl ratio they computed 6.9401 as the atomic weight for lithium, and from the LiCl/Ag ratio they obtained 6.9390, assuming in both cases the value 107.880 for the atomic weight of silver. The LiCl/LiClO$_4$ ratio was combined with the LiCl/Ag ratio to obtain a value of 107.871 for the atomic weight of silver. If the latter value is used to compute the atomic weight of lithium, the results are essentially the same as those quoted above. These workers obtained the error limits of ±0.0002 for their lithium atomic weight values by considering their final set of computed atomic weights as observed data. Such a method gives limits of precision and not of error. For example, on p. 31 of the first of the references cited, there are given seven values for the atomic weight of lithium, from which an arithmetic average is taken and a most probable error computed from the deviations from the average. Such a procedure does not take into account the systematic errors existing in the experimental work. One may, however, compute the probable error of the calculated result on the basis of the external and inter-

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

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

(5) J. A. Bearden, *Phys. Rev.*, **38**, 2089 (1931).

(6) T. W. Richards and H. H. Willard, THIS JOURNAL, **32**, 4 (1910); *Z. anorg. allgem. Chem.*, **66**, 229 (1910); Carnegie Institution Publication No. 25, 1 (1910).

nal consistency of the data by the method set forth by Birge.[7] Starting with the seven LiCl/AgCl weight ratios one may compute the most probable errors of these ratios, and make a least-squares propagation of these errors to the final lithium atomic weight values. If the probable errors of the atomic weight of lithium based on the seven determinations are computed on the basis of external and internal consistency and then their ratio is taken, the value, 1.94, is obtained. Now theory predicts that this ratio should deviate from unity by 18%; however, it varies by over five times that amount. This clearly shows the presence of systematic errors in the work even though the experimental work was performed with great precision. A partial explanation may be in the fact that one of the great problems for various workers at that time was the elimination of sodium impurity in their lithium chloride. In fact Richards and Willard[6] state that the purer they got their materials with respect to sodium impurity, the lower was their computed atomic weight for lithium. It should, therefore, not be surprising that a lower value is obtained in the present determination by the X-ray–density method which is practically insensitive to sodium impurities in the lithium fluoride.

The great consistency of the X-ray and density data employed in the present work is shown by the highly consistent results obtained in the previous application of it by the writer[2] to the determinations of atomic weights and by Birge[8] in his use of the data for the determination of the now best values for the Avogadro number and electronic charge. Thus, the value obtained for the atomic weight of lithium in the present determination is mainly dependent on the mass value of fluorine obtained from nuclear reaction data.

It may be noted that the present value for the atomic weight of lithium must be assumed in order to achieve agreement of the atomic weight of fluorine[2] from density and X-ray data with the atomic weights of fluorine obtained from chemical, mass spectrographic and nuclear reaction determinations.

[7] R. T. Birge, *Phys. Rev.*, **40**, 207 (1932).

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

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Solid Solutions of Lithium Oxide in Nickel Oxide

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The effect of gaseous atmosphere and temperature of diffusion on the solid solution of lithium oxide in nickel oxide has been studied. It is shown that the partial pressure of oxygen present during the solid solution determines its character and extent. The absence of excess oxygen prevents the formation of a vacancy free solid solution. The interoxide reaction proceeds to some extent at 600° but at this temperature it is probably limited to the surface layers. Even at 1100° the reaction within the interior of the oxide particles proceeds slowly.

Introduction

Mixed oxides have proved to be catalysts of very wide applicability and considerable interest has been shown in attempts to systematize their behavior and character. Huttig[2] and his co-workers have made intensive studies in which the physical state of such catalysts under varying temperature treatment were correlated with their subsequent catalytic activity. The greatest catalytic activity was found when intermediate states in the interoxide reaction were present. In these states, diffusion of one species over or into the other was occurring with the production of defect structures.

Verwey,[3] in studying mixed oxide systems with regard to their electrical properties, has made use of the principle of induced valence semiconductivity. For example, he has shown that the semiconductivity of nickel oxide can be altered markedly and in a controlled fashion by incorporating in the lattice lithium ions. The mixtures appeared to be homogeneous of composition $Li_\delta Ni_{1-2\delta}^{2+} Ni_\delta^{3+}O$, and up to 10 at. %, the Ni^{3+} was equivalent to the lithium added.

Hauffe[4] has used this principle as the basis of his theory of the corrosion of metal alloys and both he and Parravano have extended this to the general problem of oxide catalysis itself. Parravano[5] has shown that a correlation exists between the activation energy for the oxidation of carbon monoxide over a nickel oxide catalyst and the nature of the added ion. Hauffe[6] has used similar catalysts for the decomposition of nitrous oxide but the correlation in this case was not so simple.

The formation of these catalysts involves a high temperature diffusion of both lithium and oxygen ions into the nickel oxide matrix. Accordingly, some experiments have been carried out to investigate how the resulting solid solution depends on the temperature and the gaseous atmosphere of the diffusion process.

Experimental

Preparation of Solid Solutions.—A series of mixtures of nickel oxide and lithium oxide (containing in turn 0.00, 0.5, 1.0, 5.0, 10.0 and 50.0 atomic % lithium oxide) were prepared as follows. Finely ground nickel carbonate (80 mesh) was made into a smooth paste with the appropriate amount of a solution of lithium carbonate in very dilute acetic acid. These mixtures, with the exception of half the 5.0 at. % Li mixture, were then heated in air at 600° for three hours to decompose the carbonates. The second half of the 5.0 at. % Li mixture was heated at 600° for three hours under continuous evacuation. The seven decomposed mixtures were

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[1] Psychology Laboratory, Cambridge University, Cambridge, England.

[2] G. Huttig, *J. chim. phys.*, **36**, 84 (1939).

[3] E. J. W. Verwey, *Phillips Res. Rep.*, **5**, 173 (1950).

[4] K. Hauffe, *Werkstoffe u. Korrosion*, **2**, 131, 221, 243 (1951).

[5] G. Parravano, THIS JOURNAL, **75**, 1452 (1953).

[6] K. Hauffe, *Z. physik. Chem.*, **201**, 223 (1952).