Br^{80} (18 min.) results in much less reaction of the daughter activity with carbon tetrachloride than it does in the liquid and solid. These observations lead to the conclusion that the reaction in the condensed phases is due to the reaction of Br^{80} (18 min.) atoms with free radicals which are produced as by-products of the transition process.

2. It is suggested that chemical reactions which lead to the separation of the daughter activity from the parent activity of the Br^{80} transition may be classified under three types.

3. Chemical evidence indicates that at least 90% of the Br^{80} (4.4 hr.) $\rightarrow$ Br^{80} (18 min.) transitions occur with the emission of a conversion electron rather than a gamma ray.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Determination of Crystal Densities by the Temperature of Flotation Method. Density and Lattice Constant of Lithium Fluoride

BY CLYDE A. HUTCHISON* AND HERRICK L. JOHNSTON

Submergence in liquids of different density has been employed by mineralogists for many years as a routine method of distinguishing qualitatively between minerals of different specific gravity. The method was made quantitative by Retgers,[1] by the procedure of determining the densities of two close compositions of a binary mixture of organic liquids, in one of which the specimen would rise while in the other it would sink. Retger's method has been employed more recently as one of the relatively accurate methods of crystal density measurement[2] but has the disadvantage of relative difficulty in securing fine adjustment for close bracketing.

Lewis and MacDonald[3] used the temperature change of liquid density in conjunction with crystal "flotations," in a semi-quantitative way, as a densimetric method of determining relative atomic weights. This method is essentially the "free submerged float" method[4] employed extensively for the isotopic analysis of water. We have found it possible to develop this as a precision method of densimetric analysis which, for lithium fluoride, is capable of giving relative densities to within an error limit of about $\pm 5 \times 10^{-6}$ g./ml. and of giving absolute densities to within an error about 10 times larger. The latter could be somewhat improved upon.

Experimental

Procedure.—The details of the procedure, and techniques employed, that apply to the relative as well as to the absolute density determinations will be described elsewhere[5] and will not be elaborated here, except to outline the general steps.

1. Crystals of high purity, physically uniform, were prepared by an adaptation of the method of Kyropoulos[6] and were carefully annealed. Fragmentation along sharp fault lines occurred at a step prior to the annealing. Clear fragments were produced. Fragments that revealed no blemishes under a magnifying glass were chosen for the flotations.

2. A stable flotation liquid of the proper density, and constancy of density toward evaporation, was prepared by vacuum distillation of bromoform into a mixture of *n*-hexanol and *n*-pentanol. The composition of the final satisfactory mixture was: 115.7 g. of bromoform with 170 drops of hexanol (68 drops equal 1 ml.) and 149 drops of pentanol. This liquid was calibrated against water by hydrostatic weighings to obtain values of its density and of its density–temperature coefficient. Individual densities were reproducible to within about ± 0.00005 g./ml., and 17 points in two series of runs[5] over a 3° temperature range gave a good straight line with a slope of -2.49 $(\pm 0.01) \times 10^{-3}$ g./ml./degree.

3. Crystal fragments of lithium fluoride prepared from high purity lithium carbonate of supposedly normal isotope composition, were floated submerged in the bromoform mixture. Flotations were carried out in a glass-stoppered tube of about 15 mm. diameter, which was immersed in a small water-bath with transparent windows in the sides. The temperature of the water-bath was controlled manually to within $\pm 0.001°$ and narrow limits of temperature were established that distinguished between the rise and the fall of the crystals. A telescope with crosshair was used in making observations and it was possible to fix the flotation temperature of an individual crystal to within $\pm 0.002°$. Ordinarily it is possible to obtain

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(1) Retgers, *Z. physik. Chem.*, **3**, 289 (1899).

(2) Spangenberg, *Z. Krist.*, **57**, 497 (1922); Wulf and Heigl, *Z. physik. Chem.*, **A153**, 187 (1931); Kohler, *Z. Physik*, **78**, 375 (1932).

(3) G. N. Lewis and R. T. Macdonald, THIS JOURNAL, **58**, 2519 (1936).

(4) G. N. Lewis and R. T. Macdonald, *J. Chem. Phys.*, **1**, 341 (1933).

(5) H. L. Johnston and C. A. Hutchison, *ibid.*, **8**, Nov. issue (1940).

(6) Kyropoulos, *Z. anorg. Chem.*, **154**, 308 (1926).

agreement among a majority of the different fragments of the same isotopic composition to within ±0.002 or 0.003°. Usually those crystals which do not agree give *high* results, widely diverse among themselves. These are attributed to blemishes or undetected cracks.

4. With the aid of the density–temperature coefficient, the several values of density of the bromoform mixture were corrected individually to the temperature of crystal flotation. The average of these corrected densities is the density of lithium fluoride at the flotation temperature.

Experimental Description

(a) **Materials.**—Purification of *lithium fluoride* and preparation of the *bromoform mixture* are described elsewhere.[5] *Water* used in the hydrostatic weighings was purified by the usual methods.

(b) **The Hydrostatic Weighings.**—Densities of the bromoform mixture were determined by measuring its buoyant effect, and that of pure water, on a Pyrex glass bulb weighted with mercury. The bob had been in service for some months and had attained constant volume. Prior to the series of weighings, the bob and its 0.004″ diameter platinum suspension were thoroughly cleaned and dried. Just before the measurements the fine platinum suspension wire was heated in the flame of a Fisher burner to reduce the already small correction for surface tension (*cf.* Bartell, Culbertson and Miller, *J. Phys. Chem.*, **40**, 881 (1936)). Although this treatment may not have completely eliminated surface tension effects, it must have reduced them to a magnitude no greater than the errors imposed by other factors in the determinations.

The weights used were calibrated just before use against a set of standard weights recently calibrated by the U. S. Bureau of Standards.

The weight of the bob in vacuum (bob in vacuum and weights in vacuum) was 26.1904 g.

(c) **Thermometry.**—The density–temperature coefficient of the bromoform mixture was measured in terms of readings on a sensitive Beckmann thermometer with a uniform scale. The crystal flotation was measured in terms of the same Beckmann.

Hydrostatic weighings in *water*, for the purpose of obtaining the float volume, are expressed in terms of the readings of a 23–28° mercury in glass thermometer, graduated in intervals of 0.02°, and calibrated at even degrees by the U. S. Bureau of Standards. A comparison of the two thermometers gave: Standard 28.000° = Beckmann 4.723°.

Data

(a) **Crystal Flotation.**—Four crystal fragments were floated. Three of these floated at an average temperature (Beckmann) of 4.389° with an average deviation from the mean of 0.003°. Although this agreement is not quite so good as usually obtained[5] the influence of this factor on the final result is only 0.00001° in the density of lithium fluoride, which is less than the limits of uncertainty imposed by the results of hydrostatic weighings.

(b) **Weighings in Water and Volume of the Bob.**—Two reliable weighings in water, in addition to one obtained some months previously, were made. Each weighing was made at a different thermostat temperature. These weighings (with brass weights corrected to vacuum) are recorded in Table I together with: (1) the standard density of water at the thermostat temperature[7]; (2) the volume of the bob computed directly from the difference of weighings in water and in air; and (3) the bob volume at 28.00° computed from (2) with the aid of the thermal expansion coefficients for Pyrex.[8]

TABLE I

VOLUME OF THE BOB

T, °C.	Wt. in H_2O	d_{H_2O}	Bob volume	Volume at 28.00°
27.254	17.1170	0.9964665	9.10549	9.10557
27.795	17.1179	.9963204	9.10601	9.10603
27.612	[a]	.9963721	9.10583	9.10587
Average value for the volume at 28.00°				9.10582 ± 0.0002

[a] This is the older weighing. Some differences in the suspension make direct comparison of the water weighings of no significance. The older weighings (reduced to vacuum) were: bob in air, 25.7324; bob in H_2O 16.6596.

The average of the volumes computed from these weighings (9.10582 at 28.00°) was used to determine values for the densities of the bromoform mixture.

(c) **Weighings and Densities in the Bromoform Mixture.**—Eight weighings, at various temperatures, were carried out in the bromoform mixture. These weighings, corrected to vacuum, are given in Table II, which also gives the densities computed from these data. Corrections for the thermal expansion of the Pyrex float[8] were applied. Temperatures are recorded in terms of the Beckmann thermometer readings since the temperature–density coefficient of the liquid and the flotations of the crystals are in terms of the Beckmann readings.

TABLE II

DENSITIES OF THE BROMOFORM MIXTURE

Bob volume taken as 9.10582 cc. at Beckmann 4.723°

Detn.	*T* (Beckmann)	Weight in liquid	Density (at *T*)	Density (at *T* = 4.389°)
1	3.983	2.1572	2.63935	2.63834
2	4.226	2.1623	2.63878	2.63837
3	4.346	2.1648	2.63847	2.63836
4	4.442	2.1668	2.63825	2.63838
5	4.556	2.1694	2.63796	2.63837
6	4.685	2.1732	2.63753	2.63826
7	3.939	2.1558	2.63947	2.63835
8	4.853	2.1764	2.63718	2.63833
			Average density at 4.389°	2.63835

(d) **Density of Lithium Fluoride.**—Each of the eight determinations of density was used to compute the density of the bromoform mixture at a Beckmann temperature of 4.389°, equal to 27.67°. This was done by applying the experimental density–temperature coefficient 2.49 × 10^{-3} g./ml./degree to the entries in Column 4 of Table II. The results of these computations are given in the fifth column of the table, together with their average.

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(7) "International Critical Tables," Vol. 3, McGraw-Hill Book Co., New York, N. Y., 1927, p. 25.

(8) R. M. Buffington, THIS JOURNAL, **48**, 2305 (1926).

Since 4.389° was the temperature of crystal flotation, this average is the density of lithium fluoride at 27.67°. Correction to 25° by use of 1.00×10^{-4} as the volume coefficient of thermal expansion, based on Adenstadt's[9] interferometric determination of the linear coefficient, gives

$$d_{25} = 2.63905 \pm 0.0001 \text{ g./cc.}$$

The principal source of error in this determination is in the ±0.0002 cc. variation in the determination of bob volume (Table I), with an equal uncertainty arising from possible effects of surface tensions. Lesser errors arise from: (a) the 0.003 to 0.004° uncertainty which may be ascribed to the flotation temperature (*cf. infra*); (b) ±0.0001 g. in the weight of the bob in air and (c) an average variation of less than 0.00003 from the mean value of the weighings in the bromoform mixture (Table II).

The only direct determinations, in the literature, for the density of lithium fluoride are the inaccurate value 2.587 g./cc. determined by Henglein[10] and the value 2.639 ± 0.015 (cor. to 25°) by Spangenberg.[2]

Lattice Constant of Lithium Fluoride.—The most accurate determinations of crystal density have been for the purpose of establishing standards of X-ray wave length[11] or, through that, values of basic physical constants. The accuracy of our value for lithium fluoride is comparable to these and it appears worth while therefore to employ it to calculate the edge length of the unit cell in the lattice of lithium fluoride.

With the International values of the atomic weights of lithium and of fluorine, and with Avogadro's number taken[12] as 6.064×10^{23}, we obtain $a_{25} = 4.01736$ Å. This is subject to an uncertainty of ±0.00050 Å due to an uncertainty of 0.01 unit in the atomic weight of fluorine,[13] but to an uncertainty of only ±0.00004 Å. from the 0.0001 unit uncertainty in density.

Comparison with the more recent X-ray measurements, based on the Siegbahn scale, and with one value from electron diffraction, is shown in Table III.

TABLE III

LATTICE CONSTANTS OF LiF

Author	a, Å. (25°)
Ott[14] (1926) corrected to 25°[9]	4.0201 ± 0.0020
Moeller[15] (1937) corrected to 25°[9]	4.0205 ± 0.0002
Straumanis, Ievins and Karlsons[16] (1939)	4.01807 ± 0.00004
Finch and Fordham[17] (1936) (electron diffraction)	4.027 ± 0.005
Computed from density (F = 19.00 and N = 6.064×10^{23})	4.01736 ± 0.00004

For proper comparison, the X-ray values, which are based on Siegbahn's wave length scale which in turn is based on $a_{\text{NaCl}} = 5.62800$ Å. at 20° should be recomputed to correspond to an NaCl lattice constant based on $d_{\text{NaCl}} = 2.1638$[18] and on $N = 6.064 \times 10^{23}$. With these latter assignments a_{NaCl} at 20° comes out 5.62694 Å. and there results a correction to the X-ray values of a_{LiF} of −0.00075 Å.

When this correction is applied to Straumanis, Ievins and Karlsons' latest X-ray value for lithium fluoride the result is $a_{25°} = 4.01732$ Å. The result is in fortuitously perfect agreement with our density value of $a_{25°} = 4.01736$ Å. since an uncertainty that may approach 0.00050 Å. attaches to our value through a 0.01 unit uncer-

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(9) Adenstadt, *Ann. Physik*, **26**, 69 (1936).

(10) Henglein, *Z. anorg. allgem. Chem.*, **120**, 77 (1921).

(11) (a) O. K. Defoe and A. H. Compton, *Phys. Rev.*, **25**, 618 (1925).

d_{20} NaCl = 2.1632 ± 0.0004
d_{20} Calcite = 2.7102 ± 0.0004

(*b*) J. A. Bearden, *ibid.*, **38**, 2089 (1931).

d_{20} Calcite = 2.71026 ± 0.00003

(*c*) Y. Tu, *ibid.*, **40**, 662 (1932).

d_{18} Calcite = 2.71003 ± 0.00005
d_{18} NaCl = 2.16418 ± 0.00014
d_{18} KCl = 1.98930 ± 0.00014
d_{18} Diamond = (3.5141, 3.5142) ± 0.0001

(d) J. A. Bearden, *ibid.*, **54**, 698 (1938).

$d_{23.5}$ Diamond = 3.51536 ± 0.00004

Except for diamond all of the above determinations were made by hydrostatic weighings of relatively large crystals in air and in a liquid (such as water) whose density was either known or was determined separately. The diamond determinations were made by rough flotations in mixtures of thallous formate and thallous malonate diluted with the proper amount of water to adjust the density. The results of Y. Tu are inconsistent with those of Bearden.

(12) R. T. Birge, *ibid.*, **40**, 228 (1932).

(13) "Ninth Report of the Committee on Atomic Weights of the International Union of Chemistry," THIS JOURNAL, **61**, 223 (1939).

(14) Ott, *Z. Krist.*, **63**, 222 (1926).

(15) Moeller, *ibid.*, **97**, 170 (1937).

(16) Straumanis, Ievins and Karlsons, *Z. physik. Chem.*, **B42**, 143 (1939).

(17) Finch and Fordham, *Proc. Phys. Soc.* (London), **48**, 85 (1936).

(18) This is a weighted average of Tu's value[11] corrected to 20° (d_{20} = 2.1640 ± 0.0002) and that of De Foe and Compton[11] (2.1632 ± 0.0004). Bearden[11d] points out that there appears to be some sort of systematic error in Tu's value for calcite as well as that for diamond. Tu's measurements on diamond were comparatively crude and involved quite a different method than that he employed with the salts. His results on diamond should, therefore, not be considered in judging the reliability of his data on the salts. Corrected to 20°, Tu's value for calcite is about 0.0003 unit lower than that of Bearden, and within the limits of error of DeFoe and Compton. However, his d_{NaCl} at 20° is already 0.0008 of a unit above that of the latter authors, and outside of their expressed limits of error. A systematic error such as Bearden suggests would further increase the discrepancy. It appears to us that the intermediate assignment of $d_{20°}$ = 2.1638 is the best representation of the data and is probably within 0.0002 to 0.0004 unit of the correct value. It is apparent that d_{NaCl} should be repeated.

tainty in the atomic weight of fluorine and an uncertainty of at least 0.00020 Å. attaches to the X-ray value through an uncertainty of at least 0.0002 unit in the density of sodium chloride. The agreement is adequate, however, to indicate the possibility of using X-ray measurements on lithium fluoride, in conjunction with its density, as a means of comparing the atomic weight of fluorine with that of chlorine when improved determinations are available for the latter, or as a new foundation for a wave length standard.

The above comparison has no immediate bearing on the present dilemma regarding the experimental values of the fundamental physical constants, *e*, *m*, *N* and *h*.[19] If, however, the dilemma is settled in a manner that does not do violence to the classic conceptions of the interaction between X-radiation and the crystal lattice (and this does not appear probable) and independent methods of wave length determination are unambiguously established,[20] it will be possible (with an independent improved atomic weight of fluorine) to obtain a very precise value for Avogadro's number through density and X-ray measurements on lithium fluoride alone.

It would be possible to reduce the present limits of accuracy in the density of lithium fluoride by a factor of three to five if that were important.

Summary

A method is described for determining the densities of crystals to the fifth decimal place, which is a combination of "temperature flotation" of small crystals with calibration of the flotation liquid by hydrostatic weighings.

By this means the density of lithium fluoride was found to be $d_{25} = 2.63905 \pm 0.0001$. This value of the density was used to compute the lattice constant of lithium fluoride. With the atomic weight of fluorine taken to be 19.00 and Avogadro's number taken as 6.064×10^{23}, this yields $a_{25} = 4.01736 \pm 0.00004$ Å. However, an additional uncertainty that may be as high as ± 0.00050 Å. attaches to this due to an uncertainty of 0.01 unit in the atomic weight of fluorine.

Corrected to a wave length scale which also uses $N = 6.064 \times 10^{23}$ and takes the density of sodium chloride (20°) as 2.1638, recent X-ray measurements of Straumanis[16] yield $a_{25} = 4.01732 \pm 0.00004$ Å. in complete agreement with the above figure. An additional uncertainty of at least 0.00020 Å. attaches to this value from a minimum uncertainty of 0.0002 unit in the density of sodium chloride.

The possible future utility of a combination of density and X-ray measurements on lithium fluoride in providing a standard of wave length measurements, in determining a precise value of Avogadro's number or in comparing the atomic weight of fluorine with that of chlorine is pointed out.

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(19) For general reviews of this topic *cf.* Compton and Allison, "X-Rays in Theory and in Practice," Van Nostrand, 1935, pp. 694–704 and DuMond, *Phys. Rev.*, **56**, 153 (1939). It should be noted that in computing a lattice constant of 4.01736 Å. for LiF we are less interested in its absolute value than in its comparison with the latest X-ray value. For this purpose it is only important that we use the *same* value for Avogadro's number as employed, in conjunction with NaCl, in fixing a standard of X-ray wave length. As an absolute value $a_{\mathrm{LiF}} = 4.01736$ Å. is subject to the same proportionate uncertainty as exists in the choice $N = 6.064 \times 10^{23}$ for Avogadro's number, and may readily be corrected to such value of the latter constant as may be ultimately agreed upon.

(20) J. A. Bearden, *ibid.*, **37**, 1210 (1931); **47**, 884 (1935); **54**, 698 (1938).