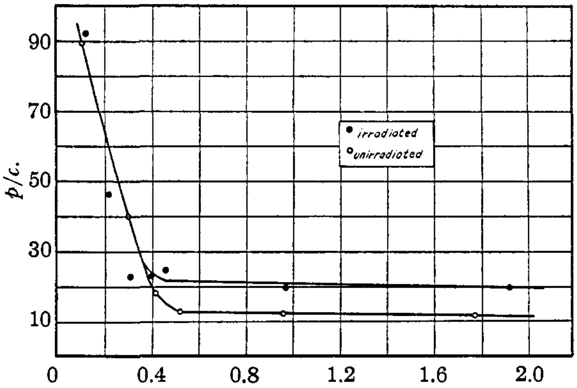
TABLE III

EFFECT OF ULTRAVIOLET LIGHT ON MOLECULAR WEIGHT OF METHYL CELLULOSE

Irradiation, hours	(M. W.) viscosity, by extrapolation	(M. W.)$_{\text{Osm.p.}}$, from approx. 2% soln.	Copper number (2% solution)
0	53,000	44,000	0.01
8		42,000	.03
30		38,000	.22
73	24,000	26,000	.95

ing properties due, probably, to a rupturing of the glycosidic linkages of the substituted "glucose anhydride" units.

Preliminary work on the effect of concentration on the osmotic pressure of methyl cellulose solutions shows that by plotting *p/c versus c* a curve is obtained (see Fig. 4) in which a break occurs at a concentration of about (0.45–0.50%) which is in agreement with that of Schulz[22] although the shapes of the curves are different. However, these curves are similar to those reported by Herz[23] for Cellit in methyl glycolacetate.



Concentration in volume %.

Fig. 4.—Variation of *p/c* with *c*.

Acknowledgments.—The authors are indebted to the Dow Chemical Company for the samples of Methocel furnished for this investigation. They also wish to thank Mr. R. G. MacDonald, Secretary of the Technical Association of the Pulp and Paper Industry, for obtaining certain information concerning end group determinations. Our special thanks go to Mr. M. C. Anderson for making some of the equipment used in this research, and also to Mr. J. R. Murphy for his help in preparing the manuscript.

Summary

Using a quartz capillary mercury arc lamp to furnish ultraviolet light, an out-gassed sample of methylcellulose in water was irradiated in a stoppered quartz flask. Viscosity, osmotic pressure, and copper number data show that the methyl cellulose molecule is degraded. A molecular weight of about 50,000 for methyl cellulose is in harmony with results obtained by other investigators for various cellulose derivatives. A modification of the Heyes micro copper number procedure for cellulose was developed and applied to the degraded methyl cellulose solutions.

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[22] G. V. Schulz, *Z. physik. Chem.*, **A158**, 237 (1932); **A176**, 317 (1936); **A177**, 453 (1936); *Z. Elektrochem.*, **42**, 692 (1936); *Angew. Chem.*, **49**, 863 (1936).

[23] M. Ulmann, "Molekulgrossen-Bestimmungen hochpolymerer Naturstoffe," Leipzig, 1936, p. 78, work of W. Herz in *Cellulosechem.*, **15**, 95 (1934).

TROY, N. Y. RECEIVED MARCH 6, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BUFFALO AND THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Atomic Weight of Fluorine Calculated from Density and X-Ray Data

BY CLYDE A. HUTCHISON AND HERRICK L. JOHNSTON

A precise value for the density of lithium fluoride, determined by a "temperature of flotation" technique, has been reported recently by Hutchison and Johnston.[1,2] In the present paper this density value is used to compute a value for the atomic weight of fluorine.

The following values are also used in the computation: (a) the ratio between the true grating spaces for calcite and lithium fluoride determined from the X-ray measurements of Bearden and Shaw[3] and of Straumanis, Ievins and Karlsons[4]; (b) the cleavage angles for calcite determined by Bearden[5]; (c) the density of calcite determined by Bearden[5]; (d) the linear coefficient of ex-

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[1] C. A. Hutchison and H. L. Johnston, THIS JOURNAL, **62**, 3165 (1940).

[2] H. L. Johnston and C. A. Hutchison, *J. Chem. Phys.*, **8**, 869 (1940).

[3] Bearden and Shaw, *Phys. Rev.*, **48**, 18 (1935).

[4] Straumanis, Ievins and Karlsons, *Z. physik. Chem.*, **B42**, 143 (1939).

[5] Bearden, *Phys. Rev.*, **38**, 2089 (1931).

pansion for lithium fluoride determined by Adenstadt[6]; (e) the molecular weight of calcite; (f) the atomic weight of lithium.

The above quantities are related by the equation

$$M_{\mathrm{F}} = \left(\frac{M_{\mathrm{CaCO_3}} \times \rho_{\mathrm{LiF}}}{\rho_{\mathrm{calcite}} \times \varphi_{\mathrm{calcite}}} \times R_{\mathrm{g}}^{3}\right) - M_{\mathrm{Li}} \qquad (1)$$

in which M denotes an atomic or molecular weight; ρ denotes a density; φ denotes the volume of a calcite cleavage rhombohedron for which the distance between opposite faces is unity; and R_{g} denotes the ratio between the true grating spaces for lithium fluoride and calcite.

The Values of the Quantities in Equation (1)

The Density of Lithium Fluoride.—The density of lithium fluoride at 20°, from the data of Hutchison and Johnston,[1] is 2.64030 ± 0.0001 g./cc. This value at 20° is computed from the value, 2.63835 ± 0.0001 g./ml.[7] determined at 27.67° by use of 1.00×10^{-4} as the volume coefficient of thermal expansion, based on Adenstadt's[6] interferometric determination of the linear coefficient of expansion.

The Density of Calcite.—The value of the density of calcite at 20° has been given by Bearden[5] as 2.71030 ± 0.00003 g./cc. This value is based on densities of calcite determined by Bearden[5] and by Defoe and Compton.[8]

The Cleavage Angles of Calcite.—The value of $\varphi_{\mathrm{calcite}}$ has been computed by Bearden[5] to be 1.09594 at 20°. This value is based upon the mean of values for the cleavage angles determined by two independent methods.

The Ratio of the Values of the True Grating Spaces of Calcite and Lithium Fluoride.—Bearden and Shaw,[3] using a double crystal spectrometer, have determined X-ray wave lengths relative to the grating space of calcite. Assuming the Siegbahn[9,3] arbitrary value of 3.02904 Å. for the *effective* first order grating space at 18° (which is equivalent to 3.02945 Å. for d_∞ at 18°[10,3] or 3.02951 Å. for d_∞ at 20°[11]) they found the copper K_{α_1} line to have a wave length of 1.537400 Å. and the chromium K_{α_1} line to have a wave length of 2.284987 Å.

Straumanis, Ievins and Karlsons[4] have determined d_∞ for LiF relative to the wave lengths of the copper K_{α_1} line and chromium K_{α_1} line. Assuming the copper K_{α_1} line to have a wave length of 1.537395 Å. and the chromium K_{α_1} line to have a wave length of 2.28503 Å., they computed the value of twice d_∞ for lithium fluoride to be 4.01808 ± 0.00004 Å. and 4.01807 ± 0.00004 Å., respectively, at 25°. This value may be corrected to 20°, using 0.34×10^{-4} as the linear coefficient of thermal expansion.[6] The value computed for 20° is 4.01739 ± 0.00004 Å. The value of R_{g} is then $4.01739/(2 \times 3.02951)$.

The Molecular Weight of Calcite.—The atomic weight of calcium given by Birge,[12] 40.075 ± 0.005, is used in computing the molecular weight of calcite. This value of the atomic weight of calcium is based on the work of Richards and Hönigschmid[13] and is in agreement with the more recent value of Kendall, Smith and Tait.[14] Hönigschmid and Kempter,[15] however, have reported a value as high as 40.085 for the atomic weight of calcium. Using the value of the atomic weight of carbon given in the 1940 table of International Atomic Weights,[16] the molecular weight of calcite is found to be 100.085 ± 0.005.

The Atomic Weight of Lithium.—The value used for the atomic weight of lithium, 6.9390, is based upon the work of Richards and Willard.[17]

Mass spectrographic determinations have led to a value of 6.937.[18] A mass spectrographic determination by Brewer[19] yielded the value 6.939.

The Atomic Weight of Fluorine

The values used in calculating the atomic weight of fluorine by Equation (1) are listed in Table I.

TABLE I

Density of lithium fluoride at 20°[1]	2.64030 g./cc.
Density of calcite at 20°[5]	2.71030 g./cc.
Value of $\varphi_{\mathrm{calcite}}$ at 20°[5]	1.09594
Ratio of the true grating spaces at 20°[3,4]	0.663045
Molecular weight of calcite[12,16]	100.085
Atomic weight of lithium[17]	6.9390

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[6] Adenstadt, *Ann. Physik*, **26**, 69 (1936).

[7] Density values are given by Hutchison and Johnston[1] as g./cc. whereas what was really determined was g./ml. The discrepancy in units results in an error smaller than the experimental error.

[8] Defoe and Compton, *Phys. Rev.*, **25**, 618 (1925).

[9] M. Siegbahn, "Spectroscopie der Röntgenstrahlen."

[10] $d = d_\infty\ (1 - 0.000135)$ where d_∞ is the grating space corrected for refraction and d is the *effective* first order grating space.

[11] This calculation is based on the thermal expansion data for calcite of C. D. Cooksey and D. Cooksey, *Phys. Rev.*, **36**, 85 (1930).

[12] Birge, *Phys. Rev. Supplement*, **1**, No. 1, 1 (1929).

[13] Richards and Hönigschmid, THIS JOURNAL, **32**, 1577 (1910).

[14] Kendall, Smith and Tait, *Nature*, **131**, 688 (1933).

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

[16] Baxter, *et al.*, THIS JOURNAL, **62**, 699 (1940).

[17] Richards and Willard, *ibid.*, **32**, 10 (1910); *Z. anorg. allgem. Chem.*, **66**, 237 (1910); *Carnegie Inst. Pub.*, No. 25, 1 (1910).

[18] O. Hahn, *Ber.*, **70**, 1 (1937); **71**, 1 (1938).

[19] Brewer, *Phys. Rev.*, **49**, 867 (1936).

The result obtained for the atomic weight of fluorine is 18.9935.

The largest uncertainty entering into the *comparison* of the atomic weight of fluorine with the molecular weight of calcite and the atomic weight of lithium is the uncertainty in the density of lithium fluoride. This uncertainty is about one part in 26,000 or ±0.0010 in the atomic weight of fluorine. (As has been stated,[1] this uncertainty could be reduced by a factor of three to five.) The atomic weight of fluorine, if $CaCO_3$ = 100.085 and Li = 6.9390, is therefore 18.9935 ± 0.0010.

Birge has estimated the probable uncertainty in the molecular weight of calcite as ±0.005. Richards and Willard[17] state the atomic weight of lithium as 6.9390 with a probable error of less than 0.0002. The uncertainty in the computation of the absolute value of the atomic weight of fluorine is largely due to the uncertainty in the atomic weight of calcium. Using Birge's reasonably stated probable uncertainty in the molecular weight of calcite the resulting probable error for the atomic weight of fluorine is ±0.0013. The atomic weight of fluorine may therefore be stated as 18.9935 ± 0.0015.

If the atomic weight of calcium is as large as Hönigschmid and Kempter's[15] value of 40.085, the atomic weight of fluorine becomes 18.996 instead of 18.994.

The atomic weights of fluorine obtained by various physical methods are summarized in Table II.

TABLE II

Mass spectrographic determinations[18,20]	18.999
Gas density method, Cawood and Patterson,[21] using CF_4	18.995
Gas density method, Cawood and Patterson,[21] using CH_3F	18.997
Gas density method, Moles and Toral,[22] using SiF_4	18.995
From X-ray and density data, Hutchison and Johnston	18.994

The value calculated in this paper is seen to be in agreement with the gas density determinations on carbon tetrafluoride and silicon tetrafluoride, but not with the mass spectrographic value.

Summary

Available X-ray and density data on lithium fluoride and calcite have been used to compute the atomic weight of fluorine.

The value of the atomic weight of fluorine is found to be 18.9935 ± 0.0015, if the molecular weight of calcite is taken as 100.085 ± 0.005. The probable uncertainty stated is largely due to the uncertainty in the molecular weight of calcite.

The computed atomic weight of fluorine is in agreement with the results of gas density determinations on carbon tetrafluoride and silicon tetrafluoride, but not with mass spectrographic determinations.

BUFFALO, N. Y.
COLUMBUS, OHIO RECEIVED JANUARY 23, 1941

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[20] This mass spectrographic value is in agreement with computations of the mass of F^{19} from nuclear reaction data, using the best available values for other masses involved (Livingston and Bethe, *Rev. Mod. Phys.*, **9**, 245 (1937)). It also agrees with theoretically computed values of the mass (Barkas, *Phys. Rev.*, **55**, 691 (1939)).

[21] Cawood and Patterson, *Trans. Roy. Soc.* (London), **A236**, 77 (1936).

[22] *Z. anorg. allgem. Chem.*, **236**, 225 (1938).

[CONTRIBUTION NO. 426 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Heat Contents of Bivalent Sulfates in Extremely Dilute Aqueous Solutions

BY A. L. ROBINSON AND W. E. WALLACE*

Young and Seligmann[1] have shown that the limiting derivative of the apparent molal heat content with respect to the square root of the concentration ($S = d\Phi L_2/dc^{1/2}$) is in striking agreement with the prediction of the Debye–Hückel limiting law for a number of salts of the 1–1 and 1–2 valence types. They also state that an incomplete study of salts of the alkaline earth metals (2–1 type) indicates similar agreement. They find, however, that existing data for salts of the 2–2 valence type, if treated by their methods, do not lead to limiting values in agreement with theory.

Recently we have applied a modification of the method of Young to new heat of dilution data for sodium sulfate at 15 and 20°.[2] The modified treatment seems to extend the usefulness of the method, particularly in the very dilute concentration region ($c^{1/2} < 0.05$), and to afford simplification of the type of equation chosen to represent

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* Research Fellow in Chemistry. The research, in collaboration with the Geophysical Laboratory, was made possible by a grant from the Carnegie Institution of Washington.

[1] T. F. Young and P. Seligmann, THIS JOURNAL, **60**, 2379 (1938).

[2] W. E. Wallace and A. L. Robinson, *ibid.*, **63**, 958 (1941).