TABLE IV

RELATIVE PARTIAL MOLAL HEAT CONTENT AND HEAT CAPACITY. CONSTANTS OF EQUATION (7)

m	$\bar{L}_{2(0)}$	α	β	$(\bar{C}_p - \bar{C}_{p0})_{18}$	$(\bar{C}_p - \bar{C}_p)_{18-25}$
0.1	− 23	4.6	0.015	5.1	6.4
.2	− 140	8.2	.023	9.0	9.1
.3	− 210	11.8	.027	12.8	11.1
.5	− 400	17.3	.036	18.6	14.4
.7	− 580	21.8	.044	23.4	17.1
1	− 830	23.5	.049	25.3	20.4
1.5	−1140	27.4	.055	29.4	(25)
2	−1390	30.6	.061	32.8	(29)
2.5	−1600	33.6	.066	36.0	(33)
3	−1790	37.0	.073	39.6	(35)
3.5	−1940	41.4	.079	44.2	(38)
4	−2020	43.2	.086	46.3	(41)

sults. However, values of $(\bar{C}_p - \bar{C}_{p0})$ up to 1 M have been determined by Randall and Rossini[6] by heat measurement. In the fifth column of the table are given values of this quantity computed from our results by the equation

$$(\bar{C}_p - \bar{C}_{p0}) = \alpha + 2\beta t \qquad (8)$$

In the last column the values computed by Rossini's equation are given.[7] Those in parentheses are extrapolated by this equation to regions of concentration where experimental results were not available. The agreement between the calorimetric and electromotive force determinations although fairly good does not equal that recently obtained with potassium hydroxide and potassium chloride solutions.[5]

Summary

1. The electromotive forces of the cells

Ag–AgBr | NaBr (m) | Na_xHg | NaBr (0.1) | AgBr–Ag

have been obtained at temperatures from 0 to 40° inclusive and at concentrations, m, varying from 0.1 to 4 M.

2. From these, the activity coefficient, relative partial molal heat content and heat capacity of sodium bromide have been calculated.

NEW HAVEN, CONN. RECEIVED AUGUST 7, 1937

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[6] Randall and Rossini, THIS JOURNAL, **51**, 323 (1929).

[7] Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

The Atomic Weight of Carbon. The Ratio of Benzoyl Chloride to Silver[1]

BY ARTHUR F. SCOTT AND FRANK H. HURLEY, JR.

In the current report of the Committee on Atomic Weights of the International Union of Chemistry,[2] the atomic weight of carbon has been changed from 12.00 to 12.01. Evidence favoring the higher value has been accumulating for the past few years as a result of gas-density and mass-spectrographic measurements, but it was not until very recently that this evidence was supported by a purely chemical determination. Such a determination was made by Baxter and Hale,[3] who obtained the value 12.010 from measurements of the ratio $C:O_2$ made by the combustion of hydrocarbons. This value is appreciably higher than the value 12.001 obtained by Richards and Hoover[4] from very careful measurements of the ratios $Na_2CO_3:2Ag$ and $Na_2CO_3:2AgBr$, perhaps the best of the older chemical determinations.

Of all the other chemical determinations of the atomic weight of carbon, only one was made by the most accurate method developed for atomic weights, namely, the direct titration of halides with silver, and this one determination, the ratio of tetraethylammonium bromide to silver measured by A. Scott in 1909,[5] was not made with the improvements in technique characteristic of modern atomic weight work. In view of this rather striking fact, it seemed desirable to attempt such a determination as a check on the recent work of Baxter and Hale. Of the innumerable organic halides which might be used for fixing the atomic weight of carbon, benzoyl chloride appeared to be the most desirable. It has a simple formula and its properties are well known. It contains seven atoms of carbon per molecule and the atomic weights needed in the calculation are all well established. It is not difficult to prepare and the parent substance, benzoic acid, is capable of a high degree of purification. Finally, its boiling point (197°) is sufficiently high to suggest that it could be separated from

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[1] Abstract of a thesis by Frank H. Hurley, Jr., presented to the faculty of the Rice Institute in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May 19, 1937.

[2] THIS JOURNAL, **59**, 219 (1937).

[3] Baxter and Hale, *ibid.*, **58**, 510 (1936); **59**, 506 (1937).

[4] Richards and Hoover, *ibid.*, **37**, 95 (1915).

[5] A. Scott, *J. Chem. Soc.*, **95**, 1200 (1909).

impurities without too much difficulty by vacuum distillation. In consideration of these facts, the measurement of the ratio of benzoyl chloride to silver seemed to offer a good opportunity for the determination of the atomic weight of carbon.

Purification of Materials

All materials used in this work were purified carefully before use. Throughout the purification work attention was paid to the exclusion of impurities which might be introduced by the containers and vessels used, and to dust and laboratory fumes. *Water, nitric acid,* and *pyridine* were purified by well-known distillation procedures and the absence of halide impurities in these substances was proven by tests. *Silver* was purified as described by Baxter and Scott[6] with the addition of an extra reduction of the silver chloride. For the final fusion of the silver, the quartz muffle furnace described by Johnson[7] was found to be very convenient. *Phosphorus trichloride,* used in the preparation of benzoyl chloride, was purified by two fractional distillations in an all-Pyrex vacuum apparatus.

Benzoic acid was made by the oxidation of Baker "Analyzed" toluene with potassium permanganate according to the directions of Ullmann and Uzbachian.[8] In order to ensure the absence of thiophenes and other sulfur-containing compounds frequently present in toluene, the material was first refluxed with mercuric acetate for several hours, then decanted and once distilled.

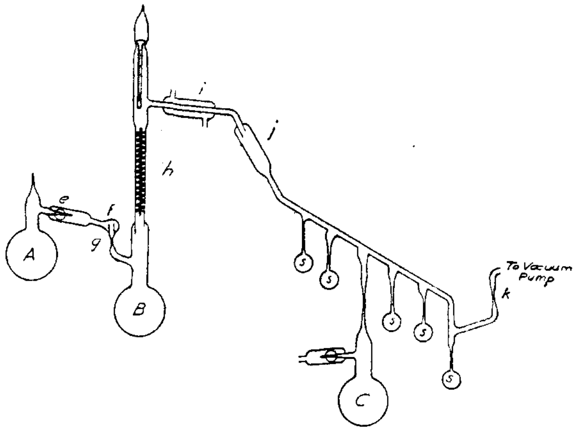

Fig. 1.—Vacuum distillation apparatus.

After the completion of the oxidation, the excess toluene was removed by distillation and the manganese dioxide filtered off. The solution was then concentrated by evaporation and the benzoic acid precipitated by the addition of concentrated hydrochloric acid to the boiling solution. The precipitation of benzoic acid from the hot solution produced large acicular crystals from which the mother liquor was washed easily. The acid was then dissolved in a solution of analyzed sodium carbonate and the solution extracted twice with ether to remove organic impurities not soluble in the carbonate. The remaining ether was removed by heating, and the benzoic acid again precipitated by the addition of hydrochloric acid to the hot solution. To remove the small amount of hydrochloric acid which might be retained by the crystals even after thorough washing, the acid was once recrystallized from water, the crystals washed twice with centrifugal draining, and then dried in a vacuum desiccator over phosphorus pentoxide. The benzoic acid was finally sublimed under reduced pressure.

Benzoyl chloride was prepared by the action of phosphorus trichloride on benzoic acid. The reaction was carried out by placing 317 g. of benzoic acid in a 2-liter flask fitted with a reflux condenser connected by means of a ground joint. To the acid in the flask was added 175 g. of phosphorus trichloride. The mixture was heated on a steam-bath until it became liquid and then for two and one-half hours longer. The resulting material consisted of two layers, the lower being a gummy, water-soluble mixture containing phosphorous acid and a yellow insoluble compound of indefinite composition.[9] The upper layer consisted principally of benzoyl chloride. This material was decanted into a clean flask.

The remainder of the purification process consisted in the repeated distillation of the benzoyl chloride in an evacuated all-Pyrex apparatus. This procedure seemed very suitable for the removal of the principal impurities, HCl, PCl_3, C_6H_5COOH, $(C_6H_5CO)_2O$, H_3PO_3, and other acids or anhydrides of phosphorus, since all of these substances have boiling points far removed from that of benzoyl chloride.

The distillation apparatus is shown in Fig. 1. The benzoyl chloride was introduced into the bulb A by suction, making use of an extra side-arm not shown in the diagram. The liquid was then heated to boiling for a short time under the reduced pressure of an aspirator in order to expel most of the air in the flask, and while still boiling the flask was sealed off. This treatment served to remove a large part of the more volatile impurities.

The apparatus to the right of the valve e was then evacuated and with the vacuum pump still running, the valve was broken with a magnetic hammer.[10] The ring-seal trap f served to prevent fragments of the broken valve-capillary from clogging the constriction g. The liquid was then distilled from A to B by heating A in a glycerol bath and cooling B in an ice-bath. Large amounts of hydrogen chloride and phosphorus trichloride were removed through the pump during the distillation. Heating was discontinued when a white solid, probably benzoic acid, began to sublime over at 100°. After further pumping for a brief period, capillary k was sealed and the vacuum pump disconnected. Only this first distillation, from A to B, was made with the pump on. In the remainder, the constriction k was sealed before the valve was broken.

The constriction g was now sealed and flask A, which contained the residue of the distillation, disconnected. Preliminary tests of the distillation procedure had shown that it was impossible to seal capillaries with which benzoyl chloride had been in contact merely by heating them with a hot, pointed flame, as is usually done. When this was done, a black char appeared inside the tube at the point of heating, indicating the decomposition of benzoyl

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(6) Baxter and Scott, *Proc. Am. Acad. Arts Sci.*, **59**, 23 (1923).

(7) Johnson, *Chemist Analyst*, **22**, 16 (1933).

(8) Ullmann and Uzbachian, *Ber.*, **36**, 1798 (1903).

(9) Wolf, Kalaebne, and Schmazer, *ibid.*, **62**, 1446 (1929).

(10) Richards and Craig, THIS JOURNAL, **45**, 1160 (1923).

chloride retained on the surface of the glass, though no wetness was ever visible. This difficulty was finally obviated by subjecting the capillaries to a prolonged baking before attempting to seal them. A special split-tube electric heater, reaching a temperature about 200°, was designed to accomplish this treatment. All capillaries were baked for thirty minutes or longer before they were sealed with a flame. With this treatment, the charring was practically eliminated.

The residue of the first distillation was a rather viscous yellow liquid consisting mainly of phosphorous acid, though considerable benzoyl chloride was also present. The distillate in B was clear and colorless.

The once-distilled material was now fractionally distilled through the column h. This column consisted of a spiral of 2-mm. Pyrex rodding wound on a central rod of Pyrex 22 cm. long. The spiral was ground to fit snugly into its containing tube, which was 10 mm. in diameter. The distillation was performed by heating B to 70–80° while ice water was run through the condenser i. Under these conditions the temperature at the top of the column varied from about 33 to 38°, depending on the rate of heating. By means of the drop-counter j, the rate of distillation could be determined. It was never allowed to exceed 8–10 drops per minute and was usually less. The reflux ratio was about 2:1. At no time was the liquid brought to boiling.

When the first of the sample bulbs s was filled, distillation was discontinued, the capillary of the bulb baked and sealed, and the bulb disconnected. Distillation was then resumed and the next sample collected. The small amount of distillate which collected in the side-arm to which the previous bulb had been connected was removed by gentle heating. The main fraction of the distillate was collected in a large bulb, C, which was equipped with a capillary valve so that the material could be redistilled.

When the distillation was completed, the apparatus was dismantled and thoroughly cleaned, then dried and reassembled for the next distillation. The remaining distillations were made in a manner similar to the one described. Before each distillation, the apparatus was well tested for leaks, and was evacuated until a McLeod gage connected to the pumping system showed a pressure due to non-condensable gases of about 10^{-5} mm. The complete distillation diagram is shown in Fig. 2. The following points regarding the various distillations may be noted.

In the first fractionation, from B to C, a small residue which did not distil at 80° was left in B.

A Widmer[11] fractionating column was used for the distillation from D to E. Since it was somewhat difficult to operate and did not appear to be especially advantageous, it was replaced by the simple spiral column in the remaining distillations. During the collection of the first sample of this distillation, the vapor temperature rose to 60°, and then fell rapidly, suggesting that hydrogen chloride was first vaporized, then redissolved in the distillate. This fact is of importance in interpreting the results of the analyses.

In order to obtain Sample 14, it was necessary to heat the distillation bulb to 100–110°, the vapor temperature rising to 45°. The reason for this is not clear, though it may have been due to a small leak in the apparatus. However, no difficulty was encountered in the subsequent fractionation, and the analysis of Sample 14 did not deviate significantly from the other analyses.

The results obtained from the analysis of the various fractions of benzoyl chloride seem to indicate that the purification by repeated distillation is a very efficient process. The material seems to have been freed from all its impurities after the third fractionation, for the three further fractionations caused no further change in composition of the various fractions, as determined analytically.

Determination of the Ratio of Benzoyl Chloride to Silver

Weighings.—Weighings were made on a Troemner balance of high sensitivity. The weights were calibrated by Richards' method using the method of calculation recently described.[12] The samples of silver were conveniently weighed on tared watch glasses by the method of double weighing, but all other weighings were made by substitution. The air density was determined immediately after each weighing by the method of Baxter,[13] and all weights were reduced to the vacuum basis. In calculating the vacuum corrections, the following densities were used: Pyrex glass, 2.25; platinum, 21.5; silver, 10.5; weights, 8.36. Weighings were reproducible to 0.02–0.03 mg.

Analytical Procedure.—The bulb containing the sample of benzoyl chloride to be analyzed was first washed well and dried. Its exterior volume was determined by weighing it in air and in water of known temperature using a triple-beam balance sensitive to 0.01 g. It was necessary to know this volume in order to calculate the vacuum correction. The bulb was then cleaned more thoroughly with "cleaning solution," followed by several hours of soaking and rinsing with water. After wiping the clean bulb with a nearly lintless cloth, it was placed in a desiccator containing fused sodium hydroxide and allowed to stand overnight to dry. Its weight was then determined accurately.

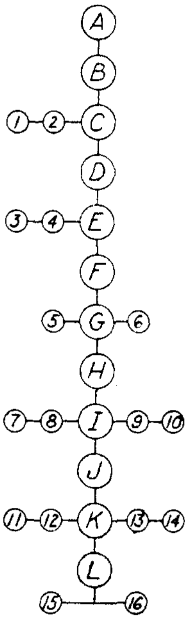

Fig. 2.—Distillation diagram.

The bulb was placed in a thick-walled flask containing 100 ml. of pyridine and 100 ml. of water, and the flask was closed with a tight-fitting, ground-glass stopper. The bulb was then broken inside the flask by violent shaking and the benzoyl chloride allowed to react with the aqueous pyridine. After standing for eight hours or longer, the flask was opened, and, if necessary, the end of the sealed capillary smashed with a stout glass rod. The solution was then decanted through a No. 42 Whatman filter into a 3-liter glass-stoppered flask. The glass fragments in the thick-walled flask were washed 15 times with 50-ml. por-

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[11] Widmer, *Helv. Chim. Acta*, **7**, 59 (1924).

[12] Hurley, *Ind. Eng. Chem., Anal. Ed.*, **9**, 239 (1937).

[13] Baxter, THIS JOURNAL, **43**, 1317 (1921).

tions of water to complete the transfer of the benzoyl chloride. They were then collected on the filter paper. This was best accomplished by first washing them into a 600-ml. beaker and then onto the filter. To remove the last few fragments from the walls of the flask, it was necessary to invert the flask over the beaker and use a wash-bottle with a nozzle bent upward. The glass fragments and filter paper were placed in a previously weighed platinum crucible and the filter paper burned off in an electric furnace. It is an advantage of Pyrex glass that its high melting point permits the use of higher temperatures for the removal of the filter paper than does soft glass, thus hastening the work. After cooling for thirty minutes or longer in a desiccator, the weight of the crucible and glass fragments was obtained. Applying a correction of 0.11 mg. for the ash of the filter paper, the weights of the glass fragments and the benzoyl chloride sample were calculated.

As previously stated, the hydrolysis of the benzoyl chloride samples was carried out in 200 ml. of 50% aqueous pyridine. The chloride samples were completely soluble in this mixture, and within a few minutes after the sample bulb was broken, the solution was perfectly clear. Preliminary hydrolysis experiments using sodium carbonate and sodium hydroxide showed that benzoyl chloride reacted with them far too slowly to be used.

After obtaining the weight of the benzoyl chloride, the equivalent weight of silver was calculated, using 12.01 as the atomic weight of carbon. A quantity of silver within 2 or 3 mg. of the calculated amount was then weighed out. The bulk of the silver consisted of fused buttons, though in some instances the last few centigrams were made up with electrolytic crystals which had been dried by heating in a vacuum. The silver, which weighed about 10 g. in each analysis, was placed in a flask fitted with a tower of bulbs and dissolved in 25–30 ml. of 1:1 nitric acid. The flask was heated on an electric hot-plate to hasten the solution. After all the silver had dissolved, it was further heated to expel oxides of nitrogen. The solution was diluted to 500 ml.

Before addition of the silver, the pyridine solution of the benzoyl chloride was acidified with 300 ml. of 1:3 nitric acid. The resultant volume was 1200–1700 ml. The addition of nitric acid did not cause the precipitation of benzoic acid, as might be expected, except in two of the analyses in which a very small amount (which later redissolved) slowly crystallized out.

The precipitation of the chloride was carried out by adding the dissolved silver to the acid solution of the benzoyl chloride in small portions with constant agitation. The last traces of the silver were removed from the flask by 10 washings with water. After the addition of the silver in this manner, the amount was adjusted to the calculated value by the addition of silver nitrate or sodium chloride from carefully prepared solutions of the purified substances. These solutions contained 0.1 mg. of silver or its equivalent of chloride per milliliter. The additions were made from calibrated burets.

The solutions were shaken vigorously several times over a period of three days to coagulate the silver chloride, then allowed to stand at least two days longer before making any nephelometric tests. The final volume was between 2250 and 2750 ml., depending on the amount of wash water which had been used.

Determination of the End-point.—The end-point of the analyses was determined nephelometrically using a nephelometer of the Richards type. The nephelometric test suspensions were prepared by the use of the "uniform" precipitation device described by Scott and Hurley.[14] After the first tests on the analytical solutions had shown whether an excess of silver or chloride was present, suitable additions of silver nitrate or sodium chloride were made, using the very dilute standard solutions already mentioned. By further tests and additions, if necessary, the analyses were brought to the end-point of equal opalescence. When three or more consecutive tests showing equal opalescences were obtained, the analyses were judged to be at the end-point. The nephelometric tests on the solutions were made over a period of four weeks. After each test the solutions were shaken vigorously and allowed to stand for thirty-six hours or longer before making another test.

Because of the rather large amount of pyridine used to dissolve the benzoyl chloride, the analytical solutions contained considerable amounts of so-called "extra compounds." The final concentrations of these substances were approximately as follows: pyridinium nitrate, 0.5 *M;* benzoic acid, 0.04 *M;* nitric acid, 0.2 *M*. That these substances might exert an effect on the silver chloride precipitate such that the end-point of equal opalescence would not be valid was a possibility which could not be ignored, although Johnson[15] found no significant effects in tests of a large number of "extra compounds" present in various atomic weight determinations. In order to make a test of this point, two very pure silver chloride precipitates which were at hand were washed 11 times with water, followed by 4 washings with 0.16 *M* nitric acid. The washings were made over a period of two weeks. Nephelometric tests were made on the fourth washing with nitric acid. Two tests on each solution gave identical results, an equal-opalescence ratio of 1.00, indicating equivalence of silver and chloride. The nitric acid was then replaced with a solution containing pyridinium nitrate and nitric acid in approximately the same concentration as in the analytical solutions. After shaking and standing for a week to allow the solution to become saturated with silver chloride, duplicate tests on the two solutions gave values of 1.00 and 1.02 for the opalescence ratio. That no significant change in the ratio occurred indicates that the "extra compounds" present in the analytical solutions are without effect on the end-point. The fact that the test solutions did not contain benzoic acid seems unlikely to vitiate the test, since the concentration of this substance in the analytical solutions was relatively so small that it could hardly have had any significant effect on the end-point.

Results of the Analyses.—The results obtained from the analysis of ten samples of the benzoyl chloride are given in Table I. These analyses formed a consecutive series and no accidents or mishaps occurred. All the weights given in the

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[14] Scott and Hurley, THIS JOURNAL, **56**, 333 (1934).

[15] Johnson, *J. Phys. Chem.*, **35**, 2237 (1931).

TABLE I

RESULTS OF ANALYSES OF BENZOYL CHLORIDE

Ag = 107.880, H = 1.0078, Cl = 35.457

Analysis	Fraction of BzCl	BzCl, g.	Init. Ag, g.	Ag added, g.	Corr. wt., Ag.	Ratio $\frac{C_7H_5OCl}{Ag}$	Atomic wt. of carbon
1	4	13.08649	10.04336	+0.00260	10.04596	1.302662	12.0050
2	5	13.12011	10.06925	.00000	10.06925	1.302988	12.0100
3	6	12.53791	9.62237	− .00080	9.62157	1.303104	12.0118
4	8	13.09014	10.04617	.00000	10.04617	1.302998	12.0102
5	9	14.61669	11.21788	− .00020	11.21768	1.303004	12.0103
6	11	12.43004	9.53960	.00000	9.53960	1.302994	12.0101
7	14	10.71976	8.22698	− .00010	8.22688	1.303016	12.0105
8	12	13.48239	10.34756	− .00020	10.34736	1.302979	12.0099
9	15	14.70047	11.28211	.00000	11.28211	1.302989	12.0101
10	16	13.80987	10.59873	− .00040	10.59833	1.303023	12.0106
				Mean, excluding Analyses 1 and 3		1.302999	12.0102
					Probable error	±0.0000035	± 0.00006

table are corrected to the vacuum basis. The initial weights of silver given in column 4 include the small additions of silver nitrate or sodium chloride needed to bring the weights to the calculated values. The additions tabulated in column 5 are those made after the nephelometric tests were begun. The total amount of silver or chloride added by means of the dilute standard solutions did not exceed 3.5 mg. except in the first analysis, in which a total of 5.50 mg. of silver was added.

Analyses 1 and 3 are excluded in the calculation of the mean values. The first analysis must be discarded not only because the result obtained differs so widely from the other analyses, but also because there is a strong presumption that fraction 4 contained a small amount of hydrogen chloride. This presumption is based on the behavior of the Widmer column during the collection of the previous fraction, already mentioned in the description of the purification. Although no explanation for the high results of analysis 3 is known, it seems preferable to reject it in the calculations. If, however, it is retained, the mean value of the atomic weight is increased by only 0.0002 unit.

The current International values for the atomic weights of hydrogen, chlorine, and silver were used in the calculations. The atomic weight of carbon calculated from the ratio of benzoyl chloride to silver is not very dependent on these antecedent atomic weights. If, as is not unlikely, the atomic weight of hydrogen is somewhat higher than the present accepted value, the value for carbon would be lowered slightly. Using Aston's latest value for hydrogen,[16] which is 1.0081 when converted to the chemical scale with the factor 1.00025, the mean value for carbon becomes 12.0100. This value is also obtained if 107.879 is used for silver.

The final value for the atomic weight of carbon calculated from these analyses, 12.0102, is in very good agreement with the value 12.0104, the mean calculated from all of the combustion analyses of Baxter and Hale, excepting those which they themselves rejected. This concordance between two entirely independent chemical determinations appears to remove the uncertainty from the third decimal place, and suggests that the value 12.010 may be safely adopted for the chemical atomic weight of carbon.

Summary

A determination of the ratio of benzoyl chloride to silver has been made and the results of eight analyses give as the mean value of the ratio the figure 1.302999 ± 0.0000035, from which the atomic weight of carbon is found to be 12.0102 ± 0.00006.

The concordance of this result with the value recently obtained by Baxter and Hale from the combustion of hydrocarbons suggests that the value 12.010 be adopted for the chemical atomic weight of carbon.

HOUSTON, TEXAS

RECEIVED JUNE 4, 1937

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[16] Aston, *Nature*, **137**, 357 (1936).