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A Revision of the Atomic Weight of Cesium

BY GREGORY PAUL BAXTER AND JOSEPH SMITH THOMAS

The atomic weight of cesium in use for some time rests upon the work of Richards and Archibald,[1] who by analyses of cesium chloride, bromide and nitrate obtained the value 132.81. Later analyses of cesium chloride by Richards and Françon[2] have confirmed this figure. On the other hand Aston[3] with the mass spectrograph has been unable to find more than one species of cesium atom and Bainbridge[4] confirms Aston's conclusion that cesium is a simple element. The packing fraction of cesium found by Aston[3] is -5×10^{-4} referred to O^{16}. If the Mecke and Childs value of the factor for conversion to the chemical scale, 1.00022, is used, the atomic weight of cesium becomes 132.904. Since the discrepancy seems to be far larger than the error of either the chemical or the physical method, we have undertaken a redetermination of the atomic weight of cesium. The result of our work is in close agreement with that obtained by Aston, although sufficient reasons for the difference between our results and those of Richards and his collaborators are difficult to discover.

Purification of Cesium Salt

Our cesium material was extracted some years ago from two specimens of pollucite found near Andover, Maine, U. S. A. After decomposition with hot concentrated nitric acid, cesium nitrate was obtained in part by crystallization, in part by precipitation of the aluminum with ammonia and decomposition of the resulting ammonium nitrate. The combined cesium nitrate, amounting to about 3600 g., was then subjected to systematic fractional crystallization through seventeen series in a vain effort to concentrate element No. 87. Spectroscopic examination of the least soluble fraction of the seventeenth series (3 g.) showed no perceptible difference from the less soluble fractions and a single analysis of a small quantity of cesium chloride prepared from this sample yielded the atomic weight 132.82.[5] The distribution of material among the fourteen fractions of the seventeenth series was as follows

132 least soluble	3 g.	137–138	1245 g.
133	25 g.	139–140	575 g.
134	112 g.	141–145	550 g.
135–136	1165 g.		

The more soluble fractions, besides sodium contained lithium, potassium, rubidium and thallium. The spectra of Fractions 132–141 were examined anew with a Féry quartz spectrograph by placing the material to be examined in a copper arc. *No trace of rubidium or potassium could be detected in any of the fractions 132–140.* Fraction 141 contained a barely visible trace of potassium and a slightly larger proportion of rubidium.

Although any one of the Fractions 132–140 was probably pure enough for the purpose, Fraction 135–136 was first selected for examination. About 500 g. of this fraction was dissolved and filtered through a sintered glass filter. The solution was then added to a hot solution of an excess of perchloric acid which had been distilled in quartz, and, after cooling, the perchlorate was washed by decantation with chilled water and centrifugally drained. Next the perchlorate was twice recrystallized from aqueous solution in platinum vessels. In order to convert the perchlorate to chloride it was ignited in 100-g. portions in a large platinum still. The fused chloride thus produced showed no evidence of having attacked the still, for it yielded a clear, colorless solution. Nevertheless, the solution was filtered through platinum sponge and the cesium chloride was subjected to recrystallization. Thirteen grams obtained from three recrystallizations was combined with 10 g. obtained by four recrystallizations from the mother liquors (Sample A_1). From the mother liquors of Sample A_1 26 g. was recovered in a similar way (Sample A_2). A spectrogram made with Sample A_1 seemed to be identical with that made with the original nitrate.

Since recrystallization of cesium dichloroiodide has been recommended by Wells[6] and Richards and Archibald for purification of cesium material, the chloride mother liquors of Sample A_2 were converted to the former salt by adding an excess of resublimed iodine and passing scrubbed chlorine into the hot solution until the iodine was dissolved. Fractional crystallization of the dichloroiodide from 10–20% hydrochloric acid followed, with recovery from the mother liquors. Four extreme fractions which had been brought to the same degree of purity, corresponding to six crystallizations of the original, were combined and converted to chloride by prolonged heating at 200–210° in an electric oven. The cesium chloride, which still contained a trace of dichloroiodide, was dissolved and filtered through sintered glass into a quartz dish and was twice recrystallized in quartz from a solution saturated with hydrogen chloride. Possible traces of iodine were removed by passing chlorine into a hot solution of the

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(1) Richards and Archibald, *Proc. Am. Acad.*, **38**, 443 (1903).

(2) Richards and Françon, THIS JOURNAL, **50**, 2162 (1928); **51**, 3677 (1929).

(3) Aston, *Proc. Roy. Soc.* (London), **A134**, 573 (1932).

(4) Bainbridge, *Phys. Rev.*, **36**, 1668 (1930).

(5) Baxter and Stewart, THIS JOURNAL, **37**, 286 (1915).

(6) Wells, *Chemical News*, **84**, 169 (1901).

crystals, and silicic acid by twice evaporating to dryness with hydrochloric acid, heating to 120°, dissolving and filtering through platinum sponge. The product was now fused in platinum, dissolved and again filtered through platinum sponge. Fractional crystallization in platinum yielded about 15 g. (Sample B_1) and the combined mother liquors a second portion of 7 g. (Sample B_2).

The mother liquors of the chloride produced by decomposition of the dichloroiodide were evaporated to dryness and the residue fused in platinum. The solution of the product was filtered through platinum sponge, and the processes of fusion and filtration twice repeated. This chloride was combined with the mother liquors of Samples B_1 and B_2 and by fractional crystallization two samples, B_3 and B_4, were recovered.

The mother liquors of Samples B_3 and B_4 were separately treated with small amounts of distilled hydrazine and heated to boiling. Although in only one could a trace of insoluble material, presumably platinum, be detected, all were filtered, combined and fractionally crystallized (Sample B_5).

Fraction 133 of the original nitrate fractionation was next purified by three crystallizations as perchlorate and one as chloride by processes closely resembling those used for Sample A (Sample C_1). The mother liquors of Sample C_1 were converted to perchlorate and Sample C_2 was prepared from the perchlorate exactly as with Sample C_1.

Finally Fraction 132, the least soluble of the original nitrate fractions, was converted to perchlorate and after three crystallizations was ignited to chloride. Since the quantity of chloride was very small, it was not recrystallized, but merely dissolved, filtered and evaporated to dryness (Sample D).

THE ATOMIC WEIGHT OF CESIUM. CsCl:Ag

Ag = 107.880 Cl = 35.457

Analysis	Sample of CsCl	Fusion atmosphere	CsCl in vacuum, g.	Ag in vacuum, g.	Ag added, g.	Corr. wt. of Ag in vacuum, g.	Ratio CsCl:Ag	At. wt. Cesium
1	A_1	N_2	8.96291	5.74636	−0.00340	5.74296	1.56068	132.909
2	A_1	N_2	9.60983	6.15841	− .00110	6.15731	1.56072	132.913
3	A_2	H_2 + 25% HCl	9.70288	6.21748	− .00062	6.21686	1.56074	132.916
4	A_2	H_2 + 25% HCl	9.53125	6.10771	− .00073	6.10698	1.56071	132.912
5	A_2	H_2	7.52304	4.82015	+ .00010	4.82025	1.56072	132.913
6	B_1	H_2 + 75% HCl	9.38363	6.01264	− .00010	6.01254	1.56068	132.909
7	$B_1 + B_2$	H_2 + 20% HCl	9.33593	5.98172	+ .00035	5.98207	1.56065	132.906
8	B_3	H_2 + trace HCl	10.83528	6.94254	+ .00160	6.94414	1.56035	132.874
9	B_4	N_2	7.70022	4.93365	+ .00050	4.93415	1.56060	132.901
10	B_5	H_2 + trace HCl	7.78342	4.98754	+ .00016	4.98770	1.56052	132.892
11	B_5	H_2 + 50% HCl	7.83724	5.02131	+ .00070	5.02201	1.56058	132.898
12	C_1	H_2 + 35% HCl	5.78546	3.70713	+ .00035	3.70748	1.56048	132.888
13	D	H_2 + 20% HCl	2.16882	1.38988	− .00020	1.38968	1.56066	132.907
14	C_2	H_2 + 35% HCl	4.02114	2.57625	+ .00030	2.57655	1.56067	132.908
						Average	1.56063	132.903
						Average, excluding Analysis 8	1.56065	132.906
						Average of Analyses 1–7	1.56070	132.911

Method of Analysis

The cesium chloride was prepared for weighing by fusion in a platinum boat in a Richards quartz bottling apparatus. The fusion atmosphere was varied considerably. Nitrogen alone, hydrogen alone, and various mixtures of hydrogen and hydrogen chloride gave similar results. The solution of the salt was always clear, and the weighing bottle and boat which were used in the last twelve analyses possessed the same weight at the end as at the beginning with only minor variations in the interval.

After being weighed the salt was dissolved and diluted until the solution was between 0.05 and 0.10 normal. A nearly equivalent quantity of pure silver was dissolved and diluted to a similar concentration and in every experiment but one slowly added to the chloride solution. In Analysis 4 the chloride solution was added to the silver solution. After about a week, during which the solution and precipitate were gently agitated, the end-point was adjusted with the aid of a nephelometer by adding hundredth normal chloride or silver solutions. Nephelometer tests were made by the pouring method[7] which has been in general use in this Laboratory for the past ten years. Slight drifts of the end-point were experienced occasionally, but ultimately disappeared. In every case the final adjustment was permanent over a period of several weeks. In one case (Analysis 8) the silver chloride was dissolved in ammonia and reprecipitated with nitric acid, without altering the end-point by an appreciable amount. Weighings were made by substitution, with the use of a counterpoise in the case of the weighing bottle and boat. Corrections for the air buoyancy were made on the basis

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[7] Scott and Moilliet, THIS JOURNAL, **54**, 205 (1932).

of the air density at the time of weighing and the specific gravities 3.97 and 10.49 for cesium chloride and silver, respectively.

From spectroscopic evidence there seems ample reason to believe that all the material was initially free from the other alkalies. Certainly further purification as the dichloroiodide produced no detectable effect. The chloride used in Analyses 1–7 was probably of slightly better quality than that used in the later analyses, since the processes of purification were simpler and the quantity of material larger. On the basis of these experiments the atomic weight of cesium appears to be close to 132.91, but the average result omitting Analysis 8 is almost as high. We are unable to suggest any explanation for the large deviation of this experiment from the others. It is striking that no one of our results even approaches the lower value found by Richards and Archibald and Richards and Françon. The difference between the older value and ours, 0.1 unit, is far larger than the experimental error of the analytical method, so that a difference in the material used in their analyses seems to be a more probable explanation of the discrepancy. Unfortunately we have been unable to discover among the materials left by the late Professor Richards any specimens of purified cesium salts. We feel, however, that our own salt was essentially free from impurities, most of which would lower rather than raise the apparent atomic weight. The same is true of the silver used for comparison. Furthermore, our value is almost identical with that found by Aston with the mass spectrograph, 132.90. It is reassuring that the chemical and physical methods agree so well in this region of the atomic weight scale.

To summarize the results of our work, by comparison of pure cesium chloride with silver we have found the atomic weight of cesium to be 132.91.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGY, YALE UNIVERSITY SCHOOL OF MEDICINE]

The First Dissociation Constant of Phosphoric Acid from 0 to 50°

BY LESLIE FREDERICK NIMS

Phosphoric acid is a comparatively weak acid, and it has the peculiarity that the acid function of its three hydrogen atoms varies greatly. The dissociation constants of this acid, of great importance to physiology and to theoretical chemistry, deserve careful study. Values given in the literature[1-10] for the first constant were determined at isolated temperatures and show only an approximate agreement (±10% in K). Therefore in the present investigation the first thermodynamic dissociation constant of phosphoric acid is obtained as accurately as possible over a wide temperature range from electromotive force measurements of cells without liquid junction. A summary of recent results obtained for other acids by similar methods is given by Harned and Embree.[11]

Discussion of the Method.—Due to the magnitude of the dissociation constant, the calculation in the usual manner is somewhat laborious. A more satisfactory method is here presented. Buffer solutions of phosphoric acid and potassium dihydrogen phosphate are measured in the cell

$$H_2/HCl\ (m_1),\ KH_2PO_4\ (m_2)/AgCl/Ag$$

The apparent hydrogen-ion molality of the solution is related to the observed electromotive force through the equation

$$\log m_H = -\frac{(E - E_0)F}{2.3026\,RT} - \log m_1 + 2A\sqrt{\mu} \qquad (1)$$

in which the limiting Debye–Hückel equation

$$\log \gamma = -A\sqrt{\mu} \qquad (2)$$

is used to approximate the activity coefficients of hydrochloric acid. The ionic strength may be expressed by

$$\mu = m_2 + m_H \qquad (3)$$

This equation when solved simultaneously with equation (1) gives an apparent value for m_H.

The first dissociation constant of phosphoric acid is

$$K_1 = \frac{(m_H)(m_2 - m_1 + m_H)}{(m_1 - m_H)}\,\frac{\gamma_H\gamma_{H_2PO_4}}{\gamma_{H_3PO_4}} \qquad (4)$$

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(1) Rothmund and Drucker, *Z. physik. Chem.*, **46**, 827 (1903).

(2) Abbott and Bray, THIS JOURNAL, **31**, 729 (1909).

(3) Sherrill and Noyes, *ibid.*, **48**, 1861 (1926).

(4) Sendroy and Hastings, *J. Biol. Chem.*, **71**, 783 (1927).

(5) Britton, *J. Chem. Soc.*, 614 (1927).

(6) Jowett and Millet, THIS JOURNAL, **51**, 1004 (1929).

(7) Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab, Math-fys. Medd.*, **9**, 5 (1931).

(8) Lugg, THIS JOURNAL, **53**, 1 (1931).

(9) Britton and Robinson, *Trans. Faraday Soc.*, **28**, 531 (1932).

(10) Jowett and Price, *ibid.*, **28**, 668 (1932).

(11) Harned and Embree, THIS JOURNAL, **56**, 1050 (1934).