The esters of thioacetic acid that were made by this method and used had the following boiling points: methyl 95–96°, ethyl 115–116°, propyl 135–137°, *iso*propyl 122–123°, normal butyl 134–135° and phenyl 110–111° at 8 mm.

The conductances were determined in cells similar to those described and used by Quam and Wilkinson.[4] The cell constants were determined with 0.02 N potassium chloride at 25°. No correction was made for the change in the cell constant due to the fact that the cells were then used at −77°. Since the thiohydrolysis is calculated from a ratio this correction will be the same in both the numerator and the denominator and will be eliminated in the calculation.

The concentrations were determined by adding from a weight buret known weights of the ester to definite volumes of liquid hydrogen sulfide. The preceding tables give the data obtained and the percentage of hydrolysis calculated from them. The phenyl thioacetate was found to show no conductance when dissolved in liquid hydrogen sulfide.

Conclusions

1. Esters of thioacetic acid are shown to be thiohydrolyzed in liquid hydrogen sulfide. The degree of thiohydrolysis increases with the molecular weight of the ester.

2. The amount of thiohydrolysis of these esters in liquid hydrogen sulfide even at −77° is several times the value for the hydrolysis of esters of similar oxygen acids in water at room temperature.

AMES, IOWA

THE ATOMIC WEIGHT OF CESIUM

BY THEODORE W. RICHARDS[1] AND MARCEL FRANÇON

Introduction

A redetermination of the atomic weight of cesium was undertaken on account of the difference in this value as found by chemical and physical methods. The modern value of 132.81 is based primarily upon the work of Richards and Archibald.[2] Earlier atomic weight determinations are adequately treated by Clarke.[3]

[4] Quam and Wilkinson, THIS JOURNAL, **47**, 989 (1925).

[1] The research here reported was completed under the direction of Professor Richards but the manuscript was written after his death. The junior author is responsible for the conclusions drawn and any opinions expressed.

[2] Richards and Archibald, Proc. Am. Acad., **38**, 443 (1903).

[3] F. W. Clarke, "The Constants of Nature," Part V, "A Recalculation of the Atomic Weights," 4th ed., **1920**, Nat. Acad. of Sciences, Washington, D. C.

By the mass spectrograph Aston[4] in 1921 found cesium to be a simple element with a mass of 133 ± 0.2. Although the possible error in his early work happens to be as great as the difference, 0.2 unit, there are very few cases of simple elements for which there is such a discrepancy between the atomic weight and the mass number; but, particularly when a negative packing exists, the differences between the true weight of the atoms of an element and an integer are usually smaller than is the case for cesium.[5]

Further interest in a chemical study of the atomic weight of cesium was stimulated by recent efforts to find "element 87,"[6] and also from certain theoretical considerations arising from Aston's discussion of the "packing effect."[7] He has defined the "packing fraction" as the divergence of the mass of an atom from an integral value, divided by its mass number. To this fraction may be related the stability of the atoms and the forces binding the protons and electrons together. A great loss of weight may correspond to a great loss of energy, which is the result of tightly bound electrons, while a small loss of weight might correspond to a loose packing of electrons. Tight packing would then indicate stability and loose packing the reverse. Cesium occurs in the region of tight packing, being only slightly removed from the minimum of Aston's curve. At one end of this curve the light elements may be supposed to build up with a loss of mass corresponding to a loss of energy[8] and at the other end the heavy elements disintegrate into lighter elements.[9] The elements of greatest stability as indicated by their abundance[10] are found to the left of cesium in the curve of packing effect and mass number. An accurate determination of discrepancies from the whole number rule should, according to this interpretation, be of fundamental importance in providing information as to the structure of atoms.

It was with due consideration of these ideas that this determination of the atomic weight of cesium was undertaken.

Procedure

Purification of Materials.—All materials were purified according to the usual methods and the usual standards of purity of reagents were

[4] Aston, *Phil. Mag.*, [6] **42**, 436 (1921).

[5] Examples of cases in which discrepancies have been accounted for recently are boron and strontium. Aston predicted an atomic weight of about 10.85 for boron, and in a redetermination of this value Baxter and Scott, *Proc. Am. Acad.*, **59**, 21 (1923), found 10.82. On the other hand, strontium, atomic weight 87.63, at first appeared to have only one mass line at 88, but lately Aston, *Phil. Mag.*, [6] **49**, 1191 (1925), found another faint line at 86.

[6] Herszfinkiel, *Compt. rend.*, **184**, 968 (1927).

[7] Aston, *Proc. Royal Soc. London*, **115A**, 487 (1927).

[8] Millikan and Cameron, *Science*, N. S., **67**, 401 (1928); *Phys. Rev.*, **31**, 921 (1928).

[9] Cabrera, *Compt. rend.*, **186**, 228 (1928); **186**, 501 (1928).

[10] See F. W. Clarke, "The Data of Geochemistry," U. S. G. S. Bulletin 770, Washington, **1924**, p. 36.

maintained.   The silver used in this work was identical with that used in other researches in this Laboratory.[11]

Cesium chloride was made from pollucite from Maine.   After the mineral had been finely ground, it was attacked with hydrochloric acid which had been diluted with an equal volume of water.   A small amount of nitric acid was added to oxidize the iron.   The solution was filtered, evaporated to dryness, treated with hydrochloric acid and water, and then these steps were repeated twice to separate out silica.

The chlorides were then converted to sulfates by the addition of sulfuric acid and cesium alums were obtained, separated and centrifuged.   From this point on quartz dishes were used.   The alums were crystallized three more times with centrifuging.   It should be noted that to obtain alums it is not necessary to add anything other than sulfuric acid to the material extracted from pollucite, the composition of which as determined by Wells[12] and Kastler[13] indicates enough iron and aluminum for this purpose. The solubility relationships of the alums[14] are very favorable for the separation of other alkali metals.   Murman[15] has recommended cesium alums for separation from potassium and rubidium.   Godeffroy[16] made use of the alums in preparing pure cesium chloride.   Our experience indicates that sodium, which forms stable alums only with the lighter of the tervalent metals, is best removed by crystallization of the alums.

To a hot, dilute solution of the cesium alums was added a hot solution of barium chloride, which had been twice recrystallized from the best obtainable material.   After digestion of the precipitated barium sulfate, the solution was filtered through a Gooch-Monroe crucible.   This cesium chloride solution was then treated with perchloric acid, carefully purified by Willard.[17]   The cesium perchlorate crystals thus obtained were centrifuged and recrystallized three times.

The transformation into chloride was accomplished by thermally decomposing the perchlorate in a large platinum boat, placed within a quartz tube, which was heated electrically.   It was necessary to carry the temperature to about 800° to decompose the trace of chloroplatinates which resulted on decomposition of the chlorate in platinum.   The fused cesium chloride was dissolved in doubly distilled water and filtered through a Gooch-Monroe crucible, to separate a few particles of platinum.   This cesium chloride was purified by two crystallizations.

[11] (a) Richards and Hall, THIS JOURNAL, **48**, 704 (1926); (b) Richards, King and Hall, *ibid.*, **48**, 1530 (1926).

[12] Wells, *Am. J. Sci.*, **41**, 216 (1891).

[13] Kastler, *Bull. soc. chim.*, **41**, 428 (1927).

[14] Locke, *Am. Chem. J.*, **26**, 166 (1901).

[15] Murman, *Oesterr. Chem.-Ztg.*, **27**, 129 (1924).

[16] Godeffroy, *Ann.*, **181**, 176 (1876).

[17] Richards and Willard, THIS JOURNAL, **32**, 4 (1910).

It was then fused in a platinum boat in the well-known bottling apparatus of quartz, described in recent publications.[18]   The fusion was made in an atmosphere consisting for the greater part of dry nitrogen with a small amount of hydrogen chloride.   The cesium chloride was cooled in a current of dry nitrogen, which was displaced when entirely cold by dry air before transference to a weighing bottle.

Cesium chloride thus prepared reacted neutral to indicators, whereas a solution of cesium chloride which had been fused in an atmosphere of hydrogen chloride alone was acid to methyl red.

The final product was examined in a Féry quartz spectrometer.   By comparison with other spectra the cesium chloride did not contain any aluminum, barium, potassium or thallium.   The presence of sodium was doubtful, although if it was present, there was only a very faint trace of it. Cesium chloride from the mother liquor seemed almost equally pure spectroscopically and did not react to any chemical tests for impurities.

Weighings were made with the usual care and the cesium chloride was compared nephelometrically with pure silver.   The following factors were used in the calculations.

Atomic weights		Vacuum corrections		Densities	
Silver.........	107.880	Silver.....	−0.000031	Weights..........	8.3
Chlorine......	35.457	Cesium chloride..	+0.00016	Silver............	10.49
				Cesium chloride...	3.97

TABLE I

ATOMIC WEIGHT OF CESIUM

Wt. of CsCl in vac., g.	Wt. of Ag in vac., g.	Wt. of Ag added or subtracted	Corrected wt. of Ag, g.	Atomic wt. of cesium
4.42344	2.83611	−0.00001	2.83610	132.802
5.01421	3.21436	− .00020	3.21416	132.832
4.14983	2.66076	+ .00023	2.66099	132.783
4.48842	2.87830	− .00083	2.87747	132.820
			Av.	132.809

The error of the average of these determinations can be evaluated in several ways.   The "probable error," calculated from 0.6745 times the mean error, is 0.012.   This is within the "experimental error" of 0.015 which is based upon the accuracy of weighing and the accuracy of determining the end-point.

The average of the analyses confirms the present accepted value of 132.81, which Richards and Archibald found by analysis of the chloride, bromide and nitrate.   However, since all of these salts were prepared from recrystallized dichloro-iodide, confirmation by analysis of a salt prepared by a different method is of importance.

[18] Richards, King and Hall, THIS JOURNAL, **48**, 1537 (1926); see also Baxter and Grover, *ibid.*, **37**, 1027 (1915).

The deviation from an integral value found corresponds to a packing fraction of -14 ($\times 10^{-4}$), which is much greater than would be indicated by Aston's curve, provided that cesium is a simple element. Another unexpectedly large packing fraction was recently found by Baxter and Butler[19] for titanium, although in this case doubtful indications of another mass line have been reported and the element may not be simple. It may well be that further investigation will prove that cesium is also complex.

Summary

An analysis of cesium chloride, prepared by the recrystallization of alums of cesium, by comparison with silver confirmed the atomic weight of cesium to be 132.81.

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THE VAPOR DENSITY AND SOME OTHER PROPERTIES OF FORMIC ACID

BY ALBERT SPRAGUE COOLIDGE

Introduction

In connection with some work on the adsorption of formic acid vapor, it became necessary to know the density of the vapor at ordinary temperatures and at pressures below the vapor pressure of the liquid. The only measurements seem to be those of Bineau;[1] Peterson and Ekstrand[2] give fragmentary data at higher temperatures and pressures. It seemed necessary to undertake direct determination of the vapor density. The acid prepared for this purpose appeared to be of exceptional purity, and certain other properties were determined for purposes of comparison.

Purification and Preservation of Formic Acid

Even at room temperature, formic acid slowly decomposes into water and carbon monoxide. Bulbs of Kahlbaum's best acid, which had presumably been stored for some time, were found to contain high pressures of the latter, while freshly imported bulbs did not. After fruitless attempts to remove the water by distillation over phosphorus pentoxide, acid sodium sulfate and magnesium perchlorate trihydrate (the first two decomposed the vapor, while the third absorbed it copiously), it was

[19] Baxter and Butler, THIS JOURNAL, 50, 408 (1928).

[1] Bineau, *Ann. chim. phys.*, [3] 18, 228 (1846).

[2] Peterson and Ekstrand, *Ber.*, 13, 1194 (1880).