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THE COMPRESSIBILITY OF SODIUM, BARIUM AND BERYLLIUM[1]

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Determinations of the coefficient of compressibility have been made during the past twenty-five years for many of the elements by the "constant volume method" developed at the Harvard Laboratories. Values for the less common elements have been determined as such elements have become available. In this paper are presented values for barium, strontium and beryllium, and also for sodium. The latter was redetermined to demonstrate the reliability of the method with the modifications necessary in handling strontium and barium.

Bridgman, measuring the linear compressibility,[2] calculated the cubic compressibility of strontium to be 8.187×10^{-6} at 30° (in kg./cm.^{2}). Shortly after the initiation of the research here presented, Bridgman published values for barium and beryllium[3] of 10.19×10^{-6} and 0.855×10^{-6}, respectively, at 30° and in kg./cm.^{2} units. Nevertheless, corroboration by an independent method was deemed to be of sufficient importance to justify publication of the results.

Preparation of Materials

Barium.—The barium was obtained through the kindness of Dr. Francis C. Frary of the Aluminum Company of America. It was prepared in a special alloy furnace which was provided with a mild steel crucible so constructed that it could be evacuated and filled with some inert gas. Before the barium was melted, the crucible was evacuated to 2 mm. residual pressure and maintained thus until the temperature rose to about 400°.

The barium was then melted in an atmosphere of argon in the steel crucible, the pressure reduced to prevent blow-holes and the barium cast in a mold in the lid of the crucible.

After its receipt the barium was cut under kerosene oil with the aid of a small coping saw and knife into a size and shape suitable for the piezometer. The pieces of barium when not in use were stored in a vacuum desiccator under exceptionally pure kerosene.

During the manipulations involved in three determinations of compressibility over a period of four days, an eighteen-gram sample gained only 1.4 mg., showing that the methods of storage and manipulation ade-

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[1] As this research was completed shortly after the death of Professor Richards, this report was prepared by the junior authors.

[2] Bridgman, *Proc. Am. Acad. Arts Sci.*, **58**, 151 (1923).

[3] Bridgman, *ibid.*, **62**, 207 (1927).

quately prevented serious oxidation. The trace of oxide thus formed was present as a superficial layer, which would be without influence on the value for the compressibility.

An examination in a quartz prism spectrometer showed the barium to be of exceptional purity: no iron and only very slight traces of strontium. Analyses indicated a barium content of 99.95%.

Kerosene Oil.—The essential requirements of the kerosene used in the piezometer as a confining liquid for barium are absolute freedom from water, sulfur and unsaturated hydrocarbons. Treatment with sodium wire over a period of one week and subsequent distillation did not yield an anhydrous water-white product. For these reasons the kerosene oil was further treated by shaking with a potassium–sodium alloy (four parts potassium to one part sodium) followed by a careful fractionation. Only the fraction distilling between 185 and 225° was used. Since the potassium–sodium alloy was a liquid at ordinary temperatures, it continually presented a fresh surface to the kerosene. This surface, in conjunction with its great chemical activity, assured the removal of any substances liable to react with barium. The oil was stored over potassium–sodium alloy until ready for use.

Mercury.—The mercury was prepared in the usual manner by treatment in a nitric acid tower and finally by distillation, according to Hulett.

Method and Apparatus

The apparatus and methods used in this research have been described in adequate detail elsewhere.[4] Only modifications of apparatus or procedure will be described here. All measurements were made at 25.00°, instead of the customary 20°. The piezometer, of the type previously used for solids, was made of Pyrex instead of soft glass. This was advantageous in making it less liable to fracture, while its temperature and pressure hysteresis did not appear to be any greater than that of soft glass. One detail of its construction, the taper of the stopper, although mentioned before, seems worthy of repetition since in recent years it appears to have been overlooked. The taper found to be most satisfactory was one in eight. With this taper no difficulty was experienced in removing the stopper, while with less taper, one in twelve or one in sixteen, this difficulty occasionally resulted in breakage of the piezometer. This increased taper also resulted in greater reproducibility of volume.

The barium was held in a thin-walled test-tube which fitted snugly in the piezometer and prevented mercury from coming in contact with it.

The piezometer containing the glass tube, mercury and about 2.5 g. of kerosene (the amount used in actual measurement of the compressibility of barium) was standardized in the usual manner.

The stopper lubricant used was a heavy Ramsay grease. 9.3 ± 0.1 mg. was placed on one spot on the stopper, which was then inserted rapidly in position and turned with considerable pressure until further movement

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[4] Richards, *J. Franklin Inst.*, **198**, 25 (1924); Richards and Saerens, THIS JOURNAL, **46**, 935 (1924).

was impossible. With this procedure practically none of the lubricant dissolved in the kerosene. A glucose–glycerine lubricant was tried but, although insoluble in kerosene, was much less satisfactory, possibly owing to the presence of small, solid particles which hindered a satisfactory seating of the stopper.

The data for the standardizations of the piezometer are tabulated in Table I in the customary manner.

TABLE I

STANDARDIZATION OF PIEZOMETER WITH OIL

Expt	Oil, g.	Mercury, g. 100–500 meg.	Mercury on basis of 2.3132 g. of oil, 100–500 meg.
1	2.3132	1.0905	1.0905
2	2.3132	1.0890	1.0890
3	2.5652	1.2014	1.0882
4	2.7027	1.2645	1.0895
5	2.4408	1.1454	1.0881
		Av.	1.0891 g.

The weights of kerosene used in the different standardization experiments (Col. 2) were not identical. To reduce these to a common basis (Col. 4), it was necessary to determine a correction factor for the oil used. The following table presents the experimentally determined values for the weight of mercury in the side arm when one gram of oil replaces one gram of mercury in the piezometer.

TABLE II

EXPERIMENTALLY DETERMINED VALUES

Expt.	Oil, g.	Mercury, g. 100–500 meg.	Oil in excess of 2.3132 g.	Mercury in excess of 1.0891	Ratio, Hg/oil
1	7.7294	3.5154	5.4162	2.4263	0.4480
2	7.8488	3.5848	5.5356	2.4957	.4508
3	7.2624	3.3106	4.9492	2.2215	.4488
4	7.6397	3.4860	5.3265	2.3969	.4500
				Av.	.4494

This factor was also used in calculating the compressibility of sodium, barium and strontium.

Compressibility measurements were first made on a sample of "C. P." sodium to determine whether the special methods necessary for the work with barium would give results, in the case of sodium, in accordance with those generally accepted. As will be seen, the results thus obtained confirm the older value[5] of 15.6×10^{-6}.

The density of sodium (0.972) used was that determined by F. N. Brink.[6]

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[5] Richards, THIS JOURNAL, **37**, 1652 (1915).

[6] Richards, Stull and Bonnet, *Carnegie Institution of Washington*, Pub. No. **76**, **1907**, p. 15.

TABLE III

COMPRESSIBILITY OF SODIUM

Oil used, g.	Mercury 100–500 meg.	$\beta \times 10^6$	Wt. of sodium in air, g.
3.3676	1.8645	15.68	4.6265
3.1311	1.7558	15.58	4.6268
	Av.	15.63	

When the details of experimental procedure had been perfected with sodium, the data recorded in Table IV were obtained with barium.

TABLE IV

COMPRESSIBILITY OF BARIUM

Expt.	Oil used, g.	Mercury, 100–500 meg.	$\beta \times 10^6$ (meg.)	Weight of barium in air, g.
1	2.3298	1.2741	10.46	18.5382
2	2.3315	1.2771	10.54	18.5388
3	2.5461	1.3721	10.49	18.5392
4	2.5694	1.3811	10.44	18.5392
		Av.	10.48	

When Bridgman's value for barium is corrected to 25° to the pressure units here used, and to the same range of pressure, β equals 10.34×10^{-6}, a reasonably good agreement for the two diverse methods.

Determination of Weight and Density of Barium

The determination of the weight of the sample of barium presented one of the most difficult problems of the research. A special apparatus was designed for complete removal of kerosene in an inert atmosphere. Argon of 99.95% purity was further purified by passage over activated charcoal chilled with solid carbon dioxide in ether. A diagrammatic sketch of the

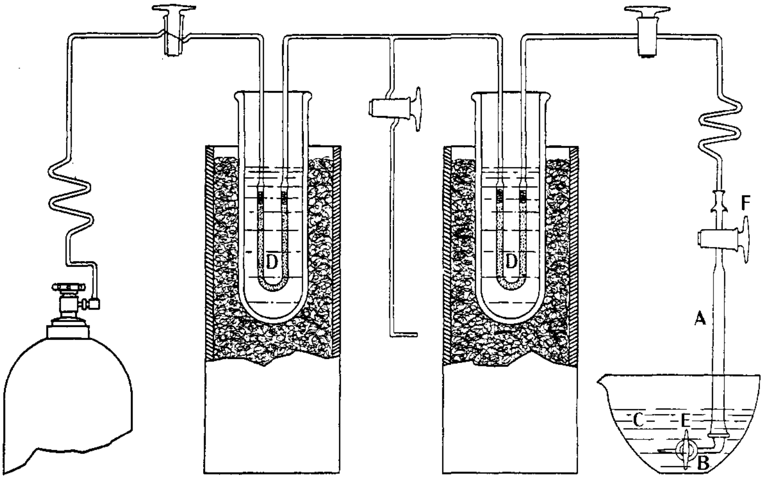

Fig. 1.

apparatus is depicted in Fig. 1. The charcoal in tubes (D,D) was first completely outgassed by heating to 500° in a high vacuum for forty-eight hours. When pure argon was desired, Dewar vessels with carbon dioxide and ether were placed over these tubes. Next, the sample of barium in the tube with kerosene was immersed in a bath of anhydrous, sulfur-free petroleum ether (C), into which the weighing tube (A) dipped. After the apparatus was swept out with pure argon, the cylindrical pieces of barium were introduced into A and the end piece (B) inserted in position. The bath of petroleum ether was removed and the barium dried in a current of argon. The stoppers E and F were closed, the tube was removed and weighed. The sample was again transferred to kerosene and the tube refilled with argon. The difference in weight gave the weight of barium in argon. A buoyancy factor was applied to obtain the weight of barium *in vacuo* and in air. The weight of barium in air was used to compute the weight of oil in the piezometer by difference.

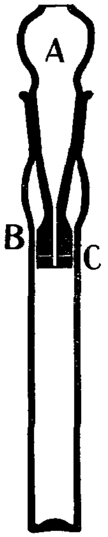

Fig. 2.

The density was determined in a new kind of pycnometer for solids, a modification of a type suggested by Dr. J. C. Woodhouse. The pycnometer used is illustrated in Fig. 2. The ground-glass stopper (A) was of the same type as that used in the piezometer, which had been found to yield a reproducible volume. A capillary tube (B) etched with a fine mark (C) extended into the piezometer. The level of the liquid was adjusted to the mark by means of a capillary pipet inserted through the hollow stopper. Excellent reproducibility of weight was obtained, a maximum variation of only 0.3 mg. being found in successive fillings and settings. The density of the kerosene was determined as 0.79424 by this method, whereas 0.79430 was obtained with a small Ostwald-Sprengel pycnometer. Even greater reproducibility might be possible by the use of a small ground-glass cap fitting on the stopper to prevent evaporation.

Two determinations of the density of barium at 25.00° gave the identical value, 3.661. This value appears to be the most reliable yet obtained.[7]

Strontium, also provided by the Aluminum Company of America, was prepared in a way similar to that used for barium. Since there were some inclusions of strontium hydroxide in the sample, it was more difficult to cut it up. It was undoubtedly on account of these inclusions that the density found (2.737) was higher than is usually reported.[8] The coefficient of compressibility at 25° was found to be 7.22×10^{-6} as the average of

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[7] Considerable discrepancy exists in the literature for the density of barium. Guntz, *Compt. rend.*, **141**, 1240 (1905), found 3.78. Biltz and Hüttig, *Z. anorg. Chem.*, **114**, 247 (1920), found values ranging from 3.44 to 3.70, using samples of 0.5 to 1.5 g. Kern, *Chem. News*, **31**, 243 (1875), found 3.75 with an impure sample.

[8] *Cf.* Glascock, THIS JOURNAL, **32**, 1222 (1910).

three experiments. This is distinctly lower than Bridgman's value of 8.32 $\times 10^{-6}$ (corrected for temperature and pressure units).

This lowering of the value is in agreement with the high density caused by the presence of compounds. Hence, this value is presented only as a preliminary one.

These determinations complete the compressibility and density data for the family group of Ca, Sr and Ba.

Comparison of their atomic volumes and compressibilities is of interest.

	Mg	Ca	Sr	Ba
Atomic weight	24.32	40.07	87.62	137.37
Density	1.73	1.53	2.55[a]	3.66
Atomic volume	13.3	25.3	34.36	37.52
Compressibility ($\beta \times 10^6$)	2.9	5.7	8.32[b]	10.48

[a] Glascock, ref. 8.

[b] Bridgman, *Proc. Am. Acad. Arts Sci.*, **58,** 201 (1923).

Beryllium

A cylinder (1.1 × 9 cm.) of beryllium, over 99% pure, was made by the Beryllium Corporation of America. It was coherent and finely crystalline. The density was found to be 1.85. Since in this case water was used as the confining liquid, it was necessary to standardize the piezometer with water. The results of these experiments will be found in Table V. The factor for the replacement of water for mercury in the piezometer has been determined[9] as 0.2044 and this factor was used to correct the weights of mercury in Table V to a common basis.

TABLE V

STANDARDIZATION OF PIEZOMETER WITH WATER

Expt	Water, g.	Mercury, g. 100–500 meg.	Mercury on basis of 2.7604 g. of water 100–500 meg.
1	2.7604	0.6319	0.6319
2	2.9156	.6643	.6326
3	2.9166	.6638	.6319
4	2.9064	.6603	.6325
5	2.8742	.6561	.6328
		Av.	.6323

TABLE VI

COMPRESSIBILITY OF BERYLLIUM

Expt.	Water used, g.	Mercury, g. 100–500 meg.	$\beta \times 10^6$
1	2.9884	0.5355	0.930
2	3.1357	.5307	.890
3	2.9743	.5334	.948
4	3.1119	.5661	.918
5	2.9871	.5360	.947
		Av.	.927

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[9] Mehl and Mair, THIS JOURNAL, **49,** 1892 (1927).

The data for the compressibility of beryllium are presented in Table VI.

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Summary

1. Coefficients of compressibility were measured by the "constant volume" method at 25° as follows: sodium, $\beta = 15.6 \times 10^{-6}$; barium, $\beta = 10.48 \times 10^{-6}$; strontium (preliminary) 7.22×10^{-6}; beryllium, $\beta = 0.93 \times 10^{-6}$.

2. The densities of the specimens used were for barium, 3.66; for strontium, 2.74; for beryllium, 1.85.

3. Special methods were developed for determining the weight and density of barium and strontium.

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NOTE

Use of the Hildebrand Hydrogen Electrode in Biological Solutions.—We have found that in certain biological solutions the ordinary Hildebrand[1] hydrogen electrode may attain equilibrium so slowly as to be entirely worthless. The Hildebrand type is obviously inferior to the enclosed electrode involving complete saturation of the solution with hydrogen, but the latter device greatly changes the *P*H (as is well known) of mixtures containing reducible substances, or of mixtures partly buffered by hemoglobin or by volatile substances such as carbon dioxide and hydrogen sulfide.

We have put an ordinary rubber bulb from an "atomizer" into our hydrogen supply line so that the hydrogen flows through the bulb. By squeezing the bulb repeatedly the Hildebrand electrode is repeatedly saturated with hydrogen. Obviously, because of possible air leaks, the system should be operated so that at all times the pressure in the hydrogen supply line is slightly greater than atmospheric. It is very important that the solution level be periodically forced *entirely* below the bottom of the platinum, this being regulated by the rate of squeezing the bulb. In this way nearly constant readings are obtainable within five minutes with a small amount of hydrogen, while the usual arrangement sometimes did not give the right *sign* of e.m.f. even after an hour with a vigorous stream of hydrogen. This difference is strikingly observed by passing the hydrogen at first without touching the bulb, the e.m.f. being erratic and sometimes off by 0.5 volt. The correct reading is then quickly attained by pressing

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[1] J. H. Hildebrand, This Journal, **35**, 349 (1913).