









# The Compressibilities of the Elements and Their Periodic Relations

BY

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IN COLLABORATION WITH

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WASHINGTON, D. C.:  
PUBLISHED BY THE CARNEGIE INSTITUTION OF WASHINGTON  
MAY, 1907

CARNEGIE INSTITUTION OF WASHINGTON PUBLICATION No. 76

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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY  
OF HARVARD COLLEGE

PRESS OF BYRON S. ADAMS  
WASHINGTON, D. C.

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# I

## THE COMPRESSIBILITY OF LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, AND CÆSIUM.

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BY THEODORE WILLIAM RICHARDS, WILFRED NEWSOME STULL, AND  
FREDERICK BONNET, JR.





## THE COMPRESSIBILITY OF LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, AND CÆSIUM.

### INTRODUCTION.

In a series of papers upon the significance of changing atomic volume,\* it has been shown that, at least in some cases, atomic volume is probably in part dependent upon the intensity of the affinities concerned in holding the material together. It has been shown, also, that even in those cases where the relationship is not at first obvious, the same tendencies may still be in action. In these obscure cases it seems probable that the difficulty of interpretation is due to the superposition of conflicting effects produced by the simultaneous action of chemical and cohesive affinity.

Reference has been made to the increasingly definite hints of this relation, to be found in the literature of the subject. As far as has yet been discovered, the first suggestion seems to have appeared nearly a hundred years ago, when Sir Humphry Davy had a clear conception of the possibility of this connection of effects, although he never amplified it. The suggestion is contained in a footnote in one of his papers; it reads as follows:

The common metallic oxides are lighter than their bases, but potash and soda are heavier; this fact may be explained on either theory; the density of a compound will be proportional to the attraction of its parts. Platina, having a weak affinity for oxygen, can not be supposed to condense it in the same degree as potassium does; or if platina and potassium be both compounds of hydrogen, the hydrogen must be attracted in platina, with an energy infinitely greater than in potassium. Sulphuric acid is lighter than sulphur; but phosphoric acid (where there is a strong affinity) is heavier than phosphorus. The oxide of tin (wood tin) is very little inferior to tin in specific gravity. In this instance the metallic base is comparatively light, and the attraction for oxygen strong; and in a case when the metal is much lighter and the attraction for oxygen stronger, it might be expected *à priori* that the oxide would be heavier than the base.†

It is interesting to note that this paragraph clearly gives to Davy the priority concerning this matter; but undoubtedly the later writers (including the present author) developed the hypothesis independently of Davy and of one another.

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\*Richards, Proc. Am. Acad., **37**, 1 (1901); 399 (1902); **38**, 293 (1902); **39**, 581 (1904).

†Humphry Davy, Collected Works, **5**, 133 (1840). We are indebted to Prof. W. D. Bancroft for his kindness in calling attention to this note.

Although it is thus evident that Davy had a distinct conception of the significance of changing atomic volume, it is equally evident that he was no more cognizant of the relation of compressibility to that problem than were others who have more recently touched upon the subject. This connection is now worthy of brief comment.

Upon consideration, it is evident that the proposed interpretation involves the assumption that chemical affinity in its action exerts pressure; this internal pressure is supposed to cause a diminution of the volume of the substance. Here the main difference between the present series of papers and the independent work of others may be especially emphasized. It is now contended that if chemical affinity exerts pressure, this pressure must have more effect in its action upon the volume of a compressible substance than upon that of a relatively incompressible one. To have any important meaning, the volume-change must be considered in relation to the compressibilities of the substances concerned.

If, then, compressibility is not merely an isolated physical fact, but rather a phenomenon of chemical significance immediately connected with the most important chemical properties of material, it becomes a highly interesting problem to determine the compressibility of as many simple substances as possible. The fact that the results are not always easy of interpretation in the more complex cases does not prevent an approximate analysis of the figures in the simpler cases; and even this approximate interpretation holds out the promise of a resulting gain in our knowledge concerning the mechanism of chemical affinity.

It was with these facts in mind that three years ago we began the study of compressibility, in the first place devising a new method for its determination, because none of the already existing methods were adequately convenient or precise. This method has already been described in detail in Publication 7 of the Carnegie Institution of Washington.\* The essential feature of the method is the comparison of the unknown compressibility with the compressibility of mercury, by first compressing mercury in a given apparatus, measuring both pressure and change of volume, and then displacing most of the mercury by the substance to be studied, and again noting the relationship of pressure to volume. Obviously in such a method as this, the compressibility of the apparatus itself is eliminated, occurring in both series of measurements. The relation of volume to pressure was easily determined by causing the mercury meniscus to make contact with a very fine platinum point in a tube of narrow diameter; and the decrease in volume was determined by adding weighed globules of mercury and noting the pressures needed to cause similar contact. Several forms of

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\*This paper by Richards and Stull appears also in more abbreviated form in Journ. Am. Chem. Soc., **26**, p. 399 (1904), and Zeit. phys. Chem., **49**, p. 1 (1904).

glass tubes or jackets were used to contain the mercury and the substance to be compressed, according to the state of this substance. Also in the course of the following investigations these forms were used, and some of them were still further modified to meet the special conditions of individual cases. In general, it may be said that the method continued to give entire satisfaction, provided only that air was scrupulously eliminated from the substances to be studied.

The present paper deals with the first part of this extended investigation, discussing the compressibility of the alkali metals. These were studied first because it was expected that they would prove to be very compressible, and because they form well-defined simple compounds involving great energy changes. In the following work other substances were tested, so that in all the compressibilities of thirty-five elements and many simple compounds were studied with sufficient care to leave no doubt as to their relative values. Highly interesting relationships were found between these values, showing not only that compressibility is closely related to cohesive pressure as indicated by boiling-point and is, therefore, periodic in the system of elements, but also other important connections between the fundamental properties of material. In the following pages are discussed both the details of the experimental investigation and some of the conclusions which may be drawn from the results.

#### THE COMPRESSION APPARATUS.

The Cailletet compression-pump used in the previous investigation served well in this one also as a means of obtaining the high pressures needed. The apparatus consists of a lever-and-screw compression-pump (*A*) filled with oil, communicating through a stout copper tube with a heavy steel barrel (*B*) provided with a stout steel screw cap (*C*). The hydraulic gauge (*D*) registering these pressures will be discussed under a subsequent heading.

As before, the glass jacket (*E*) containing the mercury and other substance to be compressed was suspended under the oil and mercury in the steel barrel, hanging from a bronze piece (*F*) held down by the screw cap. The details of the arrangement can best be seen by inspection of the accompanying diagram (fig. 1). In order to keep the apparatus at constant temperature, the barrel as far up as the screw cap was immersed in the water of a thermostat, which varied less than  $0.003^{\circ}$  throughout the whole time of the observations. This constancy was attained very simply by a submerged reservoir of toluol (*G*), which forced mercury up and down in a capillary tube, making contact with a very finely pointed platinum wire. The weak current through this contact actuated a relay (*H*), which automatically shut off the stronger heating current. The water in the thermostat was forcibly stirred by means of motor-driven paddles (*J*). The

room itself in which the whole apparatus was placed was kept constant in temperature by a gas-barometric electrical thermostat, at about half a degree below the temperature of the water of the vessel. The regulation of the temperature of the room, of course, assisted materially in promoting the constancy of the bath. The thermometer used was carefully compared with the international standard and all determinations of compressibility were made at exactly  $20.00^{\circ}$  of the international hydrogen scale.

Two types of glass tube were used to contain the alkali metals to be compressed. Because these metals could not be allowed to come into contact with mercury, the forms used in the previous work were inapplicable; but slight modifications removed the objections. The two forms used are shown in the accompanying diagram, the form A (fig. 2) having been used in the preliminary work, and the much more satisfactory and convenient form V (fig. 2) having been used in the final determinations. These were constructed of carefully annealed glass and provided with very finely ground stoppers.

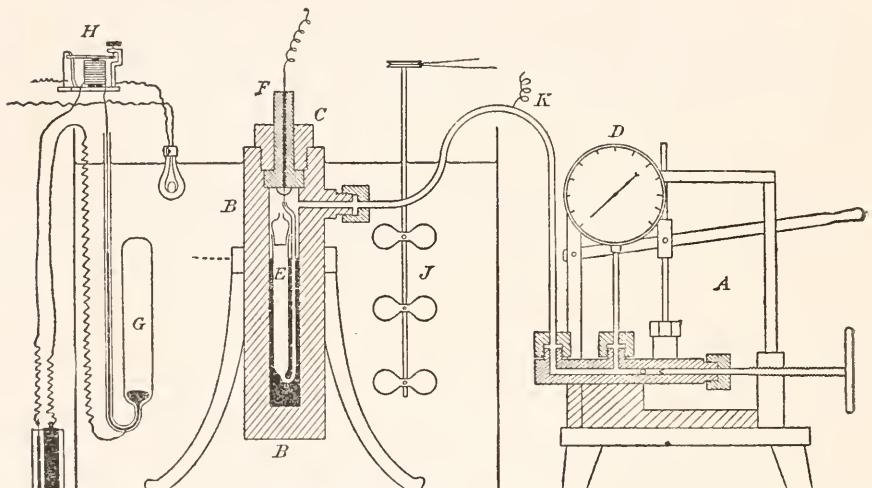


Fig. 1.—The Compression Apparatus.

It will be remembered that the tube or glass jacket was at first filled completely with mercury, and the change in volume for different pressures was measured very simply by placing the whole jacket under the liquid in the barrel of the Cailletet compression apparatus, adding successive weighed portions of mercury, and noting each time the pressure needed just to break and then again make the electrical connection between the meniscus and the platinum point (*P*). The quantity of mercury in the glass jacket was usually so adjusted that the first constant pressure reading was between

50 and 100 atmospheres, and this first reading was taken as the starting point of the determination. Minute air-bubbles were thus disarmed of possible injurious effects. As already suggested, a weighed quantity of mercury was now added through the open tube, and pressure was again applied. The added pressure necessary to break the electrical circuit corresponded to the volume of the extra mercury introduced. This process was repeated until the highest pressure was reached, and thus were found the points on a curve which represented the difference between the compressibilities of mercury and glass.

The mercury was now wholly removed, except for a small amount in the U-tube —enough to seal the bend. The rest of the left-hand side of the apparatus was then filled with paraffin oil of known compressibility, and the metal was introduced in the form of a closely fitting cylinder. The jacket was now placed once more in the Cailletet barrel, and once more the pressures corresponding to successive added portions of mercury were found. These new readings define the curve of the total compression of the liquid, the metal, and the residual mercury, all taken together. By subtracting the corresponding values from this first curve, and also that corresponding to the known weight of paraffin oil, results are obtained which represent the differences between the compression of the metal and a like bulk of mercury. From this the compressibility is very simply computed.

In the case of rubidium and cæsium an additional glass bulb was needed within the jacket. Correction for this was easily made, as will be seen.

If the platinum wire is very finely pointed, the fine tube around it about 1.5 mm. in diameter, and the mercury meniscus covered with perfectly clean water, the indications of this instrument are surprisingly constant and trustworthy. Even with a substance no more compressible than mercury it is easy to be certain of the necessary pressure within 1 atmosphere — a very small fractional error in many hundred atmospheres. The pressure at which the correction was made was taken as the true point, rather than

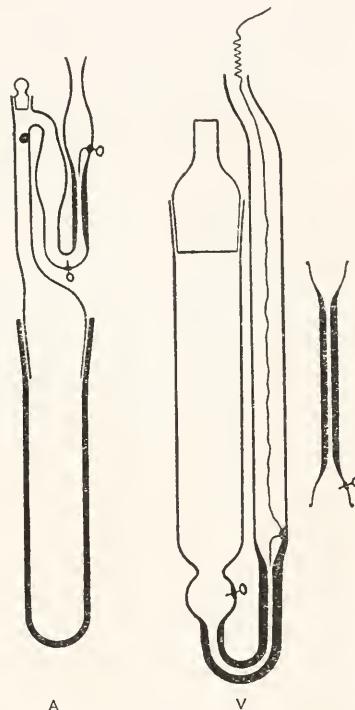


Fig. 2.—Compression Jackets.

that at which the connection was broken, since there is sometimes a slight adhesion between the point and the mercury under the last-named circumstances. Often, however, the making and breaking occurred within an atmosphere's pressure of one another, and with the most compressible substances no difference at all could be observed.

To prevent leakage of kerosene, a fixed amount (3 mg.) of rubber lubricant was always used on the glass stopper. Because this occurred in every case, any slight effect which it might have had in the readings was the same in every case, and hence was wholly eliminated from the final results.

The special precautions needed for manipulating this apparatus are sufficiently discussed in the preceding paper, to which the reader is referred for further details. (Carnegie Institution of Washington Publication 7.)

#### THE STANDARD OF PRESSURE.

The accurate determination of pressure is the most difficult part of these measurements, because all the other uncertainties are eliminated by the method of operation of the apparatus. It has already been pointed out that if the relation of the compressibility of water to that of mercury were accurately known, this could be used as a standard, but unfortunately it is not accurately known. The work of Amagat upon the compressibility of water\* is indeed in many respects admirable. His apparatus for determining high pressure — a double hydraulic press with rotary pistons — seems to have given consistent results, and to have been more satisfactory than a gas manometer would have been. Nevertheless, it is a complex apparatus, and certainly less desirable than a mercury column of constant temperature and known height. Among other defects, it is probable that the diameters of the pistons are neither perfectly constant or easily determinable with the accuracy required; these diameters must vary with the pressures. In another respect, too, Amagat's determinations of the compressibility of water are uncertain, namely, because of the fact that in his experiments the water was compressed in a kind of inverted thermometer tube, and no allowance was made for the water adhering to the sides of the stem. As the column was pressed upward by the mercury, this adhering water would tend to make the compressibilities at high pressure appear larger than they really were.

Accordingly, for the present, it was deemed best to refer in this paper, as in our former one, all the pressures to the gauges which we actually possess; and because these results are all determined in the same way, they all may be corrected when the true compressibility of water is known, by reference to our own figures for water. We hope that before very long this value may be obtained by Dr. W. Ekman at the Laboratory for the Investigation of the Sea, Christiania, Norway.

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\*Ann. de Chim. et de Phys. (6), 29, pp. 68 and 505 (1893).

The two hydraulic gauges used for the registration of the pressure were made at different times by Schaeffer & Budenberg, of Zürich, Switzerland. One of these gauges, that used in the previous work, was labeled No. 2740747, while the other, procured a year later, was labeled No. 3014491. As will be shown, the two gauges agreed very well with one another as far as 500 atmospheres, and also agreed in general with those of the Brooklyn establishment of the same firm, each gauge having been sent to Brooklyn for verification at different times. Because the agreement of our own gauges with one another was better than the agreements of the reports received from the Brooklyn firm, and because also the mean reading of our gauges gave a nearly linear curve for the compressibility of hardly compressible solids with increasing pressure, while the Brooklyn result gave curves less regular, the average reading of our two gauges was taken as the standard, and every reading of each gauge was corrected to correspond to it.

In order to compare the two gauges together, they were both attached to the same compression-pump on several occasions, and the pressure was increased step by step, sometimes 50 atmospheres\* at a time, and sometimes only 10 atmospheres at a time. The discrepancies between different comparisons at the same point never exceeded an atmosphere, and the average was taken as representing the true relation of the gauges. The corresponding corrections are given in the following table, a positive correction signifying that the gauges in question gave too low a value for the pressure. The gauges could scarcely be read more closely than to within 1 atmosphere; accordingly, the corrections are not made more precise than to within half an atmosphere.

*Corrections to be applied to gauges.  
[All the figures given below are kilograms per square centimeter.]*

Readings.	Corrections.		Readings.	Corrections.	
	Gauge 2740747.	Gauge 3014491.		Gauge 2740747.	Gauge 3014491.
50 to 110	0	0	460	-0.5	+0.5
120	+0.5	-0.5	470 to 480	0	0
130 to 230	0	0	500	-0.5	+0.5
240	-0.5	+0.5	510	-1.0	+1.0
250 to 340	0	0	520	-1.5	+1.5
350 to 400	-0.5	+0.5	530	-1.5	+1.5
410 to 440	±0	0	540 to 590	-2.0	+2.0
450	-1	+1	600	-3.5	+3.5

Although the zero points of the gauges changed somewhat during the protracted research, the relative corrections remained essentially unchanged, and were applied with confidence to all the pressure readings

\*In this paragraph the phrase "atmospheres" is used to signify a kilogram per square centimeter, in which terms the gauges were graduated.



which follow. The change in the zero-point was of no consequence, provided that it did not occur in the course of a single series of experiments, because a pressure of less than 30 atmospheres was never used; the increase in pressure was all that need be known. That the gauges were each trustworthy in any given series, many experiments demonstrated. The fact that the value of compressibility of water as determined by the gauges at the close of the experiments was found to be equal to that found at first is, further, strong evidence of the constancy of the gauges.

It is interesting to compare the value of the compressibility of a standard substance, for example water, as computed with the help of these corrected pressures, and the value for the same substances found by Amagat.\* This comparison is given in the table below, using an average of our three most careful determinations, to be recorded later.

*The compressibility of water.*

Pressure gauge.	Compressibility $\times 10^6$	
	Amagat.	Harvard.
<i>Kg / Cm<sup>2</sup></i>		
100-300	42.4	42.52
300-500	40.6	39.58

From this table it is easily seen that if Amagat's standard was correct, our 200 atmospheres space between 100 and 300 was less than one-third of 1 per cent in error, while the next 200 atmospheres were 2.5 per cent in error. Amagat makes the total compression of water for the 400 atmospheres 0.0166 of the volume, and we make it 0.01642. Whether these differences were due to the possible defects in Amagat's apparatus already mentioned, or to an incorrect standard used in graduating both our gauges, it is impossible to say.

Fortunately, this doubt, which would be a very serious matter in some cases, has no effect upon the value of our result for the present purpose. Relative compressibilities rather than absolute compressibilities are the data sought; and the gauges furnished relative results of an accuracy quite sufficient. On this account it was deemed unwise to go to the very great expense of time and money needed to procure a more accurate standard of pressure. This is particularly true, because, as has been said, the results below can very easily be corrected at any future time, whenever the difference between the compressibility of mercury and water is precisely known with reference to a really accurate standard of pressure.

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\*Ann. de Chim. et de Phys. (6), **22**, 1891 (121).

## DESCRIPTION OF MATERIALS.

## LITHIUM.

Three different bars of lithium obtained at different times were used for the determination of the compressibility of this metal. That used in the preliminary samples was slightly impure, containing either sodium or potassium, as was indicated by its specific gravity and somewhat too large compressibility. On the other hand, that used in the final determinations was very pure, giving neither sodium nor potassium lines in the spectroscope, and containing only 0.3 per cent of aluminum and 0.1 per cent of iron, according to a careful analysis made by F. N. Brink, of this laboratory, who analyzed the sodium and potassium also. The density was found by him to be only 0.534, as will be shown in a further communication. The impurity present was too small in amount to exercise a significant effect on the compressibility.

## SODIUM.

The sodium employed was the commercial article prepared by the Mallinckrodt Chemical Works of St. Louis. It was found to contain 0.035 per cent of iron, and 0.03 per cent of magnesium; but no other impurities in significant amounts were detected. This small proportion of contamination could not have affected its compressibility. The inconsiderable weight of hydrogen, which almost always exists in commercial sodium, was found by Brink to have no essential effect on the density of the metals, and therefore this also could hardly have affected the compressibility. The density was found to be 0.972, in confirmation of Brink's results upon the same preparation of sodium.

## POTASSIUM.

The potassium was a German preparation of a very high degree of purity, containing only minute traces of iron and aluminum, and 0.03 per cent of magnesium. No other impurities were found, except hydrogen, as in the case of sodium. The metal was fused under a limpid paraffin oil, and was subsequently cut and shaped to fit as closely as possible into the jacket. Its density was 0.862.

## RUBIDIUM.

This metal — the commercial article furnished by the same German firm which supplied the potassium — was very impure, in marked contrast to the potassium. It had been our intention to return to rubidium, preparing a pure specimen ourselves, after the work on caesium, but because the latter work seemed to leave no doubt that the compressibility calculated from the results with the impure metal were approximately correct, and time was

lacking, the matter was not pursued further. Only a gram and a half of the metal were at our disposal; but the treatment of this small amount was facilitated by the fact that the large quantity of potassium present liquefied it. The specific gravity of the liquid alloy was found to be 1.285, by means of a tiny pycnometer filled with kerosene, the metal being handled by a fine pipette filled with hydrogen. Assuming no contraction upon the formation of the alloy and having given the density of potassium and that of pure rubidium (1.53), it is easy to calculate that about two-thirds of the liquid must have been rubidium. This assumption is only a very approximate one; but it is supported by the density 0.89 of the liquid alloy of sodium and potassium combined in atomic proportions.\* It serves in the present case because the compressibilities of potassium and rubidium are not very far apart, and therefore considerable uncertainty in the amount of potassium does not greatly affect the result. The trace of sodium which also existed in the metal was too small an amount to cause appreciable error.

#### CÆSIUM.

The salt used for the preparation of this metal was purified according to the method of H. L. Wells by repeated precipitation as the dichloriodide. It was as pure as that used in the recent Harvard work upon the atomic weight of the metal. The sulphate was made from it, and then the hydroxide with the help of pure crystallized baric hydroxide. This was dried and fused, and ignited in an iron tube with powdered magnesium in a current of dry hydrogen. The metal which distilled over was collected in a vessel filled with hydrogen, and was transferred in the liquid state by small pipettes filled with hydrogen. The density of a similar but subsequently made specimen at 20° (in the solid state) was found by Brink to be about 1.87. No analysis of this specimen was made, but it must have been free from all impurities except traces of magnesium and such other impurities as the magnesium may have contained. Rubidium prepared in the same way was found by Brink to contain only insignificant amounts of magnesium and the merest trace of iron.

#### PARAFFIN OIL.

After many experiments upon liquids suitable for conveying the pressure to the metals, paraffin oil was found to be the only suitable substance. For the preliminary experiments a viscous, very high boiling paraffin lubricating oil was used, after having been purified by long contact with

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\*F. N. Brink made experiments on this point also, as will be shown in another paper. He, moreover, made long afterward an approximate quantitative analysis of the particular alloy of rubidium in question, confirming essentially this conclusion.

metallic sodium. For the later more exact work a more limpid oil selected from the higher boiling fractions ( $150^{\circ}$  to  $250^{\circ}$ ) of ordinary illuminating oil (kerosene) was found to be more convenient. After several distillations over chips of sodium this oil was without action on sodium and potassium when cold. We were never able to secure a sample wholly without action on cæsium; but with care a sample could be prepared which had no significant effect during the time of the compression experiments. Enough oil was prepared at once to supply all that was needed in all the experiments, so that its constants could be found once for all.

#### MERCURY.

It is very important that this substance should be pure, for obvious reasons; therefore pains were taken to purify it carefully for the present purpose.

#### PRELIMINARY EXPERIMENTS ON THE COMPRESSIBILITY OF LITHIUM, SODIUM, AND POTASSIUM.\*

At first the compression of sodium which had been solidified in a bulb-tube or in the glass jacket itself was attempted, in the hope that the metal was plastic enough to transmit the pressure to all parts. The internal friction was nevertheless found to be too great for thoroughly satisfactory compression, although it was not too great to prevent the invariable shattering of the jacket or tube by the expansion of the compressed metal upon relieving the pressure. Not many trials were needed to assure us that the metal must be cast separately into a bar fitting snugly but not too tightly into the glass jacket, and surrounded on all sides by oil. Of course, great care was needed to prevent the access to the metal of the mercury in the bulb-tube.

It is not necessary to describe these experiments in detail, because their numerical results are supplanted by the more accurate subsequent work to be recounted. Two glass jackets were used — one with a capacity of only 2 milliliters. In this latter tube the determinations of both lithium and potassium were made, and considering the small volume under investigation, it is surprising that the results were as accurate as they afterwards proved to be. The compressibility of lithium was found to be 0.000011, instead of the true value 0.000009; that of sodium was found to be 0.000018, instead of the true value 0.000015; and that of potassium 0.000032, instead of the true value 0.000031. These errors are not great

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\*These experiments were carried out by F. Bonnet, jr., and constitute his contribution to the present paper.

enough to affect the use to which the preliminary values for the compressibilities have already been put.\*

Although these early experiments are thus treated with but few words, the experience gained in them was valuable, and contributed considerably to the success of the later work. Moreover, they furnished the first data concerning the compressibilities of the most compressible series of metals, and the first evidence which showed that the usually accepted density of lithium as found by Bunsen is considerably too great. This matter will be discussed in a subsequent paper.

#### FINAL DETERMINATIONS OF THE COMPRESSIBILITY OF ALL THE ALKALI METALS.†

For this purpose the jacket indicated in fig. 2 (V) was used, a single one serving for all determinations. In the first place, it was filled with pure mercury, and then with mercury and paraffin oil, in each case having the total compressibilities of the contents measured by first adding and then removing small weighed amounts of mercury in the way already described. In every case, as has been said, 3 mg. of rubber lubricant was put on the stopper. The following table contains the figures, which are given in order to make the somewhat unusual operations more obvious.

*Observations during compression of mercury and oil.*

Jacket filled with 127.6 grams of mercury alone.		Jacket filled with mercury and 7.056 grams paraffin oil.	
Corrected pressure (Kg / cm <sup>2</sup> )	Total weights of mercury added. <i>Gram.</i>	Corrected pressure (Kg / cm <sup>2</sup> ). <i>Grams.</i>	Total weights of mercury added. <i>Grams.</i>
56	0	103	0.684
352	0.0543	225	1.760
550	0.0893	356	2.792
221	0.0308	511.5	3.898
.....	.....	332	2.602
.....	.....	170	1.287
.....	.....	34	0.000

The left-hand half of the table gives data for computing the difference between the compressibility of mercury and glass — which may be said incidentally to agree with previous results — although this fact is only useful in the present research as showing that no accidental error was made in obtaining the figures.

\*Richards, Proc. Amer. Acad., **39**, 584 (1904); Zeit. phys. Chem., **49**, 18 (1894).

†The experimental part of this work was performed by W. N. Stull.

In order to find the values corresponding to every hundred atmospheres, the observed data were plotted with great care on a large sheet of accurate coördinate paper by means of a spline, heavily weighted at each point (see fig. 4). A much reduced copy of these curves is given in fig. 4 on page 21. From these curves the following figures were found:

*Derived values concerning compressibility of mercury and oil.*

Pressure ranges.	Weights of mercury needed for successive 100 Kg/cm <sup>2</sup> with 7.056 gr. oil.	Weights of mercury with Hg. alone in jacket.	Difference = weights of mercury correspond- ing to compression of 7.056 gr. of oil less than of equal volume of Hg.
<i>Kg / cm<sup>2</sup></i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
100–200	0.895	0.0185	0.877
200–300	0.815	0.0180	0.797
300–400	0.750	0.0180	0.732
400–500	0.708	0.0176	0.690
100–500	3.168 = $W_k$	0.0721 = $W_0$	3.096 = $W_k - W_0$

Another less complete trial with the same amount of oil gave the final result 3.100 instead of 3.096 (a difference of only 0.13 per cent), and yet another with a different amount of oil gave upon calculation over to the same basis by simple proportion the value 3.090. There can be no doubt, therefore, that the trial tabulated above represents very nearly the compressibility of the oil in question.

The data needed for proceeding with the metals having thus been found, the first two of these were prepared in the following manner: The bars of lithium and sodium were hammered, cut under oil into the shape needed to fit into the jacket, washed with several successive portions of pure naphtha, warmed in a current of hydrogen, and transferred to a weighed tube containing paraffin oil. The tube was then reweighed, the difference being the weight of the metal.

Potassium, being in smaller pieces, was first fused — for one determination under oil, and for another in hydrogen — and then cast into suitable bars. Subsequently, it was treated exactly as the lithium and sodium.

On the other hand, the rubidium alloy, being liquid, needed different treatment. By alternately exhausting and admitting gas pressure into the apparatus indicated in fig. 3, the small inside weighed tube was filled with the alloy and oil. Another weighing gave the weight of oil and alloy together; and after the compression experiments the alloy was for the most part separated by a hydrogen-filled weighing-pipette, the small remainder being dissolved and determined by titration. The somewhat numerous figures need not be given; the essential outcome is recorded in the table on the following page.

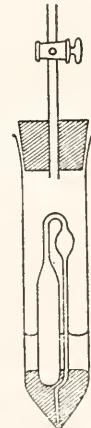


Fig. 3.

*Data and results concerning the compressibility of lithium, sodium, potassium, rubidium, and caesium.*

No. of ex- periment.	Metal.	Weight of metal = $A$ .	Weight of oil = $K$ .	Total weights of mercury added with corre- sponding pressures given beneath each weight.					Weight of mercury be- tween pres- sures 100 and 500 = $W$ .	Compress- ibility $\times 10^6$ .						
1	Li	3.381	2.089 {	0	0.410	0.816	1.226	0.221	} 1.159	8.70						
2	Li	3.285	2.192 {	92.0	221.0	364.5	516.0	193.0	72.5	0.478	0.920	1.268	0.582	.....	1.190	8.44

Average compressibility of lithium (density 0.536)..... 8.6

3	Na	6.947	$1.445 \left\{ \begin{array}{l} 0 \\ 80 \end{array} \right. \right.$	0.377	0.735	1,078	$1.231 \left\{ \begin{array}{l} 508.0 \\ 145.0 \end{array} \right. \right.$	1.148	15.1
4	Na	6.377	$1.965 \left\{ \begin{array}{l} 0 \\ 114.0 \end{array} \right. \right.$	0.482	0.972	1,296	$0.110 \left\{ \begin{array}{l} 502.5 \\ 145.0 \end{array} \right. \right.$	1.341	15.2

Average compressibility of sodium (density 0.972) . . . . . 15.1

5	K	5.661	1.909	{ 0 95	0.544	1.165	1.869	.....	{ } 1.883	30.9
6	K	4.211	3.221	{ 0 91	0.791	1.602	2.313	0.517	{ } 2.209	30.9

Average compressibility of potassium (density 0.862) ..... 30.9

$$7 \left\{ \begin{array}{l} \text{Rb} \\ \dagger \text{K} \end{array} \right. \left\{ \begin{array}{l} 0.855 \\ 0.483 \end{array} \right\} 0.373 \left\{ \begin{array}{l} 0 \\ 66 \end{array} \right. \left\{ \begin{array}{l} 0.151 \\ 200.0 \end{array} \right. \left\{ \begin{array}{l} 0.257 \\ 300.0 \end{array} \right. \left\{ \begin{array}{l} 0.452 \\ 497.5 \end{array} \right. \left\{ \begin{array}{l} 0.173 \\ 220.0 \end{array} \right. \left\{ \begin{array}{l} \text{see} \\ \text{above} \end{array} \right\} \left\{ \begin{array}{l} \\ 36 \end{array} \right\}$$

From this the compressibility of rubidium is calculated as..... 40

8	Cs	0.319	0.285 {	0 93	0.185 382.5	0.262 520.0	0.064 186.0	.....	.....	} see above	} 58
9	Cs	2.705	0.259 {	0 85.5	0.253 237.5	0.528 408	0.681 518	0.208 200	0.208	} see above	} 60.5

The latter being more accurate, the compressibility of cæsium is..... 60

Cæsium also was treated differently from the other metals. At 20° it possesses about the consistency of butter at the same temperature, and is able to transmit pressure almost as well as a liquid. It was therefore allowed to solidify in a small tube essentially like that used for the rubidium alloy, into which it had been drawn while liquid. Of course the small amount of supernatant oil was exactly weighed also.

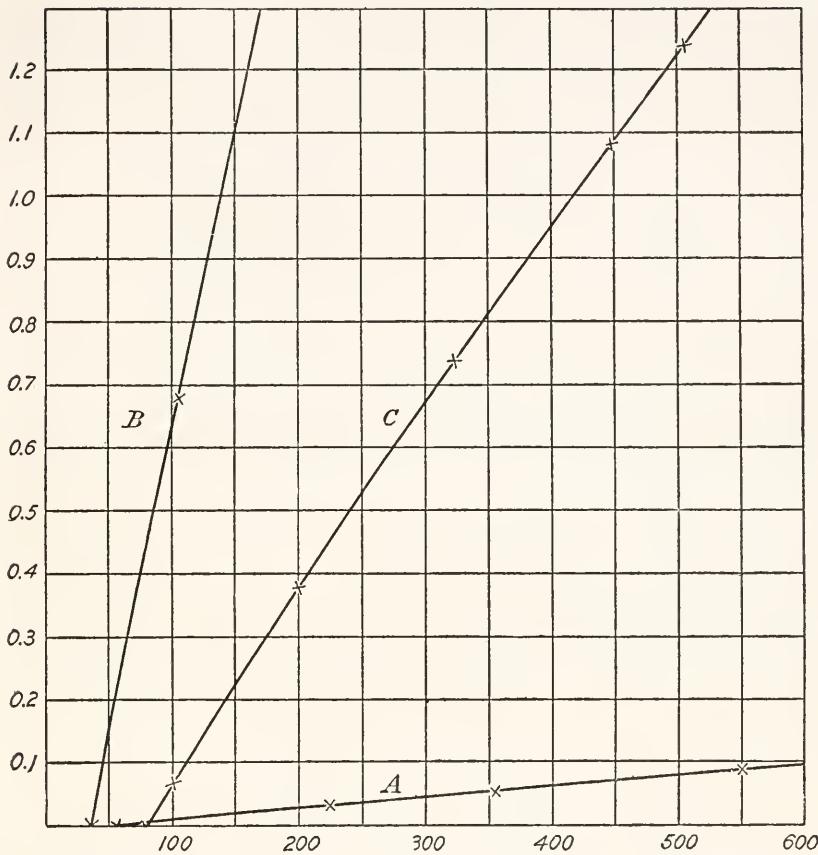


Fig. 4.—Type of Plot for Calculation.

*A*, Mercury. *B*, Sodium. *C*, Oil.

Having thus either clean bars of metal, or glass tubes containing bright metal and oil, the determination of the compressibility was a simple matter. The bars were immersed in oil and the tubes were immersed in mercury in the glass jacket; and each was compressed with weighed additions or removals of mercury as before. The results are given in the table.

The pressure interval from 100 to 500 kg. per square centimeter was used throughout the calculation of the results. Later a table is given showing in some cases the values of the compressibilities for shorter intervals, but these can not claim great accuracy. The calculation may be performed with the help of the equation given in the previous paper; but it is more simply performed in this special case in the following manner:

In the first place, the difference between the weight of mercury added for 400 kg. per square centimeter when the oil and alkali metal were in the

tube, and that when mercury alone was in the tube, was found by simple subtraction. From this remainder was taken further the weight of mercury which represented the difference between the change in volume of the kerosene present and that of the mercury it displaced. The remainder, still a weight of mercury, represented the change in volume of the metal minus that mercury which it displaced. To convert this weight of mercury into change of volume, it was necessary to divide it by the density of mercury under 500 atmospheres pressure at 20°, that is, by 13.57. The resulting volume, upon being divided by 400 times the volume of sodium, yielded as a result the difference between the compressibility of mercury and of sodium. To this was then added the average compressibility of mercury ( $3.69 \times 10^{-6}$ ) for the final result.

The calculation may be expressed algebraically as follows, causing all weights of mercury to correspond to the pressure-difference of 400 kg. per square centimeter between 100 and 500. Let  $W$  = the weight of mercury added when the alkali metal and paraffin oil were in the jacket;  $W_0$  = the weight added when mercury alone was in the jacket;  $W_k$  = the weight when oil alone was in the jacket;  $K_0$  = the weight of the oil taken in the last case;  $K$  = the weight of oil used in the first case;  $A$  = the weight of the alkali metal, and  $D$  = the density of the alkali metal, and  $\beta$  the compressibility of the metal sought. The density of mercury is assumed to be 13.57, and its average compressibility\* between 100 and 500 kg. per square centimeter is assumed to be  $3.71 \times 10^{-6}$ , then

$$\beta = \frac{[W - W_0 - (W_k - W_0) \frac{K}{K_0}] D}{400 \times 13.57 A} + 0.00000371$$

or, more conveniently for the present cases, where  $\frac{W_k - W_0}{K_0} = \frac{3.096}{7.056}$

$$\beta = \frac{(W - 0.0721 - 0.4387 K) D}{5428 A} + 0.00000371$$

A special example taken at random may make the method yet clearer. In experiment 3 below, at the start, when 6.947 grams of sodium and 1.445 grams of kerosene were in the tube, contact was made with the corrected gauge reading at 80. By first adding four successive amounts of mercury, weighing, respectively, 0.377, 0.358, 0.343, and 0.153 gram, and then removing 1.170 grams,† the following corrected pressure-readings were obtained in succession: 200, 325, 449, 508, and 100. The total weights of mercury were then plotted against the pressures as shown in fig. 4,

\*This matter is discussed at length in the third paper of the present series.

†This last figure was observed only to test the work and is not recorded in the table on p. 20.

although of course this was done on a much larger scale. The curve was satisfactory in its slight curvature and its return-point; hence the experiment was deemed successful. From the curve it appeared that  $IV = 1.148$  grams. It had previously been found that  $W_0 = 0.072$  gram and that  $W_k = 3.168$  grams, as given at the foot of the third and second columns of the table on page 19. Then

$$\beta = \frac{\left[ 1.148 - 0.072 - (3.168 - 0.072) \frac{1.445}{7.056} \right] 0.972}{400 \times 13.57 \times 6.947} + 0.00000371 = 0.0000151$$

In the cases of rubidium and caesium a slight correction was needed for the glass vessel containing the metal. This correction has already been discussed in the previous paper dealing with the compressibility of bromine and need not be further detailed here. It is enough to say that the small vessels in experiments 7, 8, and 9 weighed, respectively, 2.65, 1.21, and 2.88 grams.

Thus the elements form a series of increasing compressibility with increasing atomic weight. Lithium is not 3 times and caesium is over 16 times as compressible as mercury.

The relations of these compressibilities to one another and to other constants of the elements are of interest. In parallel columns below are given the compressibilities, the atomic weights, the atomic volumes, and finally an approximate constant obtained by dividing compressibilities by atomic volumes.

#### *Comparison of fundamental constants.*

	Compressibility. ( $\beta \times 10^6$ .)	Atomic weights.	Atomic volumes ( $V$ ).	$K = \frac{\beta}{V} \times 10^7$ .
Li.....	8.6	7.0	13.1	6.5
Na.....	15.1	23.0	23.7	6.3
K.....	30.9	39.1	45.5	6.7
Rb.....	40	85.5	56	7
Cs .....	60	132.9	71	8.4

Thus all these properties increase together, the compressibilities increasing much less rapidly than the atomic weights, but almost at the same rate as the atomic volumes, especially with the three lightest elements.

A further matter of interest may be discovered by the careful study of the curves drawn from the figures given, namely, the different magnitude of the second differential coefficient in the five cases.\* In the case of lithium and sodium the compression curve, when corrected for the mercury and oil present, is almost a straight line, while in the case of potassium, the

\*Richards and Stull, Carnegie Institution of Washington Publication No. 7, p. 44.

compressibility decidedly decreases under pressure, and in that of cæsium the decrease is very marked. The uncertainty of the pressure gauge and the subtlety of the curves make the discrimination of the changes with small differences of pressure somewhat doubtful, but a careful study of the curves led to the following probable values:

*Change of compressibility with pressure.*

	Sodium.	Potassium.	Cæsium.
100-300.....	15.2	31.5	67
300-500.....	15.0	30.3	53
Average, 100-500.	15.1	30.9	60

Thus, while sodium probably decreases in compressibility less than 2 per cent between 200 and 400 atmospheres (the mean pressure in each case), potassium probably decreases over 4 per cent, and cæsium over 20 per cent. Lithium and rubidium undoubtedly take corresponding places in the table, although the present results with these substances were not carried on upon a scale large enough to show this with certainty.

The data given are enough to show that the five alkali metals are no exceptions to the usual but not universal rule that the more compressible a substance, the more its compressibility decreases with increasing pressure. It is interesting to note also, that cæsium, having a compressibility of about the order of such liquids as bromine and chloroform, should have its compressibility change with pressure to an extent not very different from these liquids.

The results recorded in this paper will be compared with those with other substances and interpreted in the light of the theory of compressible atoms in subsequent papers.

It remains only to express the results of the work in terms of the three standards of pressure commonly in use. The megabar is the pressure of a megadyne per square centimeter, or 0.987 atmosphere.

*The average compressibility of the alkali metals  
between 100 and 500 atmospheres.*

	Kg. per cm <sup>2</sup> .	Megabars.	Atmospheres.
Lithium .....	0.0000086	0.0000088	0.0000089
Sodium .....	.0000151	.0000154	.0000156
Potassium....	.0000309	.0000315	.0000319
Rubidium....	.00004	.00004	.00004
Cæsium.....	.000060	.000061	.000062

In conclusion, the authors acknowledge with pleasure their indebtedness to the Carnegie Institution of Washington for the pecuniary aid which made this research possible.

#### SUMMARY.

The compressibilities of the alkali metals were successfully studied by the new method of Richards and Stull, slightly altered to suit the new conditions. The pressure being expressed in megabars, they were found to be: 0.0000088 for lithium, 0.0000154 for sodium, 0.0000315 for potassium, 0.00004 for rubidium, and 0.000061 for cæsium, between pressures of 100 and 500 megabars.

These numbers are almost proportional to the respective atomic volumes.

The greater the compressibility, the greater was found to be its decrease with increasing pressure.



## II

### THE COMPRESSIBILITY OF CARBON, SILICON, PHOSPHORUS, SULPHUR, AND SELENIUM.

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BY THEODORE W. RICHARDS, W. N. STULL, AND F. N. BRINK.



# THE COMPRESSIBILITY OF CARBON, SILICON, PHOSPHORUS, SULPHUR, AND SELENIUM.

## INTRODUCTION.

The preceding paper upon the alkali metals led to the conclusion that among similar elements large atomic volume is at least occasionally associated with great compressibility. Inspection of the figures for other substances quickly indicates that atomic volume is not the only property which thus takes part in determining the magnitude of the effect of pressure; but clearly there is some connection between the two properties. Therefore it seemed probable that elements possessing small atomic volume must possess slight compressibility; and with a view to subjecting the hypothesis to a striking test, carbon and silicon, which lie in the first two valleys of the atomic-volume curve of Lothar Meyer, were subjected to experimental investigation. Having found in the results with these elements a vindication of the hypothesis, other non-metals with larger atomic volume, namely, sulphur and selenium, were studied in order to obtain further light upon this relation and other possible modifying circumstances. In a previous research,\* the compressibility of yellow phosphorus was determined; it was now desired to determine if the more dense modification, red phosphorus, has the smaller compressibility which would be expected of the more compact material. Therefore red phosphorus also was studied, with interesting results.

The method of investigation was essentially similar to that employed in the case of the alkali metals, the substances being compressed under a neutral liquid in a suitable glass jacket, the extent of the compression being determined by the weights of mercury needed to make contact with a fine platinum point at various pressures. Due correction was of course applied for the contraction of the jacket and the liquids, in the simple manner already indicated.

## PREPARATION OF MATERIAL.

Several samples of carbon were employed, including charcoal of various kinds, and both natural and artificial graphite. Effort was made to secure diamonds, also, but although Mr. George F. Kunz, of Tiffany & Co., New York, has kindly interested himself in the matter, we have not yet been

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\*Richards and Stull, Carnegie Institution of Washington Pub. No. 7.

able to secure enough colored diamonds free from mechanical defects to obtain adequate measurements. The commercial value of 20 grams of colorless perfect diamonds is so great that it was questionable if the results would be commensurate with the risk involved. Accordingly, these were not used, although kindly offered. Nevertheless, it is hoped that, before long, enough suitable crystallized carbon may be obtained to complete the study of this subject.

Silicon was very kindly furnished in quantity by Mr. F. J. Tone, of the International Atcheson Graphite Company at Niagara Falls. The substance was in a compact brilliant crystalline mass, free from cracks or gas-holes, very suitable for the purpose in hand. Before use it was broken into small pieces fit for introduction into the jacket. In two experiments, 1.346 and 4.464 grams of the substance lost, respectively, 0.558 gram and 1.837 grams on immersion in water, corresponding to specific gravities of 2.41 and 2.43, respectively. The average, 2.42 ( $20^{\circ}/20^{\circ}$ ), lies between the values found by Wöhler and by Winkler. The true density, corrected to the vacuum standard, is essentially the same. In the case of very slightly compressible substances like this the knowledge of the specific gravity of the sample within 1 per cent is very important.

The carbide of silicon ("carborundum"), also made by the same firm, was studied. Large masses of crystals of this substance were gently fractured in order to open existing cracks without starting new ones. Its specific gravity was 3.20 ( $20^{\circ}/20^{\circ}$ ), as 6.277 grams displaced 1.988 grams of water; hence its density was 3.19.

Sulphur was investigated in its densest form — clear crystallized rhombic sulphur — having a specific gravity of 2.07. The other forms are too unstable under pressure to give satisfactory results. A very pure sample was obtained, which contained only negligible amounts of other substances.

Selenium, in a state of adequate but not perfect purity, was obtained from a well-known German firm, in small fragments. These were broken into somewhat smaller pieces in order to open accidental cavities. Of this material 8.959 grams were found to displace 2.0946 grams of water at  $20^{\circ}$ , indicating a specific gravity of 4.28 ( $20^{\circ}/20^{\circ}$ ), a figure identical with the value found by Saunders.\*

Red phosphorus was treated several times with carbon bisulphide to remove any yellow phosphorus which might be present, and the last traces of the liquid were evaporated.

Mercury was carefully purified as usual. Ordinary distilled water is pure enough to play the rôle required of it. Thus all the substances were prepared for compression.

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\*Journ. Phys. Chem., **4**, 491 (1900).

## THE APPARATUS.

In the course of this work, which was prolonged over two years, five glass jackets were used. These were of two types, represented in the accompanying diagrams. Jacket v was the one already used for the alkali metals, and jackets VII, VIII, and IX were of the same type, but slightly larger; jacket III was of a different and somewhat less advantageous form, devised before jacket v. The pressure of the high column of mercury on the right-hand side in this form made the danger of leakage greater than in the other; but when the stopper was properly lubricated, no trouble was experienced.

Jacket III was always lubricated around the glass stopper with 10 mg. of rubber-paraffin lubricant; jackets v, VIII, and IX always with 3 mg., and jacket VII always with 4 mg. The different extent of lubrication and the difference in the glass caused but a very slight difference in the behavior under compression of these jackets. Because the lubricant was always the same in kind and quantity with any one of the jackets, even this slight difference is entirely eliminated from the final results.

*Data concerning glass jackets filled with mercury.*

No. of experiment.	Designation of jacket.	Weight Hg in jacket.	Weights of mercury added, the corresponding increasing pressures in kilograms per square centimeter being given directly beneath each weight.				$W_0$ , weight of mercury added from 100 to 500.
1	Jacket III....	281.3	{ 0 85.5	0.0632 225	0.1094 330	0.1705 465	{ 0.1798
2	Jacket v....	127.6	{ 0 56	0.0543 352	0.0893 550	0.0308 221	{ 0.0721
3	Jacket VII...	140	{ 0 73	0.0473 306	0.0907 529	0.0180 160	{ 0.0794
4	Jacket VIII .	170	{ 0 40	0.0338 173	0.0694 325	0.0111 495	{ 0.0967
5	Jacket IX ...	150	{ 0 54	0.0125 112	0.0695 372	0.0934 480	{ 0.0878

Before giving the data for each of the elements, the behavior of the jackets alone under pressure must be detailed. The figures given in the accompanying table were found by the method already described in the paper on the compressibility of the alkali metals. In brief, the empty jacket having been weighed, it was carefully filled with mercury, and weighed again. The difference gave the values in the first column of the figures in the table. This mercury had been so adjusted as to stand slightly above the fine platinum point in the narrow limb of the apparatus. Pressure was now applied, by placing the jacket in the barrel of a Cailletet compression apparatus, until contact was just made at this point — this pressure

being recorded in the second column of figures. A small weighed globule of mercury was now added, and pressure was again applied. The weight added and the new pressure are recorded in the third column. In the same way the fourth and fifth columns of figures were found. From all these values, with the help of a plotted curve drawn through the points which they represent, were computed the values given in the sixth column of figures, headed  $W_o$ . This records the amount of added mercury needed by each jacket to cover the range of pressure from 100 to 500 kg. per square centimeter. Each jacket must have this series of experiments carefully made with it, on account of the variations in the compressibility of glass. The figures given for jacket v are merely a repetition of those given in somewhat different arrangement in a previous table.

In compressing an irregularly shaped substance, such as a mass of broken pieces, or a quantity of crystals, beneath the mercury in one of these jackets, errors are liable to arise

because the surface tension of the mercury keeps this liquid out of the finest cracks and cavities. Hence, unless further precaution is taken, the observed values for the compressibilities are always larger than the true ones. We have found this difficulty may be wholly overcome if the solid is first thoroughly surrounded by a liquid which wets it, the major part of this liquid being subsequently displaced by mercury in case the metal is without action on the solid. The film of lighter liquid wholly surrounds the solid, and is everywhere also in immediate contact with the mercury, so that no empty spaces are left.

In order to compute the results from data thus obtained with three substances in the jacket, the compressibility of the lighter liquid, as well as the quantity present, must

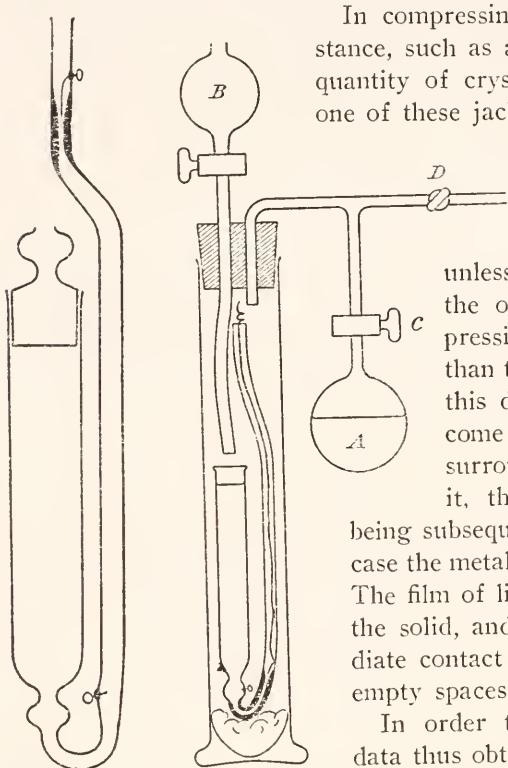


Fig. 5.—Jacket III. Fig. 6.—Apparatus for Powders.

be exactly known, just as in the case of the alkali metals which has already been discussed.

As water was the supplementary liquid most convenient to use in the present case, pains were taken to determine accurately its compressibility

before proceeding with the solid substances, so that this measurement might be strictly comparable as regards the standard of pressure, and all other conditions, with the measurements concerning the substances to be studied. Obviously, it is not necessary to determine the compressibility of water in each one of the jackets, for this quantity is one entirely independent of the form or nature of the apparatus used. Nevertheless, experiments were made with several of the jackets, in order to test their efficiency.

These compressibility determinations with water, as far as they concern the present work, may be quickly given. In a previous research\* two of us found that water decreases 0.01632 of its uncompressed volume between 100 and 500 pressure-units. In three other experiments we have found more recently the values 0.01664, 0.01652, 0.01644, and two others by Mr. J. H. Mathews gave essentially similar values, 0.01640 and 0.01639. Clearly the value is not far from 0.0164; and for most purposes this might be taken as representing very nearly the average compressibility sought, which is thus about 0.0000041. For our present purpose, however, the greatest obtainable accuracy was desired; and accordingly the following three experiments were executed under conditions as nearly as possible like those obtaining when the other substances were compressed.

*Compressibility of water (Jacket III).*

No. of experiment.	Weight of water.	Total weights of mercury added, the corresponding total pressures in kg/cm <sup>2</sup> being given directly beneath each weight.						
	<i>Grams.</i>							
...	19.187	{ 0      1.056      2.098      2.945      4.045      4.600      -0.189 51.5    148.5    247.5    330.5    442    499.5    33						
...	19.187	{ 0      1.892      3.991      4.852      .....      .....      ..... 33      2.095    417.5      505      .....      .....      .....						
...	15.377	{ 0      1.247      2.452      3.710      0.411      ..... 63.5    206.5    353.5    511      110.5      .....						

The careful plotting of these closely agreeing results leads to the conclusion that each gram of water requires 0.2031 gram of added mercury between 100 and 500 pressure-units, after eliminating the compression of the jacket. Dividing this quantity by  $400 \times 13.57$ , correcting for the volume of 1 gram, and adding the compressibility of mercury, the value  $0.00004105$  is found as the average compressibility of water, or 0.01642 as the total change in volume in water, between 100 and 500 pressure-units, referred to the original uncompressed volume. This value, nearly the mean of all the earlier work, will be taken in the work which follows as being the one most nearly comparable to the other determinations.

\*Richards and Stull, loc. cit. See also Richards, Stull, and Bonnet, this monograph, p. 14.

## THE DETERMINATIONS OF COMPRESSIBILITY.

All the preliminary data having thus been found, the solid to be studied was placed into the jacket thus prepared and tested. The operation was usually conducted and the weight of the water was usually found in the following way: The jacket containing a little mercury, its stopper already lubricated with a weighed amount of lubricant, the solid to be studied, and a bottle containing an excess of pure mercury were all placed upon the balance-pan together, and weighed to within a milligram. The solid was then placed within the jacket, water or oil was added (after exhausting the air if necessary), and mercury was carefully supplied from the bottle in sufficient quantity. After closing the jacket and cleaning it externally, it was once more weighed with the bottle and residual mercury. The gain in weight of the total load was the weight of the water or oil in the jacket.

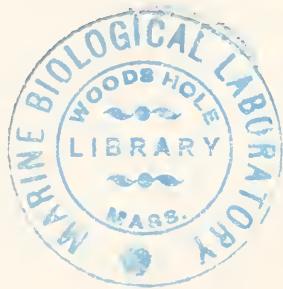
When operating with powders not attacking mercury, the following method may be used with advantage. The jacket with a small amount of mercury in it, together with an additional tube of mercury, a little platinum disk, and the lubricated stopper were weighed all together. The powder under investigation was then placed into the jacket and packed down with a glass rod. On the top of this powder was placed the platinum disk, which was firmly wedged so as to prevent the powder from being thrown out during the subsequent treatment. The apparatus was reweighed to obtain the weight of the powder. The jacket (unstoppered) was then placed into the apparatus shown in fig. 6, in which apparatus *A* was filled with dry ether, while *B* was filled with the supplementary liquid (either water or oil of known compressibility) to be used to transmit the pressure to the powder. The apparatus was then evacuated and *D* closed, and ether vapor was boiled back into the apparatus from *A*. After closing *C* the whole was evacuated again; and the process was repeated again and again, alternately exhausting and filling with ether vapor four times. The object of this treatment was to displace every trace of air in the interstices with ether vapor, which would quickly be reduced to vanishingly small proportions under pressure. The vessel was finally exhausted to 2 or 3 mm. pressure and the liquid was allowed to run down from *B*. Air was now slowly admitted, always keeping a layer of liquid above the powder. In this way all the empty space was filled by the oil or water. The apparatus was now taken out and a plug was tied down upon the top of the platinum disk. Mercury was poured into the long narrow arm of the jacket and pressure from a common bicycle pump was

applied at the upper end of this arm. Mercury was thus forced up to take the place, in large measure, of the oil or water in the jacket, and in this way the jacket was made to contain a minimum of supplementary liquid. The lubricated stopper was now put in place, and after wiping, the jacket was reweighed. Thus were obtained sufficient data for obtaining the weight of water or oil and the powder used. The compression was then carried on in the usual way.

This method must sometimes be applied also in cases where the material contains fine cracks difficult to free from air, as in many rocks and other substances with crystalline structure. It was used in the case of all the substances discussed in this paper, except carbon.

This exceptional substance, in the form of graphite, needed especially elaborate treatment on account of its porous nature. In order to remove moisture, adsorbed air, and any other volatile substances present, it was inclosed in a hard glass tube and was heated to redness for several hours in a Sprengel vacuum. After weighing, the carbon was subjected again to the same treatment for several hours more. Boiling distilled water was next allowed to run in upon the carbon and remained in contact with it for about thirty-six hours. It was hoped by this means to remove the air from the pores of the solid and fill them with water. As much of this water as possible was then replaced by mercury in the jacket, and the compression conducted in the usual way. Even with all these precautions, it was found impossible to obtain wholly consistent results with graphite, and the value given in the table must be looked upon as the maximum value. Apparently the substance contains a multitude of pores of submicroscopic minuteness which only fill with water under high pressure. It may be that these pores are only developed by the compression of the substance, or at least only opened up by this compression.

Both in the cases of carbon and silicon, several preliminary determinations gave values for the compressibility of each element somewhat lower than those given in the table; but those recorded are the last and most careful experiments, and are chosen for that reason.



## CALCULATION OF RESULTS.

Attention is now directed to the calculation of the correction to be applied for the pressure of the compressible liquid in the jacket around the substance under investigation. This is performed in a manner exactly analogous to that used for the similar correction applied in the case of the alkali metals, except that in the present case water, not paraffin oil, was the supplementary liquid used.

The compression of water between 100 and 500 pressure-units is, according to our measurements, already summarized above, 0.01642 of its bulk,\* or for 1 gram of water at 20°, 0.01645 milliliter. The difference between this compression and that of the same bulk of mercury, 0.00148 between the same pressures, is 0.01497. As the density of mercury under 500 atmospheres pressure at 20° is 13.57, the quantity  $13.57 \times 0.01497 = 0.2031$  gram more of mercury would have to be added to a jacket containing a gram of water besides the mercury than to the same jacket filled with mercury alone, over the stated range of 400 pressure-units. When water is the liquid used, these figures, 1 gram and 0.2031 gram, take the place of the values  $K_0$  and  $W_k - W_0$ , respectively, in the equation given under the alkali metals for the calculation of the results. Thus the compressibility of a substance is found from the data given below by the following equation when water is used:

$$\beta = \frac{(W - W_0 - 0.2031 K) D}{5428 A} + 0.00000371$$

where  $W$  = the weight of mercury added to the jacket containing the solid substance, mercury, and water for 400 units of pressure between 100 and 500 units.

$W_0$  = the corresponding weight of mercury, added when mercury alone is present.

$K$  = the weight of water present.

$D$  = the density of the substance under investigation.

$A$  = the weight of the substance.

0.00000371 = the average compressibility of mercury between 100 and 500 pressure-units.

As an example the case of selenium may be cited. With 2.075 grams of water and 19.48 grams of selenium of density 4.28 in jacket vii, it was found from the curve that 0.696 gram of added mercury demanded an increase in the contact-pressure from 100 to 500 kg. per square centimeter. This weight of mercury is  $W$  in the equation.  $W_0$ , the similar

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\*See p. 33.

datum with mercury alone in the jacket, was 0.079 (see table on p. 31). Hence the equation becomes

$$\beta = \frac{(0.696 - 0.079 - 0.2031 \times 2.075)4.28}{5428 \times 19.48} + 3.71 \times 10^{-6}$$

$$\text{or } \beta = 0.00000116$$

The data and results concerning the substances under investigation are recorded in the table below.

*Data concerning the compressibility of five non-metals.*

No. of experiment.	Substance.	Weight of substance.	Weight of water.	Weights of mercury added with corresponding pressures beneath each weight.						Density of substance.	Jacket No.	Compressibility $\times 10^{-6}$			
8 C.....	14.1	0.390	{ 0	0.0277	0.0974	0.1612	0.615	{ 81	150	335	508	220	{ 2.26	IX	{ not over 3
9 C.....	14.1	0.390	{ 0	0.0286	0.0800	0.1654	0.0496	{ 86	164	301	556	218	{ 2.26	IX	{ not over 3
13 Si.....	9.613	1.400	{ 0	0.0423	0.2706	0.3366	0.1140	{ 63	120	429	519	217	{ 2.42	IX	{ not over 0.16
14 Si C....	7.397	0.428	{ 0	0.0556	0.0974	0.1581	0.0921	{ 86	242	359	535	340	{ 3.19	VIII	0.21
15 P <sub>4</sub> red	12.132	3.707	{ 0	0.1575	1.0274	1.1549	0.294	{ 54	120	459	520	173	{ 2.15	VIII	8.8
<sup>1</sup> 16 S.....	17.00	10.9	{ 0	1.048	2.081	3.218	0.146	{ 82	229	379	544	103	{ 2.07	III	12.3
<sup>1</sup> 17 Se.....	19.48	2.075	{ 0	0.3424	0.7353	.....	.....	{ 102	294	524	.....	.....	{ 4.28	VII	11.6

<sup>1</sup> These two determinations were made by W. N. Stull; all the others by F. N. Brink.

### DISCUSSION OF RESULTS.

The study of these results is interesting. It is to be noted in the first place that, as was predicted, carbon and silicon have low compressibilities, although the former of these substances gives a larger value than had been anticipated. Silicon has the lowest compressibility,  $0.16 \times 10^{-6}$ , of any of the substances included in this series of papers.

In seeking for an answer to the question as to why the value for carbon should not be still lower than it is, an obvious one suggests itself at once in the different states of aggregation of the two substances. The silicon was compact and crystalline, the carbon in a loose friable mass. That carbon also is but little compressible when crystalline may be inferred from the behavior of carborundum, which is but little more compressible than silicon itself, although containing almost 30 per cent of carbon. Assuming for the moment that compressibility is an approximately additive property (an assumption which only holds true when, as in this case, no great volume-change occurs in producing a compound from the two elements) it is easy to calculate from the compressibilities of silicon and carborundum that the compressibility of crystallized carbon must be about

0.0000003, or only a tenth of that in graphite. A result of the same order would be reached by comparing the linear coefficients of expansion of diamond with that of graphite, Fizeau's values for these data being respectively 0.0000012 and 0.0000079. If Dupré's equation, connecting compressibility and coefficient of expansion

$$\beta' = \beta \frac{a' \Delta^2 T'}{a' \Delta'^2 T}$$

be assumed to hold for a single element, the compressibility of diamond computed from that of graphite would be found to be about 0.0000007. The mean between these guesses, namely,  $0.5 \times 10^{-6}$ , may be taken as the most probable value for the present, until an experimental determination is possible, of the compressibility of diamond.

The difference between actually determined compressibilities of the different allotropic states of a given element is exhibited for the first time by the comparison of the result recorded above concerning red phosphorus, with that found some years ago by Richards and Stull concerning white phosphorus.\* The former of these values, as found by the present research, is  $8.8 \times 10^{-6}$ , while the latter of these values, as found in the earlier investigation (between 100 and 150 pressure units), is  $19.9 \times 10^{-6}$ . Thus the compressibility of the more compact modification of phosphorus is less than one-half the compressibility of the less compact variety. This is a highly interesting fact not only in itself as the first instance on record of such relationship, but also in relation to the theory of compressible atoms with which it is entirely consistent, as well as in connection with the preceding discussion concerning the allotropic forms of carbon. Red phosphorus, having less than half the compressibility, is only about 20 per cent denser than white phosphorus, whereas diamond is 36 per cent denser than graphite. Accordingly, one would expect diamond to be not much more than one-quarter as compressible as graphite, if as much as this. It will be seen at once that the comparison, although of course it is capable of giving nothing more than the order of result to be expected, substantiates the approximations given above concerning carbon, and adds its share toward giving the result more weight than would be adjudged to a mere guess.

The comparison of sulphur with selenium is interesting, because, although the two elements have decidedly different atomic volumes, 15.7 and 18.5, respectively, their compressibilities are almost alike, 12.3 and 11.6 respectively; moreover, such difference as they exhibit is in the opposite direction from that in the atomic volume. Among the causes likely to bring about this greater compressibility of sulphur, its weaker cohesion, as indicated both by its volatility and its slight tensile strength, may be

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\*Carnegie Institution of Washington Publication No. 7, p. 37.

supposed to be the most probable. If the theory of compressible atoms is used as a guide, it is reasonable to suppose that when a substance is subjected to but slight internal pressure from its cohesion, an outside pressure would produce a greater change of volume than the same outside pressure would produce upon a similar substance, already much compressed. Such is the case with sulphur and selenium. This is merely carrying the arguments drawn from the fact concerning phosphorus and the inferences concerning carbon to the comparison of two similar elements, instead of simply to the comparison of the different states of the same element.

These results will be considered in relation to one another and also in relation to the compressibilities of the other elements in another paper of this series,\* as well as in a future paper in which their relations to the theory of compressible atoms will be more clearly set forth. The present investigation aims only to present the facts in order that they may go on record at once.

It remains only to state the results in terms of the three pressure standards commonly accepted.

*Average compressibilities of C, Si, P, S, and Se, between  
100 and 500 atmospheres.*

Elements.	Kg. per cm. <sup>2</sup>	Megabars.	Atmospheres.
Carbon, graphite.....	0.000003	0.000003	0.000003
Carbon, diamond.....	.0000005?	.0000005?	.0000005?
Silicon .....	.00000016	.00000016	.00000016
Carbide of silicon....	.00000021	.00000021	.00000021
Red phosphorus.....	.0000088	.0000090	.0000091
White phosphorus....	.0000199	.0000203	.0000206
Sulphur .....	.0000123	.0000125	.0000127
Selenium.. .....	.0000116	.0000118	.0000120

In conclusion, it is a pleasure to express our thanks for the generous support of the Carnegie Institution of Washington.

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\*See p. 65 of this publication.

## SUMMARY.

The method of Richards and Stull of determining the compressibilities has been applied to five more non-metals.

The compressibility of silicon was found to be not over  $0.16 \times 10^{-6}$ , silicon being the least compressible of the thirty-five elements thus far investigated.

Carbon in the state of graphite was found to be filled with minute pores which interfered with the exact determination of its compressibility. Nevertheless, this quantity may safely be said to be not greater than  $3 \times 10^{-6}$ .

The compressibility of carborundum (SiC) was found to be  $0.21 \times 10^{-6}$ , but little greater than that of silicon. From these results and from other compressibilities it is concluded that the compressibility of diamond can not greatly exceed  $0.5 \times 10^{-6}$ .

Red phosphorus was found to have a compressibility of  $9.0 \times 10^{-6}$ , less than half of the value for white phosphorus. Thus for the first time differences in compressibility caused by change of allotropic form are illustrated by actual experiment.

Sulphur and selenium were found to have, respectively, compressibilities amounting to  $12.5 \times 10^{-6}$  and  $11.8 \times 10^{-6}$ . All these values are expressed in megabars, and give the average compressibilities between 100 and 500 megabars.

### III

## THE LINEAR COMPRESSIBILITY OF COPPER AND IRON, AND THE CUBIC COMPRESSIBILITY OF MERCURY.

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BY THEODORE WILLIAM RICHARDS AND FRANCIS NEWTON BRINK.



## THE LINEAR COMPRESSIBILITY OF COPPER AND IRON, AND THE CUBIC COMPRESSIBILITY OF MERCURY.

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### INTRODUCTION.

The recent determinations of the compressibilities of the elements all depend upon that of mercury. A change in the accepted value of this constant would affect all the others. It is true that their order of succession and their order of magnitude could not be changed, and that the preceding conclusions concerning them could not be affected, by any probable deviation of the accepted value of mercury from the true one; nevertheless, before publishing so extensive an array of new data, it was thought worth while to obtain further experimental evidence concerning the very important fundamental value in question.

The new method of Richards and Stull was used for the determination of the compressibility of mercury in the following manner: The respective differences between the compressibilities of iron and mercury, and of copper and mercury were determined; and then, by adding these differences to the absolute cubic compressibilities of these metals as found from their linear measurement under compression, the absolute cubic compressibility of mercury was found.

The first part of this program was carried out by compressing the solid metals in question under water and mercury, in a glass jacket exactly like that used for the similar work with the alkali metals and the non-metals; and both experiment and calculation were wholly analogous to the procedures there described. Because the mercury could not be allowed to come into contact with the copper for fear of amalgamation, more water was needed to surround the solid in this case than in the case of iron. Even in the latter case, however, the presence of some water was found highly desirable to fill any small crevices or inequalities from which mercury was excluded because of its high surface tension.

The solid metals used were the purest commercial copper and wrought iron, hammered and carefully turned to fit the jacket. In the case of iron powerful hammering was especially necessary; in preliminary rejected determinations indication was had of the existence of fine pores in the metal. The samples used finally gave wholly satisfactory results. The mercury was carefully purified by recognized means.

As in the case of the other substances, the jacket was first filled with pure mercury, and a series of determinations was made of the pressures needed to compress small successively added weighed globules of mercury into precise contact with a finely pointed platinum wire in the narrow limb of the jacket. This procedure was then repeated with pure water in the jacket above the mercury, giving data previously detailed for the compressibility of water; and finally once more with the solid metal and a small amount of water in the same jacket. The data concerning the first two sets of determinations are given in the preceding paper; while the last of the three series of data is given in the table below, with the results calculated from them all together. The calculation is performed according to the usual equation somewhat transposed, thus

$$\beta_{\text{Cu}} - \beta_{\text{Hg}} = \frac{(W - W_0 - 0.2031 K) D}{5428 A}$$

*Determination of differences between compressibility of iron and copper and mercury.*

No. of experiment.	Metal.	Weight of metal.	Weight of water.	Weights of mercury added with corresponding pressures beneath.					No. of jacket.	Difference between compressibilities of solid metal and mercury ( $\pm \beta_M - \beta_{\text{Hg}}$ ) (100 to 500 Kg/cm <sup>2</sup> ).	
1	Cu	75.410	1.560	{ 0 61	0.116 229	0.218 383	0.312 530	0.027 100	VIII	- 0.00000320	
2	Cu	75.410	1.560	{ 0 58	0.062 148	0.170 306	0.302 515	0.166 300	VIII	- 0.00000324	
3	Cu	54.57	3.585	{ 0 76	0.123 141	0.552 378	0.782 511	0.095 127	VIII	- 0.00000319	
4	Cu	152	2.166	{ 0 90	0.123 230	0.283 427	0.413 599	0.069 167	III	- 0.00000315	
Average result for copper .....											- 0.00000319
5	Fe	69.95	0.833	{ 0 53	0.045 216	0.093 395	0.125 527	0.051 237	VIII	- 0.00000332	
6	Fe	133.2	1.925	{ 0 75	0.116 236	0.215 386	0.301 516	0.127 250	III	- 0.00000333	
Average result for iron .....											- 0.00000332

<sup>1</sup> These determinations were made by W. N. Stull a year before the other work. Jacket III, described in the preceding paper on non-metals, was used.

The results are so concordant as to leave no doubt that the difference between the compressibilities of mercury and copper is not far from 0.00000319, while the corresponding difference in the case of iron is about 0.000003325. The negative signs in the table indicate that each solid is less compressible than mercury.

APPARATUS FOR DETERMINING THE LINEAR COMPRESSIBILITY  
OF COPPER AND IRON.

The differences having been thus determined, it remained to determine the absolute linear compressibilities of copper and iron — a matter far more difficult than the preceding. The method used for this purpose was essentially the same in principle as that used by Amagat. The apparatus, however, was somewhat simpler and less liable to accidental errors. The metal whose compressibility was to be determined was turned into a thin rod, 2.6 meters long. The change in length of this rod was measured with great care upon subjection to pressure. For this purpose the rod was confined in a steel jacket of peculiar construction.

The apparatus is depicted in section in fig. 7. The jacket for containing the rod which represents the extreme ends almost in full size, and more of the arrangement on a reduced scale, consisted of a steel cylinder (*E*) nearly 3 meters long, 23 mm. outside diameter, and 7 mm. inside diameter. The steel cylinder was surrounded by a thin iron cylinder (*L L*) of 8 cm. inside diameter to contain water for maintaining a constant temperature. Screwed into the inside of the *L L* was the heavy iron rod (*K*) which acted as a support for the fixed point *A*. The water in the jacket was stirred by the up-and-down motion of metal bars bent in the shape of horse-shoes, placed 0.3 meter apart. The stroke of this complicated oscillating apparatus was about 5 inches.

Not only was the whole apparatus kept as nearly as possible at a constant temperature, but the work was done in a room the temperature of which was regulated to within  $0.1^{\circ}$ . The room was heated by a gas-stove having a hydrogen-barometric electrical regulator\* attached for controlling the supply of gas. The air in the room was kept in constant motion by means of a large electric fan.

On the upper end of *E* was screwed the nut *D*, through the center of which passed the bolt *C*. To insure a tight joint the threads of this bolt were tinned. This bolt was pierced through the center for almost its whole length by a small hole in which rested loosely the steel needle *B*. The lower end of the bolt bore a rigid but very sharp platinum point (*F*) about a centimeter in length.

Obliquely through the lower end of the steel cylinder was drilled a hole for the passage of an insulated copper wire (*M*) which was attached to the lower end of the metal rod (*R*) to be measured. This channel was made pressure-tight by the use of marine glue.

\*Regand and Fouillard, Zeitsch. wiss. microscop., **20**, 138 (1903); also Richards and Mark, Proc. Am. Acad., **41**, 119 (1905).

*G* was a steel plate perforated through the center, set with its upper surface level with the base of the water-jacket. The object of the plate was to provide a solid support for the metal rod to be measured.

This metal rod was electrically insulated by being surrounded with several pieces of loosely fitting glass tubing (*N*). The lower end of the tube

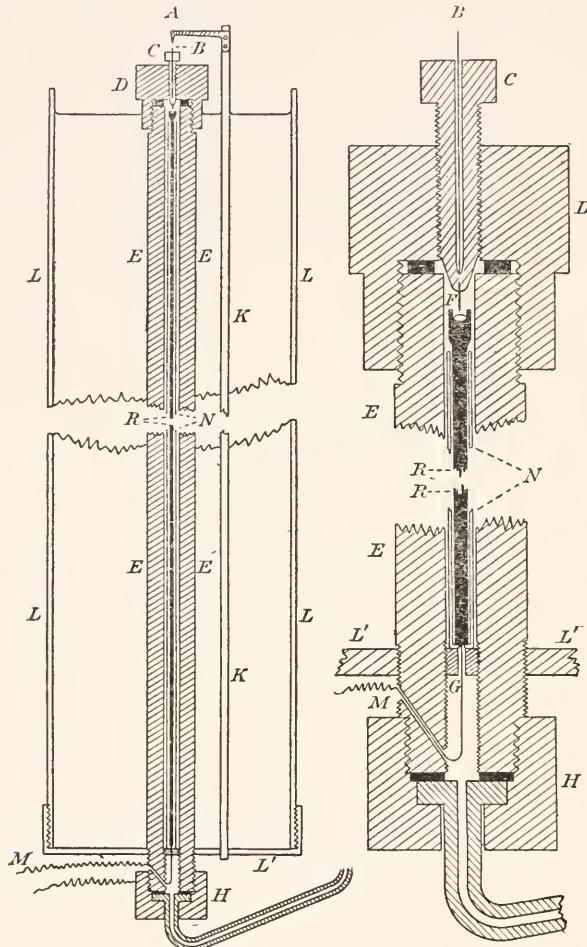


Fig. 7.—Apparatus for Determining Linear Compressibility.

incasing the base of the metal rod had been almost closed, so that the rod rested on a thickness of 1 mm. of glass. The upper part of the metal rod was somewhat larger in diameter than the shaft and contained on top a shallow cup into which was placed a drop of mercury, intended to make electrical contact with the platinum point *F*. This part of the rod was

wrapped with a piece of thin silk, except above. In this manner it was possible to insulate the rod perfectly, if the fluid transmitting the pressure was a non-conductor.

Limpid paraffin oil was used to convey the pressure, which was applied through the nut *H* at the bottom. Amagat used water, but in the present experiments it was found impossible to insulate adequately the metal rod if the steel cylinder contained this liquid.

The method of procedure was as follows: After mounting, the steel cylinder *E* and the metal rod *R* were respectively connected with the two poles of a weak galvanic cell, one side of the circuit containing a delicate index-galvanometer. All being finally adjusted, the bolt *C* was turned until the platinum point just touched the surface of the mercury in the cup at the top of the metal rod. The platinum point was carefully centered, so that in the act of turning it remained exactly in the middle of the tube, no matter whether bolt *C* was screwed in or out. The moment of contact between the point and the mercury was indicated by the galvanometer.

The index *A* was tightly fitted on the rod *K*, exactly above the top of the needle *B*. Pressure was now applied, until the circuit was broken because the metal rod had been shortened so much that the platinum point no longer touched the mercury. The pressure was allowed to fall slowly until the galvanometer showed once more a completed circuit. The pressure at the moment of making the circuit was recorded, and this process was repeated at least twenty times. It was the custom to record ten of these pressures on contact, then to release the pressure, either completely or partially, and to apply it again after a short interval, and repeat the whole process. The average of these twenty readings was taken as the pressure required to make the contact. The distance between the index *A* and *B* was now read by means of a very accurate telescope micrometer. During the whole time the water in the jacket was stirred. This served to distribute the heat of compression and to eliminate it as soon as possible.

The bolt *C* with its needle *B* was now turned so as to lower the point about 0.15 mm., a change which caused the contact to hold until about in the neighborhood of 500 atmospheres. The same process was repeated, the pressure of contact being recorded and the distance between *A* and *B* read as before. At the high pressures the pressure was not suddenly released between the readings, since this would cause the rod to shorten from cooling. Instead, the pressure, after being allowed to fall slowly over a range of about 200 atmospheres, was increased slowly before the second series of readings was taken. For the most part the two series agreed satisfactorily. From the data it is clearly possible to calculate how

much the rod has been shortened by the application of a given amount of increased pressure.

To make sure that the apparatus had undergone no accidental change during the trial, the pressure was relieved, the bolt *C* was afterwards withdrawn until the platinum point again just touched the surface of the mercury, and the initial operations were repeated, giving usually a very satisfactory agreement with their first indication.

In this manner the absolute linear compressibilities of iron and copper were determined.

To the observed linear contraction of the metal rod in this apparatus three small corrections must be applied in order to obtain the true value. These corrections are for first, the contraction of the platinum needle; secondly, the error due to the millimeter thickness of glass in which the metal rods rested for insulation; and thirdly, the contraction under pressure of the globule of mercury. All three of these corrections are negative, diminishing the value for the compressibility.

Of these corrections, the first and second may be most simply applied by adding a correction to the actual length of the metal rod. As platinum is about half as compressible as iron,\* the platinum needle was equivalent to about 5 mm. of iron; and as glass is about six times as compressible as iron, the millimeter of glass was equivalent to 6 mm. of iron. Thus the iron rod, with the platinum above and the glass below, behaved as if it were 2.68 meters long, instead of 2.67 meters. With copper the percentage correction is slightly less, but not enough to affect the significant figures given. Because these corrections of only about 0.4 per cent in all are beyond the limit of accuracy of the measurements, they might have been neglected altogether.

The third correction is more serious and less easy to apply. Its magnitude may be computed as follows: The drop of mercury weighed 0.23 gram and therefore had a volume of 16.6 c. mm. As the diameter of the cup in which it was contained was 3 mm., or its area 7.1 sq. mm., the mercury must have been nearly 3 mm. deep, allowing for the curvature of the meniscus. The globule of mercury must have changed  $0.0000037 \times 400 \times 16.6 = 0.0246$  c. mm. under pressure. This decrease spread over a cup 7 sq. mm. in area would have caused a fall of 0.0035 mm. But, on the other hand, the contraction of the cup holding the mercury would have caused this liquid to rise 0.0003 mm. if the mercury itself had not changed in volume. The difference between these values, 0.0032 mm., may be taken safely as the probable fall of the mercury under pressure in the iron cup, and 0.0031 mm. as the probable fall in the copper cup. It was assumed that the shape of the meniscus did not change appreciably,

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\*See Richards and Stull, this publication, pp. 61-62.

because the pressure of 500 atmospheres is insignificant compared with the probable internal pressure of the mercury; but nevertheless one reason for the use of the two metals was the fear that a slight change in the surface tension of mercury might change the shape of the meniscus under pressure. Obviously this would cause the opposite effect in the concave meniscus in the copper cup from that caused in the convex meniscus in the iron cup. As the total contraction of the iron rod over the same range was 0.13 mm., the presence of the mercury involved a correction of 2.4 per cent. This is most conveniently applied by making another addition to the value representing the length of the rod, which now becomes 2.74 meters, instead of 2.68 meters. In the case of the copper rod the actual length of the rod was 2.69 meters, and the corrected length 2.74 meters.

It is conceivable that yet another very slight error might be caused by the settling or lowering of the screw-diaphragm on which the rod rested, because of the widening of the steel tube under pressure. The small interior diameter of the tube must make the error from this source very slight, however; and for this reason no correction was applied for it. The difficulty could be wholly eliminated by cutting the thread in such a way that the bearing surfaces would be horizontal radially.

The micrometer by means of which the readings of changing length were made was very carefully standardized by means of an accurate millimeter scale, whose corrections had been found by the National Bureau of Standards at Washington. The scale was of course placed at exactly the same distance from the telescope as the points to be observed during this standardization. The successive measurements show a maximum deviation from the mean of about 0.02 mm., in the case of iron, and somewhat more in the case of copper. A smaller range of error would have been desirable, but because we were unable to do better than this, it was necessary to make many determinations. The deviations from exact constancy were probably due partly to temperature, for in spite of much care it was found very difficult to keep the temperature perfectly constant during an experiment.

From the linear compressibilities as thus determined, the cubic compressibilities were found simply by multiplication by three. This simple calculation involves the assumption that the rods were equally compressible in all directions—an assumption which is not unreasonable in the case of these pure elementary substances. Nevertheless, if a very high order of accuracy is sought, especial pains should be taken to be certain that the structure of the metal is identical in all directions. Probably heating almost to fusion would accomplish this. In the present case this precaution was deemed supererogatory.

In the following tables each numbered determination is given with each of its two parts separate — one in which the pressure was increased and one in which the pressure was decreased.

*Data concerning the compressibility of iron.*

[Actual length of iron rod = 2.67 meters; corrected length of iron rod = 2.74 meters; 1 division of micrometer = 0.00625 mm.]

Determination.	Corrected range of pressure.	Difference of length (micrometer divisions).	Observed linear compressibility $\times 10^9$ .	Cubical compressibility $\times 10^8$ .
1	{ + 472	+ 26	125	38
	{ - 325	- 18	127	38
2	{ + 446	+ 25	127	38
	{ - 280	- 17	138	21
3	{ + 480	+ 30	142	43
	{ - 466	- 25	121	36
4	{ + 419	+ 22	118	36
	{ - 408	- 20	110	33
5	{ + 445	+ 25	127	38
	{ - 437	- 26	134	40
6	{ + 414	+ 21	114	34
	{ - 426	- 24	127	38
7	{ + 565	+ 35	140	42
	{ - 572	- 37	147	44
8	{ + 397	+ 22	126	38
	{ - 394	- 22	127	38

$$\text{Total average } \beta_{Fe} = 0.000000385 \pm 0.000000005.$$

*Data concerning the compressibility of copper.*

[Actual length of copper rod = 2.69 meters; corrected length of copper rod = 2.74 meters; 1 division of micrometer = 0.00625 mm.]

Determination.	Corrected range of pressure.	Difference of length in (micrometer divisions).	Observed linear compressibility $\times 10^9$ .	Cubical compressibility $\times 10^8$ .
1	{ + 459	+ 39	194	58
	{ - 451	- 38	192	58
2	{ + 438	+ 29	151	45
	{ - 432	- 30	158	47
3	{ + 480	+ 36	171	51
	{ - 480	- 32	152	46
4	{ + 512	+ 42	187	56
	{ - 506	- 44	197	59
5	{ + 432	+ 29	152	45
	{ - 442	- 30	154	46

$$\text{Total average } \beta_{Cu} = 0.00000051 \pm 0.00000004.$$

It will be noted that the values for the compressibility of iron, 0.000000385, and of copper, 0.00000051, differ considerably from the values found by Amagat, respectively, 0.00000068 and 0.00000086.\* The

\*Loc. cit.

latter values are dependent upon the somewhat arbitrary and uncertain theory of Poisson, because Amagat rejected entirely his work on the linear compressibility of the metals, and was not even willing to record its results. The present direct determinations have the advantage of being free from mathematical assumptions; and if they are accepted, the mathematical method used by Amagat must obviously be modified in such a way as to reduce the result by about 42 per cent in the cases of iron and copper. This conclusion casts doubt upon the true magnitude of the coefficient of Poisson, except in the case of amorphous substances like glass, which gives fairly consistent results by the two methods.

It is now possible to compute the compressibility of mercury between 100 and 500 atmospheres, by adding the differences between the compressibilities of the solid metals and mercury to the values just given. The results are recorded in the following table:

*Compressibility of mercury between 100 and 500 atmospheres.*

$$\begin{array}{r} \text{I. } 0.000000385 + 0.000003325 = 0.00000371 \\ \text{II. } 0.00000051 + 0.00000319 = \underline{\underline{0.00000370}} \\ \text{Average . . . . . } 0.000003705 \end{array}$$

The agreement of these results must be partly accidental, as it is greater than would be expected from the large probable error of the result with copper. The figure 3.71 obtained from iron is much the surer, and will be taken as representing the compressibility of mercury. It is interesting and satisfactory to note also that the result agrees well with the figures of Amagat, when these are corrected for change of compressibility at high pressures. Amagat found 0.00000392 as the compressibility of mercury under small pressures, these being measured in ordinary atmospheres. Corrected for the decrease of compressibility with pressure, and transposed to the metric standard of pressure, this value becomes 0.00000370,\* essentially identical with the new value given above. The work of very early experimenters is sufficiently commented upon by Aimé, and of those preceding Amagat by the latter physicist. The earlier values are not to be compared with Amagat's in accuracy. The more recent value of de Metz,† 0.00000390, at 20° under small pressures, depends like that of Amagat upon the assumptions of the theory of elasticity, and is therefore no more certain than his.

On this account, the result of the present investigation (0.00000371 expressed in kilograms per square centimeter, 0.00000379 expressed in

\*Amagat, Ann. de Chim. et de Phys., (3), **8**, 257 (1843); Richards and Stull, Publication Carnegie Institution of Washington No. 7, p. 20 (1903).

†Wiedemann's Annalen, **47**, 706 (1892).

megabars, or 0.00000383 expressed in atmospheres) may be accepted as the most probable value, because it depends upon actual measurements alone. Nevertheless it is clear that with more elaborate apparatus and by the expenditure of more time, better results might be obtained in the same way. Hence these results are to be considered merely as preliminary ones, worthy of publication because they exemplify the working of an efficient arrangement of apparatus, as well as because they confirm essentially the work of others on this subject. The present results appear to be accurate enough to serve the present purpose, therefore the execution of the yet more precise determinations is left for the future, when the need for them may arise.

In this work, as well as in the preceding and following investigations, the support of the Carnegie Institution of Washington was of great assistance, and the authors express their thanks.

#### SUMMARY.

The method of Richards and Stull was used for determining the differences between the compressibilities of copper, iron, and mercury. The determination of the linear compressibilities of rods of copper and iron nearly 3 meters long, then, afforded two independent means of calculating the cubic compressibility of mercury. The results for the cubic compressibilities of the three metals are given in the following table, expressed in terms of the three standards of pressure commonly in use:

*Cubic compressibilities of copper, iron, and mercury  
between 100 and 500 atmospheres.*

	Kg / cm <sup>2</sup> (metric).	Megabars (C.G.S.).	Atmospheres (76 cm.).
Copper.....	0. 00000051	0. 00000052	0. 00000053
Iron.....	0. 00000039	0. 00000040	0. 00000040
Mercury.....	0. 0000371	0. 0000379	0. 0000383

## IV

### THE COMPRESSIBILITIES OF THE MORE IMPORTANT SOLID ELEMENTS, AND THEIR PERIODIC RELATIONS.

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BY THEODORE W. RICHARDS AND WILFRED N. STULL.





## THE COMPRESSIBILITIES OF THE MORE IMPORTANT SOLID ELEMENTS, AND THEIR PERIODIC RELATIONS.

### INTRODUCTION.

In continuing the research upon compressibilities, it was desired to obtain a series of results from many of the more important elements, in order to discover their relation to one another, and to obtain as much light as possible upon the internal structure of solids in general. Accordingly, magnesium, calcium, zinc, cadmium, copper, silver, gold, palladium, platinum, tin, lead, thallium, aluminum, iron, manganese, nickel, chromium, molybdenum, arsenic, antimony, and bismuth were all studied, and the interesting results obtained from this study are detailed below.

The method of investigation was essentially similar to that already detailed in the preceding papers upon the compressibilities of the alkaline metals and the non-metals. Because of the less violent chemical nature of most of the heavier elements, the new problem was simpler than in the case of the alkaline metals, but because, on the other hand, their compressibilities for the most part are extremely small (often less than 1 per cent of the compressibility of water), great accuracy was needed in the conduct of the experiments.

The method of procedure was in this case, as before, the following. In the first place, the amount of mercury needed in a suitably arranged glass jacket for precisely attaining electrical contact with a very finely pointed platinum wire was determined at various pressures. The metal under examination was then immersed in the mercury and a similar series of experiments was once more conducted. Because nearly all of these metals had a compressibility less than that of mercury, less additional mercury would have been needed for a given pressure when the metal was present than when it was not present, except for the fact that in order to protect the metal, some other liquid besides mercury was also put into the jacket and compressed at the same time. As has been shown in the preceding papers, the correction for this other liquid is easily and exactly applied if its compressibility is known. The following pages describe as briefly as possible the essential details of the various processes.

The materials were all carefully prepared with a view to the peculiar nature of the process to which they were to be subjected. They were carefully examined for accidental flaws, and the metals were generally hammered in order to make them as compact as possible and then if possible carefully turned in the lathe to fit the jacket, so that but little compressible liquid would be needed to surround them.

When sufficiently pure rods of metal could not be obtained in commerce, pure materials were cast in suitable form, using as a mold a piece of smooth gas pipe, sawed longitudinally, so that the casting might be easily removed from the mold. This was done with zinc, cadmium, tin, lead, thallium, arsenic, antimony, and bismuth. The cylinders were in each case satisfactory and upon superficial smoothing showed no signs of cracks or flaws. The brittle substances arsenic, antimony, and bismuth were smoothed by filing instead of by turning.

Magnesium was turned from a bar of pure commercial material. The calcium was very kindly sent us by Professor Edgar F. Smith, of the University of Pennsylvania. It was not perfectly pure, containing nearly 1 per cent of silicon and some iron, but was pure enough to give a sufficiently accurate idea of its compressibility. Its density was determined by F. N. Brink, and found to be 1.54.

The copper was turned from a compact hammered copper rod. The results with this metal agreed closely with those obtained by Brink, described in another place.

Of silver two samples were used. The first sample was in the form of fine rods about 3 mm. in diameter, being about 99.5 per cent pure. In this form much water had to be used in order to fill the interstices in the jacket. Accordingly, the results are less trustworthy than those obtained with the second sample, and although approximately confirming them, are not worthy of a place in the table. The latter sample was very pure, having been prepared especially for this research, together with specimens of gold, palladium, and platinum, through the kindness of Baker & Company, of Newark, New Jersey. This firm prepared cylinders of these four metals in very satisfactory condition, and loaned us the large specimens of costly material without charge. The ingots of precious metal were all cast, hammered, and drawn, and finally turned to fit one of the glass jackets. They were all of a very high degree of purity, a fact which was shown by the specific gravities. The cylinder of gold weighed 149.861 grams; its loss of weight in water at 20° was 7.770 grams; therefore the specific gravity of the gold was 19.29. The palladium weighed 94.657 grams; its loss of weight in water at 20° was 7.783 grams; there-

fore its specific gravity was 12.16. The platinum weighed 166.534 grams; its loss of weight suspended in water at 20° was 7.793 grams; therefore its specific gravity was 21.37. These values, which have not been reduced to the vacuum standard or to 4°,\* are all near the accepted values, corresponding to the pure metals. In the following table the true densities, corrected to the vacuum standard, are given.

The thallium contained a trace of lead, but since the compressibility of thallium is not far from that of lead, this trace could have produced no essential effect upon the results. The weight of the bar in air was 89.458 grams, and its loss of weight in water was 7.540 grams. Therefore its specific gravity at 20° was 11.86.

The iron was a piece of wrought iron, commercially pure. Manganese was obtained from two sources, one, a sample from a German firm intended to be pure, and another, undoubtedly purer, kindly given us by the Roessler & Hasslacher Chemical Company of New York. To this firm also we are much indebted for their interest in our investigation and for their gifts of material. The two samples of manganese had slightly different densities, but were not very different in their behavior.

Of chromium two samples were used, one specimen prepared by Goldschmidt's method — a sample of the very earliest product of this method shortly after its invention — the other, a much purer sample, furnished by the Roessler & Hasslacher Company and stated by them to contain 99 per cent of chromium. Between these two samples there was a very great difference in compressibility, the first sample being far less compressible. We are inclined to think that this first sample contained a silicide of chromium or some other less compressible compound, and therefore accept the later result with chromium of known purity as the more accurate.

Nickel was placed in the jacket in the form of the small cubes in which the pure material may be procured in commerce. These cubes are permeated in every direction with fine pores or channels, and upon applying pressure to the mercury in which they are immersed, this mercury is driven into the innermost recesses of the lumps, giving false values for the compressibilities. Various devices were tried in the effort to stop these channels, but finally, the simple expedient of hammering each lump heavily on all sides proved to be very efficient and prevented the entrance of any appreciable amounts of mercury into the interior of the metal.

The molybdenum used in the experiments was a sample also kindly furnished by the Roessler & Hasslacher Company. Its purity was stated by them to be 98 per cent.

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\*This reduction causes so small a change in the values as to have no important effect in the present work. The uncorrected values are given here for the sake of more ready comparison with the work of others, which is usually not corrected.

The manganese, chromium, and molybdenum were all used in the form of small broken pieces, treated essentially in the way recommended for powders. Some difficulty was experienced in the last case from minute cracks, but it is believed that the final results are free from error from this cause. These various preparations of metal were one by one subjected to pressure under mercury in several glass jackets in the manner so often described. The mercury was all carefully purified by recognized methods.

#### THE APPARATUS.

The various jackets used for this work have been described in the foregoing papers. Of these, jacket v was that used for the determinations of the alkaline metals already discussed, and jacket vi was exactly similar to it, having been made out of a piece of the same glass tube; jacket viii was of similar form, but was larger; jackets iii and iii $\alpha$  were of a somewhat different form,\* used before the other form had been devised, and on the whole less convenient to manipulate, but no less accurate in operation than jacket v; iii had already been used for sulphur; iii $\alpha$  was made from iii after this had been accidentally broken, and the weights of mercury needed to fill it at various pressures were calculated from those found for iii, through the bracketed value in the last column of the table given below. For each of the other jackets these weights were determined by special series of experiments, recorded below.

*Data concerning glass jackets filled with mercury.*

No. of experiment.	Jacket.	Weight Hg. in jacket.	Weights of mercury added, the corresponding increasing pressures being given in kilograms per square centimeter directly beneath each weight.				$W_0$ Weight of mercury added from 100 to 500.	$100 W_0 M$ Kg Cm <sup>2</sup> .
1	iii	281.3	{ 0 85.5	0.0632 225	0.1094 330	0.1705 465	{ 0.1798	0.0639
2	iii $\alpha$	284.4	{ 0 85.5	0.0638 225	0.1106 330	0.1724 465	{ 0.1818	[0.0639]
4	v	127.6	{ 0 56	0.0543 352	0.0893 550	0.0308 221	{ 0.0721	0.0565
5	vi	125.7	{ 0 84	0.0309 255	0.0730 493	0.0035 103	{ 0.0713	0.0566
6	viii	170	{ 0 40	0.084 173	0.069 325	0.111 495	{ 0.0967	.....

The data for these jackets are repeated together in the above table for convenience of reference. The table is so similar to others which have been given before that no further explanation is needed, except as regards one point concerning it. The last column is printed to show the differences caused by differences in the kind of glass used in the jacket; it gives

\*See fig. 5, p. 32.

the weights of added mercury reduced in each case to 100 grams of mercury contents of each jacket, over the range of 400 kg. per square centimeter just mentioned. It will be noted that the jackets v and vi, made of the same piece of glass tube, agree exactly. The respective extreme values correspond to compressibilities of glass equal to 0.0000021 in the case of jacket III, and 0.0000023 in the case of jacket v. Similar differences in the compressibility of different kinds of glass were noted by Amagat.

The column headed  $IV_0$  contains the outcome of these measurements needed for subsequent work with the respective jackets.

In the mercury or in water above the mercury held by these jackets, the metals to be studied were one by one immersed with all the precautions discussed in previous papers. Amalgamable metals were never allowed to touch the mercury; and even when the mercury entirely surrounded the cylinder of a metal not capable of amalgamation, a little supplementary liquid was needed to fill accidental fine cavities from which mercury was excluded by its surface tension. The weight of this water present was of course always carefully found, as its compression was usually larger than that of the metal to be studied. In a few cases, indicated by foot-notes in the table on pp. 61 and 62, paraffin oil was used instead of water.

#### CALCULATION OF RESULTS.

The general treatment of the calculation of the results has been sufficiently discussed in the preceding papers. The equation needed when water is used as the supplementary liquid is described in the paper on the non-metals,\* and the similar one when oil is used in the paper on the alkali metals.<sup>†</sup>

In case paraffin oil is used, its appropriate coefficient for K (the weight of the supplementary liquid) must be specially determined. Two samples of oil were used in the following work. One possessed a compressibility corresponding to a coefficient for K of 0.438%, being the sample which had previously been used for the alkali metals. The other was less compressible, for 7.082 grams in jacket VIII required only 0.760 gram of added mercury at 148 units of pressure, 2.491 at 387 units, and 3.371 at 526 units, starting with no added mercury at 50 atmospheres. These figures correspond to a coefficient for K of 0.3830. The first sample of oil was used with magnesium and calcium and the more dense specimen of manganese; the other sample was used with the less dense sample of the last-named metal.

Two cases may be given in detail, as typical examples of the method, one in which paraffin oil was used to surround the metal, and another in

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\*Loc. cit., p. 36.

<sup>†</sup>Loc. cit., p. 22.

which water served. Experiment 7, the compressibility of magnesium, 13.67 grams of metal hammered and turned down in a lathe to fit the jacket were immersed in 0.843 gram of oil in jacket v. Enough mercury was placed in the narrow limb of the jacket to cause contact to be made under 103 metric pressure-units. Mercury was added in three successive stages, until when 0.4149 gram of mercury had been added, contact was made under 520 pressure-units. From the curve (or in this case, because the pressure readings are near 100 and 500 respectively, directly from the data) it is easy to see that 400 units of pressure correspond to 0.398 gram of added mercury. Because the density of magnesium is 1.74, the calculation is as follows:

$$\beta = \frac{(0.398 - 0.0721 - 0.4385 \times 0.843) 1.74}{5428 \times 13.67} + 0.00000371$$

or

$$\beta = 0.00000268$$

*Experiment 1.* — *The compressibility of zinc.* — 108.2 grams of pure zinc was cast, hammered, and turned to fit jacket III, in which it was immersed in 3.906 grams of water. The point of the first contact was 42 pressure-units. Successive amounts, of 0.2997, 0.6084, and 0.9139 gram of added mercury were found to correspond to 183, 339, and 499 metric pressure-units, respectively; and on taking out all but 7.5 mg. of this mercury the pressure went back to 39 pressure-units, almost the same as at first. The latter point is to be considered as more reliable than the first, but the difference is too slight to have a great effect on the results. From these figures it is easily found that the mercury needed between 100 and 500 pressure-units is 0.790 gram, and the calculation becomes

$$\beta = \frac{(0.790 - 0.1798 - 0.2031 \times 3.906) 7.15}{5428 \times 108.2} + 0.00000371$$

or

$$\beta = 0.0000015$$

The figures given in the table on p. 61 were found or calculated in the same way, so that further explanation is superfluous. All the data necessary for the calculation are given in the table, except the values  $W_0$  corresponding to the various jackets. These data are to be found in the table on page 58, entitled "Data concerning glass jackets filled with mercury." The final results have each been recalculated at least three times, in order to be sure that no error could have crept in during the somewhat elaborate computation.

Moreover, besides being calculated in the way described, they were also calculated directly from the observed points in each case, reading the corresponding values on the water and mercury curves, without drawing

curves for each single metal. This method of calculation brought essentially the same results.

We are greatly indebted to Mr. F. N. Brink for his kindness in making determinations Nos. 29 to 31 inclusive, as well as Nos. 34 to 37 inclusive, and for his assistance in independently recalculating the results. There are included in the table also repetitions of two of his determinations of copper and iron (13 and 27) given in the paper immediately preceding this one.

The close agreement of successive determinations, and especially the consistent verdict of the independent results of the two different experimenters (except in the single case of chromium), furnish good reasons for trust in the approximate accuracy of the results. The series is nevertheless not to be regarded as the final word upon the subject, but rather as a preliminary attempt to solve an experimental problem of no small difficulty. It bears the same relation to an ideal research on this subject that a sketch bears to a finished picture.

*Data concerning the compressibilities of twenty-one metals.*

No. of exper- iment.	Metal.	Weight of metal = $A$ .	Weight of oil (or water) = $K$ .	Weights of mercury added with corresponding pressures given beneath each weight.						Density of metal.	Jacket.	Compre- ssibility $\times 10^6$
8	Mg	13.67	10.843	{ 0 0.1567 0.3065 0.4149 0.0665 103 243 399 520 160 }						1.74	v	2.7
9	Ca	12.17	11.734	{ 0 0.3138 0.7501 1.0046 0.2262 71 194 388 515 160 }						1.53	v	5.4
10	Zn	108.2	3.906	{ 0 0.2997 0.6084 0.9139 0.0075 42 183 339 499 39 }						7.13	III	1.5
11	Cd	139.7	3.073	{ 0 0.2556 0.4912 0.7314 0.1859 50 200 346 499 159 }						8.60	III	1.9
12	Cu	152	2.166	{ 0 0.1229 0.2826 0.4125 0.6880 90 230 427 599 167 }						8.92	III	0.56
13	Cu	75.41	1.560	{ 0 0.116 0.218 0.312 0.270 61 229 383 530 100 }						8.92	VIII	0.51
14	Ag	81.63	0.859	{ 0 0.0478 0.0954 0.1431 0.0637 68 211 364 525 260 }						10.5	VI	0.82
15	Au	145.89	1.089	{ 0 0.0858 0.1727 0.0319 ..... 83 293 533 160 ..... }						19.24	v	0.47
16	Au	149.85	0.797	{ 0 0.0691 0.1034 0.0040 ..... 72 348 500 87 ..... }						19.24	VI	0.46
17	Pd	94.65	1.1065	{ 0 0.1569 0.1055 0.1730 0.0543 102 240 365 548 211 }						12.13	v	0.36
18	Pd	94.65	1.0555	{ 0 0.0857 0.1597 0.0201 ..... 90 313 527 141 ..... }						12.13	v	0.38
19	Pt	166.53	0.1400	{ 0 0.0526 ..... ..... ..... 110 538 ..... ..... }						21.31	v	0.20
20	Pt	166.53	0.148	{ 0 0.0500 ..... ..... ..... 129 545 ..... ..... }						21.31	v	0.22
21	Sn	121.6	2.393	{ 0 0.213 0.4218 0.6173 0.0957 59 228 404 572 133 }						7.29	III	1.67
22	Pb	188.6	2.293	{ 0 0.2232 0.4561 0.0210 ..... 49 212 396 63 ..... }						11.37	III	2.2

<sup>1</sup>The first sample of paraffin oil was used here. In all the other experiments except Nos. 28 and 29 water was used.

*Data concerning the compressibilities of twenty-one metals.—Continued.*

No. of experiment.	Metal.	Weight of metal = $d$ .	Weight of oil (or water) = $K$ .	Weights of mercury added with corresponding pressures given beneath each weight.					Density of metal.	Jacket.	Compressibility $\times 10^6$ .
23	Tl	89.52	1.101	{ 0 101	0.1235 291	0.2586 511	0.0504 177	.....	{ 11.83	vi	2.06
24	Tl	89.45	1.034	{ 0 57	0.1204 252	0.2769 517	0.1199 251	.....	{ 11.83	vi	2.07
25	Al	45.62	2.112	{ 0 56	0.113 168	0.2710 333	0.398 473	0.0440 99	{ 2.60	iii	1.28
26	Fe	133.2	1.925	{ 0 75	0.1162 236	0.2153 386	0.3009 516	0.1265 250	{ 7.86	iii	0.38
27	Fe	69.95	0.833	{ 0 53	0.045 216	0.093 395	0.125 527	0.051 237	{ 7.86	viii	0.39
28	Mn	25.52	10.486	{ 0 117	0.0923 329	0.2203 510	.....	.....	{ 7.37	v	0.64
29	Mn	0.48	20.204	{ 0 42	0.050 230	0.104 432	0.128 528	0.059 260	{ 7.22	viii	0.69
30	Ni	36.62	0.294	{ 0 50	0.0302 210	0.0630 367	0.0950 528	0.058 340	{ 8.7	viii	0.24
31	Ni	36.62	0.294	{ 0 77	0.034 250	0.066 395	0.0908 528	1.057 357	{ 8.7	viii	0.29
32	Cr	32.0	4.899	{ 0 45	0.3930 181	0.8361 342	1.247 499	0.1600 100	{ 6.9	iiia	0.22
33	Cr	40.9	0.388	{ 0 80	0.068 258	0.165 520	0.045 198	.....	{ 6.9	iiia	0.24
34	Cr	26.47	0.674	{ 0 70	0.062 214	0.151 424	0.180 490	0.056 300	{ 7.06	viii	0.73
35	Cr	27.52	0.654	{ 0 63	0.051 184	0.101 305	0.179 492	0.056 197	{ 7.06	viii	0.78
36	Mo	27.77	0.400	{ 0 30	0.052 190	0.108 364	0.160 523	0.094 267	{ 9.56	viii	0.22
37	Mo	27.77	0.400	{ 0 50	0.052 332	0.110 442	0.131 515	0.059 242	{ 9.56	viii	0.31
38	As	24.47	2.041	{ 0 57	0.202 185	0.432 336	0.689 508	0.217 193	{ 7.53	iiia	4.2
39	Sb	97.8	4.449	{ 0 116	0.384 271	0.685 399	1.105 580	0.067 90	{ 6.71	iii	2.2
40	Bi	146.5	4.258	{ 0 63	0.337 197	0.804 391	1.051 495	0.048 83	{ 9.80	iii	2.8

<sup>1</sup> The first sample of paraffin oil was used here. In all the other experiments except Nos. 8, 9, and 29 water was used.

<sup>2</sup> The less compressible paraffin oil was used in this case. See p. 59.

It will be noticed that in some cases the determinations have been made in duplicate, either because of the experimental opportunity presented by the temporary possession of large quantities of pure rare metals or because of doubt concerning one of the determinations. In most cases this duplication was not considered necessary, because the method employed of adding successive amounts of mercury and then taking out most of that which had been added (in order to determine if the system had altered during the compression) practically amounted to a multiple reduplication of the work. Any inaccuracy in any of the readings would have been detected at once from the form of the curve. Thus it may be said that

each of these experiments is essentially at least a three-fold repetition of the same process, and those experiments which were duplicated gave a yet higher degree of certainty.

The study of the curves shows that changing pressure produces practically no effect upon the compressibility of these comparatively incompressible substances. Such change as may occur is beyond the accuracy of the method, and can only be determined when larger quantities are used. This is in accord with Amagat's experience with glass, which is much more compressible than most of the metals.

There are only a few older results with which to compare these, but all which have been found are higher than those given in the table on pp. 61, 62. Regnault measured the compressibility of copper, and Amagat measured this quantity also, as well as the compressibilities of steel and lead. The more recent work of Lussana\* included tin, lead, cadmium, zinc, and copper; it was executed by an ingenious method, and yielded results much higher even than Amagat's. It is interesting and significant to note that in spite of the great discrepancy in the absolute values, the relative values of the five metals as given by Lussana correspond approximately with the relative values recorded above. Lussana places the five elements in the following order, beginning with most compressible, and ending with the least: Lead, cadmium, tin, zinc, and copper. The results in the table above fall in the same order of succession. Hence, although the absolute values obtained by Lussana were not far from twice as great as ours, the relative values do not contradict ours. Because relative values rather than absolute ones were chiefly sought in the present research, the present results are published with confidence that they will be of use even if time should show that Lussana's scanty figures are more absolutely accurate. It may be added that careful scrutiny has not yet been able to discover any plausible reason for supposing that our low values are less than the truth. The divergence of the results gives interesting evidence of the great difficulty in determining the compressibilities of very incompressible substances.

#### COMPARISON OF RESULTS.

Before summing up the results in the large table and those previously found concerning the elementary substances, it may be illuminating to compare these magnitudes with other well-known compressibilities. The compressibility of mercury is somewhat less than one-tenth of that of water, which is usually considered as a rather incompressible substance. A few of these compressibilities are not far from that of mercury, espe-

\*Regnault and Amagat, Landolt-Börnstein Tabellen (2d Edition), p. 278 (1894). Lussana, *Il Nuovo Cimento* [5], **4**, 371 (1902); **5**, 153 (1903); **7**, 355 (1904). The latter very recent work became known to us only after the completion of our own work.

cially calcium and arsenic. Several others are somewhat less, although more than half as large, namely, magnesium, zinc, cadmium, lead, thallium, antimony, and bismuth. Tin, aluminum, sulphur, manganese, and chromium are only about one-fifth as compressible as mercury, and copper is still less compressible. Gold, palladium, and iron are yet less affected by pressure; and platinum, nickel, and molybdenum have a compressibility not much more than one-twentieth of that of mercury, or one two-hundredth of that of water. The determination of these very small quantities is of course subject to considerable percentage of inaccuracy, but at least it seems probable that the values given are not in excess of the true values.

It becomes now a matter of interest to compare the compressibilities of the different elements in a more careful and systematic manner. This is most conveniently done by arranging all the values which have been found for the solid and liquid elements in a table in the order of the atomic weights. Such a table is given below. In it are recorded not only the compressibilities reported in the present paper, but also those found by Richards and Stull, three years ago, and those concerning the alkali metals, and certain non-metals given in the preceding papers. Of these determinations two, namely, those concerning sulphur and selenium, were determined by us at the same time as the elements discussed above. They were printed in a foregoing paper merely in order that all the work might be arranged as systematically as possible. In this table of compressibilities the values are given in terms of the megabar—a megadyne per square centimeter—as the unit of pressure, instead of the kilogram per square centimeter. This absolute unit is about 2 per cent greater than the latter-named technical unit, and 1.3 per cent less than the “atmosphere.” In most of the present cases the difference between these standards does not exceed greatly the experimental limit of error. The values may be easily transposed into terms of the atmosphere by adding in each case 1.3 per cent. In comparing these results it must be borne in mind that all depend upon the still somewhat uncertain compressibility of mercury, and that any change in this latter value would affect each other value by the same actual amount (not the same percentage amount). No change of the value for mercury could affect the sequence in the order of magnitude of the results, which for the present purpose is the really essential matter. There are given also the atomic weights, the atomic volumes of these various substances.

*The compressibilities, atomic weights, and atomic volumes of a majority of the commonly solid and liquid elements.*

[Compressibility of mercury = 0.00000371.]

Element.	Average compressibility, (i. e., average fractional change of volume caused by 1 megabar pressure) between 100 and 500 megabars, $\times 10^6$ .	Approximate atomic weight (O = 16)	Atomic volume.
Lithium.....	8.8	7.0	13.1
Carbon :			
Diamond .....	0.5	{ 12.0	{ 3.4
Graphite .....	3	{	5.4
Sodium.....	15.4	23.0	23.7
Magnesium.....	2.7	24.4	13.3
Aluminum.....	1.3	27.1	10.1
Silicon.....	0.16	28.4	11.4
Phosphorus :			
Red.....	9.0	{ 31.0	{ 16.6
White.....	20.3	{	14.4
Sulphur.....	12.5	32.1	15.5
Chlorine.....	95	35.5	25
Potassium.....	31.5	39.1	45.5
Calcium.....	5.5	40.1	25.3
Chromium.....	0.7	52.1	7.7
Manganese.....	0.67	55.0	7.7
Iron.....	0.40	55.9	7.1
Nickel.....	0.27	58.7	6.7
Copper.....	0.54	63.6	7.1
Zinc.....	1.5	65.4	9.5
Arsenic.....	4.3	75.0	13.3
Selenium.....	11.8	79	18.5
Bromine.....	51.8	79.9	25.1
Rubidium.....	40	85.5	56
Molybdenum.....	0.26	96	11.1
Palladium.....	0.38	107	9.3
Silver.....	0.84	107.9	10.3
Cadmium.....	1.9	112.5	13.0
Tin.....	1.7	119	16.2
Antimony.....	2.2	120	17.9
Iodine.....	13	127	25.7
Cæsium.....	61	182.9	71
Platinum.....	0.21	195	9.1
Gold.....	0.47	197	10.2
Mercury.....	<sup>1</sup> 3.71	200	14.8
Thallium.....	2.6	204	17.2
Lead.....	2.2	207	18.2
Bismuth.....	2.8	208	21.2

<sup>1</sup> Standard.

In tracing the relationship between the data recorded in this table, the first fact which impresses the observer is that compressibility is a property as definitely periodic as any other property of the elements. This is clearly demonstrated by the diagram appended, which shows the relation between the atomic weight and the compressibility of the elements, plotted in the same manner as the well-known atomic volume curve of Lothar Meyer (fig. 8).

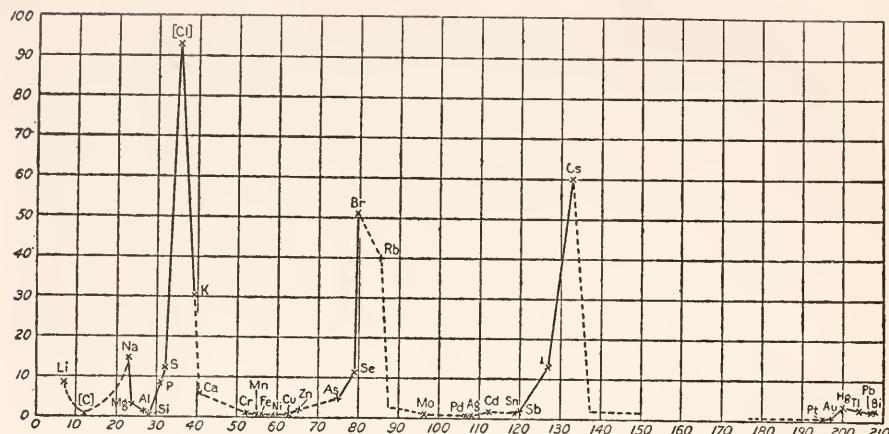


Fig. 8.—Atomic weight—compressibility curve.

Upon comparing the individual data concerning the compressibilities and atomic volumes, it is seen that in many cases these are more or less parallel properties, as has already been shown concerning the alkali metals. This parallelism, however, seems to hold, even approximately, only between similar elements. The comparison of magnesium, calcium, zinc, cadmium, and mercury gives the compressibilities and the atomic volumes in parallel sequence, as in the case of the alkali metals. Tin and lead bear a similar relation to each other; but with the less compressible elements possessing very high boiling-points, this parallelism seems to cease, and on comparing elements of different character, the relation completely fails.

Often the coefficients of expansion are seen likewise to be parallel with the values of the compressibilities, especially in those cases where the atomic volumes are nearly identical. Evidently, however, the relationship between these quantities is not that demanded by the rule of Dupré:

$$\beta' = \frac{\beta a' \Delta^2 T'}{a \Delta'^2 T}$$

For example, if sodium is taken as 0.000015, potassium should be, according to Dupré's rule, 0.000021, but it is in reality 0.000031; the coefficients of expansion being, respectively, 0.000072 and 0.000083. Again, according to Dupré's rule, sulphur should be ten times as compressible as selenium; but they are, as a matter of fact, almost alike. It is not necessary, however, to go as far afield as this to discover the uncertainty of Dupré's rule. The single case of water, having at 1° and 100° the coefficients of expansion of — 0.000006 and + 0.00077 respectively, and the compressibilities of 0.000051 and 0.000048 respectively, would prove that it is not infallible, although it takes cognizance of causes which undoubtedly affect compressibility. No surprise need be excited by this lack of parallelism,

for compression always tends toward producing a smaller volume in a system, while warming does not necessarily tend to produce a greater volume.

In every case it will be observed that volatility, which may be ascribed to lack of cohesive tendency, seems to be associated with increased compressibility, other things being nearly equal. This is seen most strikingly on comparing the compressibility of chlorine, bromine, and iodine, but it is manifest also in other cases; for example, in the cases of arsenic and antimony, or sulphur and selenium. This effect of decreasing the cohesive tendency is entirely in accord with principles which were laid down in the recent communications from this laboratory concerning the significance of changing atomic volume.\* It is reasonable to suppose that substances already much compressed by their own great internal pressure would not be sensitive to outside pressure. Further consideration of these relationships will be taken up at a subsequent time in connection with the compressibilities of simple compounds, for which a large amount of data is at hand awaiting codification and discussion.

In conclusion it is a pleasure to acknowledge the generous support of the Carnegie Institution of Washington, which alone has made the present investigation possible.

#### SUMMARY.

Attention is called to the summaries of the preceding papers, given on pages 25, 40, and 52.

In this last paper has been described the application of the method of Richards and Stull to the determination of the compressibility of twenty-one metallic elements.

The compressibilities of these elements between 100 and 500 atmospheres were found to be as follows, expressed in terms of megabars multiplied by  $10^6$ : Magnesium, 2.7; calcium, 5.5; zinc, 1.5; cadmium, 1.9; copper, 0.54; silver, 0.84; gold, 0.47; palladium, 0.38; platinum, 0.21; tin, 1.7; lead, 2.2; thallium, 2.6; aluminum, 1.30; iron, 0.40; manganese, 0.67; nickel, 0.27; chromium, 0.7; molybdenum, 0.26; arsenic, 4.3; antimony, 2.2; bismuth, 2.8.

This series of values depends entirely upon work at Harvard, except as regards the standard of pressure. It is independent of other investigations on compressibilities.

It is shown by comparing these values with those of other elements previously found in the chemical laboratory of Harvard College, that compressibility is a periodic property of the elements and that it is probably in part associated with the same causes which determine atomic volume and volatility.

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\*Richards, Proc. Am. Acad.



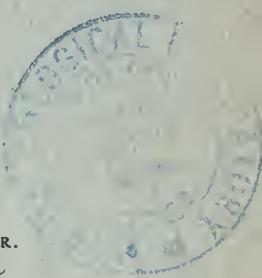
# The Compressibilities of the Elements and Their Periodic Relations

BY

THEODORE WILLIAM RICHARDS

IN COLLABORATION WITH

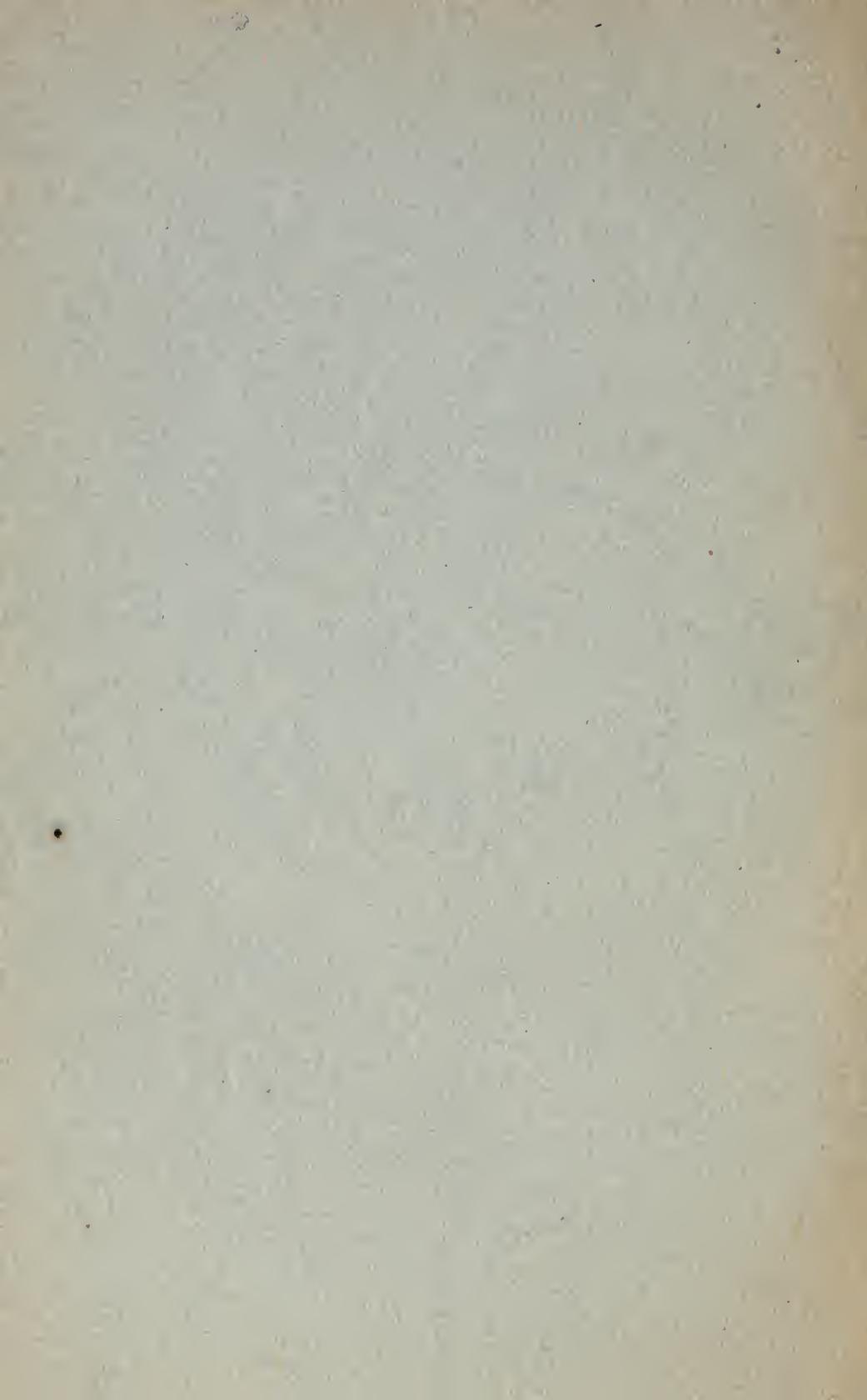
W. N. STULL, F. N. BRINK, AND F. BONNET, JR.



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