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CONCERNING THE COMPRESSIBILITIES OF THE ELEMENTS, AND THEIR RELATIONS TO OTHER PROPERTIES.

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In an extended paper published eight years ago, a number of experiments were described, having for their aim the determination of the compressibilities of thirty-five elements.[1] The object was to determine especially the periodicity of the compressibilities in relation to the atomic weight and to other properties of these fundamental substances. All the values were referred to that of mercury, although it was explicitly recognized at that time that the value for mercury was somewhat in doubt.[2] This was done, because such an error, if present, must affect each value equally:—the doubt could not invalidate the main point of the work; therefore, instead of spending much time, labor and money upon the determination of the absolute compressibility of mercury, the experimenters studied the various other elements. When the compressibility of mercury became more accurately known, the results could all be easily corrected to the better standard without additional experimental work.

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[1] Richards, Stull, Brink and Bonnet, *Pub. Carnegie Inst. Wash.*, No. 76 (1907).

[2] *Ibid.*, on page 64 the following statement was made: "In comparing these results it must be borne in mind that all depend upon the still somewhat uncertain compressibility of mercury....."

This time now seems to have come. The recent work of Bridgman at high pressures and that of the author in conjunction with E. P. Bartlett,[1] and yet more recently with J. H. Hodges,[2] at lower pressures have put this quantity in the list of those very accurately determined; accordingly, it is appropriate that the older results should be corrected to the true standard.

Moreover, a better standard of pressure is now available. The two Bourdon pressure gages used in 1903–1907 were not perfect, and could be relied upon only for relative results, as was fully recognized at the time.[3] Fortunately, since this earlier work was finished, two new independent and entirely satisfactory absolute pressure gages have been at our disposal, and the old Bourdon gages have been compared with them, so that in this respect also the older results may be corrected and put upon a more permanent footing.

A study of the relation between each of the old gages and Bridgman's absolute standard is given in a diagram in an earlier paper.[4] The Bridgman gage, when connected with our extremely accurate gage, gives essentially identical results,[5] so that one may feel confident of the joint indication. From the mean of several comparisons of the old Bourdon gages with the new absolute standard, the following table of corrections to be applied to the average between the two old gages has been compiled:

CORRECTIONS TO AVERAGE OF BOURDON GAGE.

Reading.	Cor.	Reading.	Cor.	Reading.	Cor.
50	+0.5	250	+1.0	450	+2.0
100	0.0	300	0.5	500	+2.0
150	+1.0	350	+2.0	550	0.0
200	+1.0	400	+2.0	...	...

This table, which agrees essentially with the diagram already mentioned, is made out, for convenience, upon the assumption that the 100-atmosphere point was without error, as this was always the starting point. No effort was made to record the values more nearly than to within 0.5 atmosphere, because the early work was not carried beyond this degree of refinement. These values, then, are the corrections to be applied to the recorded pressures of 1907 in order to bring them to the true standard. Evidently the error between 100 and 500 is only about one-half of one per cent. of the interval, so that the figures are but little altered by the correction. Accordingly, the new values for the compressibilities differ from the old ones (given in the early publication) in most cases

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[1] Richards and Bartlett, THIS JOURNAL, 37, 470 (1915).

[2] As yet unpublished.

[3] *Pub. Carnegie Inst. Wash.*, No. 76, 14 (1907).

[4] THIS JOURNAL, 34, 793 (1912).

[5] Richards and Shipley; investigation as yet unpublished.

only by the addition to each compressibility of the quantity 0.00000016—the error of the formerly assumed value of the compressibility (0.00000379) of the standard substance, mercury (now taken as 0.00000395).[1] In the cases of iron, copper, lead and molybdenum, the new values, determined more accurately with the help of E. P. Bartlett,[2] have been substituted for the old ones, which after correction were not very different, but which were doubtless less trustworthy. The new results of the same investigation giving data for tungsten and tantalum have also been included in the table, and so has a preliminary value determined here with the help of J. H. Hodges for boron, this substance having been kindly furnished in a very pure state by Dr. Weintraub of the works of the General Electric Company, at Lynn, Mass. This last research has not yet been published.

The table below contains the recalculated record of the compressibility of 38 elements, of which 35 are solid under the conditions of measurement and 3 liquid. These values are all expressed as $\frac{(\Delta v)_{100-500}}{v_0 \Delta p}$, that is, in terms of the average fractional change of volume caused by 1 megabar's pressure between 100 and 500 megabars, referred to the volume of the uncompressed substance. The values, as has been said, are all determined at 20° by reference to mercury, the compressibility of which is recorded below. If this last named value should be found to demand a slight further correction at some future date, the same actual correction will apply additively to each figure given.

The megabar (or megabarie) is chosen as the measure of pressure, because this logical absolute unit, having received international recommendation, bids fair to become the scientific standard of the future. Being the pressure of one megadyne per square centimeter, it is almost 2% greater than the kilogram per square centimeter, and 1.3% less than the "atmosphere." In many 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%.

In addition to the compressibilities of these several elements, the table records also in subsequent columns the atomic volumes, densities, melting points recorded in absolute temperature, coefficients of expansion and, finally, international atomic weights, since the compressibilities will

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[1] Credit should be given to Grüneisen for pointing out that an error of about 0.0000002 probably existed in the earlier published results, although he was not able to guess the cause of the error. The reason for taking mercury as 0.00000395 instead of 0.00000396 as found by Richards and Bartlett will be explained in a coming paper by one of us in conjunction with J. H. Hodges. (See Grüneisen, *Ann. der Physik.*, [4] **25**, 849 (1908); also footnote, *ibid.*, [4] **26**, 397 (1908).)

[2] *Loc. cit.*

Compressibilities, Atomic Volumes, Densities, Melting Points, Coefficients of Expansion and Atomic Weights of a Majority of the Commonly Solid and Liquid Elements at 20° C. between 100 and 500 Megabars (if the Compressibility of Mercury = 0.00000395).

	Average compressibility at 20° (see above) $\times 10^6$.	Atomic volume.	Density at 20°.	Melting point (absolute temp.).	Cubic coefficient of expansion $\times$ 100,000.	International atomic weight (1914).
Lithium	9.0	13.1	0.534	453	19.	6.94
Boron	0.3	4.7	2.34	2800[1]	...	11.0
Carbon, diamond	Very small	3.4	3.51	Very high	0.3	12.00
Carbon graphite	3.0	5.4	2.26	Very high	7.2	12.00
Sodium	15.6	23.7	0.971	371	22.0	23.00
Magnesium	2.9	13.3	1.74	927	7.8	24.32
Aluminium	1.47	10.1	2.60	930	7.2	27.1
Silicon	0.32	11.4	2.42	1733	2.3	28.3
Phosphorus, red	9.2	14.4	2.15	863[2]	?	31.04
Phosphorus, white	20.5	16.6	1.82	317	36.0	31.04
Sulfur	12.9	15.5	2.07	384	18.0	32.07
Chlorine	[95](?)	25.0*	1.42*	171	....	35.46
Potassium	31.7	45.5	0.862	335	25.0	39.10
Calcium	5.7	25.3	1.53	1073	....	40.07
Chromium	0.9	7.7	7.06	1823	....	52.0
Manganese	0.84	7.7	7.37	1533	....	54.93
Iron	0.60	7.1	7.85	1790	3.6	55.84
Nickel	0.43	6.7	8.7	1725	4.2	58.68
Copper	0.75	7.1	8.92	1356	5.0	63.57
Zinc	1.7	9.5	7.13	692	8.7(?)	65.37
Arsenic	4.5	13.3	7.53	1073	1.6	74.96
Selenium	12.0	18.5	4.28	490	13.0	79.2
Bromine	52.	25.1	3.12	266	....	79.92
Rubidium	40.	56.0	1.53	312	[30](?)	85.45
Molybdenum	0.46	11.1	10.23	2773	1.1	96.0
Palladium	0.54	9.3	12.13	1822	3.8	106.7
Silver	1.01	10.3	10.5	1234	5.7	107.88
Cadmium	2.1	13.0	8.60	594	7.4	112.40
Tin	1.9	16.2	7.29	505	6.7	119.0
Antimony	2.4	17.9	6.71	903	3.3	120.2
Iodine	13.0	25.7	4.94	386	25.0	126.92
Cesium	61.	71.0	1.87	301	[33](?)	132.81
Tantalum	0.53	10.9	16.67	3123	2.3	181.5
Tungsten	0.27	9.6	19.23	3300(?)	1.1	184.0
Platinum	0.38	9.1	21.31	2020	2.7	195.2
Gold	0.64	10.2	19.24	1336	4.3	197.2
Mercury	3.95	14.8	13.55	234	18.	200.6
Thallium	2.3	17.2	11.83	574	9.0	204.0
Lead	2.33	18.2	11.37	600	8.8	207.2
Bismuth	3.0	21.2	9.80	543	4.0	208.0

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[1] Personal communication from Dr. Weintraub.

[2] Smits and Bokhorst, *Amst. Acad.*, 17, 969 (1915).

be shown to have relations with each of these data. The values for melting points and coefficient of expansion were most of them taken from the Landolt-Börnstein Tables (1912). Nearly all the other data (including most of the atomic weights) were determined at Harvard. The numbers given in brackets [ ] were not determined directly, but have been approximately calculated on the basis of analogous data. The coefficients of expansion of solid cesium and rubidium are estimated roughly, assuming that the difference between the solid and liquid form is about the same in the case of cesium as in that of potassium, and that the value for rubidium is, approximately, half way between that of potassium and cesium. These estimates are sufficiently exact for the purpose in hand. Cubic coefficients of expansion are taken as 3α,—the letter α designating linear coefficients.

It is interesting and satisfactory that such of these results for compressibility as concern the elements studied by Grüneisen are now in reasonable accord with the results obtained by him with the help of the theory of elasticity, as already pointed out in the joint paper with E. P. Bartlett. The comparison with the scanty work of others, as shown by the figures on the 48th page of the Landolt-Börnstein Tables (1912), also shows so good an agreement that there is every reason to believe the figures given above to represent closely the true values of the constants in question. Therefore, they are worthy of further study, especially as regards their mutual relations and their relations to other properties.

On comparing the results concerning compressibility with one another, the first point to which attention may be called is the fact that three of the elements included in the table are in the liquid condition, namely, chlorine, bromine and mercury. This fact prevents the compressibilities of these substances from being strictly comparable with those of the others, because the available evidence seems to show that at the same temperature liquids are usually much more compressible than the solids crystallized from them. At the time of publishing the early work, this fact, although suspected, could not be definitely stated, because no measurements had ever been capable of proving the point; but since that time data concerning several cases have been obtained.

The first published and perhaps the most striking of these is the comparison of the compressibility of common ice and water, especially because ice, having the greater bulk, might be supposed to show a greater compressibility than liquid water, if such a contingency were ever possible. Nevertheless, investigation has shown that the compressibility of ice is only about one-quarter of that of water at neighboring temperatures.[1] Other cases are those of *o*- and *p*-cresol, substances which likewise can be conveniently investigated both in the solid and the super-

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[1] Richards and Speyers, This Journal, 36, 491 (1914).

cooled liquid condition at neighboring temperatures. These determinations, not previously published, were carried out several years ago in Boylston Hall, Cambridge, with the help of J. H. Mathews. Solid *o*-cresol, having the density 1.0176 at 20°, was found to possess the average compressibility between 300 and 500 megabars of 23.8×10^{-6}; and solid *p*-cresol, having the density 1.389 at 20°, was found to possess the average compressibility between 300 and 500 megabars of 21.8×10^{-6}, not much over half the values for the compressibilites of these substances in the supercooled liquid state over the same range (42.1 and 41.8).[1] These results are strikingly confirmed by results since obtained by Bridgman with the help of an indirect thermodynamic method.[2] He found as a minimum value for the difference between the compressibilities of solid and liquid orthocresol under 1 atmosphere's pressure the quantity 0.0000191 (reduced to the megabar standard), almost exactly in concordance with the difference between the values given above, considering that our determinations were made at a higher pressure. The more recent work of Harry Essex[3] on solid and liquid benzene points in the same direction, for he found these to be 0.000077 and 0.000025, respectively. Bridgman's indirect method confirms these observations by predicting a difference between these two data of 0.00005. Thus the compressibility of solid benzene is only about one-third of that of the liquid.

Evidently, then, the compressibility of *solid* chlorine is not likely to be over 50×10^{-6}, and might be as low as 25×10^{-6}, or less than that of potassium. It is, moreover, fairly certain that the compressibility of solid bromine must be under 30×10^{-6}, or distinctly less than that of rubidium, while that of solid mercury is doubtless less than that of liquid mercury.[4] Although, therefore, the evidence is fairly conclusive, it is perhaps safest to omit these liquids from the comparisons. Let us, then, plot the compressibilities of the usually solid elements in relation to their atomic weights in a curve more or less parallel to the corresponding values of the several atomic volumes, in the manner depicted in the early paper and again in the Faraday lecture of 1911.[5] In the diagram, the low-

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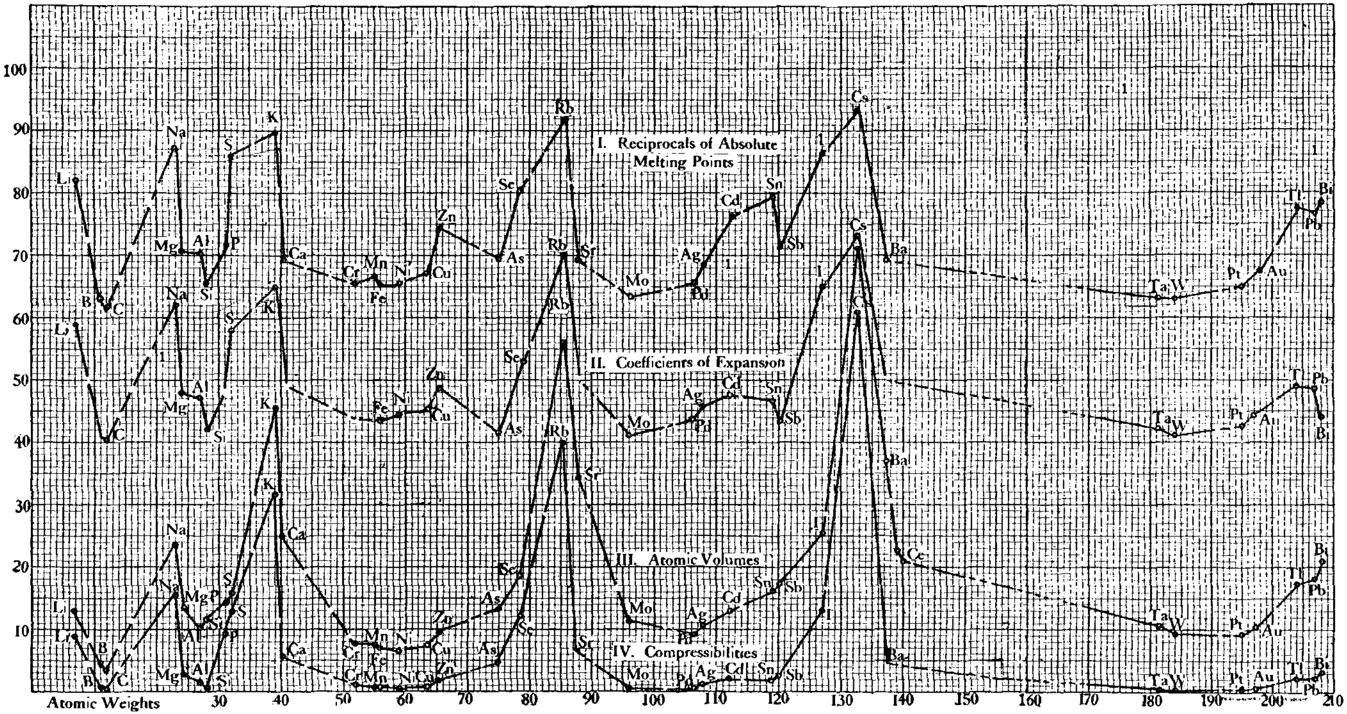
[1] Richards, Stull, Mathews and Speyers, THIS JOURNAL, **34**, 989 (1912).

[2] Bridgman, *Phys. Rev.* (1915).

[3] Harry Essex, Doctor's Dissertation, Göttingen, 1914. *Z. anorg. Chem.*, **88**, 190 (1914). The values are both those found at 20°.

[4] Bridgman, *Proc. Am. Acad.*, **47**, 423 (1911). The difference between the compressibilities of solid and liquid mercury seems to be less than that in the other cases, perhaps because of its simple molecular structure.

[5] "The Fundamental Properties of the Elements," *Science*, **34**, 537 (1911). According to an unpublished suggestion of Professor Bridgman, these properties might equally well be plotted in relation to the *atomic numbers* instead of atomic weights. The curves thus plotted are perhaps a little smoother than the ones given, but are essentially similar. The idea of atomic numbers was probably first suggested by J. A. R. Newlands (*Chem. News*, **10**, 94 (1864)).



PROPERTIES OF THIRTY-FIVE SOLID ELEMENTS.

Atomic weights are plotted as abscissae, other properties as ordinates.

Curve I represents reciprocals of absolute melting points, being plotted as $\frac{10,000}{T_m} + 60$.

Curve II represents cubic coefficients of expansion, being plotted as $300,000\,\alpha + 40$.

Curve III depicts atomic volumes.

Curve IV depicts compressibilities, multiplied by one million.

est curve of all represents compressibilities and the one just above it, atomic volumes. To these have been added a curve depicting the coefficients of expansion (Curve II, next above the atomic volume curve) and another (Curve I) giving the reciprocals of the melting points (expressed in terms of absolute temperature[1]) for reasons which will soon be apparent. To avoid complication in the diagram, only the denser forms of carbon and phosphorus are depicted in the curves; if white phosphorus had been included, it would have made a marked subsidiary peak in each curve—all of the properties here depicted being consistently represented by much larger values in the case of white phosphorus than in that of red phosphorus. In most cases no attempt is made to indicate the properties of other intervening elements not included in the table above. The omissions are indicated in each case of brief gaps in the curves, which may easily be identified by the atomic weights.

Let us now examine these curves in more detail. Turning first to the relation between the two lowest lines, representing atomic volumes (Curve III) and compressibilities (Curve IV), it is clear, as it was in 1907, that, roughly speaking, solids with large atomic volumes have large compressibilities. The new additions, tantalum and tungsten (each of which possesses very small atomic volume considering its high atomic weight), are seen, consistently, to possess also very small compressibilities, as would be expected. The relation of the newly determined boron to each of the varieties of carbon also corresponds to this rule; its compressibility and atomic volume are probably both greater than that of diamond, but both less than that of graphite.

Not only these two curves show signs of relationship, however. The likeness of the two upper curves to one another is very striking—this shows, of course, that in general, substances with low melting points have large coefficients of expansion—a fact in general long known, although the striking similarity of the curves is less familiar. Moreover, both of these upper curves, consistently with the two lower curves, likewise show peaks with the alkali metals and valleys with the heavier metals, although the subordinate convolutions are much more prominent in the two upper curves than in the lower ones.

A glance at the four curves at once suggests that there must be a fundamental connection between all these properties; and their close parallelism tempts one to seek a mathematical relationship between them, in spite of the inevitable complexity of the situation and the interdependence of each property not only upon each other of these, but also on many others. A preliminary attempt has been made to find such a relation-

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[1] Attention is called to the interesting significance of absolute melting points as pointed out by Sudwik (*Z. physik. Chem.*, **88**, 632 (1914)).

ship, and although the outcome is not especially satisfactory, it is, perhaps, worth a brief recounting.

In the first place, one immediately concludes that atomic volume is not the only dimension which determines compressibility; since, for example, sodium and calcium, which have nearly the same atomic volumes, have widely different compressibilities. Silver and gold show like deviations. What other properties are concerned? Qualitative search among the data quickly leads to the conclusion that density is not quite adequately represented by its occurrence in the expression of atomic volume. In many cases, even with like atomic volumes, the denser element has the lesser compressibility. Again, those substances which are easily melted or volatilized seem to have a larger compressibility than would be warranted by their atomic volumes and densities; one is driven to infer that the compressibility of a solid is much increased by lowness of its melting point.

To make the matter more explicit, a few specific cases may be cited. For example as already stated, gold and silver have nearly the same atomic volumes; and they possess also nearly equal melting points. They have different densities, however, and the denser is the less compressible. This seems to be a general characteristic, which can be traced in many other places in the table.

Again, as has already been mentioned, sodium and calcium have nearly the same atomic volumes, and not very different densities, but they have very different melting points. Here it appears that the substance with the higher melting point (namely, calcium) has a much lower compressibility. A similar comparison may be made between copper and iron, although the difference is here not so marked. Comparing zinc and palladium, we find that greater density and higher melting point are both associated in palladium with a much lower compressibility than that of zinc.

On the other hand, sodium and potassium have nearly the same density and melting point, but their atomic volumes are very different. In this case and in many other cases otherwise similar, the compressibilities are nearly proportional to the atomic volumes (that is, to the atomic weights divided by the densities).

Bearing these facts in mind and noticing also that substances like cesium and phosphorus, which melt very near the temperature of experimentation, have abnormally large compressibilities, several attempts were made to formulate definitely the relationship, but, as was expected, no exact equation was found. The various attempts may all be represented by the general expression:

$$\beta = \mathrm{K}f_1(\mathrm{A})/f_2(\mathrm{D})f_3\mathrm{T}_m, \qquad (1)$$

when β = compressibility, A = atomic weight, T_m = absolute melting point, K an empirical constant, and f_1, f_2 and f_3 various functions of the quantities in question. The simplest of these trial equations giving reasonably good results took the following form:

$$\beta = 0.00021 \frac{A}{D^{1.25}(T_m - 50^\circ)} \qquad (2)$$

A few of the best agreeing values, thus calculated (arranged according to the natural groups of the elements, and compared with the actual values) are given in the table below:

COMPRESSIBILITIES, CALCULATED AND FOUND.

(Each multiplied by one million.)

	Calc.	Found.		Calc.	Found.
Lithium	8.0	9.0	Magnesium	2.8	2.9
Sodium	15.6	15.6	Zinc	1.9	1.7
Potassium	34.0	31.7	Cadmium	2.9	2.1
Rubidium	40.0	40.0	Molybdenum	0.50	0.46
Cesium	52.0	60.0	Tungsten	0.29	0.27
Copper	0.66	0.75	Iron	0.52	0.60
Silver	1.02	1.01	Palladium	0.60	0.54
Gold	0.79	0.64	Platinum	0.46	0.38

This is a moderately good showing, and although some of the other elements are more divergent (especially silicon, where the calculated value is nearly four times as great as the observed value) nevertheless, all of the figures are of the right order of magnitude. Considering that the atomic weights range from 7 to 208, the densities from 0.53 to 21.3, the melting points from 28° to 4000° or over, and the compressibilities from 0.27 to 60 (over two hundredfold the lowest), this degree of consistency is perhaps as good as could be expected.

It is perhaps worthy of note that some of the elements giving discrepant results also give discrepant results with regard to the law of Dulong and Petit—namely, silicon, phosphorus, sulfur, as well as carbon, for which the calculated values of the compressibilities are, respectively: 1.2, 14, 8.2 and 0.13. There is perhaps a tendency toward a specific value for the "constant" K with each group of elements; for instance, to take a widely divergent group, since sulfur and selenium give (with $K = 0.00021$ as above) theoretical values only on the average about 56% of the observed values, the assumption $K = 0.00038$ would have given satisfactory values for these nonmetals, and perhaps also for tellurium. Bearing this in mind, one may perhaps be able to predict the values of the compressibilities even in a group behaving abnormally if one member of the group is known.

To return to a more normal group, it is clear that the prediction of the approximate compressibility of strontium and barium, for example (elements not yet subjected to experimental investigation as regards this property), becomes a very simple matter. On substituting in the trial equation found above the values for the densities and melting points of these elements as found by Guntz, the compressibility of strontium is calculated to be over 0.000006 and that of barium 0.000004. Because the value for calcium calculated in the same way is not very far from the observed fact (0.000005 instead of 0.000006) one has a right to infer that these predicted figures also are not very far from the truth. An actual case of verified prediction is that of boron, which was computed from the equation to be 0.29×10^{-6} and was afterwards found to be 0.30×10^{-6}.

In the table (p. 1652) giving the calculated values for several groups of elements, and also among other groups, it is noticeable that (except in the case of cesium) the equation gives too high values with the larger atomic weights. This could be corrected, of course, by raising the quantity A to a fractional power. The equation $\beta = 0.00067\ A^{0.75}/D^{1.25}(T_m - 50°)$ gives much better results for copper, silver, gold, iron, platinum and all the heavier elements, but not such good results for the alkali metals. Therefore, it seems not worth while thus to complicate the equation for the present, until more is known about the quantitative effect of each unknown tendency among those which determine the magnitude of compressibility.

A somewhat similar equation based upon coefficients of expansion, instead of the reciprocals of the absolute melting point, could obviously be constructed, since the general shapes of the two curves are so similar; but hardly enough values are known for coefficients of expansion to make this profitable at the present time. The parallelism may be supposed to arise because each of these properties (namely, the tendency to melt and the tendency to expand on heating) may be referred to the same fundamental cause, each being increased by lack of cohesion.

No pretense is made that the foregoing equation is an exact statement of all the many-sided bearings of compressibility, and doubtless a better equation could be devised, if one assumed more complicated functions; but for the present the further pursuit of the quest seemed not worth the necessary time. It is at least of interest that an expression has been found capable of giving the approximate order of magnitude of the compressibilities of different substances, computed from the atomic weights, densities and melting points; this seems to show that the basis of the equation really represents some of the more important tendencies which are at work.

Attention may be called to the fact that the general nature of the equation is somewhat similar to that of the equation of Dupré, which gives, with fair approximation, the compressibility of numerous carbon compounds, namely (at constant temperature), $\beta = K\ \alpha/D^2$, the chief difference being that the effect of diminishing cohesiveness is expressed in one case by increase of $1/f_2(T_m)$ and in the other case by increase of α (the coefficient of expansion)[1]—the other two quantities being closely parallel, as has been shown. The equation of Dupré, however, seems to put somewhat too much emphasis upon density to be applied to the elements.

The comparison of the new empirical equation with the outcome of recent considerations by Grüneisen is not without interest, although the latter applies only to "monatomic" elements. He advanced a hypothesis assuming that a monatomic solid substance always melts when its volume is increased by a definite fraction δ above that which it occupies at the absolute zero;[2] that is to say, when

$$\frac{v_m - v_0}{v_0} = \delta = 0.08 \text{ approximately,} \tag{3}$$

in which v_m is the atomic volume at the melting point and v_0 is the atomic volume at the absolute zero.

From this equation, which he supported empirically, he evolved the expression:

$$\frac{1}{T_m}\left(\frac{dT_m}{dp}\right) = (n+2)\beta_0\frac{1}{q}, \tag{4}$$

in which T_m is the absolute melting point, n a constant (approximately 4), β_0 the compressibility of the element the absolute zero (not very different from that at the temperature of the room), and q the ratio of the coefficient of expansion at the melting point to the average coefficient of expansion, as follows:

$$q = \left(\frac{\partial v}{\partial T}\right)_{T_m} : \left(\overline{\frac{\partial v}{\partial T}}\right)_{0\ldots\ldots T_m} \tag{5}$$

Equation 4 is in a form into which it is possible to introduce the Clapeyron-Clausius equation for gram-atomic latent heat of melting (Q). Making this substitution and designating the change of atomic volume upon melting by $V'_m - V_m$, Grüneisen obtained the expression:

$$Q = \frac{V'_m - V_m}{(n+2)\beta_0} q \tag{6}$$

In this form Grüneisen's equation does not seem, at first sight, to be closely related with the new empirical equation (2) above; but by substituting for the latent heat of melting (Q) a quantity found empirically by J. W. Richards in 1897:[3]

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[1] Perhaps the most careful recent study of coefficient of expansion is that of Grüneisen (*Ann. Physik.*, [4] **33**, 33 (1910)), who compares many of the values with the equation of Thiesen, *Verh. deutsch. physik. Ges.*, **10**, 410 (1908). See also *Ann. Physik.*, [4] **26**, 393 (1908).

[2] *Verh. deutsch. physik. Ges.*, **14**, 330 (1912). Needless to say, it is not always easy to decide whether a solid element is monatomic or not.

[3] Richards, *Chemical News*, **75**, 278 (1897).

$$Q = 2.1T_m \text{ or plausibly } Q = 1.06RT_m,$$

and transposing the equation, we obtain the following:

$$\beta_o = \frac{V'_m - V_m}{1.06(n + 2)RT_m} q \qquad (7)$$

Now, taking account of the fact that n is nearly a constant, and that q probably never varies far beyond the limits 1.2 and 1.5, we may combine all these quantities with R in K and write approximately:

$$\beta_o = K \frac{V'_m - V_m}{T_m} \qquad (8)$$

That Equation 8 is not general is shown by the fact that it gives a negative (and therefore impossible) compressibility for bismuth; but bismuth is probably not monatomic, and therefore would not come within Grüneisen's moderate claim. Nevertheless, Equation 8 is seen to point with monatomic elements in the same direction as the new empirical equation (2) above, for the absolute melting point finds its place in the denominator in (8) as well as in (2), and the numerator in (8) contains the difference between the atomic volumes in the solid and liquid condition. This would naturally be greater, as a rule, the greater the atomic volume, which occupies the numerator in Equation 2. To give four values selected at random, the values for $V'_m - V_m$ for lead, sodium, potassium, and cesium are, respectively, 0.6, 0.6, 1.2, and 2.0, while the atomic volumes are the nearly proportional figures, respectively, 18.2, 23.7, 45.5 and 71. Hardly enough values for $V'_m - V_m$ are known to trace the possible slight additional effect of varying density; but the general similarity of Equations 8 and 2 is clear. Of the two, Equation 2 seems to be the better, not only because it never leads to an absurdity with substances solid at 20° C., but also because data for it are plentifully at hand.

The further comparison of these considerations with the well-known recent molecular theory of solid bodies of Einstein, Debye, Grüneisen, and others, would be a matter of interest, but will be deferred to another occasion. It will be remembered that this theory is based upon certain assumptions concerning the relation of energy and frequency of hypothetical internal atomic oscillations to specific heat and other thermodynamic properties. For a brief but fairly recent interesting review of this work, the reader may be referred to Grüneisen's recent brochure.[1]

Attention may be called to the fact that the tendencies depicted by Equation 2 are, in a general way, those which would be expected from the prediction of the theory of compressible atoms. An atom much distended because of a loose internal makeup might be supposed to be

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[1] Grüneisen's "Molekulartheorie der Festen Körper," 1913. Professor E. W. Washburn has kindly suggested in a private communication the interest of such a comparison of the new approximate empirical equation with the hypothetical ones.

highly compressible; and so might one much distended because not greatly pressed upon by outside cohesive pressure. Both of these tendencies would cause small density and accordingly large atomic volume; and the second of these tendencies would add low melting point. Therefore, the general form of the equation is plausible.

The case of tungsten is especially striking. The atomic volume is small, considering its large atomic weight (that is to say, its density is great) and its melting and boiling points are so high that this metal is now chosen as the most suitable for the filaments of electric lights. All these properties would seem to indicate cohesiveness; and a body under the pressure of such extremely high cohesion would be supposed to have a very small compressibility, which as a matter of fact it has—the value being 0.00000027, the smallest of any element thus far carefully studied.

In conclusion, the contents of this paper may be summarized by stating that the compressibilities of all the 38 elements determined at Harvard have been reduced to the new standard for the compressibility of mercury as determined at the Jefferson Physical Laboratory and the Wolcott Gibbs Memorial Laboratory of Harvard University. The new values for the compressibilities are now in accord with the less extended work of Bridgman, Grüneisen, and others. Attention is directed to probable relations between the compressibilities and the atomic volumes, densities, coefficients of expansion, and melting and boiling points of many of these elementary substances; and an approximate empirical equation is proposed for the calculation of these compressibilities.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE SURFACE TENSIONS OF WATER, METHYL, ETHYL AND ISOBUTYL ALCOHOLS, ETHYL BUTYRATE, BENZENE AND TOLUENE.

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This investigation is a part of a series of investigations having for their object the study of the fundamental properties of liquids. It is hoped that when a number of these properties have been determined with great accuracy, the essential relations between them may be discovered with greater certainty than is possible at present.

A glance at the published data[1] concerning surface tension leads one to conclude that much remains to be done. For example, the values

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[1] See, for example, "Landolt-Börnstein Tabellen," p. 113 (1912). The recent interesting research of Morgan upon the drop-method has developed since that time (THIS JOURNAL, 30, 360 (1908), and many other references given in THIS JOURNAL,