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ON THE DENSITY OF SOLID SUBSTANCES WITH ESPECIAL REFERENCE TO PERMANENT CHANGES PRODUCED BY HIGH PRESSURES.

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To many it may seem that a paper at this time on the density of solids is superfluous, in view of the large amount of work which has been done on this subject heretofore. But any one who studies the voluminous literature pertaining to the subject will find that our knowledge of the true specific gravity of many pure solid substances is still far from satisfactory; for the reason, namely, that the density of a solid is really much more an individual property of the particular sample of material used than a general property of the chemical substance. This is especially evident from the work of Kahlbaum, Roth and Siedler[1] on the specific gravities of certain metals. As an example, we may take copper, for which in the tables of Landolt-Börnstein-Meyerhoffer, we find the following densities given:

Copper, cast........................	density = 8.300–8.921
Copper, wire........................	8.930–8.949
Copper, hammered..................	8.919–8.959
Copper, electrolytic.................	8.884–8.952

with a general mean value of 8.933. Now the very careful determinations of Kahlbaum gave for pure distilled copper the value 8.9326, which after pressing to 10,000 atmospheres for 11 hours had increased to 8.9377; which, in turn, diminished again to 8.9317 after 1 hour at 20,000 atmospheres pressure. From the foregoing, it is evident that the density of a substance so common as metallic copper is known only to the second

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[1] *Z. anorg. Chem.*, 29, 197, *et seq.* (1902); *Verhandlungen der Naturforsch. Ges. Basel*, 15, 9 (1903).

decimal place, at most, and that our knowledge of the density of the element copper is still less certain.

The above divergence is without doubt due to differences in the molecular configuration of the metal as a whole; for example, to the presence in varying amount of some form differing from the usual. The uncertainty due to this cause can be excluded by studying the after-effects of various factors on substances which crystallize well and without inclusions, and do not readily yield an amorphous or allotropic modification. Salts fulfil many of these conditions, and possess the further advantage that direct microscopic observation is a certain criterion of the actual homogeneity of the crystals. Such microscopic examination is necessary; for, as Retgers[1] showed, there are outstanding differences between the recorded values of the density of salts, which, while doubtless attributable in part to faulty experiment, result in the main from a lack of homogeneity of the material; that is, the differences found are due to the occurrence in the material of inclusions or of vacuoles in varying amount.

In view of these facts it was decided to test the after-effect of high pressures on the densities of some well defined crystallin substances. Since, however, one effect of very high pressures in some cases is a partial comminution of the material, it was necessary to ascertain if a change in density follows the reduction of a substance to powder, especially as contradictory statements with reference to this question appear in the literature.

In the present paper we propose to discuss the effect of various factors upon the density of solids. Much of the material presented has been derived from the somewhat scattered papers referred to in the text: our excuse for recapitulating it here is that many of the facts observed and the permissible conclusions to be drawn from them are apparently by no means generally known. Before proceeding to treat of the factors which may influence the real or apparent density of a solid, it is advisable to discuss the methods by means of which accurate determinations of the density of a solid may be made.

The Methods for the Determination of the Density of Solid Substances.

The more important of these are five in number: (1) the volumetric method; (2) by means of the volumenometer; (3) the flotation method; (4) by the method of Archimedes; (5) by means of the pyknometer.

(1) The volumetric method, as its name implies, consists in determining by direct measurement the volume of a definit weight of material; but, owing to the difficulty of obtaining sufficiently perfect geometrical forms, this method is not applicable where the highest accuracy is desired.

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[1] J. W. Retgers, "Determination of the Specific Gravity of Salts Soluble in Water," *Z. physik. Chem.*, 3, 289 (1889).

(2) As regards the use of the volumenometer for determining the volume and hence the density of a substance, several types of instrument have been described, but none of them are accurate to better than 0.1%, and accordingly are insufficient for the purposes of the present investigation. We have constructed a modified type of the volumenometer described by A. Lo Surdo,[1] the accuracy of which, we had hoped, would be one part in 10,000. This accuracy we have so far been unable to attain; but until certain minor changes in the apparatus have been made, it will be impossible to make a definit report as to the precision attainable with this form of instrument.

(3) The flotation method possesses certain advantages, especially for the mineralogist, since a small fragment of material suffices, and the determination takes only a short time; on the other hand its applicability is limited by the lack of transparent liquids of sufficient density. In this method a heavy liquid is diluted with a lighter liquid until a small piece of the substance to be investigated remains suspended in the liquid. The density of the solid is then, of course, equal to that of the liquid, which is obtained by means of the Westphal balance or by any other appropriate method.[2]

(4) The method of Archimedes is well known. The most serious source of error is that caused by the action on the suspending wire of surface tension at the upper boundary of the liquid. This effect can be made very small, however, by using an extremely fine platinum wire previously coated with platinum black.[3] For metals or other materials, which may be put in compact form, this is perhaps the most accurate method of density determination. With a weight of metal of 50 grams, the error should not exceed 2 or 3 parts in 100,000, if attention is paid to the temperature of the liquid.

(5) The principle of the pyknometer method is so well known that no description is required. It has at various times been proposed to use, as the pyknometer liquid, substances or solutions of high density in place of water in order to increase the accuracy of the results. Among the better known of the liquids which have been suggested are thallium ethylate, solutions of various borotungstates and a solution of the double iodide of mercury and potassium. It has however been pointed out[4] that there is some important objection to the use of each of these as a

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[1] *Sci. Abstr.*, 10, 2 (1907); from *Nuovo Cimento*, 12, 41 (1906).

[2] See for instance Merwin, *Am. J. Sci.*, 32, 425 (1911). Also Andreae (*Z. physik. Chem.*, 76, 491 (1911)), who by the use of a dilatometer is able to obtain results of a high order of accuracy.

[3] Cf. Kohlrausch, *Praktische Physik*, 11 Aufl., p. 40.

[4] Kahlbaum, Roth and Siedler, *Z. anorg. Chem.*, 29, 197–224 (1902). The reader, desirous of a full discussion of the accuracy of the various methods, is referred to this paper, and to a paper by J. W. Retgers, *Z. physik. Chem.*, 3, 289 (1889).

pyknometer liquid, particularly so when used with metals. For salts or any substances soluble in water where the use of water is precluded, xylene is a very suitable liquid. It possesses the advantage that air bubbles are very easily removed from it; and while its rate of evaporation is greater than that of water, no serious error from this source need be apprehended.

In general the pyknometer method (using water or xylene as the liquid) or the method of Archimedes is the most suitable for accurate work; we accordingly made use of these methods, the former for salts and other fragmentary material, the latter for metals. With the method of Archimedes, the temperature of the liquid was read to 0.1° in order to calculate the true density of the substance.

Determinations by the pyknometer method were made according to the procedure recommended by Day and Allen[1] except that the later measurements were made with a new type of pyknometer bottle, which was devised to obviate certain difficulties incident to the use (especially in the case of fine powders) of the usual type of bottle with tapered stopper. This type has been found so satisfactory in every respect that in all the later experiments we have used it altogether, for coarse as well as for fine powders.

An Improved Form of Pyknometer for the Density of Solid Substances.

The essential feature of this new form, which is illustrated in Fig. 1, is the plane ground joint, between stopper and bottle. The neck is made fairly thick, partly for the sake of strength, partly so as to minimize heat transfer when the bottle is held by the neck between the fingers. The two surfaces making up the ground joint should be *optically flat*, but not necessarily highly polished. Considerable care should therefore be exercised in grinding them properly, as the success or failure of the bottle depends upon the excellence of the joint. As a criterion of the quality of the joint, the stopper should be pressed forcibly on to the bottle with a slight rotary motion; if the grinding has been sufficiently well done, the bottle may be lifted by the stopper. In making this test the stopper should be dry, that is without grease or lubrication of any kind. Another requisit of success is that the pyknometer should be made in such a manner that no deep groove exists at A (see figure),[2] or indeed that there be no recess from which excess of water cannot readily be wiped away.

Pyknometers of this form have the following important advantages:

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[1] Publication No. 31, Carnegie Institution of Washington, p. 55; *Am. J. Sci.*, [4] **19**, 93 (1905); *Z. physik. Chem.*, 54, 1 (1905); or see W. F. Hillebrand, U. S. G. S. *Bulletin*, **422**, p. 48.

[2] The bottles, which were made for us by the Emil Greiner Company, New York, were not entirely satisfactory as regards the grinding or freedom from grooves at the place indicated. However, by selecting two or three of the better ones, and grinding them further ourselves, we were able to obtain satisfactory results.

(1) The loss in weight by evaporation of the pyknometer liquid is negligible (for water it is of the order of 1 mg. in 24 hours). The pyknometer may therefore be allowed to stand in the balance case until temperature and moisture equilibrium is attained before it is weighed. (2) No grease or other lubricant is required on the joint; hence this obviates the uncertainty as to the weight of a variable, though small, amount of such grease. (3) Any small particles of grit or dirt which may accidentally lodge on the ground surfaces can be quickly and easily wiped off.

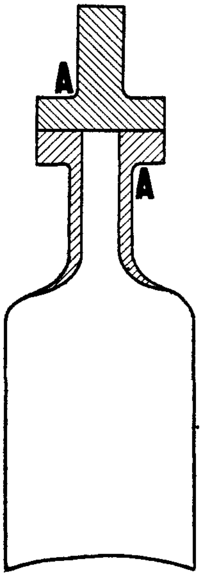

Fig. 1.—Improved form of pyknometer bottle.

For these reasons this new type of pyknometer bottle gives considerably greater accuracy than the older forms; moreover, after very little practice its manipulation is quite as simple as with the older forms. After a few preliminary trials we were able to make successive fillings and weighings, both with water alone and with the sample plus water, which did not differ by more than 0.2 mg. This is illustrated by the following records, which are part of the results of an actual determination of the density of ground quartz which passed through a "200-mesh" sieve: weight of pyknometer filled with water at 25°, 29.6111 grams; after refilling, 29.6112; weight of pyknometer and quartz filled up with water at 25°, 34.1957 grams; after refilling, 34.1957; after standing 18 hours in balance case, 34.1953.

In order to secure good results with this form of pyknometer it is highly important that attention be paid to the following details of manipulation: the loosely-stoppered bottle is immersed in a thermostat, the temperature of which should be constant to 0.01°, to such a depth that the water-level is 2 or 3 mm. below the ground joint, and is allowed to remain at least fifteen minutes. Enough distilled water at the temperature of the thermostat is then poured into the bottle to fill it to overflowing (less than 1 cc. will usually be required). The neck of the pyknometer is then held firmly with one hand while with the other the stopper is pushed on firmly with a sliding and slightly rotary motion. While the pressure is still being maintained[1] the pyknometer is removed from the thermostat and wiped dry around the stopper with a soft cloth. The bottle may then be grasped by the neck and the wiping completed. It is advisable as a precaution to pass the corner of a piece of filter paper around the stopper

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[1] The purpose of this is to prevent the occurrence of a slight leak which may be caused by the apparent expansion of the liquid when the bottle is removed from the thermostat; this apparent expansion is due to the fact that under these circumstances the bottle cools slightly and contracts, while the temperature of the water remains practically unchanged.

and top of the pyknometer in order to remove any drops of water which may adhere. After standing ten minutes (or more) in the balance case, the pyknometer is ready to weigh.[1] Great care should be taken not to heat it by the hand, or otherwise, while it is being wiped and removed to the balance case. If these directions are followed the stopper will adhere firmly and not fall off even if the bottle is turned upside down.

The Correction of Densities to Vacuum.

To all determinations of density which purport to be accurate a correction for the buoyancy of the air must be applied. The error due to this cause can be eliminated by making separate corrections on each of the weights involved in the determination; but it is much easier, and less liable to error, to make the correction to vacuum in one operation. This may be done by means of the formula given below, or by reference to Table I; these results are applicable to any method in which density is measured by finding the weight of a certain liquid displaced by a given weight of the substance.

If s is the density of the substance as calculated from the uncorrected weights, S its true density, and L the true density of the liquid, then it can be shown that the vacuum correction to be applied to the uncorrected density, s, is $0.0012\ (1 - s/L)$.[2]

The values of $0.0012\ (1 - s/L)$ for densities up to 20 and for liquids of density 1 (water),[3] 0.852 (xylene), and 13.55 (mercury) are given in Table I.

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[1] It is, of course, advisable to use a counterpoise.

[2] Let s = density of substance calculated from uncorrected weights
S = true density of substance
L = true density of liquid
W_s = uncorrected weight of substance
W_l = uncorrected weight of liquid displaced by substance

Then by definition, $s = LW^s/Wl$. (1)

Assuming D to be the density of the balance weights, $W_s(1 + 0.0012(1/S + 1/D))$ and $W_l(1 + 0.0012(1/L + 1/D))$ are the true weights of the substance and liquid respectively (assuming that the weighings are made under normal atmospheric corrections, so that the weight of 1 cc. of air is 0.0012 gram).

$$\text{Then the true density } S = \frac{W_s[1 + 0.0012(1/S + 1/D)]}{W_l[1 + 0.0012(1/L + 1/D)]} L.$$

But from (1) $W/_sW_l = s/L$. Substituting this in the above we obtain ultimately,

$$S = \frac{s + 0.0012}{L + 0.0012} L.$$

$$\text{Then the correction, } S - s = \frac{0.0012(L - s)}{L + 0.0012}. \qquad (2)$$

Since L is always large as compared with 0.0012 the denominator of the above expression may be taken as equal to L, making

$$S - s = 0.0012\ (1 - s/L).$$

[3] A table of the corrections when using water is given in Ostwald's *Lehrbuch der Allgemeinen Chemie*, 2 Aufl., I, p. 285; but the sign of the correction as given there is wrong.

It is to be noted that when the density of the substance is greater than that of the liquid (as is usually the case) the true density is smaller than the apparent or uncorrected density. In other words, the correction is negative and is therefore to be subtracted from the apparent density. All of the original results given in this paper have been corrected in this manner for the buoyancy of the air.

TABLE I.—VACUUM CORRECTIONS FOR DENSITY (COR. $= 0.0012\ (1 - s/L)$).

Density of substance (s).	Correction: density of liquid = 1 (H_2O).	Correction: density of liquid = 0.852 (xylene).	Correction: density of liquid = 13.55 (Hg).
0.8	+0.00024	....	....
0.9	+0.00012	....	....
1	0.0000	—0.0002	+0.0011
2	—0.0012	—0.0016	+0.0010
3	—0.0024	—0.0030	+0.0009
4	—0.0036	—0.0044	+0.0008
5	—0.0048	—0.0058	+0.0008
6	—0.0060	—0.0073	+0.0007
7	—0.0072	—0.0087	+0.0006
8	—0.0084	—0.0101	+0.0005
9	—0.0096	—0.0115	+0.0004
10	—0.0108	—0.0129	+0.0003
11	—0.0120	....	+0.0002
12	—0.0132	....	+0.0001
13	—0.0144	....	0.0000
14	—0.0156	....	0.0000
15	—0.0168	....	—0.0001
16	—0.0180	....	—0.0002
17	—0.0192	....	—0.0003
18	—0.0204	....	—0.0004
19	—0.0216	....	—0.0005
20	—0.0228	....	—0.0006

Effect of Powdering a Solid upon its Density.

More than a century ago, Hassenfratz[1] published a paper in which he claims that by breaking up a piece of glass weighing about 50 grams into 2520 pieces,[2] a change in density ensued; but his experiments are in part discordant among themselves and are by no means accurate enough to decide the point at issue. His work may therefore be left out of account entirely; it has been mentioned here solely because its conclusions have been quoted occasionally.

The second paper, in point of time, dealing with this question, is one by G. Rose;[3] it deserves mention if for no other reason because it has been widely cited and frequently by authors who apparently have not read through the original. Rose worked, on the one hand, with gold

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[1] *Gilbert's Ann.*, 1, 369 (1799); *Ann. chim.* (Paris), No. 77, 188 (An 6).

[2] How this was accomplished without loss of material is not stated.

[3] *Pogg. Ann.*, **73**, 1 (1848).

and silver in the massive state, and with natural barite; on the other hand, with powders produced by precipitating these substances by chemical agency; and he found that in each case the density of the powder was the greater. He is careful to state, however, that this is no absolute proof that the density of a substance in a powdered condition is greater than that of a block of the same substance, since we cannot be sure of the complete identity of the substance in the two forms. Indeed, we now know that in very many cases the form of a substance when precipitated is different from that observed in nature or obtained by fusion. Rose's work, therefore, affords no information on the influence of the state of division of a substance on its specific gravity.

The Earl of Berkeley[1] has measured carefully the densities of two sizes of fragments of natural barium sulfate. For particles remaining on a sieve, the openings of which were 0.57 mm. on a side, he finds a density which averages 4.4702, while that of particles remaining on a sieve with 0.35 mm. openings averages 4.4700. The difference between the two densities is less than 0.005%—within the error of experiment. The difference between the sizes of the particles in the two cases, however, is so comparatively small that the evidence here adduced is insufficient to decide the point at issue.

It may be noted, in passing, that the above work of Rose has been cited[2] in support of an observation of Spring,[3] according to which the amount of water required to fill the spaces of a given mass of sand is greater than would be expected if it were merely a phenomenon of occupying the air spaces. Spring's experimental work on this point is altogether insufficient to decide the question; his conclusion is based on the *assumption* that 26% of the total volume occupied by the sand consists of air spaces; even then the difference observed was only 0.8 cc., or but 0.25% of the total volume of the sand. In what follows it will be shown directly that this conclusion is false, since the density of solid substances, determined by the pyknometer, is found to be independent of the size of the particles, so long as these are strictly homogeneous, or even to show a slight decrease as the size of particle decreases; whereas, according to Spring's conclusion, the density should increase as the size of the particles decreases. A number of other early papers are cited by Spring in his first paper[4] dealing with the change of densities of solids; these are all, however, concerned with changes of density produced by crystallization, vitrification, by tempering, hammering or annealing, and will be considered later.

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[1] *J. Chem. Soc.*, 91, 60 (1907).

[2] Cameron and Bell, *Bull.* 30, Bureau of Soils, Department of Agriculture, p. 43 (1905).

[3] *Mémoires Soc. Geol. Belg.*, 17, 13–33 (1903).

[4] *Bull. Acad. Roy. Belg.*, [3] 6, 507 (1883).

Our experiments were made with quartz and potassium sulfate. The material was passed through a series of sieves, rated as 40, 60, 80, 100, 120, 150, and 200 meshes to the linear inch; the various samples were collected and dried at 200° for half an hour.[1] The earlier determinations of densities were made with the old style of pyknometer; the later ones with the new style described above. The liquids used were water and xylene,[2] the latter being used exclusively with the salts.

TABLE II.—d_4^{30} OF K_2SO_4 PARTICLES OF VARIOUS SIZES.

Old Style Pyknometer.	d_4^{30}.
Between 40 and 60 mesh..............	2.657_4 2.657_4
Between 100 and 120 mesh...........,	2.656_2
Finer than 200 mesh..................	2.656_3

The results with potassium sulfate are brought together in Table II, which shows that the difference in density between the fine and the coarse powder is here scarcely greater than the error of experiment. A microscopical examination of the potassium sulfate showed that the crystals were free from inclusions or inhomogeneities of any kind.

For quartz the results shown in Table III were obtained. In this table each value of density represents a determination on a separate sample of material. It will be noted that with increasing fineness, the density increases by a small but definit amount reaching a maximum with particles 0.05 mm. in diameter (200 *A*) and then decreasing in the case of the very finest material (200 *B*).

This seemed difficult to account for until we discovered that, although a previous microscopical examination of one lot of ground quartz indicated that it was quite homogeneous, nevertheless the coarser particles of the lot from which our samples were taken contained a number of minute gaseous and solid inclusions; the finer particles (200 *A*), however, were almost entirely free from such inclusions. This fact accounts for the greater density of the 200 *A*. It is of interest to note in this connection that H. E. Merwin[3] found the density of a number of fragments of clear quartz from different localities to be 2.6495 at 20°. Correcting the density to 25°[4] it becomes 2.6490—almost identical with the density of the 200 *A* material. This shows with great certainty that there is no difference in density between fragments of quartz 1 cm. in diameter and particles 0.05 mm. in diameter.

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[1] Special experiments showed that the density of even the finest material was not appreciably affected by exposure to the air for 48 hours.

[2] For which d_4^{30} = 0.85262.

[3] *Loc. cit.*

[4] See *Smithsonian Physical Tables,* 215–216 (1904).

TABLE III.—d_4^{25} OF QUARTZ PARTICLES OF VARIOUS SIZES.

Old Style Pyknometer.

	Between 40 and 60 mesh.	Between 100 and 120 mesh.	Finer than 200 mesh.
	2.648_7	2.646_6	2.649_2
	2.645_5	...	2.648_1
	2.645_6	...	2.646_8
	2.647_1	...	2.647_1
	2.646_6	...	2.648_5
	2.647_2	...	2.649_5
	...	...	2.648_3
	...	...	2.646_3
Average....	**2.646_8**	**2.646_6**	**2.648_0**

New Style Pyknometer.

Between 40 and 60 mesh.	Between 80 and 100 mesh.	Finer than 200 mesh.	200 *A*.[1]	200 *B*.[1]
2.6471	2.6478	2.6488	2.6492	2.6483
2.6469	2.6476	2.6477	2.6486	2.6477
....	....	2.6483	....	....
....	....	2.6481	....	....
2.6470	**2.6477**	**2.6482**	**2.6489**	**2.6480**

With potassium chloride, the crystals of which contain a considerable number of holes, the density of the fine powder is considerably higher than that of the coarse material, as the following results indicate:

TABLE IV.—d_4^{30} OF KCl PARTICLES OF VARIOUS SIZES.

Old Style Pyknometer.

	With sifted samples.	With ground and sifted samples.
Between 20 and 40 mesh.	1.978_6	...
Between 80 and 100 mesh.	1.982_9	...
Between 100 and 120 mesh.	1.983_7	1.981_8
Between 150 and 200 mesh.	1.984_1	1.982_8

It may be remarked that the density of the finest product was the same independently of whether it had been obtained by simply separating the fine crystals originally present or by grinding up some of the material of size between 20 and 40 mesh and subsequently sizing it between the 150- and 200-mesh sieves. These experiments suffice to show that when homogeneous material, free from cracks or holes, is powdered, the change of density thereby produced is but little greater than the error of the method employed. It may be noted, however, that the change, if real,

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[1] A quantity of the powdered quartz which passed through a 200-mesh sieve was separated by a process of sedimentation into two nearly equal fractions. The coarser fraction (200 *A*), as seen under the microscope, consisted of sharp grains very uniform in size, namely about 0.05 mm. across. The finer material (200 *B*) was composed of particles, the size of which ranged from 0.02 mm. on down to the limit of vision of the microscope and probably beyond it.

is in both cases a decrease; and this may be a manifestation of the same phenomenon which is observed when metals are strained.[1]

The After-Effect of Pressure on the Density of Solids.

For the experiments on the residual effect produced by very high hydrostatic pressures on the density of homogeneous crystals, we again used potassium sulfate, of size between 40 and 60 mesh. This size was chosen simply for the sake of convenience of manipulation; for from the preceding paragraphs it is evident that the effect of pressure does not depend upon the size of the crystal, so long as the material is strictly homogeneous.

The pressure bomb, of which a drawing to scale is given in Fig. 2, is of vanadium steel; it is 6 inches in length, 4 inches in internal diameter, with 1 inch diameter of bore. The plunger, of glass-hard steel, is a slip fit, but leak of oil past the plunger is prevented by the slice of soft rubber, *A*. Pressure was applied by means of a 500-ton hydraulic press, of which the platens are represented by *P P* in the figure. The figure also shows the arrangement by means of which the bomb centers itself. Without some such arrangement as this, it is next to impossible to obtain a rectilinear thrust parallel to the axis of the bomb; and, if this condition does not hold, leaks soon develop, and can be cured only by enlarging the bomb and by grinding a new and somewhat larger plunger to fit it.

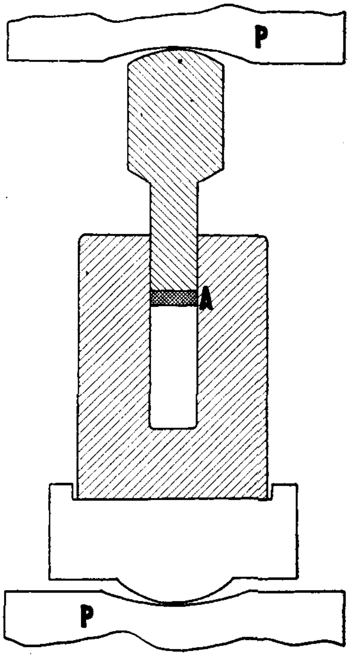

Fig. 2.—Shaded parts represent the bomb and plunger to scale; the other parts represent diagrammatically the press, platens *P P*, and the arrangement by means of which the bomb centers itself as pressure is applied to the plunger. *A* is the slice of rubber stopper.

The procedure was as follows: A quantity of about 10 grams of the substance was, in the earlier experiments, enclosed in a little bag of thin sheet rubber, the mouth of which was then tied tightly; but, as it was found impossible wholly to exclude the liquid used for compression, in the later experiments the substance was just placed within a copper tube, 1 cm. in diameter, closed at one end. The vessel containing the material was placed in the bomb and surrounded by paraffin oil (or by aqueous glycerol in some cases); the plunger was inserted, and the pressure was applied by means of a hydraulic press and continued for an hour or longer. The amount of pressure was calculated from the total com-

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[1] Cf. *postea*.

pressive force exerted by the press, as measured on a hydrostatic gauge; the values given are only approximate, as no allowance was made for friction; they cannot, however, be in serious error. After the release of the pressure, the material was well washed with gasoline to remove the paraffin oil, and after heating for half an hour to 200°, its density was determined as described above. The results follow:

TABLE V.—AFTER-EFFECT OF HIGH PRESSURE ON THE DENSITY OF K_2SO_4.

Density before compression	2.657_4
Density of one sample of same after 1 hour at 10,000 atmospheres	2.656_8
Density of a second sample of same after 1 hour at 15,000 atmospheres	2.655_8

Here again the differences are of the same magnitude as the error of experiment; again, however, it may be noted that the change, if it exists at all, is a decrease.

Spring[1] in his experiments on the after-effect of pressure on specific gravity of solids, compressed gradually in the dry state without the use of oil; the substance was subjected to pressure for a period of about three weeks, and after its density had been determined, to a second compression lasting some days. The amount of pressure was calculated to be some 20,000 atmospheres, but was probably considerably less, owing to the great friction incidental to such a method of compression. His experimental results on salts are contained in Table VI.

TABLE VI.—SPRING'S RESULTS ON THE AFTER-EFFECT OF PRESSURE ON THE DENSITY OF SALTS.

	Before compression.	After first compression.	After second compression.	Mean change produced by compression.
KCl	1.980	2.071	2.068	+0.090
KBr	2.505	2.704	2.700	+0.197
KI	3.012	3.110	3.112	+0.099
K_2SO_4	2.653	2.651	2.656	0.0
$(NH_4)_2SO_4$	1.773	1.750	1.760	—0.018
NH_4 alum	1.641	1.629	1.634	—0.009
K alum	1.758	1.756	1.750	—0.005
Cs alum	1.988	2.000	2.005	+0.014
Cr alum	1.828	1.823	...	—0.005
Tl alum	2.320	2.314	2.314	—0.006

This shows that the differences between the density after the first and that after the second compression are small and irregular; hence they are doubtless due to experimental error, which, to judge from the procedure employed, could easily have amounted to 0.005. The mean changes produced by compression are large and positive for the halides of potassium, just as one would expect from a microscopical examination, which shows that the crystals of all three substances are usually

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[1] *Bull. Acad. Roy. Belg.*, [3] 6, 507 (1883).

not homogeneous, but contain small holes and flaws; with the other substances, excepting ammonium sulfate and cesium alum, the changes are hardly greater than the probable experimental error, while with potassium sulfate there was no change, in agreement with what we have found. On account of the anomalous change in density of ammonium sulfate found by Spring, we investigated the effect of hydrostatic pressure on the density of this substance; the procedure was identical with that described above except that prior to the determination of the density some of the samples were heated to 115° for half an hour; others, however, were dried in a vacuum desiccator and not heated at all. The results, presented in Table VII, of both sets of experiments are concordant, and show again that no after-effect has been produced by pressure.

TABLE VII.—INFLUENCE OF PRESSURE ON THE DENSITY OF $(NH_4)_2SO_4$.

(*a*) Samples heated to 115° before determination of the density.
  Before compression.................................. $= 1.765_6$
  After 2 hours at 12,000 atm.......................... $= 1.767_1$
(*b*) Samples unheated.
  Before compression.................................. $= 1.763_7$
  After 1 hour at 8,000 atm............................ $= 1.763_9$

From the foregoing it is evident that the change of density observed after powdering a well-defined crystallin substance, or subjecting it to pressure, is in the direction of an increase only when the original substance contained cracks or holes; that is to say, an increased density is due entirely to accidental circumstances; with strictly homogeneous crystallin substances, on the other hand, the change of density is usually less than 0.001, and, if real, is in the direction of a decrease.

The Permanent Effect of Pressure on the Density of Metals.

That pressure may cause a *decrease* in the density of most metals has been known now for some time, though this phenomenon appears not to have attracted as much attention as it deserves in view of its bearing on the question of the constitution of metals. It was first shown for a number of metals by Kahlbaum, though it had been observed in isolated instances several times previous to him, but had not evoked much comment. H. Rose[1] observed that hammering silver caused a diminution in its density. Marchand and Scheerer found that pressed copper was, except for cast copper, the lightest, and further, that the density of bismuth decreased after compression.[2] Several investigators[3] of the density of lead, who obtained results in part discordant, agree that its density is lessened by hammering and drawing, and sometimes by pressure.

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[1] *Pogg. Ann.*, 73, 1 (1848).

[2] Erdmann, *J. prakt. Chem.*, 27, 209 (1842).

[3] See F. Reich, *Pogg. Ann.*, 119, 541.

In 1862, C. O'Neil[1] found that sheet copper diminished in density by hammering, but regained the original value on subsequent annealing. Similar observations were made by A. Riche;[2] by alternately hammering and annealing blocks of steel or bronze, he found that though the hammering usually increased the density, the process of annealing caused a further increase in each case, instead of a decrease as might be expected. The next paper in point of time dealing with this subject is that of Spring,[3] who determined the densities of seven metals before and after compression, using a method of experiment exactly similar to that described above in the case of the salts. Spring found that the second compression produced only very slight changes—decreases for two metals, lead and zinc, and increases for tin, bismuth, antimony, cadmium, and aluminium. The foregoing isolated instances would of themselves not deserve much confidence were they not confirmed by the very careful and trustworthy work of Kahlbaum and his collaborators.[4] The latter distilled a number of metals *in vacuo*, subjected them for 11 hours to a pressure of 11,000 atmospheres, determined the densities, and in five cases out of seven subjected the metal for 1 hour to still higher pressures (Pb, Cd, Au to 12,000 atm.; Cu, Ag to 20,000 atm.); the densities were determined before and after each compression, with an uncertainty of probably not more than ±0.0001. His results are reproduced in Table VIII.

TABLE VIII.—INFLUENCE OF PRESSURE ON THE DENSITY OF METALS DISTILLED IN VACUO (KAHLBAUM AND COLLABORATORS).

	Original density. d.	After 11 hours at 11,000 atm. d'.	After 1 hour at higher pressure. d''.	$d - d'$.	$d' - d''$.
Zn.	6.9225	7.1272	. . .	0.2047	. . . .
Sb.	6.6178	6.6909	. . .	0.0731	. . . .
Pb.	11.3414	11.3457	11.3298	0.0043	—0.0159
Cd.	8.6482	8.6477	8.6390	—0.0005	—0.0087
Au.	18.8858	19.2653	19.2646	0.3795	—0.0007
Cu.	8.9326	8.9377	8.9317	0.0051	—0.0060
Ag.	10.4923	10.5034	10.4993	0.0111	—0.0041

From this it is evident that the first compression caused an increase, as might be expected, in the densities of all the metals with the exception of cadmium; but that the second application of pressure caused in every case a diminution, which was so great for three of the metals—lead, cadmium and copper—that the final density is actually lower than that originally observed, before any pressure had been applied.

Kahlbaum investigated very thoroughly the possible experimental

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[1] *Fortschritte der Physik*, 18, 10.

[2] *Compt. rend.*, 69, 323 (1869).

[3] *Bull. acad. roy. Belg.*, [3] 6, 537 (1883), to which we are indebted for some of the references above.

[4] *Verhandl. Naturforsch. Ges. Basel*, 15, 9 (1903); in part in *Z. anorg. Chem.*, 29, 197 (1902).

errors, but was forced to the conclusion that the above variations represent real changes in the metals. To account for these changes he advances a somewhat fanciful *ad hoc* explanation on the basis of attractive and repulsive forces between the atoms, but makes no attempt to correlate these changes with other simultaneous changes in the metals. For instance, Kahlbaum remarks that his cylinders of metal had lost their polish and had suffered considerable deformation after compression, and especially after the second compression, but he had noticed these facts only incidentally. We now know that the oil (castor oil) used by Kahlbaum must have been nearly, if not altogether, solid at the higher pressures; consequently the metallic cylinder was then subjected to considerable differential compression, instead of to a simple hydrostatic pressure, as Kahlbaum apparently assumes was the case. This fact accounts for the deformations which he observed.

The more recent investigations instituted by Kahlbaum[1] on the changes in specific gravity of metals produced by deformation and by subsequent annealing confirm his previous results and those of Spring. He drew, or pressed, wires of various metals and alloys, measured their density, annealed them and again measured their density. The densities of wires which had been twisted a large number of times were also determined before and after annealing. A summary of his results is presented in Table IX. It will be noted that densities of the metals in the soft (annealed) state are greater in each case than the densities in the hard (drawn or twisted) state.

TABLE IX.—KAHLBAUM'S RESULTS ON THE DENSITIES OF WIRES.

Metal.	Original density of wire.	Density after annealing.	Difference.	Density after twisting.	Density after annealing.	Difference.
Au	19.2506	19.2602	0.0096	19.2220	19.2322	0.0102
Al	2.6995	2.7031	0.0036	...	...	....
Cd	8.6397	8.6434	0.0037	...	...	....
Ni	8.7599	8.8440	0.0841	8.8273	8.8412	0.0139
Cu–Al	8.2237	8.2377	0.0140	...	...	....
Pt–Ir	21.4766	21.4938	0.0172	21.3150	21.3309	0.0159
Pt, commercial	21.4170	21.4320	0.0150	21.4112	21.4284	0.0172
Pt, pure	21.4336	21.4403	0.0067	21.3985	21.4319	0.0327
Wood's alloy[2]	9.6661	9.6735	0.0074	...	...	....
Alloy IX[3]	9.2837	9.2940	0.0103	...	...	....
Alloy VIII[4]	9.7711	9.8223	0.0512	...	...	....

It remained for Spring[5] to suggest the most probable explanation for

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[1] Kahlbaum and Sturm, *Z. anorg. Chem.*, 46, 217 (1905).

[2] Composition: Bi 50%, Pb 25%, Cd 12.5%, Sn 12.5%.

[3] Composition: Bi 47.75%, Pb 18.39%, Cd 13.31%, Sn 20.55%.

[4] Composition: Bi 52%, Pb 32%, Sn 16%.

[5] "The Effect of Compression in Diminishing the Density of Certain Substances and the Probable Cause of the Phenomenon." *Rec. trav chim. Pays-Bas*, **23**, 1 (1904); *J. chim. phys.*, **1**, 593 (1903).

these changes in density: Namely, that a diminution in density occurs only in those cases in which a deformation has taken place. The gist of his argument is briefly as follows: That the substance, while it is being deformed, behaves as if it were partially liquid; that, when deformation has ceased, the substance may not wholly return to its original crystallin state, but partially remains in a state analogous to that of an under-cooled liquid, or, in other words, in an amorphous or glassy condition; and, since the density of the amorphous form is usually less than that of the corresponding crystallin form, the net effect would be a diminution in the observed density. If this reasoning be correct, it follows that metallic bismuth when deformed should show an increase of density; and Spring found this to be so. He fashioned wires of various metals by squeezing the metal through a hole 2 mm. in diameter, and made thin sheets by hammering; the densities were determined, the wires and sheets annealed and the densities again determined, with the following results:

TABLE X.—SPRING'S RESULTS ON THE CHANGE OF DENSITY OF METALS PRODUCED BY DEFORMATION.

	Density at 16° of			Mean difference.
	Wire.	Hammered sheet.	Annealed metal.	
Pb	11.3351	11.3348	11.3410	—0.0060
Sn	7.3011	7.3016	7.3137	—0.0123
Cd	8.6558	8.6603	8.6633	—0.005
Ag	10.2485	10.2531	10.2696	—0.019
Bi	9.8522	...	9.8354	+0.0168

These results are in agreement with those of Kahlbaum, except for the metals tin and bismuth, which the latter did not investigate. The anomalous behavior of bismuth as compared to that of the other metals is very important if true, since it furnishes strong evidence in support of Spring's theory.

Experiments with Bismuth.

Bismuth Cylinders.—In order to test this alleged behavior of bismuth, careful measurements were made of the densities of bismuth cylinders, first, after subjection to high pressures and again after annealing them. The bomb used for these experiments was of "type D" chrome-vanadium steel. The dimensions were: outside diameter 60 mm., diameter of bore 12 mm., length 80 mm. Pressure was applied directly to the metal by means of a hardened steel plunger. The whole sat beneath the press, and pressure was applied to the plunger as previously described on page 573. The cylinders were turned down to the proper diameter in a lathe; the diameter of cylinders I and II was practically the same as that of the hole in the bomb, while the diameter of cylinder III was 2 mm. less. The latter cylinder, therefore, when subjected to pressure was probably first crushed to some extent and then welded together again at the higher pressures. As will be seen later, the density of this cylinder changed in a direction opposit to that of the other two. The pressure applied to each cylinder was about 15,000 atmospheres. Density was determined by the principle of Archimedes. The suspending wire was of platinum 0.1 mm. in diameter and was platinized according to the procedure of Kohlrausch. The cylinders were annealed by heating in a beaker filled with paraffin oil, and then slowly cooled to room temperature. After being wiped free from oil with a cloth, washed with "petroleum ether," and carefully dried, their densities were again determined. The results corrected to vacuum and to 25° follow:

Table XI.—d_4^{25} of Metallic Bismuth, under the Conditions Stated.

	Cylinder I. 33 g.	Cylinder II. 32 g.	Cylinder III. 41 g.
Density after pressing to 15,000 atm...	9.8012	9.7886	9.8001
After heating to 200° for 1 hour.......	9.8022 9.8020	....	9.7997
After heating to 240° for 2 hours......	9.8028	9.7898	9.7971

Since the act of forming wires from metals deforms them greatly, it was expected that bismuth wire might show a greater density change on annealing than the compressed cylinders. Accordingly a quantity of bismuth wire 1 mm. in diameter was made by pressing it out from a small bomb through a hole of that size. Wire was thereby produced which was initially flexible but broke upon being bent back and forth three or four times.

Density of Bismuth Wire.—About 20 grams of this wire were broken up into lengths of 6 or 8 cm., the pieces were bent into a circular shape and tied together with a weighed platinum wire. The density of the bundle of wires was then determined by the principle of Archimedes, special precautions being taken that no air bubbles remained in or on the bundle of wire. To make sure that this was the case, the wire was covered with air-free water in the beaker in which it was to be suspended. The beaker was then placed in a vacuum desiccator and the water caused to boil under reduced pressure for 10–15 minutes. Two determinations of the density of the wire gave 9.7693 and 9.7692 (corrected to vacuum and to 25°). After annealing at 230° for 2 hours the density was 9.7767 and 9.7768.

It will be seen that the density change upon annealing either the cylinders or the wire is in the same direction as with other metals, except in the case of cylinder III. The amount of change is small but undoubtedly greater than the error of experiment, which is probably not greater than ±0.0005. The increase of density observed with cylinder III we attribute to the inclusion of air at high pressure during the probable crushing mentioned above. A small amount of air included in this manner, while having little effect on the density after compression, could expand during the process of annealing and thus give rise to the apparent decrease in density. This explanation may also account for the abnormal change in density observed by Spring, if indeed he made his density determinations on bismuth *before and after annealing.*[1]

General Discussion of the Experimental Data.

Supposing these figures for the effect of pressure on the density of metals to be correct—and the magnitude of the differences surely greatly exceeds the probable experimental error—it may now be regarded as proved that deformation of a metal causes a change—usually a decrease—in its density.

Additional evidence in favor of this point of view is afforded by other papers. Gray and Mees[2] noticed that when hard drawn iron, brass, German silver, and pianoforte steel wires were stretched with increasing loads, a slight diminution in density set in when the elastic limit was reached. Grunmach[3] stretched a bar of Siemens-Martin steel until it ruptured, and afterwards made a series of very careful density determinations throughout the length of the bar; he found that the density of both portions of the bar was constant and unchanged except at the broken ends, at which the density was less by 0.040 and 0.050, respectively.

From the foregoing examples, then, it is evident that deformation of metals is accompanied by a change—practically always a decrease—of density. This explanation conflicts with none of the available trustworthy experimental evidence on the densities of metals,[4] and furthermore, it serves to correlate these facts with a number of phenomena observed by Beilby.[5] Beilby's argument may be presented in his own words, it being premised that he uses the terms "crystallin" and "amorphous" to denote a homogeneous and a heterogeneous assemblage of molecules, respectively.

"Metals ordinarily occur in two distinct phases: the hardened or amor-

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[1] For a discussion of this ambiguity cf. Kahlbaum and Sturm, *Z. anorg. Chem.*, 46, 303–5 (1905).

[2] *Phil. Mag.*, [5] 29, 355 (1890).

[3] *Ann. Physik*, 67, 227 (1899).

[4] The density data brought together in tables, *e. g.*, in Landolt-Börnstein-Meyerhoffer—cannot be made use of for such comparisons; the densities must be determined upon the *same* sample (1) when deformed and (2) after annealing, in order to obviate the effect of accidental circumstances—flaws, etc.—an effect which might easily exceed the effect sought.

[5] For the present purpose, the best paper is in *Phil. Mag.*, [6] 8, 258–76 (1904), in which Beilby summarizes all his work up to that date. But see also *Proc. Roy. Soc. London, (A)* 72, 218, 226; 76, 462; 79, 463. The more important conclusions have been republished as reports, or abstracts, of lectures delivered by Beilby, in *Chem. News*, *British Association Reports*, and elsewhere.

phous, which will be referred to as the A phase, and the annealed or crystallin, which will be referred to as the C phase. The A phase is transferred into the C phase by the agency of heat, the C phase is transferred into the A phase by mechanically-produced flow. In the transformations $A \leftrightarrows C$ there are two intermediate mobil phases M and M'; so that the transformation may be written $A \longrightarrow M' \longrightarrow C$ and $C \longrightarrow M \longrightarrow A$. The argument is based on evidence drawn from:

(1) The distinct mechanical properties of the two phases A and C.

(2) The microstructure of these and the evidence which it supplies of the existence of the mobil phases M and M'.

(3) The (*a*) optical, (*b*) electrical, (*c*) thermochemical properties of the phases A and C."[1]

Evidence was obtained in favor of these views with the malleable and ductil metals—gold, silver, platinum, copper and lead—and also with the brittle and crystallin metals—antimony and bismuth—the behavior of which falls perfectly in line with that of the former; further, with iron and nickel, which however possess other properties which occasionally render their behavior less plain and simple. The evidence presented in the case of silver, which occupies a fairly central position in respect to hardness and tensil strength, is here recapitulated, in order to show its character.

(1) The tensil strength of silver may be raised from under 10 tons per square inch to over 20 tons by rolling, hammering or wire-drawing. A strip of silver may be made quite hard and springy by hammering, but loses all its spring after heating to 260°.

(2) "The micro-structure of annealed silver, if the metal is in a sufficiently massive form, is always crystallin, and consists of grains built up of lamellae of similarly oriented units. In attenuated forms, like leaves or thin films, the structure is determined by surface tension, and has none of the characteristics of crystallin aggregation. The micro-structure of hardened silver is vitreous looking on the surface, and finely granular immediately below the surface. The forms assumed by surfaces and edges are rounded and smooth, and suggest the flow of a viscous liquid. When the glassy surface is carefully removed by a solvent, the granular structure underneath is more fully disclosed. By further action of the solvent the granular layer may be completely removed, disclosing the crystallin grains of the C phase more or less deformed or broken up. It seems probable that the granules which are thickly distributed through the vitreous layer are produced by the breaking down of the lamellae and the setting free of the units of which they are built up. The granules and their vitreous matrix always appear at surfaces of flow, the thickness

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[1] Beilby, *Phil. Mag.*, [6] 8, 261 (1904).

of the layer being determined by the thoroughness of the flow at that particular place."[1]

(3) (*a*) In beaten leaves or films, silver in its hardened state is highly reflecting; by heating to 250–300° the leaf or film becomes transparent and loses much of its reflecting quality; but by flowing or burnishing the annealed leaf or film its opacity and reflecting power are restored.

(*b*) The electrical conductivity of a silver wire in the annealed state is 8–10% higher than that of the same wire in the hardened state. A thermo-junction composed of a hardened and an annealed wire of silver gave 0.17 microvolt per degree of difference between the hot and cold junctions; at 260° the electromotive force fell to zero, as the hardened wire then passes into the soft condition. Similar observations have been made by other observers, using various metals.[2]

(*c*) Berthelot[3] found that the heat of solution in mercury of hammered silver was 2.03 cal., as compared with 0.47 cal. for annealed silver, and 0.10 cal. for crystals of electrolytic silver.

Thus by collecting the observations on the mechanical, optical, electrical and electrochemical properties of the hard and soft forms, it is seen that these all, without exception, support the view that there is a well-marked difference between the two states; further that they group themselves on either side of a transition temperature common to all; we are therefore justified in regarding these forms of a metal as distinct phases. The transformation from soft to hard cannot be brought about by reducing the temperature below the transition point, provided that no strains are set up thereby;[4] but it is readily effected by mechanical means: for instance, in even the lightest and finest polishing this transformation or flow takes place to some extent at, and very near to the surface. When the metal is subjected to more drastic treatment, such as hammering or pressing, the effects penetrate to a greater and greater depth, and the transformation "takes place at all points where the strain reaches the stage at which mobility of the molecule is induced by the movement of one portion of substance against another." Thus "exceedingly thin layers of the *A* phase are formed throughout the whole mass of strained metal. Slipping is easy so long as fresh moving surfaces are forthcoming for the supply of the mobil phase; but when all the available crystallin phase has become encased in the unyielding amorphous phase, plasticity *under these particular stresses comes to an end.*"

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[1] *Loc. cit.*, pp. 262–3.

[2] Magnus Maclean, *Proc. Roy. Soc. London*, (*A*) 64, 322; 66, 165. Spring, *J. chim. phys.*, 1, 600 (1903).

[3] *Compt. rend.*, 132, 234–41 (1901).

[4] Muir found that hardening by quenching results from the overstraining of the successive layers of material in a rod or mass of metal (*Proc. Roy. Soc. London*, (*A*) 71, 89).

"In the more easily flowed metals the surface film formed by polishing may vary from 1000–5000 $\mu\mu$ in thickness, while in the less easily flowed metals they may be 500 $\mu\mu$ or less. At surfaces which have moved over each other very slightly, films of only a comparatively few molecules might be formed."

Beilby was unable by any means to destroy all traces of the crystallin phase, even in the thinnest strips of gold or silver foil; indeed it has not been possible to produce more than a small percentage amount of the amorphous phase. Hence the properties of the latter can only be very imperfectly ascertained. All the evidence, however, tends to show that this amorphous phase is closely analogous to an undercooled melt, *i. e.*, it bears much the same relation to the crystallin metal as a silicate glass bears to the crystallin silicate.

On this view then we should expect as one of the results of the deformation, and consequent flow, of metals, a change of density in the same direction as that produced on melting; which agrees with the results actually found with the metals, bismuth excepted. Too much stress must not be laid on this exception, which may after all be only apparent. For though under ordinary conditions melted bismuth is denser than solid bismuth, it by no means follows that the melt produced at the pressures required to cause the metal to flow should be denser than the solid. As an illustration consider the behavior of water[1] with pressure: at pressures up to about 2200 atmospheres water is in equilibrium with ordinary ice (ice I), and the melting point decreases with increase of pressure up to that point; but at pressures greater than 2200 atmospheres, the melting curve rises again, and we have the water in equilibrium with other forms of ice, all of which are *denser* than the liquid water.

The plausibility of this view of the decrease of density of metals which have been deformed is increased by certain other considerations, which however, can only be referred to here. It is shown, namely, in another paper from this laboratory[2] that many of the properties of metals can be simply correlated if we assume that every *permanent* deformation of a crystallin solid is conditioned by, and consequent upon, a *real* melting; the whole of the solid does not, of course, melt, but only those portions of it which at any instant bear the brunt of the strain. On the basis of this assumption—the reasonableness of which is supported by a large variety of observations on the general behavior of metals—the possibility of accounting for changes of density following deformation is apparent; a plausible account of the mode of occurrence of these changes could easily be given, but at present it seems premature to do so.

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[1] Tammann, *Krystallisieren und Schmelzen*, pp. 315–44. Bridgman, *Proc. Amer. Acad.*, 47, 441 (1912).

[2] Now in course of publication. A preliminary note was published in *J. Washington Acad. Sci.*, 1, 260 (1911).

Summary.

(1) With a new and improved form of pyknometer we have determined the density of salts and other substances with an accuracy of 3 or 4 units in the fourth decimal place, that is, within 0.02%. In many cases, however, such accuracy is unnecessary since the variations of density due to inhomogeneities of the material may be much greater than this.

(2) Powdering a crystallin substance does not change its density by an amount which we can detect with certainty, provided that the material is homogeneous and free from cracks and holes; but if the substance is not homogeneous, then, as might be expected, the fine powder is denser than the coarse particles.

(3) Neither does very high hydrostatic pressure produce any aftereffect on the density of strictly homogeneous crystallin compounds.

(4) But if the pressure be not uniform, then the density of a metal which has been subjected to such compression—or has been deformed in any other way—usually increases first (owing presumably to the filling up of pores and cracks) and then decreases, sometimes even so as to reach a final density less than the original value. Subsequent annealing of the specimen causes a renewed increase of density. The direction of the change of density on compressing bismuth is, contrary to Spring's conclusion, the same as that for other metals, namely a decrease of density following upon deformation. The bearing of these results upon the question of the "flow" of metals is discussed: they are shown to be in harmony with the idea that the "flow"—or indeed any deformation—of a metal is a manifestation of a real melting produced by the unequal strains set up during the process.

(5) Finally it is important to emphasize the fact that the density of most substances is somewhat variable, owing to a lack of complete homogeneity of the material. In consequence of this, slight changes of density cannot be regarded as good evidence for the occurrence of any transformation or chemical reaction—whether produced by subjecting the system to compression or by other means.

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THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF THE ALCOHOLS IN LIQUID HYDROGEN CHLORIDE.

By E. H. Archibald.

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In previous papers,[1] results have been given of a study of the electrical conductivity of solutions of the alcohols in liquid hydrogen bromide, and of the organic acids in liquid hydrogen chloride and bromide. These

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[1] This Journal, 29, 665 (1907); 29, 1416 (1907).