Compressions and Polymorphic Transitions of Seventeen Elements to 100,000 kg/cm^2

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IN the following I give the numerical results of the first measurements above 50,000 kg/cm^2 made by the method, already anticipated in a brief note,[1] in which the entire pressure apparatus is immersed in a liquid which is itself exposed to a hydrostatic pressure between 25,000 and 30,000 kg/cm^2. The details of the method are only briefly indicated here; I expect to publish in another place a fuller description and discussion.

The piezometer in which the material is compressed is shown in Fig. 1; it consists of a cylinder completely pierced with an axial hole. The compression is applied by two Carboloy pistons acting from each end. The piezometer is compound, consisting of an inner core of Carboloy, made slightly tapering on the outside, forced into an outer sleeve of heat-treated alloy steel. By this means the Carboloy cylinder starts under an initial compression in addition to the compression of 25 or 30,000 kg/cm^2 exerted by the confining liquid. The additional compression afforded by the steel sleeve is further increased by the external hydrostatic pressure because of the differential compressibility of steel and Carboloy, steel being about three times more compressible than Carboloy. The piezometer is six-tenths filled with the material to be measured A; this is prevented from leaking past the Carboloy pistons by conical steel retaining rings. The assembled piezometer is placed inside the cylinder of the apparatus for reaching 30,000 kg/cm^2, which is filled with an amount of isopentane, determined by preliminary trial, such that the piston of the 30,000 apparatus just makes up on the double pistons of the piezometer when the pressure in the 30,000 apparatus has reached approximately 25,000 kg/cm^2. Further motion of the piston of the 30,000 apparatus now produces the double result of increasing the pressure in the fluid of the 30,000 apparatus and at the same time increasing the pressure on the material in the piezometer. Because of the small amount of this material, compared with the total amount of fluid in the 30,000 cylinder, a motion of the piston sufficient to increase the pressure on the contents of the piezometer to 100,000 kg/cm^2 increases the pressure in the surrounding liquid by a much smaller amount. The precise increase of pressure in the surrounding liquid depends on the compressibility of the contents of the piezometer; for the materials described below it averaged something of the order of 3000 kg/cm^2, and might on occasion rise to 5000 kg/cm^2.

The extra force required to push the piston of the piezometer is measured electrically from the change of resistance of a hardened steel grid. This has already been described to some extent[2] and will be further described in the detailed paper. The compression coefficient of the grid was determined by independent measurement, as was also the pressure coefficient and the pressure coefficient of the compression coefficient. The compression coefficient is about 15 percent less at 25,000 than at atmospheric pressure. The confining pressure exerted by the liquid of the 30,000 apparatus was independently measured with a manganin gauge, which has already been described.[3] The piston displacement of the piezometer was obtained from a measurement of the piston displacement of the 30,000 apparatus, made with a jeweled Ames gauge, graduated to 0.0001 inch and reading by estimation to 0.00001

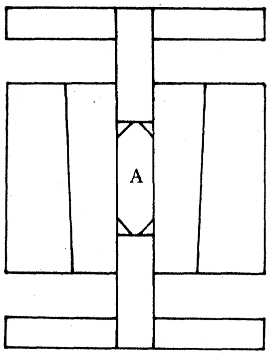

FIG. 1. Scale drawing of the high pressure piezometer. The outside diameter is 7/16 inch.

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[1] P. W. Bridgman, Phys. Rev. **57**, 342 (1940). See also R. W. Goranson and E. A. Johnson, Phys. Rev. **57**, 845 (1940).

[2] P. W. Bridgman, J. App. Phys. **12**, 461 (1941).

[3] P. W. Bridgman, Proc. Am. Acad. **74**, 1 (1940).

inch. The method is a differential method; the difference of piston displacement is determined when the piezometer is filled with the material under investigation and when filled with some standard reference material. In this way most of the various distortions in the apparatus are eliminated. The reference material should have a small compressibility; for this purpose gold was chosen, which is as incompressible as iron and has the further advantage of mechanical softness, thus reducing hysteresis effects due to friction. To convert differential compressions to absolute compressions the compression of gold must be assumed; this was extrapolated from my measurements up to 12,000 kg/cm^2, corrected for my improved values for iron, by Murnaghan's formula. This formula has shown itself surprisingly good at high pressures, and in view of the small absolute value of gold in comparison with that of the substances listed here, the error in the absolute values introduced by the extrapolation should not be important. The assumed compressions for gold are 0.0255 at 50,000 and 0.0483 at 100,000. The results thus obtained are differential in another sense, because they are for the compressions taken from 25,000 as zero. The total compressions have to be obtained by combining the measurements here with previous measurements up to 25,000 kg/cm^2. Such measurements have been made for most of the materials of the following.

It is not possible to eliminate all correction for distortion by making the method differential, but the differential displacements must be corrected by the fractional change of cross section of the piezometer. Here appears a great advantage in making the piezometer of Carboloy instead of steel, because its elastic constants are three times higher. The correction was determined by calculation from the independently determined elastic constants and was 3.3 percent at the maximum. There was practically no permanent set of the piezometer under this distortion—another advantage of Carboloy.

The magnitude of the piston displacement for the range 25,000 to 100,000 kg/cm^2 varied from 0.020 inch for gold to 0.063 inch for barium. The readings lie on smooth curves to within 0.0002 or 0.0003 inch. The principal error in the method arises from friction; the effect of friction was eliminated as far as possible by taking the mean of increasing and decreasing readings. Because of friction a higher pressure has to be applied to the Carboloy pistons than can be applied, on the average, to the contents of the piezometer; the pressure on the piston was often pushed beyond 110,000 to get 100,000 in the piezometer. The error from friction is relatively small for the highly compressible softer metals, but for metals much less compressible than zinc becomes serious enough to limit the applicability of the method. In nearly all cases the results are the mean of two independent set-ups. A check on the results is afforded by the agreement of these results, and also by the agreement of the results between 25,000 and 50,000 with those previously obtained. I believe that, in general, the final accuracy is between one and two percent.

A number of the substances have new polymorphic transitions in the range; the establishment of such transitions is the most positive of the results obtained. If the volume discontinuity of the transition is less than 0.15 percent of the initial volume, however, it would escape detection, as also if the transition is too sluggish.

The numerical results are given in a table of compressions (Table I); that is, fractional changes of the initial volume at atmospheric pressure, at pressure intervals of 10,000 kg/cm^2. The results are for room temperature, which averaged 23°. The data for the transitions are given as footnotes; the difference of the two compressions is the volume change at the transition. Thus the volume change at the transition of calcium, which occurs at 64,000 kg/cm^2, is 0.013, or, otherwise expressed, the volume at 64,000 of the low pressure modification of that amount of calcium which occupies 1 cm^3 at atmospheric pressure at 23° is 0.771 cm^3, and the volume at the same pressure of the same number of grams of the high pressure modification is 0.758 cm^3.

Because of their simple structure, which makes them amenable to theoretical treatment, perhaps the most interesting of the substances are the alkali metals. It is unfortunate, therefore, that the accuracy is materially less for them than for the other materials. The reason is that the usual technique could not be followed. These metals chemically attack and rupture the piezometer, so that it was necessary to enclose them completely in a sheath of copper, which occupied two-thirds of the total volume. The rigidity of copper is so high that the accuracy is materially reduced, particularly at the lower pressures. The results given in Table I were obtained by a graphical compromise, in which much weight was given to the former results up to 45,000 or 50,000 kg/cm^2. The previous results differ principally from the present ones in the same range in their greater decrease of compressibility with pressure, the compressions now found being greater than would be found by an extrapolation of the previous results. The compression of copper enters these results. This was assumed as given by Murnaghan's formula; the assumed compressions were 0.0325 and 0.0608 at 50,000 and 100,000 kg/cm^2, respectively.

An attempt was made also to get the compressibility of caesium, but the results were incomplete because of rupture of the apparatus. It is probable that the compression is of the order of 15 percent greater than that of rubidium, but this statement must be used with some reserve.

An interesting question in connection with the alkali metals is whether any of them have high pressure transitions analogous to the transition of caesium at 23,000 kg/cm^2. None was found. The fractional change of volume at the transition of caesium is 0.006; this is small, but not smaller than several found and tabulated above. It is, therefore, highly probable that, if there are transitions of the other alkali metals, their volume change is materially smaller than the change of caesium.

In the case of three metals of the table, cadmium, thallium, and arsenic, there are no sufficient measurements of the compressions at low pressures; the values given for 10,000 and 20,000 were obtained by estimation from comparison with similar elements or from the initial compressibility in the first few hundred kg/cm^2. The results for arsenic are obtained from only a single run. The piezometer fractured on the next filling in a way to suggest chemical attack.

Seven new transitions have been found above 50,000 kg/cm^2. The transition of antimony had been looked for because of the close similarity of the crystal structures of antimony and bismuth; the magnitude of the change of volume at the new transition of antimony is not far from that of the first transition of bismuth, so that the behavior of antimony may be parallel to that of bismuth but on a much extended pressure scale. Bismuth has two new transitions at high pressure, making now six modifications in all. There is a rather close parallelism between the transitions of bismuth and those of water. Each of the alkali earth metals has two transitions; the low pressure transition of calcium is somewhat obscure and has been smoothed over in the table. The parallel-

TABLE I. *Compression of seventeen elements.*

PRESSURE KG/CM^2	Li	Na	K	Rb	Ca		Sr		Ba		Zn	Cd	In	Tl	Sn	As	Sb		Bi		Se	Te	
10,000	0.074	0.117	0.183	0.233	0.058		0.075		0.086		0.016	0.022	0.023	0.023	0.018	0.047	0.025		0.028		0.089	0.045	
										(*d*)													
20,000	.125	.182	.268	.316	.103		.122		.159		.031	.042	.045	.043	.034	.083	.047		.052		.149	.079	
								(*b*)												(*h*)			
30,000	.164	.232	.329	.371	.139		.172		.211		.046	.060	.064	.061	.049	.109	.066		.158		.187	.111	
40,000	.201	.273	.377	.419	.168		.209		.253		.061	.076	.081	.079(*f*)	.064	.132	.083		.174		.208	.138	
																				(*i*)			(*l*)
50,000	.237	.310	.419	.462	.195		.239		.288		.075	.091	.097	.103	.077	.152	.098		.192		.227	.214	
60,000	.272	.343	.457	.501	.220		.266		.318(*e*)		.088	.104	.112	.119	.091	.171	.112		.205		.243	.225	
						(*a*)		(*c*)												(*j*)			
70,000	.305	.372	.492	.539	.252		.298		.361		.100	.116	.126	.132	.103	.188	.124		.222		.258	.234(*m*)	
80,000	.336	.397	.522	.575	.268		.317		.382		.111	.127	.140	.145	.114	.204	.136		.232		.271	.250	
																		(*g*)					
90,000	.366	.419	.549	.608	.284		.335		.402		.122	.138	.153	.157	.125	.219	.185		.240(*k*)		.283	.258	
100,000	.394	.440	.573	.638	.298		.352		.420		.132	.148	.165	.169	.136	.233	.197		.261		.295	.267	

(*a*) Transition at 64,000. Compressions: 0.229 and 0.242.
(*b*) Transition at 25,000. Compressions: .143 and .152.
(*c*) Transition at 65,000. Compressions: .279 and .287.
(*d*) Transition at 17,000. Compressions: .135 and .141.
(*e*) Transition at 60,000. Compressions: .318 and .337.
(*f*) Transition at 40,000. Compressions: .079 and .086.
(*g*) Transition at 85,000. Compressions: 0.142 and 0.179.
(*h*) Two transitions at 25,000. Extreme compressions: .064 and .150.
(*i*) Transition at 45,000. Compressions: .180 and .186.
(*j*) Transition at 65,000. Compressions: .211 and .216.
(*k*) Transition at 90,000. Compressions: .240 and .252.
(*l*) Transition at 45,000. Compressions: .152 and .207.
(*m*) Transition at 70,000. Compressions: .234 and .241.

ism between the alkali earth metals cannot be as close as superficially appears, because at atmospheric pressure calcium and strontium are face-centered cubic, whereas barium is body-centered. It is surprising that these simple cubic structures permit so many other forms.

Selenium is probably a mixture of amorphous and crystalline material. On the initial application of pressure it experiences some permanent change, but a single application apparently forces it into a more or less well-defined condition. The results obtained now agreed well in the common range with the former measurements to a pressure maximum of 50,000 kg/cm^2. The very sharp drop of compressibility of selenium in the neighborhood of 25,000 is to be noted. The curve of compression of selenium against pressure is quite different in character from that of all the other elements, dropping off with pressure at a much more rapid rate. The amorphous material doubtless functions more like a liquid than a crystalline solid.

As in all this work, I am indebted to the Carboloy Company for the Carboloy. I have received financial assistance from the Milton Fund of Harvard University, and the skillful assistance of my mechanic Mr. Charles Chase was essential.

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Heat Transfer and Superfluidity of Helium II

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In our recent researches, when studying the heat transfer of helium II in capillaries, we established the existence of a counter current in the liquid.[1] An analysis of the experimental results indicated that the transfer of heat into the kinetic energy of the current might take place in a thermodynamically reversible way. From these experiments it was suggested that the helium II flowing in thin films could be in a different energy state.

In the present experiments we studied the flow of helium through a narrow slit, about 10^{-5} cm, obtained by means of two optically polished quartz disks in the same way as in the viscosimeter by the aid of which we originally established the superfluidity of helium II.[2] By making the helium flow through this slit under the influence of a temperature gradient in a container with a good heat insulation it was possible to show that the flowing helium has zero entropy. The difference of the heat content Q(cal./g of free helium and helium flowing through the slit obtained at a number of temperatures is plotted by crosses in Fig. 1.

From a simple thermodynamic analysis of this phenomenon it follows that if the helium II is forced through a narrow channel under a pressure p; then in the case of thermohydrodynamically reversible phenomena a temperature difference ΔT will be caused which can be determined from the following expression.

$$p = A\rho Q(\Delta T/T), \qquad (1)$$

where ρ is the density of the helium and A the mechanical heat equivalent.

By means of the same apparatus the existence of the temperature difference ΔT was established and measured. In such a way we have an independent means of determining the value of Q from expression (1). On the curve in Fig. 1 these values of Q are plotted by circles. The coincidence of Q determined by two different methods shows that the thermohydrodynamic processes of helium II are reversible.

The reversibility of the thermohydrodynamical processes in helium II must evidently be attributed to the lack of the sources of energy

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[1] P. L. Kapitza, J. Exp. Theor. Phys. **11**, 1 (1941); J. Phys. USSR **4**, 177 (1941).

[2] P. L. Kapitza, Rec. Acad. Sci. USSR [18] **28** (1938); Nature **74**, 141 (1937).