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Absolute Measurements in the Pressure Range up to 30,000 kg/cm^2

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The first task for any program of accurate measurements in a new pressure range is the establishment of various landmarks. The most important of these are pressure fixed points, similar to the familiar fixed points of thermometry, for the reproduction and measurement of pressure. After the pressure scale is established perhaps the most fundamental sort of measurement that can be attempted is of compressibility. The most convenient method is a differential method, which assumes as known the absolute compressibility of a substance of reference. The establishment of one absolute compressibility is therefore the next task after the establishment of the pressure scale. In this paper I briefly summarize the results of recent measurements of these two kinds; full details are in course of publication elsewhere.

In my previous measurements[1] of various pressure effects up to 12,000 kg/cm^2 the working pressure gauge was a coil of manganin wire. A preliminary investigation with an absolute pressure gauge of the free-piston type had shown that the change of electrical resistance of manganin is nearly linear with pressure in that range, so that the manganin gauge could be calibrated by the determination with it of a single pressure at some pressure fixed point. For this pressure fixed point the freezing pressure of mercury at 0°C was chosen. This was measured in the first place with the absolute gauge and taken in all my work to be 7640 kg/cm^2. In extending the pressure range by a factor of 2.5 the first question to be answered is whether the manganin gauge continues linear. I have already made a preliminary investigation of this point,[2] and had come to the conclusion, from a comparison of the way in which the resistances of various metals extrapolate together and from rough measurements of pressure in terms of the force on the piston, that the manganin gauge is not probably in error by more than one or two percent at 25,000 kg/cm^2. It appeared therefore that in extending the accurate calibration a single new fixed point near the end of the range would be adequate. Of the phenomena which might be used to determine such a fixed point it appeared that a phase change, as had been employed before, was by far the most convenient. Transition measurements in the pressure range up to 50,000 of some 60 substances afforded extensive material for selection.[3] Of all these substances bismuth is by far the most suitable. The transition between modifications I and II of bismuth occurs at about 25,000 kg/cm^2 at room temperature, it has a conveniently large volume change, about 4.5 percent, it runs fairly rapidly with little excess pressure in either direction to start the transition and with very narrow region of indifference, and the temperature dependence is so slight that thermostatic temperature control is not necessary.

The exact transition pressure must be established by some sort of absolute procedure. An absolute gauge of the free-piston type operating with a liquid is probably not feasible, for I believe that difficulties set by leak and viscosity in the liquid will prevent the use of this type of gauge to pressures much exceeding my previous maximum of 13,000 kg/cm^2. But some sort of measurement of pressure in terms of the force exerted on a piston probably remains the simplest. This can be done by directly compressing the bismuth undergoing transition with a piston, measuring the force on the piston, and determining when the transition occurs by the discontinuous change of volume. The errors in this procedure arise from friction and distortion of the vessel under pressure. Friction is minimized by using the minimum amount of packing, making the ratio of area to thickness of the bismuth as large as possible so as to minimize the piston motion during transition, and making readings with increasing and decreasing pressure.

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[1] P. W. Bridgman, *The Physics of High Pressure* (Bell and Sons, London, and Macmillan, New York, 1931).

[2] P. W. Bridgman, Proc. Am. Acad. Sci. **72**, 157 (1938).

[3] P. W. Bridgman, Proc. Am. Acad. Sci. **72**, 46, 227 (1937–38).

With proper precautions the mean of increasing and decreasing pressure is surprisingly constant, and the total difference between increasing and decreasing pressure may under favorable conditions be as little as 3 percent, meaning an absolute friction of not more than 1.5 percent and an error of the mean of much less. Correction for distortion of the pressure vessel is less than it otherwise would be because of the external support which is necessary in order to withstand rupture. The distortion of the cross section was only 0.5 percent at 25,000; this figure was checked in two ways. An approximate calculation by ordinary elasticity theory gave about this value, and a more rigorous evaluation of this correction was made with an independent piece of apparatus with which the distortion was measured with a sliding contact arrangement mounted within the cylinder, which was filled with an insulating liquid.

The final values found for the pressure fixed points were:

At 30°, 25,420 kg/cm^2.
At 75°, 23,350 kg/cm^2.

The manganin gauge may now be calibrated against the previous mercury fixed point at 7640 and the new bismuth point, and the change of resistance expressed by a quadratic formula in the pressure. As previously surmised, the relation is very nearly linear. Pressures at 30,000 obtained by linear extrapolation from the mercury point are in error by only about one percent, and in an unexpected direction, the linearly extrapolated pressure being too low. This means that the pressure coefficient of manganin decreases with increasing pressure; in almost all other cases the coefficient increases. Different manganin gauges, even those cut from the same spool of wire, have slight differences in the second-degree term, so that every coil must be calibrated at two points for the most accurate results.

With the manganin gauge calibrated in this way, the freezing pressure of mercury at 30° was found in two determinations to be 13,700 and 13,730 kg/cm^2. The mean of these, 13,715 may be taken as a new fixed point, the freezing pressure of mercury at 30.0°C. Calibration with this instead of the former fixed point at 0° is somewhat more convenient because by putting suitable amounts of both bismuth and mercury in the apparatus the calibration may be made with a single set-up. It is also an advantage to have a point at approximately the middle of the pressure range.

The pressure scale having been established, the absolute compressibility of some one substance may next be determined. As in my previous work, the substance chosen was pure iron. The method demands a measurement of the relative change of length of an iron rod with respect to the pressure vessel by a sliding electrical contact device, plus a measurement of the distortion of the vessel. The latter was accomplished by using two probe rods reaching to nearly the interior wall of the pressure vessel through small drilled holes. The accuracy with which the second-degree term in the compressibility is determinable varies, other things being equal, as the square of the pressure range. The new determinations should therefore give this term more than six times as accurately as before. Part of this advantage is sacrificed, however, by the necessity for using a shorter specimen because of the more serious restrictions on the dimensions of the vessel. The effect to be measured is small, the maximum relative displacement being 0.05 cm. In spite of every effort, I did not succeed in eliminating capricious irregularities in the results, so that the only course was the accumulation of many observations and least-squares reduction of the results. Twenty-five different set-ups of the apparatus were made and some 400 individual observations, uniformly spaced over the entire pressure range, both with increasing and decreasing pressure. The new final result for the *linear* compressibility of pure iron at 24°C is:

$$-\Delta l/l_0 = 1.942 \times 10^{-7} p - 0.23 \times 10^{-12} p^2,$$

pressure in kg/cm^2.

The apparatus was not well adapted to a determination of the temperature coefficient. In the absence of new measurements, the best that can be done is to use my previous temperature coefficient. This would give for the linear compressibility at 75°C:

$$-\Delta l/l_0 = 1.964 \times 10^{-7} p - 0.23 \times 10^{-12} p^2.$$

The new second-degree term is smaller by a factor 3.3 than the former one (23 against 75). This is the direction of change which several theoretical physicists have pointed out was probable. I can see no possibility, however, of reconciling with the present experimental data reduction by a factor as large as 10 or even 100, as has been suggested.

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Compressions to 50,000 kg/cm^2

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The object of this note is to present a compact summary of the numerical results obtained in series of measurements with new apparatus of the volume decrements of about 40 binary cubic compounds together with a few of the more compressible elements up to pressures of 50,000 kg/cm^2. The detailed paper, to be published presently in the *Proceedings of the American Academy of Arts and Sciences*, will contain, in addition to the material to be expected in such a paper, such as a description of the apparatus and discussion of the methods of calculation and the probable errors, a tabulation of the compressions at pressure intervals of 5000 instead of 10,000 kg/cm^2, and at approximately −80°C in addition to room temperature.

The novel feature of the new apparatus is the more effective external support afforded the pressure vessel, there being now two stages of support instead of one as formerly.[1] This materially increases the life of the vessels, permits the attainment of somewhat higher pressures, and decreases the distortion of the vessel and the error from uncertainty in the distortion.

All results are the mean of two or more independent measurements, which usually did not differ by more than 5 percent. One more significant figure is given in Table I than would be justified by the absolute accuracy; the retention of another figure is demanded if the differences are to be smooth. The method is such that the accuracy is less at the ends of the range; the relative values are probably most accurate in the range from 10,000 to 40,000. The probable error varies with the material. The nine compounds of calcium, strontium and barium are probably the least satisfactory. The compressibility of the sulfides of these is probably too high because of presence of a comparatively large amount of amorphous material, and the selenides and tellurides had a tendency to chemical instability.

The figures given in the table are in cm^3 for a specified number of grams, and are ostensibly fractional changes of the volume at atmospheric pressure and room temperature. The volume decrements listed are for room temperature, which may be taken as 23°. The actual measurements were of volume decrements in cm^3 of a known number of grams. To get the fractional volume changes the observed changes must be multiplied by a factor depending on the atmospheric density. The number of grams listed with each substance is the assumed atmospheric density, in most cases the x-ray density as given in Wyckoff. If better densities are later determined, the figures of Table I may be corrected by simple factors.

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[1] P. W. Bridgman, Proc. Am. Acad. Sci. 72, 207 (1938).