COMPRESSIBILITY OF SOLIDS

By Dewey B. Larson

The work of P. W. Bridgman during the past fifty-odd years, together with some contributions by other investigators, has produced a very extensive body of experimental knowledge of the behavior of matter under very high pressures. Since the volume relationships under pressure are obviously connected very closely with the properties of the inter-atomic and inter-molecular force systems, these relationships are of particular scientific interest and numerous attempts have been made to derive mathematical expressions which would reproduce the compressibility data, none of which has achieved more than a moderate degree of success. This present article will show that a very simple expression derived from purely theoretical sources produces values for solid volumes under pressure which are in agreement with Bridgman's results throughout the entire range of solid substances covered in his investigations. Subsequent articles in this series will demonstrate that an extension of the same theoretical treatment to the more complex force systems of the liquid state enables the formulation of related mathematical expressions which are capable of reproducing the experimental liquid volume values within the probable experimental error, thus providing a complete theoretical coverage of the entire compression process.

In a recently published work[1] the author developed some general theoretical relations between the inter-atomic forces at short range (as in the solid state) and the forces effective at greater distances (as in the gaseous state). Applying these relationships to compressibility, we find that Boyle's Law, $PV = k$, which expresses the general compressibility relation in the gaseous state, can be extended to the solid state in the form

$$PV^2 = k \qquad (1)$$

In the same theoretical development it was brought out that the fixed inter-atomic distance in the solid state is the result of an equilibrium between an outward force generated by the rotation of the atoms of matter and an inward force due to the inherent properties of space-time.[2] This inward-directed force is constant and is equivalent to a pressure. The pressure term in equation (1) therefore includes this initial pressure, P_0, as well as the externally applied pressure. In the subsequent discussion the symbol P will be used to designate the external pressure only and on this basis equation (1) becomes

$$(P + P_0) \, V^2 = k \qquad (2)$$

Compression values are normally expressed in terms of relative rather than absolute volumes, the reference volume being the volume at zero external pressure where equation (2) has the form

$$P_0 V_0^2 = k \qquad (3)$$

Dividing equation (2) by equation (3) and rearranging, we have

$$(V/V_0)^2 = P_0/(P \neq P_0) \hspace{3cm} (4)$$

According to equation (4), if we plot the reciprocals of the squares of the relative volumes against the corresponding pressures we should obtain a straight line, the slope of which is determined by the magnitude of the initial pressure. Fig. 1(a) is a curve of this kind for the element tin, using Bridgman's experimental values.[3]

In view of the well-known tendency toward polymorphic transitions in the solid state, it is not to be expected that the effective initial pressure will always remain constant throughout the experimental range of pressures as it does in the case of tin. On preparing similar curves for other substances we find that over half of the elements investigated by Bridgman actually do follow this straight line pattern up to the experimental pressure limit but approximately twenty percent of the elements and a still larger percentage of the compounds undergo a transition in which the effective initial pressure increases without any volume discontinuity. The P vs. $1/V^2$ curve for such a substance consists of two straight line segments connected by a smooth transition curve, as in Fig. 1(b) which shows Bridgman's values for silicon.

In addition to the changes of this type, commonly termed second order transitions, some solid substances are subject to first order transitions in which there is a modification of the crystal structure and a volume discontinuity at the transition point. Generally the effective initial pressure changes during such a first order transition and the resulting volumetric pattern is similar to that of KCl, Fig. 1(c). With the exception of some values which are rather erratic and of questionable validity, all of Bridgman's results follow one of these three patterns or some combination of them. The antimony curve, Fig. 1(d), illustrates one of the combination patterns. Here a second order transition between 30,000 and 40,000 kg/cm^2 is followed by a first order transition at a higher pressure.

The experimental second order transition curves are smooth and regular, indicating that the transition process takes place freely when the appropriate pressure is reached. The first order transitions, on the other hand, show considerable irregularity and it appears evident from the experimental results that in many substances the structural changes at the transition point are subject to a variable amount of delay due to internal conditions within the solid aggregate. In substances of this kind the transition does not take place at a well-defined pressure but rather occurs somewhere within a relatively broad transition zone and the exact pattern may vary considerably between successive series of measurements. Furthermore, there are many substances which appear to experience similar delays in achieving volumetric equilibrium even where no transitions take place and the compression curves suggest that quite a number of the reported transitions are actually volume adjustments which merely reflect delayed response to the pressure applied earlier. In the tellurium curve, for example, there are presumably two transitions, one between 40,000 and 50,000 kg/cm^2 and the other between 70,000 and 80,000 kg/cm^2, yet the experimental volume at 80,000 kg/cm^2 is very close to the value calculated on the basis of a single straight line relation. It is quite probable therefore that this element actually follows the same linear volume relationship at least up to the vicinity of 80,000 kg/cm^2. Whether or not there is a second order transition beyond this pressure is uncertain.
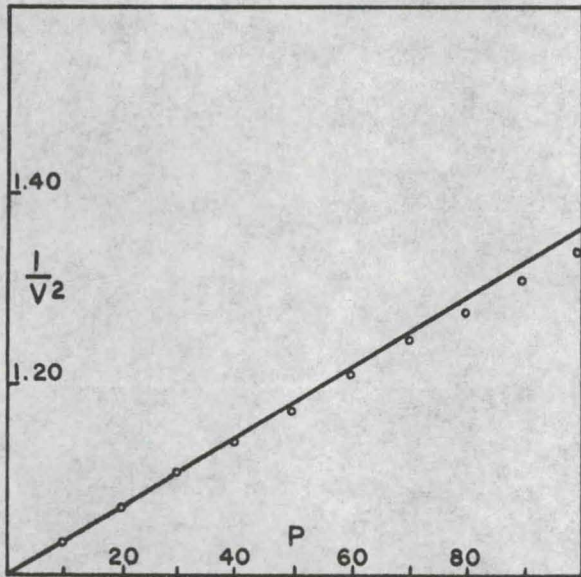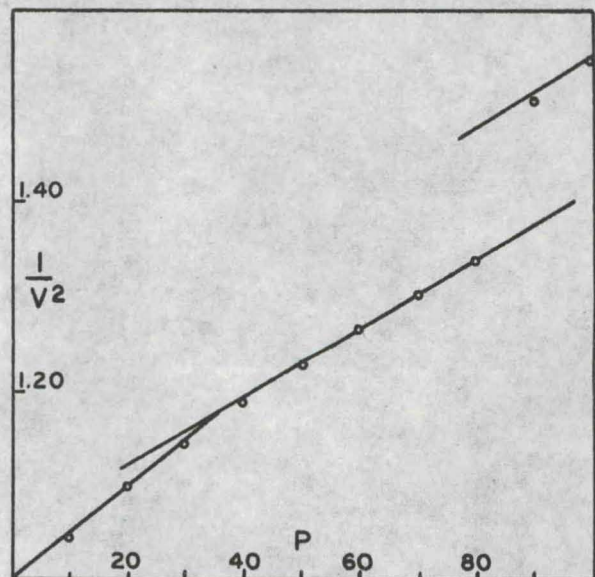
(a) Tin
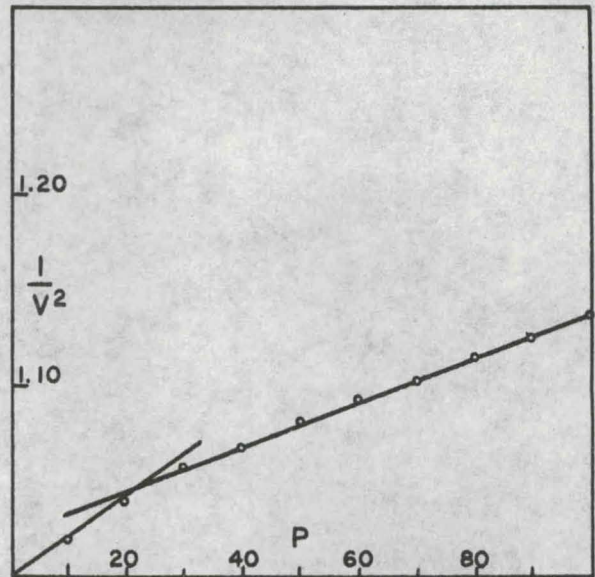
(b) Silicon
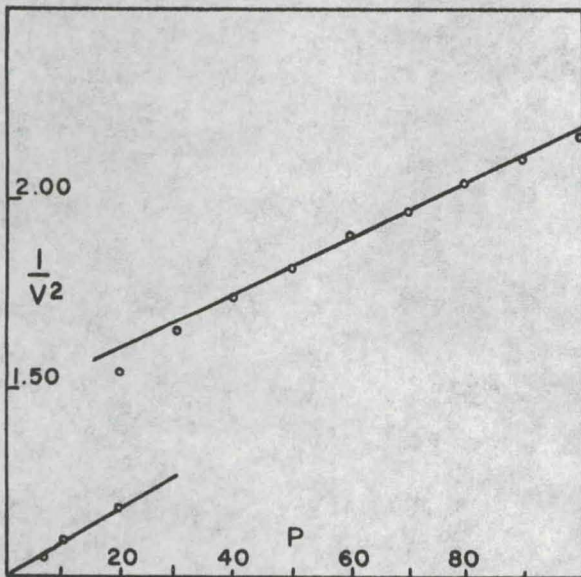
(c) Potassium Chloride

(d) Antimony

FIG. I

COMPRESSIBILITY PATTERNS

The deviations from the theoretical curves which are found in the experimental volumes of substances with relatively high melting points are almost without exception of a random nature and are readily explained on the foregoing basis. The compression curves for substances with low melting points show systematic deviations from linearity at the lower pressures, but this is a normal pattern of behavior resulting from the proximity of the change of state and the amount of the volume deviation in each case can be calculated by methods which will be described in the subsequent discussions of the liquid volume relations.

For purposes of numerical calculation it will be convenient to express equation (4) in the form

$$V/V_0 = P_0^{\frac{1}{2}}/(P \neq P_0)^{\frac{1}{2}} \tag{5}$$

In the course of this present investigation substantial progress has been made toward developing a method of calculating the initial pressures directly from the chemical composition but in order to keep the length of this article within reasonable limits it will be desirable to defer the discussion of such developments to a later date and to obtain the values of P_0 which will be needed for present purposes from the initial compressibilities or from the slopes of the P vs. $1/V^2$ curves. The compressibility is the rate of change of volume under pressure and is obtained by differentiating equation (5):

$$\frac{1}{V_0} \frac{dV}{dP} = \frac{P_0^{\frac{1}{2}}}{2(P \neq P_0)3/2} \tag{6}$$

The initial compressibility may be derived from equation (6) by letting P equal zero. The result is

$$\frac{1}{V_0} \frac{dV}{dP} (P = 0) = \frac{1}{2P_0} \tag{7}$$

We thus find that the initial pressure effective in the lower pressure range is equal to the reciprocal of twice the initial compressibility of the substance under consideration. Those of the initial pressures used in this report which have been derived from equation (7) are listed in Table I, together with the initial compressibilities on which they are based. Inasmuch as any extraneous volume, such as that due to voids, is eliminated in the early stages of compression, the measured values of the initial compressibility are not characterized by any high degree of accuracy and an empirical correction has therefore been applied in most cases to compensate for the inaccuracies. In making such corrections consideration has been given to the theoretical relationships now under development and with the benefit of the information derived from this source the values of the initial pressures have generally been carried out to one more significant figure than would be justified on the basis of empirical calculations alone.

It has been found from a study of the changes in effective initial pressure during second order transitions that there are three possible values which this pressure may assume for any particular crystal arrangement of a specific substance, and that these three values are related by the factors 1, $1\frac{1}{2}$, and 2. The factor effective at zero pressure has been determined empirically for each substance and is indicated in Table I. As would be expected from Le Chatelier's principle, the changes in this factor take place in the upward direction and we may deduce that

in all substances it will ultimately reach the upper limit, 2, if the pressure is carried to a sufficiently high level. This suggests that the large proportion of elements with no transitions in the experimental range is merely a reflection of the relatively narrow range of pressures covered, and that some of the deviations at the upper ends of the experimental curves, such as those in Fig. 1(a), are indications of approaching transitions. After the upper limit of the compression factor is reached no further second order transitions will take place. It is, of course, possible that first order transitions due to modification of the crystal structure may occur beyond the last second order transition but the volume decreases due to this cause are generally small where the change takes place at a very high pressure, and it should therefore be safe to extrapolate the compression curves considerably beyond the present experimental limits: a point which is particularly significant in the fields of geophysics and astrophysics.

Table II gives the results of the application of equation (5) to those elements which were studied by Bridgman all the way up to his pressure limit of 100,000 kg/cm^2 and which have no transitions within the experimental range. Table III is a compilation of data for some of the other elements whose volumetric behavior is similar but which were not investigated beyond 30,000 or 40,000 kg/cm^2. In both tables the elements have been arranged in the order of increasing compressibility.

The alkali metals are among the substances investigated over the full range to 100,000 kg/cm^2 but these elements have not been included in Table II because there is considerable uncertainty as to the validity of the experimental results at the higher pressures. The data for lithium up to 40,000 kg/cm^2 have, however, been given in Table III to show that where the situation is not complicated by proximity to the melting point these alkali metals do follow the normal compression pattern in the range most favorable for accurate measurement. Values for titanium and beryllium up to 40,000 kg/cm^2 are also included in this table. Bridgman gives a measurement at 100,000 kg/cm^2 for each of these elements which is somewhat below the projection of the linear compression curve. This is probably an indication of an intervening transition but since there are no intermediate values available it is not possible to verify this conclusion.

Table IV extends the coverage to representative elements of the classes that are subject to transitions within the experimental range of pressures. No attempt has been made thus far to develop a method of calculating the exact pressures at which the transitions take place in each substance, and the upper branch of each curve has therefore been fixed by the use of a reference point derived from the experimental data at some appropriate pressure above the transition. In some instances where the initial compression is modified by voids or other irregularities or where transitions occur below the level of the first measurement, it has been necessary to use a reference point of the same nature for the lower branch of the curve, but in most cases the reference point for this lower branch is the actual 1.00 relative volume at zero pressure as would be expected on a theoretical basis. Transitions reported by the observers or assumed in the theoretical calculations are indicated by horizontal lines in the appropriate columns.

Compressibility patterns of compounds are theoretically identical with those of the elements and examination of the experimental data verifies this theoretical

conclusion. As might be expected from the less uniform composition, first order transitions are somewhat more common in the compounds but otherwise there is no distinction between the compressibility curves of compounds and those of elements. A full coverage of the compounds studied by Bridgman therefore serves no particular purpose at this time and although the compressibilities of all of these substances have been calculated in the course of this investigation the tabulated comparisons of the theoretical and experimental volumes have been limited to a few represent- ative examples of each of the principal patterns. These data are given in Table V. Organic solids and others with similar low melting points have been omitted as the factors determining the compressibility of such substances can be covered more conveniently after the liquid volume relationships have been discussed.

References:

1. Larson, D. B., The Structure of the Physical Universe, published by the author, 755 N. E. Royal Court, Portland 12, Oregon, 1959. Page 19.

2. Ibid. Page 28.

3. For a bibliography of Bridgman's reports of his high pressure work see his book, The Physics of High Pressure, G. Bell & Sons, Ltd., London, 1958.

TABLE I - Initial Pressures

	Initial Comp. x 10^6 Obs.	Adj.	Comp. Factor	Initial Pressure (M atm.)		Initial Comp. x 10^6 Obs.	Adj.	Comp. Factor	Initial Pressure (M atm.)
W	.29	.28	$1\frac{1}{2}$	1815	Ag	.99	.91	1	550
Pt	.36	.31	2	1614	Ti	.80	.97	2	515
Ru	.35	.34	2	1461	Zr	1.10	1.09	2	459
Rh	.37	.38	$1\frac{1}{2}$	1324	Ge	1.38	1.13	1	441
Ta	.48	.41	1	1215	Zn	1.7	1.56	1	320
Mo	.35	.46	2	1096	Cd	1.95	1.86	1	269
Co	.54	.54	1	924	Sn	1.70	1.88	1	266
Pd	.53	.55	1	913	Tl	2.83	2.48	1	202
Au	.58	.55	$1\frac{1}{2}$	909	Pb	2.37	2.48	1	202
Fe	.59	.57	1	883	Sb	2.4	2.63	1	190
Ni	.52	.57	1	883	La	3.51	4.10	1	122
Nb	.57	.615	2	813	Ca	5.70	6.25	$1\frac{1}{2}$	80
Cu	.72	.70	1	715	Sr	8.2	6.94	$1\frac{1}{2}$	72
Be	.86	.77	$1\frac{1}{2}$	646	Li	8.7	7.7	$1\frac{1}{2}$	65

TABLE II - Relative Volumes Under Compression

P (M kg/cm²)	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
	U $P_0 - 665$		Zr $P_0 - 474$		Zn $P_0 - 331$		Cd $P_0 - 278$		Sn $P_0 - 275$	
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10	.992	.990	.990	.989	.985	.984	.982	.981	.982	.982
20	.985	.981	.980	.978	.971	.970	.966	.963	.966	.966
30	.978	.974	.970	.969	.958	.958	.950	.940	.949	.951
40	.971	.968	.960	.960	.944	.939	.935	.924	.934	.936
50	.964	.960	.951	.946	.932	.925	.921	.909	.920	.923
60	.958	.955	.942	.937	.920	.912	.907	.896	.906	.909
70	.951	.951	.934	.929	.909	.900	.894	.884	.893	.897
80	.945	.947	.925	.922	.898	.889	.881	.873	.880	.886
90	.939	.944	.917	.916	.887	.878	.869	.862	.868	.875
100	.932	.941	.909	.910	.876	.868	.858	.852	.856	.864

P (M kg/cm²)	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
	In $P_0 - 221$		Tl $P_0 - 209$		Te $P_0 - 106$		Sr $P_0 - 74$	
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10	.978	.977	.977	.977	.956	.955	.939	.925
20	.958	.955	.955	.957	.917	.923	.887	.878
30	.938	.936	.935	.939	.883	.889	.844	.845
40	.920	.919	.916	.921	.852	.862	.806	.812
50	.903	.903	.898	.897	.824	.786	.772	.761
60	.887	.888	.881	.881	.799	.775	.743	.734
70	.871	.874	.865	.868	.776	.766	.717	.702
80	.857	.860	.850	.855	.755	.750	.693	.683
90	.843	.847	.836	.843	.735	.742	.672	.665
100	.830	.835	.822	.831	.717	.733	.652	.648

TABLE III – Relative Volumes Under Compression

P (M kg/cm²)	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
	Ir $P_0 - 1875$		W $P_0 - 1875$		Pt $P_0 - 1668$		Ru $P_0 - 1510$		Rh $P_0 - 1368$	
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10	.997	.997	.997	.997	.997	.9965	.997	.997	.996	.996
20	.994	.9945	.994	.994	.994	.993	.993	.9935	.993	.993
30	.992	.992	.992	.9905	.991	.9895	.990	.990	.990	.989
	Ta $P_0 - 1255$		Mo $P_0 - 1132$		Co $P_0 - 955$		Pd $P_0 - 943$		Au $P_0 - 939$	
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10	.996	.995	.996	.996	.995	.995	.995	.975	.995	.994
20	.992	.990	.991	.993	.990	.990	.990	.990	.990	.989
30	.988	.9855	.987	.989	.985	.985	.985	.985	.984	.984
	Fe $P_0 - 912$		Ni $P_0 - 912$		Nb $P_0 - 840$		Cu $P_0 - 739$		Ag $P_0 - 568$	
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10	.994	.994	.994	.995	.994	.994	.993	.993	.991	.991
20	.989	.989	.989	.990	.988	.989	.987	.986	.983	.982
30	.984	.983	.984	.985	.982	.983	.980	.980	.974	.974
	Be $P_0 - 667$		Ti $P_0 - 532$		Lu $P_0 - 237$		Dy $P_0 - 220$		Er $P_0 - 220$	
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10	.993	.991	.991	.990	.980	.9775	.978	.975	.978	.977
20	.985	.981	.982	.981	.960	.957	.958	.954	.958	.957
30	.978	.974	.973	.974	.942	.939	.938	.935	.938	.939
40	.971	.967	.964	.967	.925	.924	.920	.919	.920	.9225
	Ho $P_0 - 220$		Gd $P_0 - 205$		Sm $P_0 - 159$		Yb $P_0 - 73$		Li $P_0 - 67$	
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10	.978	.977	.976	.976	.970	.968	.938	.930	.933	.929
20	.958	.956	.954	.955	.943	.941	.886	.877	.877	.874
30	.938	.937	.934	.937	.917	.9175	.842	.834	.831	.831
40	.920	.920	.915	.9215	.894	.895	.804	.800	.791	.796

TABLE IV - Relative Volumes Under Compression

P (M kg/cm²)	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
	Si 485,969		Ge 456,684		Al 385,514		Th 292,389		Pb 209,313	
0	1.000	1.000	.997	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10	.989	.990	.986	.985	.987	.987	.983	.983	.977	.9785
20	.980	.981	.976	.973	.975	.975	.967	.968	.955	.959
30	.973	.974	.964	.964	.963	.966	.952	.952	.937	.941
40	.968	.968	.956	.956	.963	.958	.938	.937	.924	.925
50	.963	.962	.949	.949	.954	.951	.924	.924	.911	.911
60	.958	.957	.942	.942	.946	.944	.901	.913	.898	.898
70	.954	.952	.935	.935	.938	.937	.898	.904	.887	.886
80	.949	.948	.929	.929	.930	.929	.901	.897	.876	.875
90	.944	.944	.923	.923	.923	.922	.891	.891	.864	.864
100	.940	.940	.917	.917	.915	.915	.882	.886	.853	.855

P (M kg/cm²)	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
	Sb 196,294		Pr 159,239		La 126,252		Ca 83,111		Ba 55,82.5	
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	.982	1.000
10	.975	.975	.970	.967	.963	.963	.945	.942	.903	.914
20	.953	.9535	.943	.940	.929	.933	.898	.897	.841	.841
30	.931	.934	.917	.916	.899	.904	.861	.861	.789	.789
40	.914	.917	.894	.896	.876	.882	.832	.832	.747	.747
50	.901	.901	.877	.878	.861	.863	.806	.805	.711	.712
60	.888	.888	.863	.863	.848	.846	.782	.780	.679	.682
70	.876	.876	.849	.849	.835	.832	.760	.748	.636	.639
80	.864	.864	.836	.836	.822	.819	.740	.732	.615	.618
90	.813	.815	.823	.823	.810	.808	.721	.716	.599	.598
100	.803	.803	.811	.811	.798	.798	.704	.702	.581	.580

TABLE V - Relative Volumes Under Compression

P (M kg/cm²)	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
	NaCl 139,209		NaBr 125,251		NaI 103,155		KCl 106,212		AgCl 232	
0	1.000	1.000	1.000	1.000	.987	1.000	1.000	1.000	1.000	1.000
10	.966	.962	.962	.957	.942	.944	.954	.952	.980	.979
20	.935	.932	.928	.922	.903	.902	.916	.916	.961	.960
30	.907	.907	.898	.893	.868	.868	.768	.777	.943	.942
40	.882	.885	.870	.868	.839	.840	.753	.756	.926	.926
50	.863	.865	.846	.847	.818	.816	.738	.738	.910	.910
60	.847	.848	.827	.829	.799	.795	.725	.723	.895	.896
70	.831	.832	.814	.814	.781	.777	.712	.710	.880	.883
80	.817	.817	.801	.801	.764	.761	.699	.698	.866	.871
90	.803	.803	.789	.789	.748	.747	.688	.688	.854	.860
100	.790	.790	.778	.778	.734	.734	.676	.679	.841	.835
	CsBr 113,151		ZnSe 458		PbTe 248		NH₄Cl 106,211		NH₄NO₃ 130,260	
0	.982	1.000	.978	1.000	.990	1.000	1.000	1.000	.982	1.000
10	.941	.947	.968	.978	.971	.9745	.955	.951	.947	.950
20	.905	.905	.958	.961	.953	.953	.917	.918	.915	.914
30	.873	.870	.949	.950	.936	.935	.882	.891	.885	.885
40	.844	.840	.939	.940	.920	.920	.860	.867	.860	.860
50	.814	.814	.929	.930	.884	.884	.842	.846	.835	.838
60	.794	.792	.920	.921	.869	.869	.828	.828	.820	.820
70	.776	.773	.912	.912	.855	.855	.813	.812	.807	.806
80	.757	.757	.903	.904	.842	.842	.799	.798	.796	.794
90	.743	.742	.895	.895	.830	.831	.786	.785	.784	.785
100	.728	.728	.887	.887	.818	.820	.773	.773	.773	.778

755 N. E. Royal Court
Portland 12, Oregon
Nov. 12, 1959

Dr. H. Tracy Hall
Dept. of Chemistry
Brigham Young University
Provo, Utah

Dear Dr. Hall:

There is enclosed herewith an advance copy of a paper on the compressibility of solids which I believe should be of interest to you. Perhaps this subject is not directly involved in your field of specialization but the paper is more than a discussion of this particular subject; it has been prepared as a typical example of the kind of results that are obtained by a completely new approach to problems of this nature: an approach which is equally applicable in any other field of physical science, including your own, whatever that may be.
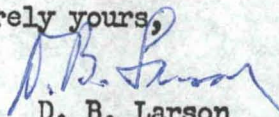
This method of approach is made possible by a totally new concept of the relationship between space and time which I have formulated as a result of findings during many years of intensive study of basic physical processes. I have expressed this new concept in the form of two postulates: one as to the physical nature of space-time and the other as to its mathematical behavior. It is possible to show that a development of the necessary consequences of these two postulates, without the introduction of any other factors of any kind, defines a theoretical universe which is identical with the actual physical universe wherever comparisons can be made. (I want to emphasize that the preceding sentence means just exactly what it says. I do not assume the existence of matter, for example, neither does it appear in the theoretical universe because it is known to exist in the actual physical universe; it is there because an entity with all of the characteristics of matter must exist if my fundamental postulates are valid. The same is true of radiation, electric charges, magnetism, gravitation, and so on. They are all necessary and unavoidable consequences of the postulates and hence they are component features of the theoretical universe which I have derived from the postulates.)

Application of the new concepts to any specific field such as that of compressibility merely requires a further development of the consequences of the postulates; that is, an elaboration of the general findings to bring out more of the "fine structure". Almost invariably this new approach reveals some hitherto unknown relationship which, when properly applied, simplifies and clarifies the entire situation. In the specific case of compressibility I find from the newly developed theory that Boyle's Law, $PV = k$, the general compressibility relation applicable to the gaseous state, can be extended to the solid state in the modified form $PV^2 = k$. The thermal motions of the gas and the solid have heretofore been regarded as entirely dissimilar and the existence of a simple compressibility relation of this kind has not even been suspected, but the data given in the enclosed article show that the solid volumes computed on this basis are in agreement

with the experimental values throughout the entire range of pressures and substances for which experimental results are available. This not only confirms the status of the modified form of Boyle's Law as an exact and generally applicable relationship, but also serves as a verification of the basic theory from which this expression was derived: one of the almost unlimited number of such verifications that can be made.

As you have no doubt deduced from the foregoing, my treatment of this subject matter is quite unorthodox, and because of the many complications which enter into the publication of a very extensive work of an unorthodox character and the impracticability of releasing such closely interrelated results piecemeal, I have found it advisable to publish a preliminary abridged report of my work in book form at my own expense so that the major results can be made available for general use without further delay. I am trying to distribute the copies of this book that are now on hand in the manner that will do the most good and I would like to get them into the hands of persons who are particularly interested in new viewpoints on basic subjects. If your impression of the compressibility discussion is sufficiently favorable to warrant taking the time to examine the underlying theory I will be pleased to send you a copy. If you wish, you can just make a notation on page one of this letter, with any corrections of the address that my be in order, and mail it back to me.

Sincerely yours,

D. B. Larson