

COMPRESSIBILITY OF SOLIDS AND TAIT'S LAW: I: P-V RELATIONSHIPS OF THE ALKALI METALS

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Abstract—It has been shown, using both Swenson's data at 4.2°K and Bridgman's data at room temperature, that the alkali metals, which do not follow Bridgman's empirical law, do follow Tait's Law. Both Bridgman's empirical equation and Levitt's high pressure empirical approach are shown to be special cases of Tait's Law. Bridgman's series of data up to 40,000 kg/cm² is shown to be about as reliable as his 100,000 kg/cm² data. Use of the Tait equation, which is founded on the strict theoretical ground of association theory, allows data to be smoothed on a theoretical basis rather than on a strictly empirical one. Since Tait's Law is derived without assumptions from the general association equation of state, it has now been shown that this equation of state is applicable to gases, liquids and most likely solids. Data for solids which is not consistent with this treatment should be held as suspect or non-continuous over the pressure range being considered.

1. INTRODUCTION

A number of investigations⁽¹⁻⁴⁾ have shown empirically that Tait's Law [equation (1)] which describes the isothermal compressibility, is obeyed quite exactly by large numbers of pure liquids, organic and inorganic; by mixture of liquids; and by solutions of ionic salts.

$$-\left(\frac{\partial v}{\partial p}\right) = \frac{J}{L+p} \quad (1)$$

This empirical law has been theoretically derived from the association equation of state^(5,6) and the meaning of the experimental parameters, J and L , has been given in terms of the quantities entering from association theory.⁽⁷⁾ From this development by association theory it appears that the structure of liquids is essentially similar to that of polycrystalline solids. It is well known that polycrystalline solids consist of small crystallites in which the arrangement of the atoms or molecules is symmetrical; these crystallites are connected by defect regions which contain smaller aggregates or single atoms. In a similar way, it appears that liquids consist of clusters of atoms or molecules separated by defect regions, which contain voids and smaller aggregates. Just as the crystallites in

polycrystalline solids are held together by defect regions, so the liquid clusters are held together by the defect molecules.

The outstanding difference between the two states is concerned with the differences in symmetry of packing that exist. While solid crystallites exhibit exact symmetries which may be 3-, 4-, or 6-fold (or even less), the symmetries in liquids are not exact and are approximately 5-fold. By exact symmetries it is meant that no matter what the order of the symmetry is, each atom or molecule in the crystal array has an assigned position around which it vibrates. The balance of forces in the array is such that the equilibrium position of each atom can be considered fixed or, put in other words, that there is a high potential barrier around each site. On the other hand, in liquids the symmetry in the cluster is apparently an approximate 5-fold symmetry.⁽⁸⁾ In contrast to the exact symmetries existing in solids, atoms packed in 5-fold symmetry give rise to many small voids in the structure. Because of the arrangement of these voids, many equivalent structures (degenerate) exist. The energy barrier between these structures appears to be exceedingly small, so that the atoms in the liquid structure upon vibration do not always return to a fixed equilibrium position.

This is why the symmetry is only an approximate symmetry and not an exact one. Five-fold symmetry does not allow the packing of atoms in space to proceed in an exactly ordered fashion. Because of the mobility in the geometric orientation of the molecules in the clusters, the acquisition of information regarding their structure is quite difficult. However, it has been shown geometrically, that in clusters of small size, 5-fold symmetry gives rise to more bonds than close packing does. From this fact comes the stability of the five-symmetric structure in liquids and also the difficulties associated with the conversion of liquids to solids (homogeneous nucleation).⁽⁹⁾

Going back to Tait's Law, it seems strange that liquids having one sort of symmetry should obey Tait's Law for the isothermal compressibility, while polycrystalline solids which are very much like liquids except in the matter of symmetries, should follow other laws. This is especially so in view of the meaning ascribed to the Tait coefficients by association theory. This paper is then devoted to an examination of the behavior of solids undergoing isothermal compression in light of Tait's Law.

2. THEORY

The experimental difficulties in determining the isothermal compressibility are considerable.⁽¹⁰⁾ These difficulties are further compounded by the fact that there has been in the past no theoretical generalization, which could be used to evaluate the meaning of the values that come from such measurements. This lack has resulted in the representation of the various experimental results in a variety of empirical or semi-empirical laws.⁽¹¹⁾ Bridgman in his work has found that he could express the compressibility of many but not all solids empirically by using the first two terms of an alternating power series in terms of the pressure [equation (2)].

$$-\Delta v/v_0 = AP - BP^2 \pm \text{higher terms} \quad (2)$$

This particular series which was probably chosen by Bridgman on purely empirical grounds of good fit can be shown to have a theoretical basis and to be a truncated version of Tait's Law. Differentiating equation (2) we have

$$-(\partial v/\partial P)_T = Av_0 - 2Bv_0P \pm \text{higher terms} \quad (3)$$

The expansion of the denominator in Tait's Law [equation (1)] yields

$$-(\partial v/\partial P)_T = J(L+P)^{-1} \\ = J \left(\frac{1}{L} - \frac{P}{L^2} + \frac{P^2}{L^3} - \frac{P^3}{L^4} + \dots \right) \quad (4)$$

It can readily be seen that equation (3) is identical to equation (4) if

$$Av_0 = J/L \\ 2Bv_0 = J/L^2 \quad (5)$$

etc. for higher terms.

In Bridgman's work he found that the higher terms could be neglected for most solids. The necessary condition here is that

$$P/L \ll 1$$

If this condition holds then a slight adjustment of the retained coefficients will fit the data, especially if a too precise fit is not demanded. Further, the experimental discrepancies in the data render exact fits unnecessary.

Another empirical approach at high pressures was presented by LEVITT⁽¹²⁾ which he portrays as "A limiting law at the upper end of the pressure range." He has applied this approach to gases, liquids and solids at high pressures with success. His approach leads to equation (6)

$$-\left(\frac{\partial v}{\partial P}\right)_T = \frac{v^2}{BP} \quad (6)$$

with B a constant. If one compares this with the Tait equation [equation (4)], one sees that at high pressures where $P \gg L$, if one sets

$$B = v^2/J \quad (7)$$

we can obtain equation (6). Since $(\partial v/\partial P)$ decreases with the rise in pressure, the volume approaches a constant value and thus, as a first approximation, v^2 and hence B may be taken as constants. Thus this empirical approach is an approximation form of the Tait equation. In another publication we show the exact nature of this approximation.⁽²⁴⁾

It can be concluded that, in the limits at least, Tait's Law is obeyed by most solids. The question then arises: Is Tait's Law obeyed by such substances whose compressibilities cannot be expressed by the simple two-term power series of

Bridgman? The hypothesis is that many compounds follow Tait's law although he did not use it. BEECROFT and others have shown various temperatures could fit their alternating power series by truncating the series and empirically fitting the bits of evidence. Tait's Law should be a simple Bridgman law. What is needed are sets of data and pressure values for the simple law.

Such data are available for alkali metals. Bridgman's runs on the alkali metals at 100,000 kg/cm² temperature. The data given are entitled "Data for 100,000 kg/cm² compressions" (14) and "Data for 100,000 kg/cm²" (15). The values of the compressibility at 4.2°K have been reported at 77°K. The work is not sufficient to compare with recent work. The results for such pressures up to 100,000 kg/cm² has not been reported other than as reported in a

The calculation was done on a computer. The specific volume was generally

Bridgman? The first evidence in favor of this hypothesis is the work of COOK⁽¹³⁾ who has found that many complex substances, such as explosives, follow Tait's Law upon isothermal compression, although he did not recognize that the equation he was using was indeed Tait's Law. Further, BEECROFT and SWENSON⁽¹⁷⁾ have determined compressibilities on sodium up to 20,000 atm. at various temperatures and have found that they could fit their data fairly well with a three-term alternating pressure series. Essentially, they are truncating the series in equation (4) at the third term and empirically adjusting the constants. These two bits of evidence point towards the idea that Tait's Law should be valid for solids, for which the simple Bridgman approximation is insufficient. What is needed to define the whole validity of the law are sets of data over wide ranges of temperature and pressure on substances which do not obey the simple law.

Such data is available in the literature on the alkali metals. Bridgman reports several different runs on the alkali metals, some of which go up to 100,000 kg/cm². This work was done around room temperature. The various sets of data that Bridgman gives are contradictory. The latest of these⁽¹⁰⁾ are entitled "The compression of 39 substances to 100,000 kg/cm²", here called Br III, and "Rough compressions of 177 substances to 40,000 kg/cm²",⁽¹⁴⁾ here called Br II. These two sets of data were reported simultaneously although the work was done on different apparatus. An earlier set of values, called here Br I, also range to 100,000 kg/cm².⁽¹⁵⁾ The results of SWENSON⁽¹⁶⁾ giving the values of the compressibilities to 10,000 atm. at 4.2°K have been analyzed. Swenson also reports work at 77°K but the details given in the paper are not sufficient for a complete analysis. In some recent work BEECROFT and SWENSON⁽¹⁷⁾ have given results for sodium at various temperatures for pressures up to 20,000 atm. Analysis of this data has not been included. Much data on substances other than alkali metals is available and will be reported in a subsequent paper.

3. CALCULATIONS

The calculations were done on an IBM 1620 computer. The data was all converted to pressure-specific volume data. Since the number of points was generally limited and unequally spaced, the

data were converted by Lagrangian interpolation⁽¹⁸⁾ (5 or 7 point) to a table of equally spaced values; Newton's interpolation formula⁽¹⁹⁾ did not yield as consistent a set of data. From this table of data the value of $(\partial P/\partial v)_T$ was determined numerically using a 7 point Lagrangian differentiation.⁽²⁰⁾ If the Tait equation [equation (4)] is rewritten as

$$(\partial P/\partial v)_T = -\frac{L}{J} - \frac{P}{J} \quad (8)$$

then determining the best straight line of $(\partial P/\partial v)_T$ versus P will give us L/J and $1/J$ from which L and J can be computed readily. This was accomplished by a least squares technique, minimizing the mean square deviation in $(\partial P/\partial v)_T$ and considering the error in P to be negligible. This technique was tested on values determined from an analytic curve and gave excellent agreement. One point needs to be mentioned; since the values of $(\partial P/\partial v)$ are part original data and part interpolated data, the curve of these combined data will systematically reproduce the random variations of the original data. The derivatives derived from this data will accordingly mirror these systematic deviations in a magnified fashion giving rise to a curve that crosses the straight Tait line several times in a seemingly systematic way. The systematic portion of this curve is however a computational artifice and should not be considered a systematic deviation.

The lithium data

Figure 1a presents the graph of the derivative versus the pressure for the Bridgman work. The straight line is the least squares fit using the combined Br II and Br III data. The two sets of data do not seem to form a thoroughly consistent straight line. Apparently the derivatives of the Br II set are lower than those of the Br III data, in agreement with the findings of Bridgman who stated that the 40,000 kg/cm² apparatus gives a somewhat greater compressibility in the range 25,000 to 40,000 kg/cm² than the 100,000 kg/cm² apparatus.⁽¹⁰⁾ This discrepancy is found with all the alkali metals considered here and is greatly amplified by the use of the derivative rather than the volume.

In addition to the variations due to the use of two different apparatus, the disagreement between

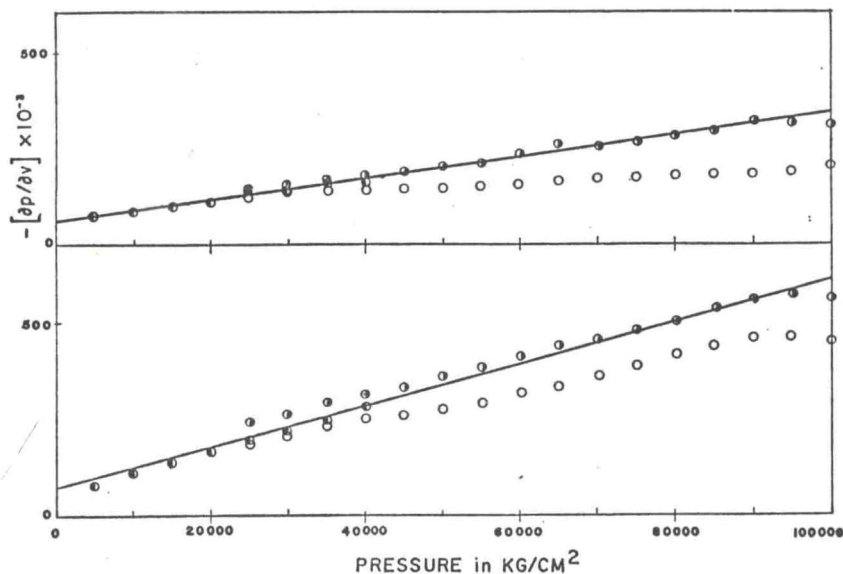


FIG. 1a. Graph of $-(\partial p/\partial v)_T$ vs. pressure in kg/cm^2 for lithium data of Bridgman at room temperature. \bullet Bridgman III experimental points, \circ Bridgman II experimental points and \circ Bridgman I experimental points. — represents the least squares line obtained using the Br II and Br III data. 1b. Graph of $-(\partial p/\partial v)_T$ vs. in kg/cm^2 for sodium data of Bridgman at room temperature. \bullet Bridgman III experimental points, \circ Bridgman II experimental points at \circ Bridgman I experimental points. — represents the least squares line obtained using the Br II and Br III data.

these sets of data may be attributed partly to the fact that an aluminum sheath was used in performing the Br III measurements, while no such encasement was used in the Br II data.

Also shown on Fig. 1a, although not used to determine the best straight line, is the Br I data. It is quite evident that these points do not fit the same straight line. Similar disagreement is found with all the metals considered except Cesium for which there is no Br I data. Factors responsible probably are: (1) the values reported as Br I were 'corrected' by Bridgman so as to agree with an earlier set of measurements which he believed to be superior; (2) a copper sheath was used around the sample. The fact that the copper is harder than the aluminum sheath used in the Br III determinations may partially account for this discrepancy. An indication that the copper sheath is at least partly responsible for the discrepancy is given by the one run of lithium without this sheath in the Br I set of measurements, where the compression was much smaller.

Using the individual data of Br II and Br III leads to an excellent fit of the points to a least squares line, but we considered the combined Br II, Br III line a better compromise.

Figure 2 presents the Swenson data at 4.2°K . Here the derivative scale is eight times greater, and the pressure scale is ten times greater than in the graphs of the Bridgman data. This same scale is used to present all sets of Swenson data. In this instance the lowest three reported values of Swenson have been omitted. Inclusion of these points lead to a rather poor fit of the points to the straight line. The omission of these points is justified on the grounds that they were not measured values but obtained by extrapolation, and were admittedly rather poor. These three lowest points were discarded for each case of Swenson data presented.

Table 1 gives the coefficients of the best straight lines through the various sets of data.

The sodium data

Figure 1b shows the combined data for Br II

Metal

Lithium

Sodium

Potassium

Rubidium

Cesium

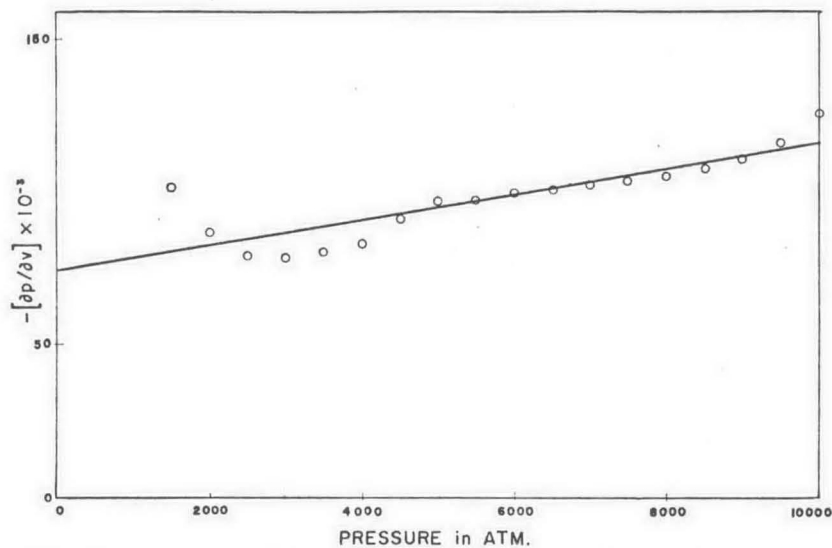


FIG. 2. Plot of $-(\partial p/\partial v)$ vs. pressure in atm for the Swenson lithium data at 4.2°K . \circ Swenson experimental values. — least squares line obtained from the Swenson experimental values.

Table 1. Tait constants of the alkali metals

Metal	Data	Temp.	$J \text{ cm}^3$	$L, \text{ kg/cm}^2$	Comments
Lithium	Br I	Room	0.13135	152092.0	
	Br II	Room	0.38805	23769.0	
	Br III	Room	0.40657	33561.6	
	Br II-Br III	Room	0.37210	24211.7	best value at Room Temp.
	Swenson	4.2°K	0.23646	17543.8 atm	1st 3 pts. omitted
Sodium	Br I	Room	0.25933	24612.2	
	Br II	Room	0.18222	10313.8	
	Br III	Room	0.21390	28094.1	
	Br II-Br III	Room	0.18556	14416.8	best value at Room Temp.
	Swenson	4.2°K	0.20303	15025.0 atm	1st 3 pts. omitted
Potassium	Br I	Room	0.32762	21792.7	
	Br II	Room	0.18413	3455.65	best value at Room Temp.
	Br III	Room	0.13680	-6828.0	
	Br II-Br III	Room	0.14521	-2911.1	
	Swenson	4.2°K	0.21976	7363.7 atm	1st 3 pts. omitted
Rubidium	Br I	Room	0.44719	73493.8	
	Br II	Room	0.10566	2912.5	
	Br III	Room	0.10839	6626.7	
	Br II-Br III	Room	0.10446	3660.75	best value at Room Temp.
	Swenson	4.2°K	0.10097	4221.7 atm	1st 3 pts. omitted
Cesium	Low pressure				
	0-23,300 kg/cm^2	Room	0.11229	5453.45	
	Med. pressure				
	23300-40000 kg/cm^2	Room	0.10301	-36.138	
	High pressure				
50000-100,000 kg/cm^2	Room	0.01856	-39421.8		
Swenson	4.2°K	0.10590	4466.95 atm	1st 3 pts. omitted	

and Br III of sodium. Once again the derivative values of the Br II set are low as expected. The Br I derivative data again is low but seems to run more or less parallel to the newer data in a manner that suggests a constant error.

Figure 3a presents the Swenson data at 4.2°K and represents a much better fit of the points to the curve than does the lithium at this temperature.

An analysis of the rather extensive set of sodium

data run at various temperatures by Beecroft and Swenson was also run.⁽¹⁷⁾ This study will be presented in the near future.

The potassium data

Potassium presents a particularly difficult problem. In Fig. 4 is presented the Bridgman data. Up to about 60,000 kg/cm² Br II and Br III points seem to present a single set of data. Br I seems to

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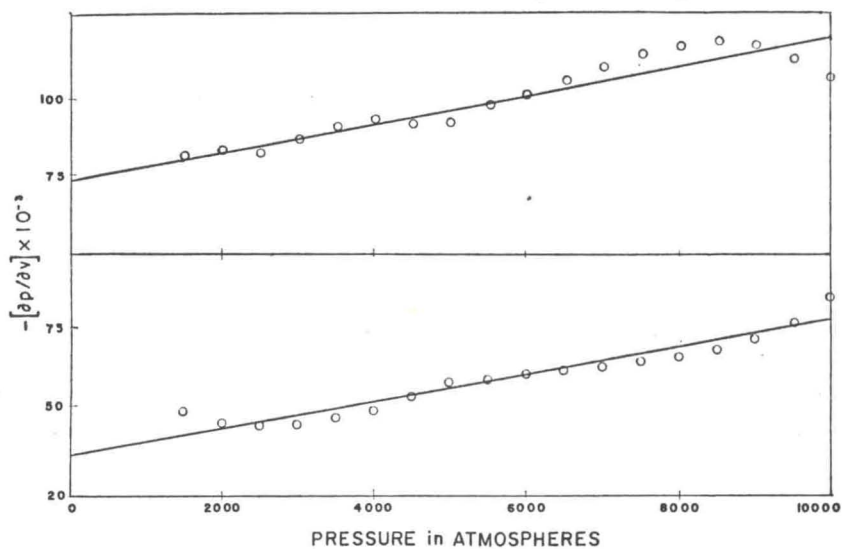


FIG. 3a. Plot of $-(\partial p/\partial v)_T$ vs. pressure in atm. for the Swenson sodium at 4.2°K; \circ Swenson experimental values. — least squares line obtained from the Swenson experimental values. 3b. Plot of $-(\partial p/\partial v)_T$ vs. pressure in atm. for the Swenson potassium data at 4.2°K. \circ Swenson experimental values. — least squares line obtained from the Swenson experimental values.

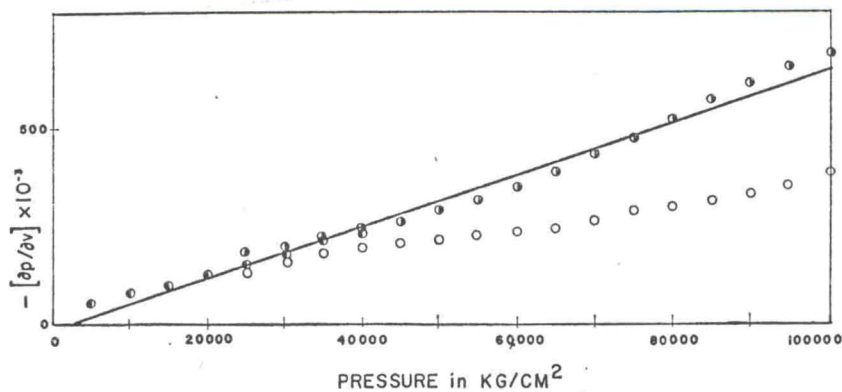


FIG. 4. Plot of $-(\partial p/\partial v)_T$ vs. pressure in kg/cm² for the Bridgman potassium data at room temperature. \bullet Bridgman III experimental values, \circ Bridgman II experimental values and \circ Bridgman I experimental values. — least squares line obtained by using the Br II and Br III potassium data.

$-[\partial p/\partial v] \times 10^{-3}$

agree to about 30,000 kg/cm² and then deviates badly. What the points above 60,000 kg/cm² in Br III mean is open to question. The values of L are unusually low for the Br II, Br III and the combined Br II-Br III data compared to those of lithium and sodium. The negative values obtained for the combined Br II-Br III and Br III are to be regarded with extreme suspicion. While

negative values of L are possible,⁽⁷⁾ they generally occur at much higher temperatures closer to the critical point. In view of the uncertainty in Bridgman's temperatures it can only be hoped new determinations will be made.

The Swenson potassium data at 4.2°K are presented in Fig. 3b, and except at the ends a fine fit is indicated.

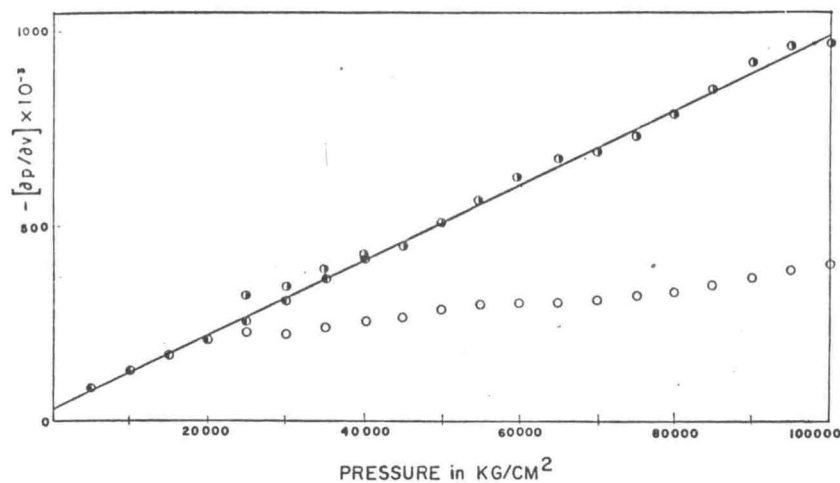


FIG. 5. Plot of $-(\partial p/\partial v)_T$ vs. pressure in kg/cm² for the Bridgman rubidium data at room temperature. ● Bridgman III experimental values, ● Bridgman II experimental values and ○ Bridgman I experimental values. — least squares line obtained by using the Br II and Br III rubidium data.

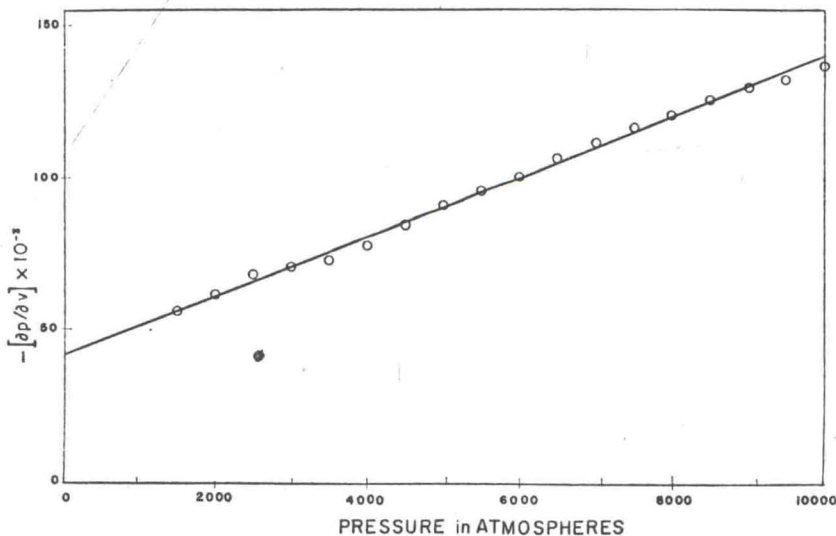


FIG. 6. Plot of $-(\partial p/\partial v)_T$ vs. pressure in atm for the Swenson rubidium data at 4.2°K. ○ Swenson experimental values. — least squares line obtained by using the Swenson values.

The rubidium data

Figure 5 shows the least squares curve for the combined Br II and Br III data of rubidium. It is immediately evident that the two sets seem to form a single set with the Br II, just slightly lower as expected. Br I data, as shown, again deviates badly from the newer measurements being much lower. In addition the higher points show opposite deviation and thus must be looked at with a high degree of suspicion.

Figure 6 shows the Swenson 4.2°K rubidium data as exhibiting an excellent fit.

The cesium data

It has been established that cesium undergoes a transition from the body-centered cube to the face-centered arrangement⁽²¹⁾ at approximately 23,300 kg/cm². Another transition has been reported and considered to be due to an electronic transition at about 45,000 kg/cm².⁽²²⁾

It was thus necessary to treat each range between transition points as an independent set of data. The data from 0 to 23,300 kg/cm² were treated individually as a low pressure set, the data from 23,300 kg/cm² to 40,000 kg/cm² were treated as a medium pressure range set, and finally a high pressure set of data extended from 50,000 to 100,000 kg/cm².

Figure 7 (changed scale) presents the low and medium range set of data. Each set fits its individual least squares line very nicely. Figure 8 is a representation of the high pressure data in an expanded scale and is a rather poor fit. Figure 9 presents the Swenson 4.2°K data of cesium, which again fits well.

From the results of the analysis of the cesium data it can be inferred that a very poor fit of the data points to the least square line indicates, that some sort of transition point may exist in the range being considered.

The Volumes

The real test of the merit of the values of J and L is the fit the volumes derived from them are to the experimentally determined values of the volume. Considering equation (1) it is evident that:

$$v = v_0 - J \ln \left(\frac{P+L}{P_0+L} \right) = v_0 - J \ln \left(\frac{P+L}{\text{const}} \right) \quad (9)$$

It is thus seen that once values of J and L are chosen it is possible to calculate the volume at any pressure, P . P_0 and v_0 are some arbitrary reference pressure and volume with v_0 being the volume at

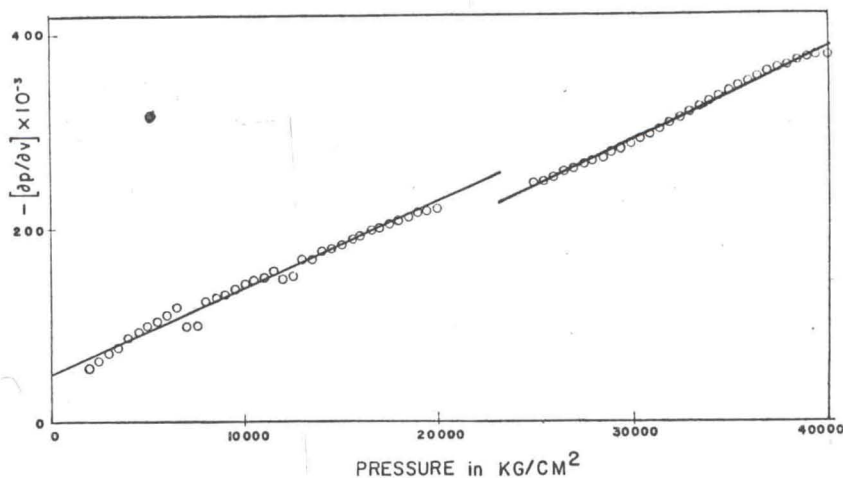


FIG. 7. Plot of $-(\partial p/\partial v)_T$ vs. pressure in kg/cm² for the Bridgman low and medium pressure range for cesium. Range from 0 to 23,300 kg/cm² represents the low pressure data as points and the least squares line as the solid line. In the medium pressure range the data are represented as points and the least squares line as a solid line on the graph between 23,300 kg/cm² and 40,000 kg/cm².

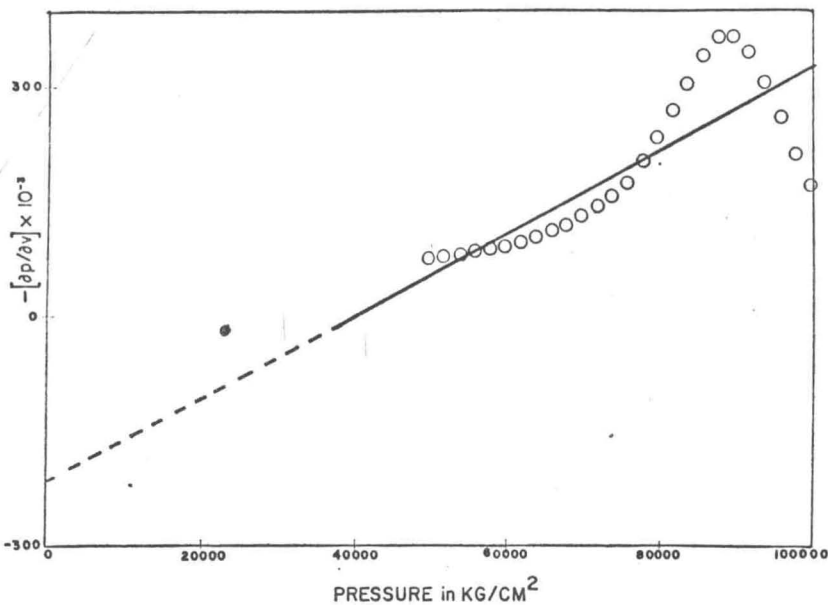


FIG. 8. Plot of $-(\partial p/\partial v)_T$ vs. pressure in kg/cm^2 for the high pressure Bridgman cesium data at room temperature. \circ experimental values. — least squares line obtained from using the experimental values.

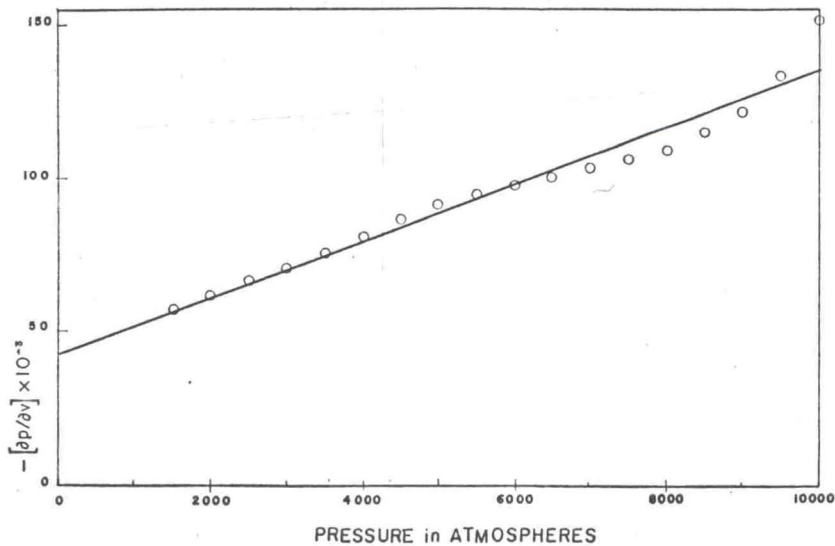


FIG. 9. Plot of $-(\partial p/\partial v)_T$ vs. pressure in atmospheres for the Swenson cesium data at 4.2°K . \circ Swenson experimental values. — least squares line from Swenson values.

P_0 . Equation (9) may also be written as

$$(P_0 + L) \exp(v_0/J) = (P + L) \exp(v/J) \\ = \text{const.}[\exp(v_0/J)] = H \quad (10)$$

where const. is a constant indicated as $(P_0 + L)$ in equation (9). Two methods of the evaluation of the volume are possible once L and J are decided upon. First a value of P_0 may be chosen to correspond to the pressure at volume v_0 and the constant becomes $(P_0 + L)$. The second method may be indicated by equation (10).

Now H may be evaluated at each pressure used and the average value taken as the overall value of H . This method has two immediate advantages over the previous method; (a) all points are treated as equals in the evaluation of the constant and thus eliminating the weakness of allowing one pressure to dominate the constant; (b) once an average value has been determined the deviation of the individual values from this average may be computed and values having deviations greater than a set limit may be discarded and a new average computed. The theoretical volumes obtained by this approach appeared to agree better with the experimental volumes than did the volumes computed using the approach based on equation (9) for all the alkali metals. Table 2 gives the data obtained by

this method and also indicates the number of points eliminated.

Figure 10 shows the specific volume versus pressure graph for the Bridgman data of lithium, sodium, potassium and rubidium. The points are the experimentally determined points of Br II and Br III and the solid line represents the value of the volume as calculated using equation (10) with the values of J and L used being those obtained for the combined Br II and Br III data.

Figure 11 shows the curves for the three sets of cesium data. Again the curves are derived from the J and L values and the points are experimental. From this graph it would seem that the fit is fairly good for the three sets of data.

The first method proved to be less satisfactory than that based on equation (10).

One other factor should be noted in Fig. 10, that is, that in all cases the Br II and Br III volumes blend into each other as a single set of data so that on consideration of the volumes, it is not easily seen that the two sets of data are not continuous. Once the derivative curve is used the discontinuity becomes apparent. That is to say the use of the derivative approach magnifies any difference between the sets of data if present.

Figure 12 shows the volume vs. pressure curve obtained for the Swenson data. An excellent fit is again evident.

Table 2. Results of the evaluation of H of equation (10)

Metal	Data	No. of pts.	$H \times 10^{-6}$	Comments
Li	Br II	10	2.9710	No pts. discarded
Li	Br III	10	2.9459	1 pt. discarded
Li	Comb. Br II-III	19	3.6224*	No pts. discarded
Na	Br II	10	3.0521	1 pt. discarded
Na	Br III	10	2.3664	1 pt. discarded
Na	Comb. Br. II-III	19	3.2259*	3 pts. discarded
K	Br II	10	2.12937*	2 pts. discarded
K	Br III	10	6.2631	1 pt. discarded
K	Comb. Br II-III	19	5.1668	4 pts. discarded
Rb	Br II	10	1.8065	2 pts. discarded
Rb	Br III	10	1.8434	1 pt. discarded
Rb	Comb. Br II-III	19	1.97998*	No pts. discarded
Cs	Low P Range	7	0.58228	No pts. discarded
Cs	Medium P Range	4	0.58677	No pts. discarded
Cs	High P Range	5	2443.7	No pts. discarded

* Best choice values.

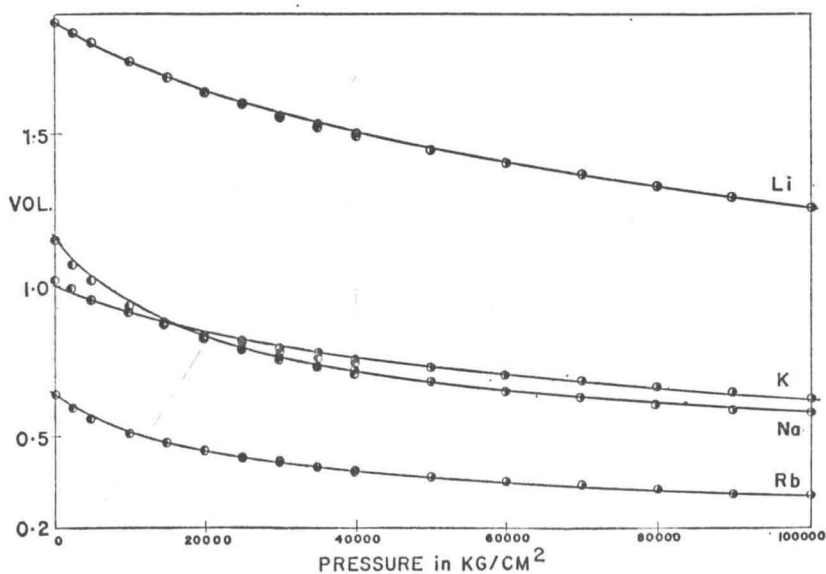


FIG. 10. Plot of specific volume vs. pressure in kg/cm^2 for the Bridgman and data of lithium, sodium, potassium, rubidium at room temperature. \circ Bridgman II experimental values, \bullet Bridgman III experimental values, — represents, in each case, the theoretical values for the specific volumes obtained by using equation (10) with the proper J and L values for each metal obtained from the combined Br II-Br III least squares curve of $-(\partial p/\partial v)_T$ vs. pressure for the individual metals and the proper H value for the metal as indicated in Table 2 for the combined Br II-Br III determinations.

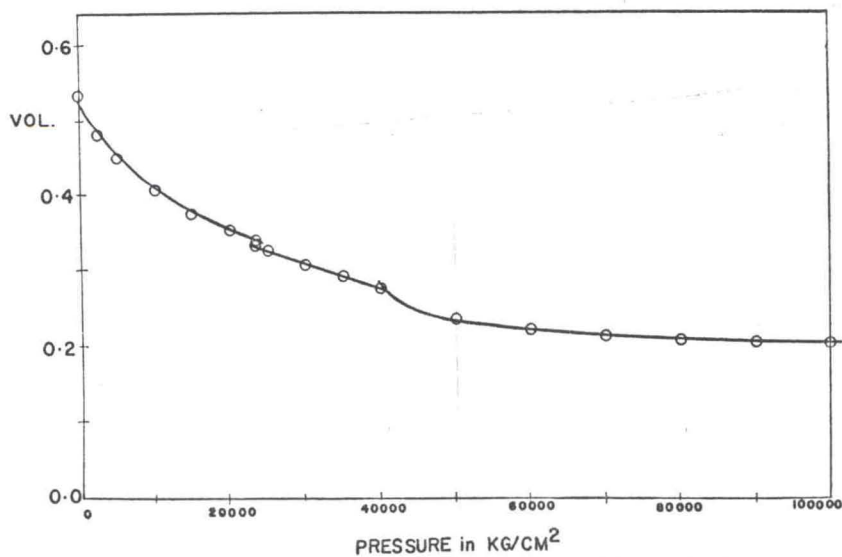


FIG. 11. Plot of specific volume vs. pressure in kg/cm^2 for the Bridgman cesium data at room temperature. The three sets of data: low pressure, medium pressure and high pressure, are presented as points. The solid lines represent the theoretical specific volumes as calculated using equation (10) with the proper J and L values indicated in Table 1 and the proper H values as indicated in Table 2.

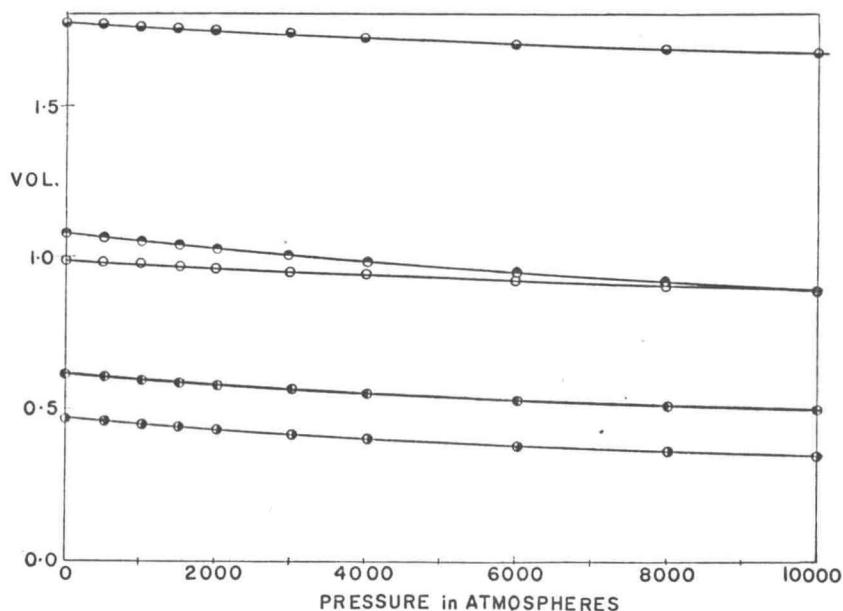


FIG. 12. Plot of specific volume vs. pressure in atm for the five sets of Swenson data at 4.2°K. ● Swenson's experimental specific volumes for lithium, ○ Swenson's experimental specific volumes for sodium, ◐ Swenson's experimental specific volume for potassium, ◑ Swenson's experimental specific volumes for rubidium and ◒ Swenson's experimental specific volumes for cesium. The solid line represents the theoretical specific volumes as calculated using equation (10) with the proper J and L values for the metal and the proper H value as indicated in Table 2.

4. DISCUSSION

Considering the evidence presented here it would seem that a plot of P versus $(\partial P/\partial v)_T$ is truly a straight line for the alkali metals; that is, that Tait's Law is applicable. The question of whether Tait's Law is obeyed by all solids cannot be decided unambiguously without examining more materials. Particularly interesting will be an examination of the rare gas solids, data for which is presented by STEWART.⁽²³⁾ These values will be analyzed shortly.

The precision of Br II and Br III data is about equal, with the Br II values being slightly lower, except in the case of potassium, where some curious deviations occur. These probably are of experimental origin but perhaps have deeper meaning.

Since Tait's Law appears to be the actual law obeyed by the alkali metals and perhaps many other substances, it can be used to smooth experimental data on compressibility. The volume versus pressure graph indicates the soundness of the

values of J and L chosen, a poor fit indicating that a redetermination of the values is in order.

In this discussion the comparison has been between liquids and polycrystalline solids. How is this fact to be reconciled with the fact that the compressibilities of single crystals are identical to those of polycrystals? The resolution of this apparent dichotomy is linked with a deeper investigation of the consequences of the fact that at least certain solids obey Tait's Law. Tait's Law can be derived free of assumption from the general equation of state. An examination of this equation shows that the average particle size (degree of association) is strongly dependent on the pressure. A fuller discussion of this subject and the various conclusions that must be drawn from the application of the general equation will be presented in a subsequent paper.

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