PHYSICAL REVIEW *JANUARY, 1926* *VOL. 27*

THE FIVE ALKALI METALS UNDER HIGH PRESSURE

By P. W. Bridgman

Abstract

Effect of high pressure on the melting constants, electrical resistance and volume of the alkali metals.—(1) *New data for Rb and Cs,* presented in detail elsewhere, are given in three tables. Then, since similar data have previously been obtained for Li, Na and K, the results of a comparative study of all five alkali metals under pressure are given and discussed. (2) *Melting constants.* The general character of the melting phenomena is the same for the alkali metals as for other substances; the melting curve continues to rise indefinitely with increasing pressure, with neither maximum nor critical point. Above 10000 kg/cm^2 there is a reversal of the normal melting points of Na and K, and a moderate graphical extrapolation indicates other reversals also, so that at high pressures we may expect a complete reversal of the order of normal melting temperatures, Cs being the highest and Li the lowest. The fractional change of volume on melting is the same within 25 percent for Na, K, Rb, and Cs, as is also the latent heat of melting per gm atom; for Li the values are only about one-fourth as large. (3) *Electric resistance.* K shows the greatest relative decrease of resistance with pressure above 1400 kg/cm^2; Rb occupies electrically an intermediate position between K and Cs. The effect of pressure on the resistance of Cs is unique in that there is a minimum (at 4000 kg/cm^2). This minimum seems to have no connection with the crystal structure of the solid, but will probably be shown by the liquid also at higher pressures. At low pressures Cs has the maximum negative pressure coefficient of resistance and at high pressures the maximum positive coefficient of all pure metals measured. At high pressures the curve of pressure coefficient of resistance of Cs against pressure has a point of inflection which could not be predicted from the behavior at lower pressures; if other metals behave similarly above the present experimental range, it is possible that the resistance of all metals will eventually pass through a minimum. Such a change for Rb may be expected below 20000 kg/cm^2. This reversal of resistance may be an indication of the first beginning of a quantum break-down, suggested more strongly by the volume relations. The discontinuity of resistance at melting is approximately constant for all the alkalies. (4) *Volume.* Cs is the most compressible solid element yet measured directly. Instead of the atom the electron seems to be the significant unit of structure for volume since the volume per electron and the compressibility per electron do not vary greatly throughout the alkali series, whereas atomic volume and atomic compressibility vary greatly. At atmospheric pressure the electronic volume of K is abnormal, standing between that of Li and Na, but at high pressures there is a reversal. At high pressures the electronic compressibilities of all the alkalies are roughly equal (2.2 to 3.5×10^{-29} at 12000 kg/cm^2), except for K, which is twice as compressible per electron (5.9×10^{-29}). The initial high relative compressibilities of Cs and Rb decrease rapidly with pressure, crossing that for K below 8000 kg/cm^2, while the high compressibility of K persists over a wide pressure range with comparatively small drop. All the evidence indicates an abnormally open electronic structure for K. (5) *Comparison with compressibility of electron gas.* Numerically the compressibility of all the alkalies is of the order of magnitude of that of a perfect gas under a high internal pressure, taking the electron as the gas unit. For K, the compressibility has passed a turning point within the experimental range, and appears to be ultimately headed for the perfect gas value. This may be the beginning of the quantum break-down, which is complete only at remotely high pressures. On the theoretical side, Schottky's theorem, in conjunction with the extrapolated behavior of compressibility, indicates the same break-down at high pressures.

INTRODUCTION

IN a paper now being published by the American Academy, data are given for several of the properties of rubidium and caesium under high pressure. Similar data have been previously published for Li, Na, and K,[1] so that the materials are now at hand for a systematic study of the effect of pressure on the properties of all the alkali metals. The data include the pressure-volume relations, and the effect of pressure on melting and electrical resistance. It is the purpose of this paper briefly to summarize the new data, and then to make a comparative study of the behavior of the five metals under pressure. Such a study may be expected to be of special significance because the effects of pressure on these metals are unusually large; Cs, for example, is by far the most compressible element solid under usual conditions, and is even more compressible over a wide range of pressure than the most compressible organic liquids, such as ether. From a study of these metals, if at all, we may expect light on the question of the ultimate behavior as pressure is increased indefinitely. Recent astronomical speculations deal with densities of 50000; such densities can exist only when the quantum structure of the atoms has entirely broken down and matter is resolved into a gas of electrons and nuclei. Some such break-down of the quantum orbits must of course take place at ordinary temperatures if the pressure is high enough; one of the questions that we shall consider here is whether the high pressure behavior of these metals suggests at all the beginning of such an atomic disintegration.

THE NEW DATA

Melting. The melting data for Rb and Cs are summarized in Table I. In broad features the behavior is the same as that found for all other substances under pressure; the curve of melting temperature against pressure is concave toward the pressure axis, the curve of the change in volume on melting, ΔV, against pressure is convex toward the pressure axis, and the latent heat is comparatively constant. The increase of the

---

[1] P. W. Bridgman, Phys. Rev. **3**, 154-157 (1914); **6**, 31 and 102 (1915); Amer. Acad. Proc. **56**, 67, 76, and 82 (1921).

latent heat of Cs under pressure is rather greater than usual. These new data on the most compressible metals give no reason to alter the conclusion previously drawn as to the character of the melting curve, namely that the melting curve probably rises indefinitely with continually decreasing curvature, but with neither maximum nor critical point.

TABLE I

Melting data for rubidium and caesium

Pressure (kg/cm^2)	Rubidium Temp.	 ΔV (cm^3/gm)	 Latent heat (kg · m/gm)	Caesium Temp.	 ΔV (cm^3/gm)	 Latent heat (kg · m/gm)
1	38°.7	.0185	2.76	29°.7	.0136	1.65
500	48 .7	163	2.73	41 .4	118	1.68
1000	57 .9	145	2.70	51 .9	105	1.72
1500	66 .5	130	2.66	61 .4	96	1.76
2000	74 .5	119	2.67	70 .2	88	1.80
2500	82 .0	112	2.72	78 .3	83	1.88
3000	89 .1	106	2.76	85 .7	78	1.99
3500	95 .9	101	2.78	92 .4	75	2.14
4000				98 .5	72	2.29

A word should be said about the character of the melting. The melting points found for these metals are materially higher than those usually listed in the literature and the melting was very sharp, both evidence of high purity. It is more than usually difficult to obtain these metals pure; the impurity difficult to remove is not another metal, but oxide, which dissolves in the metal like a foreign metal and depresses the freezing point. Purification demands long slow distillation in high vacuum at the lowest possible temperature. The criterion of sharp freezing is one of the most delicate for high purity, and results should not be accepted for these metals unless the freezing is sharp. Thus the results recently published by Bidwell[2] on the thermo-electric properties of Rb and Cs, which he interprets as due to some sort of internal change in the metals, I believe are much more likely to be due to dissolved impurity. Bidwell's metals left much to be desired as to sharpness of freezing.

Electrical resistance. The data on electrical resistance are too numerous to summarize here, but the most important results, those for the solid metals, are summarized in Table II. It is to be emphasized that the resistance measurements on the solid were made on bare wires; internal stresses introduce too large errors if the metal is enclosed in a glass capillary as has usually been done. In addition to the data of Table II, the detailed paper gives the resistance of the liquid under pressure,

---

[2] C. C. Bidwell, Phys. Rev. **23**, 357-376 (1924).

the temperature coefficients at atmospheric pressure, a study of the effect of pressure on the temperature coefficient of the solid, and the change with pressure of the discontinuity of resistance on melting.

By far the most important of the new results is the establishment of the minimum resistance of solid Cs. Initially, at atmospheric pressure, the resistance of Cs decreases more rapidly than does that of any other metal, but the rate of decrease rapidly diminishes, until near 4000 kg/cm^2 there is a flat minimum, and from here on the resistance increases smoothly. This is the only example of a minimum yet found.

TABLE II

Electrical resistance data for Rb and Cs

Pressure (kg/cm^2)	Relative resistance of solid bare wire to values for 1 kg/cm^2, at 0°C Rubidium 0°	Rubidium 35°	Caesium 0°
1	1.000	1.205	1.000
1000	.845	.982	.863
2000	.733	.840	.779
3000	.648	.740	.729
4000	.583	.663	.709
5000	.531	.602	.713
6000	.490	.553	.728
7000	.456	.514	.756
8000	.428	.481	.794
9000	.406	.455	.833
10000	.387	.434	.879
11000	.372	.418	.931
12000	.360	.406	.994

In a previous paper I made a preliminary announcement that Cs has a second polymorphic modification at high pressures, and that the resistance of this modification increases with pressure. This was an error; the apparent discontinuity which I ascribed to a polymorphic modification turns out to be connected in some way with the separation of impurity and disappears entirely when the purity is sufficiently increased, so that we are left with the perfectly smooth passage of the resistance through a minimum.

The discontinuity of resistance between solid and liquid is approximately constant along the melting curve, decreasing slightly with rising pressure for Rb, and increasing slightly for Cs. The same approximate constancy of the ratio of resistance of solid to liquid has been found for other metals. The temperature coefficient of resistance of solid Rb decreases from 0.00481 at 1 kg/cm^2 to 0.00365 at 11000, but for solid Cs the temperature coefficient decreases from 0.00496 at 1 kg/cm^2 to 0.00366 at 6000, and then increases again to 0.00418 at 12000. This is the first example found of a temperature coefficient increasing with rising pressure; it is doubtless connected in some way with the minimum of resistance.

With the improved technique now available, results found previously for K were re-examined. Measurements on the temperature coefficient of K in glass had previously shown a very marked decrease beyond 6000 kg/cm^2,[3] a decrease shown by no other metal. The measurements were now repeated with bare wire, with the results that very little decrease was found beyond 6000, a result agreeing with that for all other metals. Doubtless the former results were due to the constraints exerted by the walls of the glass capillary.

Pressure-volume relations. The pressure-volume relations are summarized in Table III. The pressure range is here 15000 kg/cm^2 against the 12000 cf my other work. The greater range was probably responsible for a somewhat lower accuracy, particularly at the upper end of the range. In the detailed paper will also be found a few values for the volume of the liquid phase and also rough measurements of the thermal expansion. The data show that Cs is the most compressible of the solid elements directly measured (indirect inference, however, shows that at least solid hydrogen and helium are much more compressible,[4] but direct observations on these will not be feasible for a long time). At 12000 kg/cm^2 the volume of Cs has been reduced by very nearly the same amount as that of ether, but there is an essential difference in that the

TABLE III

Relative volumes for Rb and Cs
(Referred to values for 1 kg/cm^2)

Pressure (kg/cm^2)	Rubidium 50°C	Caesium 50°C
1	1.000	1.000
1000	.953	.941
2000	.914	.898
3000	.883	.866
4000	.857	.839
5000	.836	.816
6000	.819	.796
7000	.803	.777
8000	.789	.760
9000	.777	.745
10000	.766	.731
11000	.756	.718
12000	.746	.706
13000	.737	.694
14000	.729	.683
15000	.721	.672

---

[3] P. W. Bridgman, Amer. Acad. Proc. **56,** 140 (1921).

[4] P. W. Bridgman, Amer. Acad. Proc. **59,** 198 (1924).

compressibility of Cs is less affected by pressure than is that of ether. The initial compressibility of Cs is less than that of ether and its compressibility at 12000 greater, so that at higher pressures (20000 kg/cm^2, for example) the volume of Cs will be very materially less than that of ether.

Comparative Discussion

Melting data. In Fig. 1 are plotted in one diagram the melting points of the five alkali metals as a function of pressure. The most interesting feature is the crossing of the curves for Na and K, so that above 10000 kg/cm^2 the melting point of K is higher than that of Na, reversing the normal order. The diagram suggests strongly that there are other crossings at higher pressures; it seems almost certain that K will cross Li, and highly probable that Na will also cross Li. It is more difficult to estimate the future course of the curves for Rb and Cs, because these are given over only a small range, but it is not at all improbable that

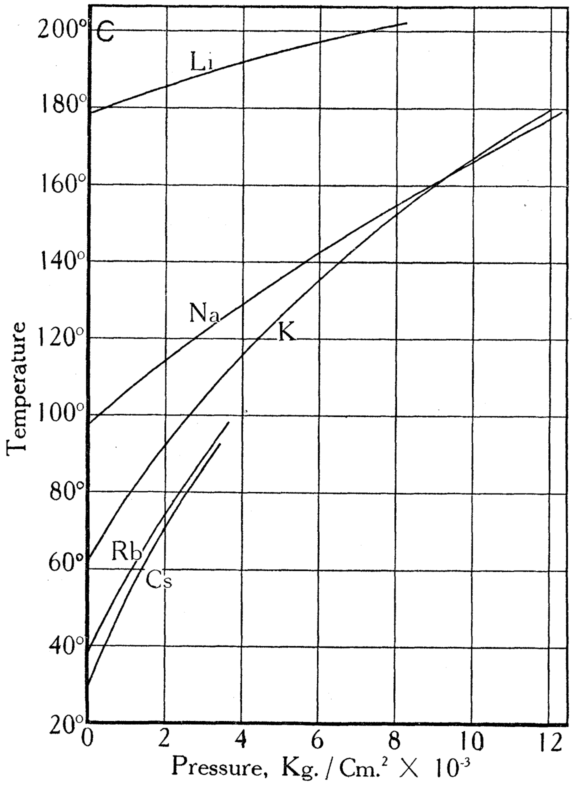

Fig. 1. The melting temperatures of the alkali metals as a function of pressure.

these two curves will eventually cross all the others, so that at sufficiently high pressures the order of melting may be Cs, Rb, K, Na, and Li, the reverse of the usual order. This is not at all an unnatural state of affairs. At high pressures we may expect the atoms to become so packed in together that they find difficulty in melting; this packing effect will increase with the complexity of the atom, and the most complicated atom, Cs, will have the highest melting point.

The pressure at which this reversal of the ordinary melting points will be accomplished may be estimated by graphical extrapolation to be of the order of 25000 kg/cm^2. Such a pressure is comparatively low, much too low to produce those ultimate effects to be expected at extreme pressures when the quantum orbits break up. Under such pressures it will be shown that the volume relations of K differ from those of the other metals; it might be thought that the crossing of the melting curves is similarly an effect due to the unique behavior of K. This, however, I do not believe to be the case; the shape of the melting curves themselves, and also the fact that if melting temperature at atmospheric pressure is plotted against atomic number, K will be found to lie smoothly with the other metals, both suggest that K is not unusual with regard to melting. The peculiar volume relations of K to be discussed later do not seem strongly to affect the melting behavior.

The other melting data relating to change of volume and latent heat are also significant. It is evident that melting is an atomic phenomenon, and the five alkali metals should be compared on an atom for atom basis. Table IV shows the latent heat of melting at atmospheric pressure per gm atom. On passing from the solid to the liquid state approximately the same heat is absorbed per atom by all the alkalies (except Li). Under high pressure the latent heats vary in a complicated way, but not by large amounts, so that over the entire pressure range the generalization holds that the latent heat of melting per atom is approximately the same.

TABLE IV

Melting data at atmospheric pressure

Metal	Latent heat (kg · m/gm · atom)	Fractional change of volume
Li	49	.0060
K	215	.0231
Cs	219	.0256
Rb	236	.0284
Na	271	.0271

Table IV shows also that, except for Li, the fractional change of volume on melting is approximately the same, that is, on passing from the solid to the liquid state an atom of an alkali metal experiences a definite fractional increase of volume.

Lithium is unique in its melting phenomena. The reason doubtless is to be sought in the structure of the atom; the number of electrons is so small, only three, that the external symmetry of the atom must be much lower than that of the other four alkalies.

Electrical resistance. Unlike many of the other properties, the electrical resistance of the alkali metals does not vary smoothly in the same direction throughout the series. Thus the specific resistance at 0°C at atmospheric pressure decreases from Li to Na, and then increases again from K to Rb to Cs. The numerical values of the specific resistance are respectively 8.6×10^{-6}, 4.3, 6.1, 11.6, and 19. A somewhat more satisfactory basis for comparison is the "conductivity per atom," which is obtained by dividing the specific conductivity at a temperature one half the characteristic temperature by $N^{1/3}$, where N is the number of atoms per cc. This is discussed more in detail in my forthcoming Solvay Conference report. If "conductivity per atom" is plotted against atomic number, a comparatively smooth curve will be found with a very pronounced maximum between K and Rb. A similar reversal within the series is shown by the pressure effects. In Fig. 2 the relative resistance at 0° is plotted against pressure. It is evident that there is some sort of a turning point between K and Rb.

The resistance of most metals decreases with rising pressure, but there are seven metals whose resistance increases. Among some 50 metals studied, the series of the alkali metals includes the numerical extremes of maximum positive and maximum negative pressure coefficients of resistance.

It is of interest that the abnormal pressure effects of both Li and Cs do not seem to be associated with the crystal structure of the solid but are more intimately connected with the atoms themselves. This is shown by the fact that the resistance of Li increases under pressure in the liquid as well as in the solid state. A corresponding experiment could not be made on the resistance of liquid Cs because within the temperature range of these experiments the liquid freezes at a pressure below that of the minimum resistance. But at 97° the freezing pressure is very close to that of the minimum resistance. The resistance of solid and liquid at this temperature was plotted in one diagram as a function of pressure, multiplying the resistance of the solid by such a factor as to remove the discontinuity at the freezing point. In this way a curve was obtained passing perfectly smoothly through the melting point. The obvious inference is that the crystal structure of the solid has nothing to do with the minimum, and that at higher temperatures the resistance of the liquid as well will show a minimum.

A question of great importance for theories of resistance is whether the minimum resistance shown by Cs, the most compressible of the metals, will be shown by the other metals also at pressures high enough. This question can be answered only by some sort of extrapolation. Such an extrapolation is not easy from the curves of resistance given in Fig. 2. If, however, we plot $(1/w)(\partial w/\partial p)_T$ as a function of pressure, where w is resistance, we get something more suggestive as to the behavior at high pressure. For Cs, this quantity starts negative and crosses the axis at the pressure of the minimum, which is about 4400 kg/cm². The curvature against pressure is convex upward at pressures below 8000 kg/cm², but here there is a point of inflection, and above 8000, $(1/w)(\partial w/\partial p)_T$ increases at an accelerated rate with increasing

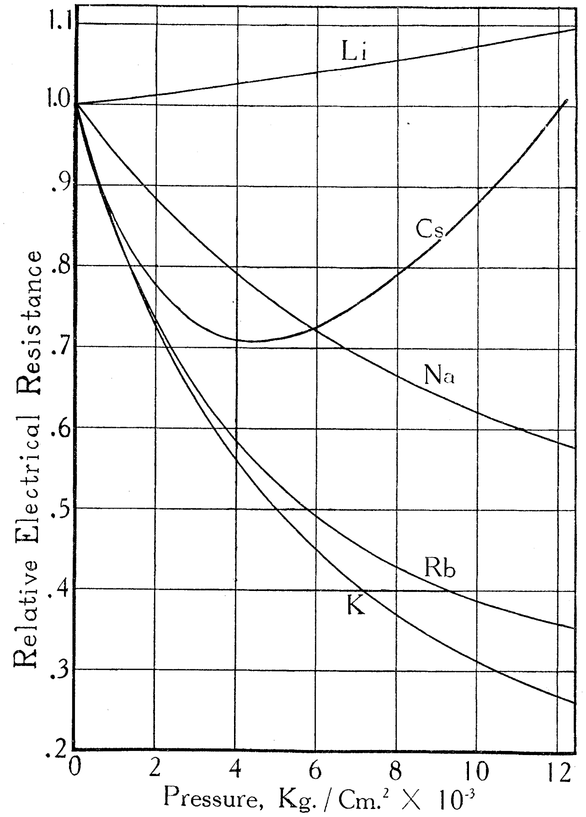

Fig. 2. The relative electrical resistances at 0°C of the alkali metals as a function of pressure.

pressure. If this inflection is characteristic of the behavior of other metals at still higher pressures, then the resistance of each of them must also ultimately pass through a minimum. The shape of the curve for Rb indicates that this may well occur at some pressure below 20000 kg/cm^2.

We next have to ask what is the theoretical significance of this minimum resistance. The theory of electrical resistance which I have developed[5] represents the conduction electrons as passing through the substance of the atoms and encountering resistance where they make the jump from atom to atom. A minimum resistance is to be thought of as due to the fact that as the pressure is increased a point is reached beyond which the electrons find it increasingly difficult either to make the jump from one atom to the next or to get through the atom. Such interference with the electron is not surprising in a complicated structure distorted at high pressure. The minimum resistance is perhaps in Cs to be regarded as the first shadowing forth of the ultimate disintegration of the quantum orbits under extreme pressure. It is significant that the effect is first found in the most compressible metal with a complicated atomic structure.

Volume relations. In discussing melting phenomena we have seen that the atom is the significant unit of structure, as is shown for example by the fact that the latent heat of melting per atom is nearly the same for the four heavy alkalies. This is as we would expect, since the atoms pass as a unit from the liquid to the solid phase. But now that we are to discuss volume relations, it will appear that the electron, the ultimate constituent of the atom, is the more significant unit of structure; this is suggested by the fact that the contributions made to the volume or to the compressibility per electron vary much less from one alkali to another than do the contributions per atom.

We first compare the volume per electron in the five metals as a function of pressure. The volume per electron is obtained from the volume per atom by dividing by the atomic number plus 1 (that is, we are obtaining the average volume occupied by one discrete piece of electricity, whether positive or negative, the nucleus counting as one). The volume per atom is the atomic weight multiplied by 1.66×10^{-24} (the weight of the atom of hydrogen) divided by the density. Thus we find, for example, the volume per electron of Li at atmospheric pressure is $6.94\times1.66\times10^{-24}/4\times.53=5.43\times10^{-24}$ cm^3.

---

[5] P. W. Bridgman, Phys. Rev. **19**, 269-289 (1917); **17**, 161-194 (1921); **19**, 114-134 (1922); Report of the Solvay Conference, Brussels, 1924 (not yet published).

In Fig. 3 is plotted the volume per electron as a function of pressure. Li has the largest and Cs the smallest electronic volume, that is, the quantum orbits are closely packed in Cs but loosely packed in Li. The electronic volume of Li at atmospheric pressure is 2.6 fold greater than that of Cs. On the other hand, if we compared atomic volumes, we would find the volume of Li to be least, and that of Cs greatest, 5.3 times that of Li. The variability of volume throughout the series of the alkalies is thus twice as great when expressed in terms of the atom as when expressed in terms of the electron.

At atmospheric pressure the electronic volume of K is greater than that of Na, a reversal of order. At high pressures, however, the curves for K and Na cross. This is the first of several pieces of evidence that the electronic structure of K is abnormally loose.

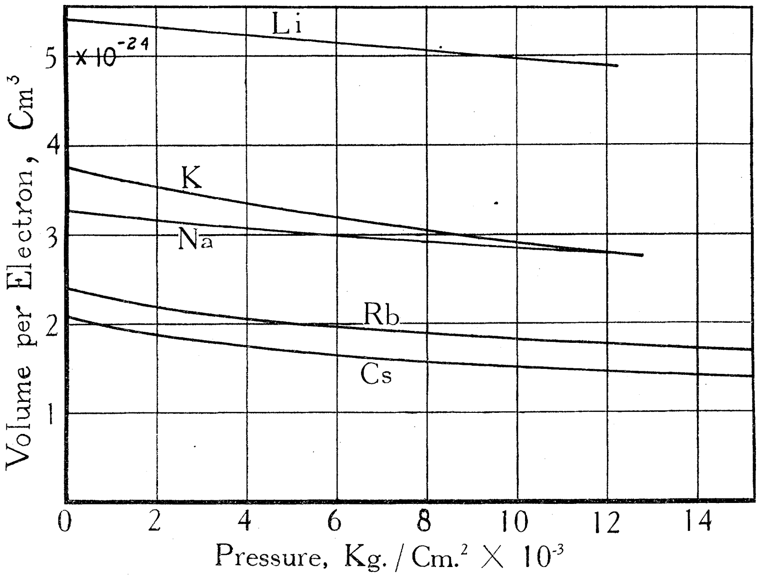

Fig. 3. The volume per electron in cm³ of the alkali metals as a function of pressure.

It is evident from Fig. 3 that the shapes of the curves of electronic volume against pressure are distinctly different for the different alkalies. This difference is brought out much more strikingly in Fig. 4 in which is plotted the instantaneous compressibility, $(1/v)(\partial v/\partial p)_T$, as a function of pressure. If the curves of volume against pressure were of the same shape, the curves of $(1/v)(\partial v/\partial p)_T$ against pressure would be the same for all the metals. This is evidently far from being the case. Not only are the absolute values of $(1/v)(\partial v/\partial p)_T$ quite different, but the shapes of the curves are very different. This has a bearing on speculations of Richards[6] as to the internal pressures of the alkalies. In endeavoring to find some rational basis for extrapolation, he made the assumption that the pressure-volume curve at low pressures of a comparatively incompressible alkali was of the same shape as the pressure-volume curve at high pressure of a more compressible alkali; that is, if all the ordinates of the pressure-volume curve of one metal were multiplied by an appropriate constant and then the curve slid bodily along the pressure axis, the curve so found would coincide with the prolongation into a region as yet unreached experimentally of the pressure-volume curve of another alkali. In particular, he applied this method of extrapolation to Na and K. At the time that he did this, these data for Cs and Rb were not available. These new data show definitely that the assumed connection between the different metals

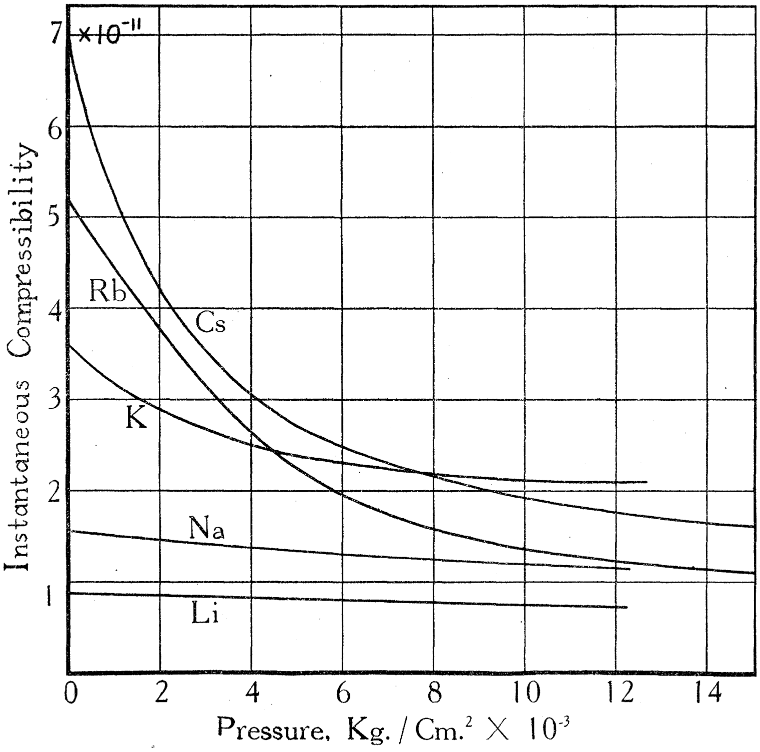

Fig. 4. The instantaneous compressibility $(1/v)(\partial v/\partial p)_T$ in Abs. C.G.S. units, of the alkali metals as a function of pressure.

---

[6] T. W. Richards, Jour. Amer. Chem. Soc. **45**, 422-437 (1923).

does not exist, for if it did, the curves could not cross in the way they do. Richard's method of extrapolation can therefore be regarded as only roughly suggesting what to expect at high pressure; it is probable, however, that the approximation was sufficiently good for the purpose for which Richards used it.

The most striking feature of Fig. 4 is the crossing of the curves for Cs and Rb by that of K; this means that K retains its compressibility to an abnormal degree at high pressures. This again points to a looseness of internal structure. Another striking feature is the great progressive change in the character of the curves throughout the series. In 12000 kg/cm^2 the compressibility of Li drops to 0.83 of its initial value, whereas that of Cs drops to 0.23. The rapid drop of compressibility with increasing pressure is partly due, especially for the more compressible metals, to a taking out of "slack" from the structure by pressure. In the most complicated structure, that of Cs, the possibility of taking out slack is most rapidly exhausted, giving the most rapid drop of compressibility with increasing pressure.

The extent to which the "slack" in the structure is responsible for the initial behavior is further indicated by Table V which shows the compressibility per electron, that is, the actual loss in volume per electron under a pressure increase of 1 kg/cm^2, at 1 and 12000 kg/cm^2, for the 5 metals. Under 12000 the approximate constancy of the compressibility per electron for all the metals (except K) is striking, especially when compared with the initial variability. Li has the greatest compressibility per electron at high pressure, as we would expect because of its more open structure. However, the difference is not as great as might be expected. At 12000 the electrons are packed 3.3 times more loosely in Li than in Cs, but the compressibility is only 1.4 times greater. K is an outstanding exception, both in its initial compressibility (too great to lie in a smooth series with the others) and in its persistent compressibility at high pressures, about twice as high as the average of the others.

TABLE V

Volume compression per electron per kg/cm^2

	Electronic compression	
Metal	Atms. pressure	12000 kg/cm^2
Li	4.7×10^{-29}	3.5×10^{-29}
Na	5.1	3.2
K	13.5	5.9
Rb	12.5	2.2
Cs	14.5	2.5

Finally we have to consider whether there is any indication within the pressure range reached experimentally of the beginning of the breakdown of the quantum structure which we may expect must be inevitable if the pressure can only be pushed high enough. An inquiry of this sort must, of course, be highly speculative. We take as our clue the recent speculations of astronomers that in the interiors of the stars matter may be disintegrated into a gas of electrons and nuclei.

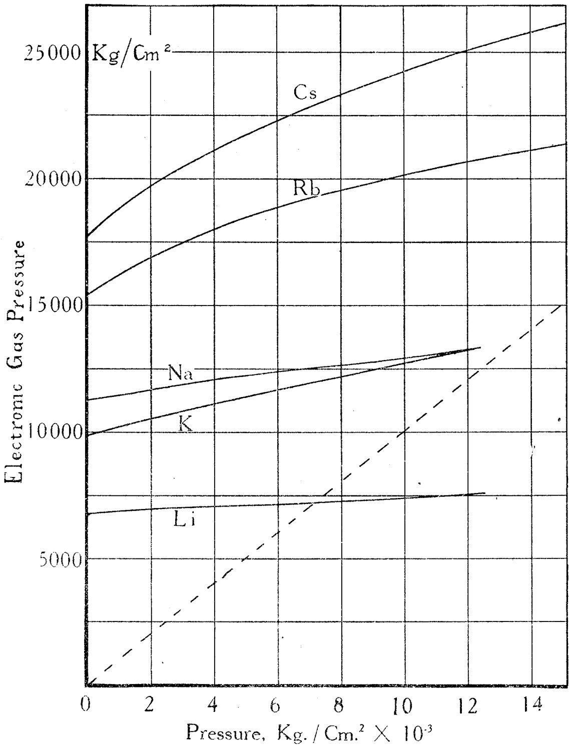

Fig. 5. The electronic gas pressures (that is, the pressures which would be exerted by the electrons and nuclei if they were in the condition of a perfect gas under the actual volume of the metal) of the alkali metals at 0°C as a function of external pressure.

It is in the first place to be noticed that the pressures which would be exerted by these alkali metals if electrons and nuclei constituted a perfect gas are not excessively high. The material for such a calculation is already at hand; we have merely to divide the reciprocal of volume per electron (number of electrons per cm^3) by 2.7×10^{19}, the number of gas molecules per cm^3 at 0°C at 1 atmosphere. In this way the curves of Fig. 5 were obtained. The pressures are of the order of tens of thousands of kilograms per cm^2, which is the order of experimentally obtainable pressures. It is therefore not extravagant to think that experimentally obtainable pressures may at least initiate the reversion to the perfect gas condition. The direction in which the quantum forces act is shown in the figure by the location of the gas pressure curve with respect to the 45° line. The curve for Li crosses this line at 7000; above 7000 the electrons in the perfect gas state would not be able to withstand the external pressure, so that if the quantum forces were removed the structure would collapse. Hence above 7000 the quantum forces distend the structure, whereas below 7000 they prevent it from flying apart. It is also evident from the figure that below 15000 kg the quantum forces in Na and K will change from an expansive to a compressive character. It seems probable that Rb and Cs will similarly change at considerably higher pressures.

When the structure breaks down completely into a perfect gas, the gas pressure curve will coincide with the 45° line, or at least will run parallel to it. The figure shows that any such state of affairs is remote, but there are two indications of the beginning of an approach to it. In the first place, it is evident that K comes nearest of the three lightest alkalies to satisfying this condition, because the slope of its gas pressure curve is closest to 45°. But if there is ever going to be coincidence or parallelism with the 45° line, it is evident that the gas pressure curve must be concave upwards, whereas at low pressures all the curves are concave downward, as is shown in the figure most unmistakably by the entire course of the curves of Rb and Cs. Now this necessary reversal of curvature is indeed shown, well beyond experimental error, both by K and Li, although the effect is not large enough to be well marked in the diagram, and probably is shown by Na also, although it is not so certain that experimental error may not enter here.

The effect is exhibited more clearly if we consider the compressibility instead of the volume. The question is whether the compressibility of the solid alkali metals has features in common with the compressibility of a perfect gas. The compressibility of a perfect gas is $(1/v)(\partial v/\partial p)_\tau = -1/p$. But when we attempt to apply this expression to our solid metals we encounter the difficulty of not knowing the internal pressure. We avoid this difficulty by eliminating p by dividing both sides of the equation by v_e, where v_e is the average volume occupied by one electron, using the gas law $pv_e = 1.35\times 10^{-16}\tau$, and obtain:

$$\frac{1}{v_e}\left[\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau\right] = \frac{-1}{1.35\times 10^{-16}\tau} = -2.4\times 10^{13} \text{ at } 300^\circ\text{K}.$$

The material is at hand for a calculation of $(1/v_e)(1/v)(\partial v/\partial p)_\tau$, which we will call the "gas function," as a function of pressure. The results are shown in Fig. 6. It is significant that the gas function is of the order of magnitude of -2.4×10^{13}, which is the value it would have if the solid were to act like a perfect gas under some unknown but high pressure and in which the *kinetic unit is the individual electron.* If we assumed that the atom were the unit, the gas function would be of a different order of magnitude. The approach of the gas function to the value of a perfect gas is closest for Cs and most remote for Li. In speculating now as to the behavior at very high pressures, the shape of the curve for the gas function is significant. The curves for Cs and Rb are still receding from the perfect gas value at the highest pressures reached experimentally, whereas for K a reversal has been reached at 7000 or 8000 kg/cm², and above this pressure the gas function of K has started to approach more closely to the value for a perfect gas. It is tempting to see in this the beginning of the quantum breakdown.

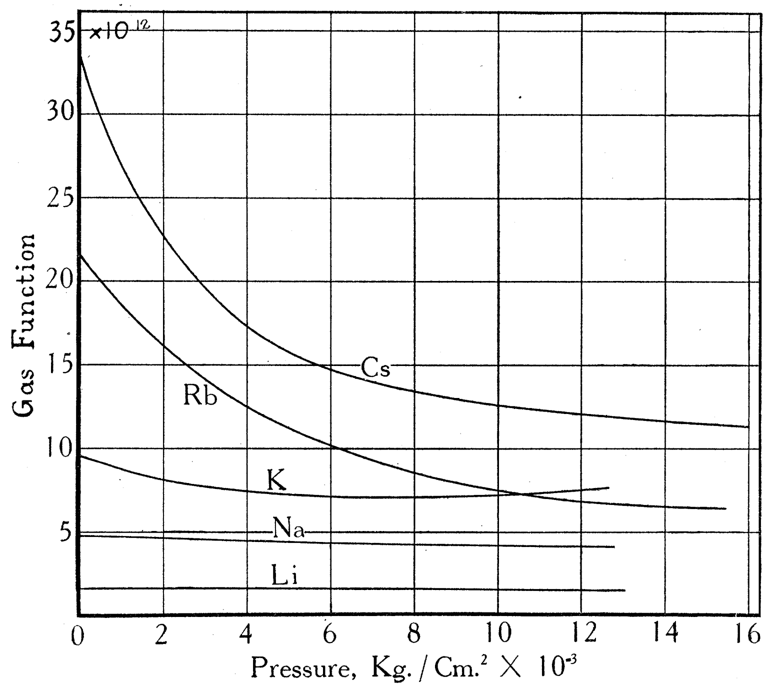

Fig. 6. The "gas function" $(1/v)(1/v)(\partial v/\partial p)_T$ of the alkali metals as a function of external pressure. If the metals acted like a perfect gas of electrons and nuclei, the gas function would have the constant value 24×10^{12}.

Apart from this experimental evidence, we may obtain some theoretical light on the question of the ultimate behavior under exceedingly high pressures from a theorem due to Schottky.[7] He finds for any system in which there are forces between the elements given by the ordinary inverse square laws of electromagnetism and in which the elements move under these forces as if they had mechanical mass, whether or not the motion is in addition subjected to quantum forces, the following equations:

$$\left(\frac{\partial \bar{L}}{\partial p}\right)_\tau = 3v + \tau\left(\frac{\partial v}{\partial \tau}\right)_p + 4p\left(\frac{\partial v}{\partial p}\right)$$

$$\left(\frac{\partial \bar{E}}{\partial p}\right)_\tau = -3v - 2\tau\left(\frac{\partial v}{\partial \tau}\right)_p - 5p\left(\frac{\partial v}{\partial p}\right)_\tau ,$$

where $\bar{L}$ is the average internal kinetic energy of motion of the elements, and $\bar{E}$ is the average electromagnetic potential energy. The total internal energy $\bar{U}$ of the system is of course given by $\bar{U} = E + \bar{L}$. The equations in the form above were not given by Schottky, but may be deduced from equations given by him by using the ordinary thermodynamic relation

$$\left(\frac{\partial \bar{U}}{\partial p}\right)_\tau = -\tau\left(\frac{\partial v}{\partial \tau}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_\tau .$$

At 0°K we have rigorously

$$\left(\frac{\partial \bar{L}}{\partial p}\right)_\tau = 3v + 4p\left(\frac{\partial v}{\partial p}\right)_\tau$$

$$\left(\frac{\partial \bar{E}}{\partial p}\right)_\tau = -3v - 5p\left(\frac{\partial v}{\partial p}\right)_\tau .$$

These relations are also approximately true at other temperatures, for on substituting numerical values for ordinary solid metals it appears that the term $\tau(\partial v/\partial \tau)_p$ is unimportant. Now in the equations as last given the term v is positive and $p(\partial v/\partial p)_\tau$ is negative. At zero pressure only the term v contributes, and $\bar{L}$ increases with increasing pressure and $\bar{E}$ diminishes. But with increasing pressure v diminishes and $p(\partial v/\partial p)_\tau$ increases. Will the second term eventually become larger than the first? We attempt to answer this by plotting $-(p/v)(\partial v/\partial p)_\tau$ against pressure for the five alkali metals. Fig. 7 shows the result. If $-(p/v)(\partial v/\partial p)_\tau$ becomes equal to 0.6, the direction of variation of $\bar{E}$ changes, and if it reaches 0.75, the direction of variation of $\bar{L}$ changes.

---

[7] W. Schottky, Phys. Zeits. **21**, 232 (1920).

Again K is the most suggestive metal. For it, $(p/v)(\partial v/\partial p)_T$ is nearly linear against pressure; as a matter of fact at low pressures the curve is slightly concave toward the pressure axis, but at high pressures it becomes slightly convex. $(p/v)(\partial v/\partial p)_T$ therefore rises at an accelerated rate as pressure increases, and the critical value 0.6 will be reached at a pressure near 30000 kg. The curves for the other metals are also flattening out at a rapid rate, so that is it probable that for all the alkalies the critical value will be eventually exceeded.

What now is the significance of the change of L and E? Initially the state of affairs is plain. In general an increase of L means an increase of rapidity of motion of the electrons in their orbits, which means an approach on the average to the attracting nuclei. The same approach to the nuclei which increases L brings the electrons into stronger parts of the fields of the nuclei and thus at the same time provides for the decrease of E. This approach to the nuclei may be thought of as signifying a compression of the atoms under pressure, as Schottky suggested, or it may be thought of as follows. As we proceed through the series of the chemical elements from simpler to more complex, it is well recognized that the electron orbits penetrate more and more deeply toward the nucleus, and at the same time become more eccentric. The same sort of thing may very naturally be produced also when we push the electron orbits into closer juxtaposition by increasing pressure, so

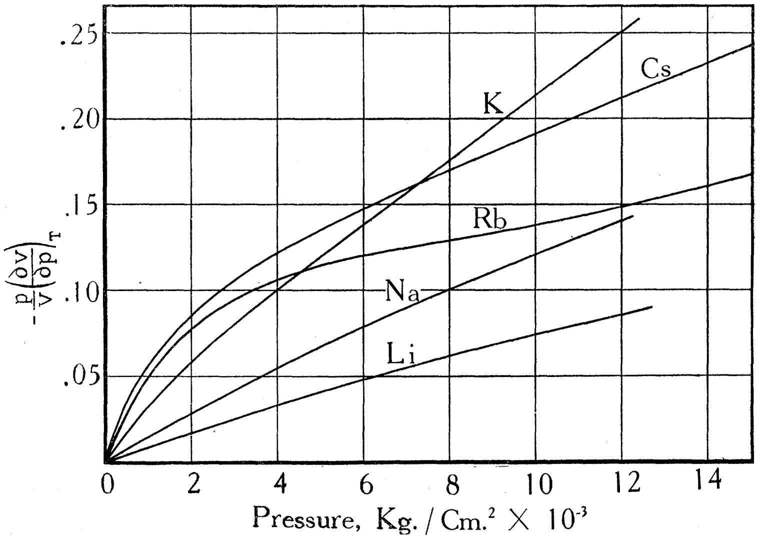

Fig. 7. The function $-(p/v)(\partial v/\partial p)_T$ of the alkali metals as a function of external pressure.

that the initial increase of L and decrease of E with increasing pressure is accounted for by a deeper penetration of the orbits toward the nuclei. But now at higher pressures, how are we to account for a decrease of L and an increase of E, if according to our argument this means orbits described at greater distances from the nuclei? The difficulty is overcome if the electron orbits break down, allowing an approach to a more uniform distribution in space of electrons and nuclei. The electrons now do not penetrate so closely to the attracting nuclei, so that on the average L is smaller and at the same time E increases, both in spite of a continued decrease of total volume. But this sort of break-down means an approach to the condition of a gas. It thus appears that the dilemma to which Schottky's theorem, in conjunction with the experimental behavior of the compressibility of the alkali metals, forces us, is resolved by a break-down of the quantum orbits at sufficiently high pressures, and an approach to the condition of a gas.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
October 4, 1925.