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The known, steady state, pressure-temperature field available for scientific exploration today is given approximately by Fig. 1. The so-called "new-area" was opened for study by the author's design of an apparatus called the "Belt." It was in this apparatus that the author succeeded in making diamonds from "carbonaceous material" at the General Electric

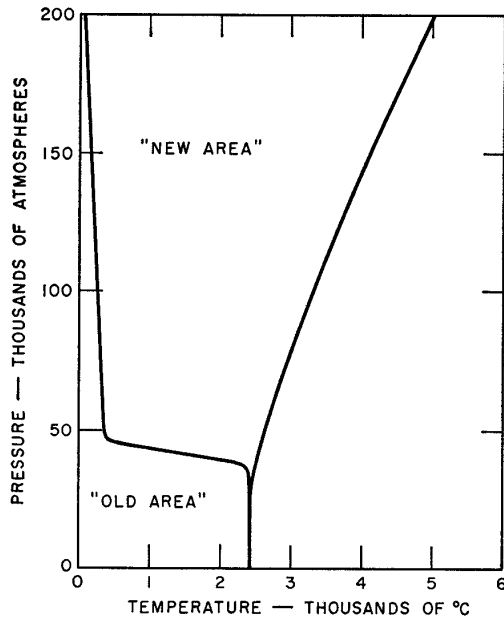


FIGURE 1. Comparison of the old pressure temperature region with the new region now available.

Research Laboratory late in 1954. Unfortunately (for those of us who are anxious to explore this new area) the apparatus is unavailable. It has been classified secret by the U.S. Government because of the importance of industrial diamonds to our national defense.

Comparison of Compressive Energy with Heat Energy

The extent of the changes produced in a mole of matter by its interaction with energy is qualitatively proportional to the quantity of energy put in. In the case of heat energy, the energy put into a system is measured as $\int C_dT + \Sigma \Delta E$ latent. In the case of compressive energy the energy put into a system is measured as

$$\int PdV = V_0 \int Pd\left(\frac{\Delta V}{V_0}\right)$$

The heat capacity of water as a function of temperature from 0 to 1000 degrees K is shown in Fig. 2. The area under the curve plus the latent heats of fusion and vaporization equals about 20,000 calories per mole which, then, is the heat energy put into the H₂O system in

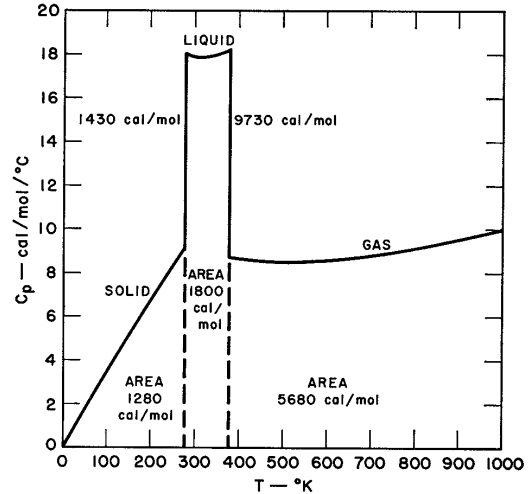


FIGURE 2. Heat capacity vs. temperature for water.

raising its temperature from 0 to 1000 degrees K at 1 atmosphere pressure.

The area under the upper curve of Fig. 3 gives the energy put into a mole of Rb metal in increasing the pressure on the material from 1 to 100,000 atmospheres. This energy equals 25,400 calories per mole. The area under the

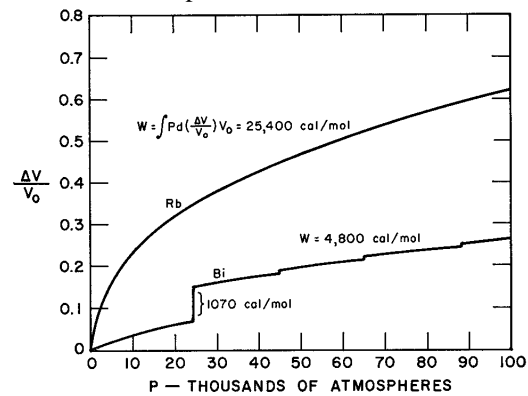


FIGURE 3. Relative change in volume vs. pressure for Rb and Bi.

lower curve gives 4800 calories for compressing bismuth to 100,000 atmospheres.

A comparison of the energies involved in the two cases just cited indicates that pressures of 100,000 to 200,000 atmospheres could cause

energy changes in condensed systems of the same order of magnitude as those brought about by temperature changes of 1000 to 2000 degrees K; i.e., these are the energies involved in ordinary chemical reactions. One can expect, then, a variety of changes to be produced in matter by these pressures comparable in number and scope to those changes produced in matter by these temperatures. One cu cm kilatmosphere per mole is equivalent to 12.19 degrees (where degrees is equal to the energy divided by k).

The broad, general effects of pressure and temperature are diametric opposites. The application of increasing temperature to a solid system causes the atoms to increase their average distance apart. The solid eventually passes through a liquid to a gaseous phase so that the final result of sufficiently high temperature, (where $P \sim 1$ atmosphere) is that the atoms become separated by large distances and occupy only a small portion of the total volume. On the other hand, increasing pressure causes the average distance between atoms to decrease. Pressure (at ordinary temperatures) can cause a gas to condense to a liquid and then become a solid. Further increase in pressure can cause collapse of electronic shells and eventually (in theory at least) pressures of the orders of billions of atmospheres can cause nuclei to be forced within the critical distance of $\sim 10^{-13}$ cm where nuclear fusion will occur.

Thermodynamics, Reaction Rates, and Pressure-Temperature Effects

To produce a chemical change, both the thermodynamic free energy and the free energy of activation for the rate process must be favorable. A system is characterized thermodynamically when the pressure, temperature, volume, and specific heat as a function of temperature are known. The rate process is similarly characterized when the same quantities are known for the activated state. Suppose we are interested in a reaction $A \rightleftharpoons B$, where A represents any number of reactants and B represents the product or products desired. The reaction becomes increasingly favorable thermodynamically as the free energy ΔF for the reaction as written becomes less than zero. We may set $\Delta F = 0$ and write an equation

$$P = T \frac{\Delta S}{\Delta V} - \frac{\Delta E}{\Delta V}.$$

A plot of P vs. T gives a plot as shown in Fig. 4 where the slope of the line equals ΔS and the P -axis intercept equals $\Delta E/\Delta V$.

The reaction, $A \rightleftharpoons B$ becomes increasingly favorable (thermodynamically) in P - T regions above this line whereas the reverse reaction

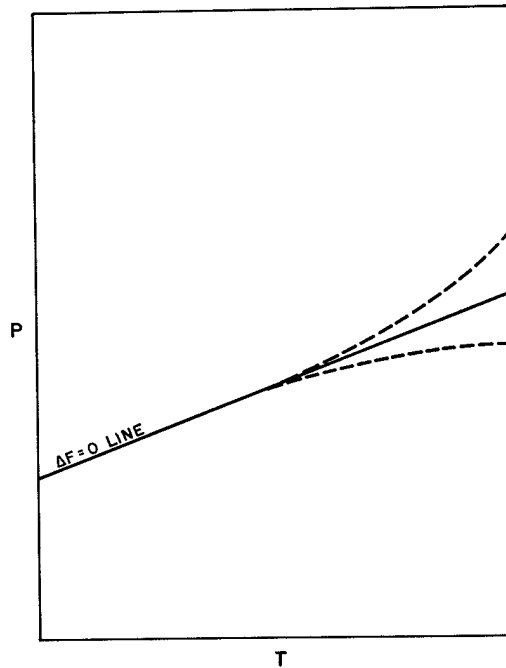


FIGURE 4. Free energy equals zero line on pressure-temperature diagram.

$B \rightleftharpoons A$ becomes increasingly favorable below the line. Actually, ΔS , ΔV , and ΔE are not constants but depend on P and T so that the $\Delta F = 0$ line can deviate in either direction from the straight line as shown by the dashed curves of Fig. 4. For reactions in which ΔF is to be thermodynamically favorable by the application of high pressure, ΔV and ΔS are in general negative.

We may, for the reaction $A \rightleftharpoons B$, decide that a minimum amount of B must be produced within a given time in order that the reaction be of interest or of use to us. If a minimum rate of m moles per second is set, an equation for the elementary rate determining step can be written:

$$m = (kT/h)e^{-\frac{\Delta F^\ddagger}{RT}} \text{ where}$$

$$\Delta F^\ddagger = P\Delta V^\ddagger + \Delta E^\ddagger - T\Delta S^\ddagger$$

or by rearrangement and substitution:

$$P = \frac{RT}{\Delta V^\ddagger} \ln T - \frac{RT}{\Delta V^\ddagger} \ln \frac{k}{mh} + \frac{\Delta S^\ddagger}{\Delta V^\ddagger} T - \frac{\Delta E^\ddagger}{\Delta V^\ddagger}$$

$$\text{let } \ln \frac{K}{mh} = C, \text{ then } P$$

$$= \frac{R}{\Delta V_{\ddagger}^{\ddagger}} \left(T \ln T + \left(\frac{\Delta S_{\ddagger}^{\ddagger}}{R} - C \right) T - \frac{\Delta E_{\ddagger}^{\ddagger}}{R} \right)$$

When DV_{\ddagger}^{\ddagger} is positive, a plot of P vs. T for the above equation gives a curve of the general type

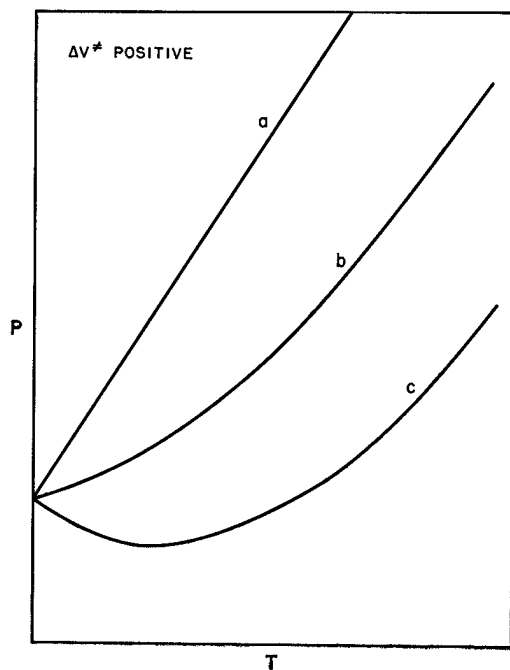


FIGURE 5. Minimum rate curves for positive $\Delta V_{\ddagger}^{\ddagger}$ on pressure-temperature diagram.

(a), (b), or (c) of Fig. 5. The following generalizations can be made concerning these curves.

- (1) The steepness of the ascending portion of the curve depends on $R/DV_{\ddagger}^{\ddagger}$ (the smaller DV_{\ddagger}^{\ddagger} , the steeper and more (a) like).
- (2) The position of the minimum is given by

$T_{min} = e^{\left(C - \frac{\Delta S_{\ddagger}^{\ddagger}}{R} \right)}$, therefore, the smaller DS_{\ddagger}^{\ddagger} the larger the T at which the minimum occurs and hence the curve tends to be (c) like.

- (3) The shift along the P axis is controlled by $DE_{\ddagger}^{\ddagger}/R$. The larger the $(+DE_{\ddagger}^{\ddagger})$ the greater the downward shift of the curve.

In a $P-T$ region below (a) curve of Fig. 5, the elementary rate process go faster than the pre-chosen value determined by C . Above the curve the rate is slower. A curve, such as (a), (b), or (c) of Fig. 5, is valid and has meaning only in a $P-T$ region where the thermodynamic DF is negative; i.e. in the region above the $DF = 0$ curve of Fig. 4. Only in these regions is it permissible to neglect the rate of the back reaction $B \rightarrow A$ as has been done in this treatment. Therefore, if the $DF = 0$ curve and the minimum

rate curve are plotted on the same graph, the region of overlap gives the $P-T$ region in which the rate and thermodynamics should be favorable for formation of the products. The situation is

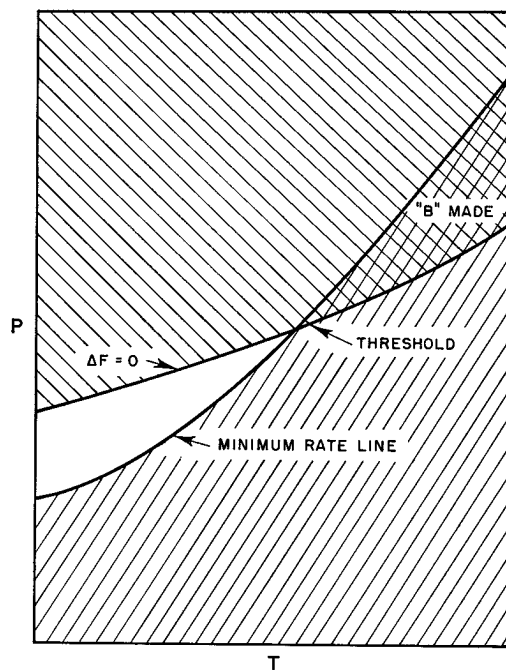


FIGURE 6. Free energy equals line and minimum rate line on pressure-temperature diagram showing region of overlap where products are formed.

shown in Fig. 6. Actually DV_{\ddagger}^{\ddagger} , DS_{\ddagger}^{\ddagger} , and DE_{\ddagger}^{\ddagger} are somewhat dependent on P and T as were their counterparts in the thermodynamic considerations. This dependence modifies the $P-T$ curve but does not change its general character.

The observed rate of a reaction may differ from the rate of the elementary process such as that just considered. This may be due to geometrical, nucleation or other considerations. For instance, in a solid-state phase change, the number of atoms in a position to react may be only a small fraction of the atoms present. However, these "key" atoms can, when they ascend the potential barrier, place additional atoms in a position to ascend a much lower barrier so that the observed rate proceeds several times faster than that at which the "key" atoms pass over their barrier. In this case C in the rate equation would be a larger number and the minimum rate curve would tend to be more like Fig. 5 (c).

When DV_{\ddagger}^{\ddagger} is negative, the minimum rate curves are of the type shown in Fig. 7. In this case, the rate goes faster than the pre-chosen

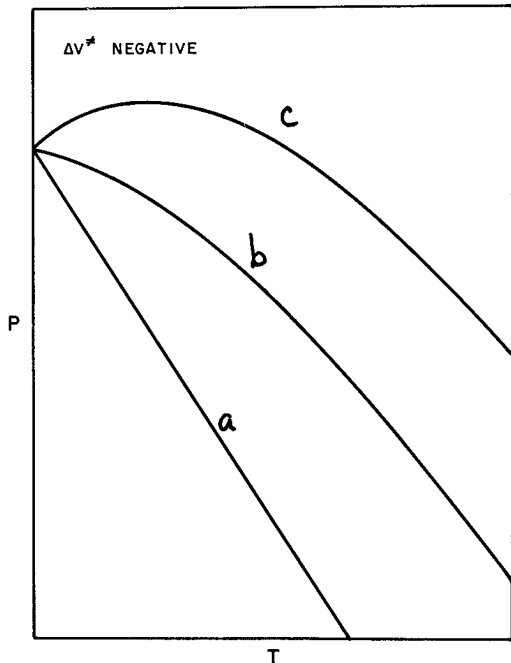


FIGURE 7. Minimum rate curves on pressure-temperature diagram for ΔV^\ddagger negative.

value in a $P-T$ region above the curve. The following considerations apply to Fig. 7.

- (1) The steepness of the descending portion of the curve depends on R/DV^\ddagger (The smaller $|DV^\ddagger|$, the steeper and more like (a))
- (2) The position of the maximum is given by

$T_{max} = e^{\left(C - \frac{\Delta S^\ddagger}{R} \right)}$, therefore the smaller DS^\ddagger , the larger the T at which the maximum occurs and hence the curve tends to be more like (c).

- (3) The larger the $+DE^\ddagger$, the greater the shift of the curve upward.

Graphite-Diamond Conversion

Let us explore the possibility of the direct conversion of graphite to diamond at high pressure and high temperature, along the lines discussed above. The $DF = 0$ curve for $A \leftrightarrow B$, where A is graphite and B is diamond, is shown in Fig. 8. Above this curve, diamond is the thermodynamically preferred form. This curve has been calculated from thermodynamic data known only at relatively low pressures and temperatures. The degree of uncertainty concerning its position increases with increased pressure and temperature.

The minimum rate curve was calculated in the following way:

(1) A reasonable working volume for an extremely high-pressure, high-temperature laboratory apparatus is about 0.1 cu cm. If this volume were initially filled with graphite and if 10 percent of 0.01 cu cm were transformed to microscopic diamond uniformly distributed throughout the graphite, x-ray techniques would allow the detection of this diamond. Let us assume that the investigator would be willing to maintain pressure and temperature for one week (604,800 seconds) in order to obtain this much diamond (0.002,92 mole). This corresponds to a rate of conversion of 2.90×10^{15} molecules per second. Therefore $\ln \frac{k}{mh} = C = 15.8$

If the same reaction path is followed in the conversion of graphite to diamond as is followed in the reverse transformation, a study of the readily accessible reaction diamond \rightarrow graphite would give data that could be used in estimating the rate for graphite \rightarrow diamond. Eyring and Cagleⁱ have calculated DV^\ddagger and DE^\ddagger from the published data available. The smallest value of DV^\ddagger allowed by the data is +10 cu cm per mole (the smaller DV^\ddagger , the faster the rate). Internal energy of activation DE^\ddagger , equals +60,000 cal/mole (the heat of vaporization of graphite is 170,000 cal/mole). The largest conceivable value for DS^\ddagger is $\sim +34 \times 60,000/170,000 = +12$ E.U. where 34 is estimated entropy of vaporization of graphite (the larger DS^\ddagger , the faster the rate).

Substitution of these values in the rate equation gives the minimum rate curve (a) shown with the $DF = 0$ curve of Fig. 8.

Curve (a) does not intersect the $DF = 0$ curve at any point. Increasing DS^\ddagger to 24 E.U. (a most improbable value) gives curve (b). This

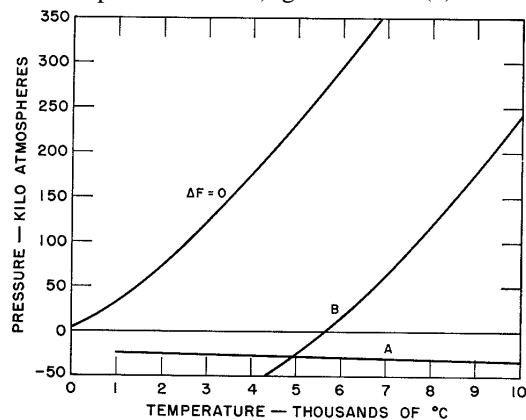


FIGURE 8. Free energy equals zero line and minimum rate line of graphite-diamond synthesis on a pressure-temperature diagram. A is graphite and B is diamond. $\Delta S^\ddagger = 12$ E.U., $\Delta S^\ddagger = 24$ E.U.

curve also falls short of intersecting the $DF = 0$ curve. These results would indicate that diamond can not be formed directly from graphite. Experiment confirms this conclusion at pressures to 100,000 atmospheres and temperatures to approximately 3000 degrees C.

Systems of Interest for Study at High Temperature, High Pressure

In general, almost any system is worthy of investigation in the "new" high-pressure, high-temperature area. The most fruitful field, however, will probably be found in the investigation of systems with normally open structures. This includes crystals whose structures are not closely packed and systems with "open" electronic structures such as the elements of the first transition group which have unfilled $3d$ orbitals. I anticipate continuing work in the following areas:

Melting Point as a Function of Pressure

The melting points of substances are profoundly affected by pressures of the order of 200,000 atmospheres. For example note the 600 degrees lowering of the melting point of germanium recently reportedⁱⁱ. Of course, germanium is an exception to the general rule that melting point of some refractory materials has been increased by well over 1000 degrees C by the application of extremely high pressures. This fact makes it possible to work at higher temperatures at high pressure than would be possible at one atmosphere. As a matter of fact, it is quite possible to work with a "liquid" refractory under high pressure conditions. A liquid can flow only if it contains "holes" into which the molecules can move. At 200,000 atmospheres the number of holes in a molten refractory can be severely reduced and the material will be extremely viscous.

Work on the melting points of substances at high pressure has considerable significance in that it should throw some light on the old question as to the nature of the melting point curve as pressure is indefinitely increased. Is there a critical point between liquid and solid analogous to the gas liquid situation? Is it impossible to melt some substances, such as graphite?

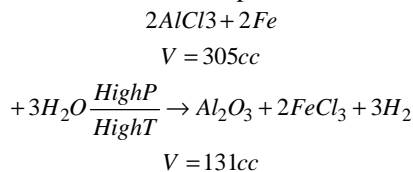
Mineral Synthesis

An interesting result of recent high-pressure, high-temperature work is the synthesis of a new dense silica, Coesite, not found in

natureⁱⁱⁱ. I have experimented with sodium silicate solutions at pressures to 100,000 atmospheres at temperatures near 450 degrees C in an effort to produce a silica phase even more dense than Coesite. No new phase has been found. The experiments indicate a rather steep threshold pressure for Coesite formation at $32,00 \pm 2000$ atmospheres. Near 60,000 atmospheres the external habit of the Coesite crystals is changed. Below 60,000 atmospheres crystals tend to grow singly with hexagonal outlines. From 60,000 to 100,000 atmospheres, the crystals tend to grow in a planar group containing four hexagons. I have found it possible to produce Coesite directly from quartz (without catalyst or mineralizer such as water) at pressures in the vicinity of 100,000 atmospheres and temperatures over 2000 degrees C. Mineral growth is greatly facilitated by the use of a catalyst (or, as some may prefer, a solvent or mineralizer). At high pressure, high temperature all the oxides show sufficient solubility in water that they can be regarded as a universal catalyst for mineral formation. A very wide array of materials are effective in catalyzing mineral synthesis from the oxides. These include urea, ammonium salts, carbonates, phosphates, sulphates, nitrates, borates, and, of course, water.

To synthesize a mineral, the required oxides are placed with the catalyst, the pressure is raised to the desired value followed by the application of the desired temperature. Temperature is then lowered followed by pressure reduction.

It is not always necessary nor desirable to use oxides. Pure metals or their salts will often do. Hydrogen is often produced if the metals are used, but manages to escape through the hot container. This continuous removal of hydrogen at high-pressure, high-temperature makes it possible to always drive the reaction in the desired direction because of the very favorable volume decrease, for example:



Almost any mineral with a known structure, not in closest packing, presents possibilities for production of a more dense phase at high-pressure, high-temperature. Often the more dense phase will "lock-in" and remain stable when temperature is reduced to normal followed by reduction to normal pressure.

The production of many new minerals that incorporate heavy elements and the less familiar elements of the periodic table presents a particularly fruitful area for research.

Of course laboratory mineral synthesis has great import in the field of geology. Future work at extreme pressure and temperature will do much to give new information on the interior of the earth and geological processes.

The Synthesis of Hard Materials

Man-made industrial diamonds will, I'm sure, be readily available commercially within a few years. Diamond is, of course, the hardest material presently known to man. What are the possibilities of making a material harder than diamond? The answers can be found in the consideration of the qualities that make materials macroscopically hard. A necessary condition is high concentration of bond energy; i.e., high cohesive-energy density (ced). A subsidiary requirement is high bond symmetry in three dimensions. Diamond and graphite have the highest cohesive energy densities of any known substances. Graphite is soft, however, because it fails to meet the symmetry requirement. Since

cohesive energy density equals $\Delta \frac{E_{vap}}{V}$ materials with high heats of vaporization and small molar volumes will have high ced's. Compounds with the highest ced's are to be found among the borides, carbides, nitrides, oxides, and sulfides. Some of these materials do not have high-three-dimensional bond symmetry. Since high pressure tends to force atoms into positions that give maximum symmetry, subsection of selected borides, carbides, nitrides, etc. to high-pressure, high-temperature, might give a stable structure of higher hardness. For example, boron nitride, which has a graphite-like structure and is slippery and soft, might be transformed into a hard, diamond-like material by use of proper catalyst at high-pressure, high-temperature.

Pressure Effects on Electronic Configurations

It is possible that extremely high pressures might affect the stability sequence for atomic orbitals. Such effects might most readily be detected in changes of electrical conductivity. Such a situation might exist in the phenomenal increase of electrical resistance of cesium discovered by Bridgman^{iv} (Cesium has completely empty 5d orbitals). He found the resistance to rise rapidly to a sharp cusp near 54,000 atmospheres followed by a rapid drop. The resistance found at 54,000 was 11 times the

resistance at one atmosphere. No volume discontinuity is associated with this sharp cusp. Experiments I have performed with cesium give a much sharper cusp than that obtained by Bridgman. Indeed it seems that if the necessary pressure could be fixed with enough precision, the peak of the cusp would show a resistance of many powers of ten higher than that at one atmosphere. Immediately on passing this sensitive pressure point the electrical resistance drops rapidly to a low value again—a most interesting phenomena. Incidentally, this sharp cusp makes an ideal pressure-reference point.

I think more of this type phenomena is to be expected at pressures near 200,000 atmospheres and above. The effect of high temperature on these phenomena should be studied. It might be possible to synthesize compounds from elements with empty atomic orbitals in which these elements display unknown and unexpected bonding behavior. Some of these structures may remain stable following return to ordinary conditions.

The conversion of ammonia to metallic form at pressures somewhat over 200,000 atmospheres will soon become a reality. Hydrogen is expected to become metallic near 500,000 atmospheres and minerals such as olivine near 1,500,000 atmospheres. These phenomena will result from pressure effects on electronic energy levels.

ⁱ Eyring and Cagle, *Zeits. für Electrochem.* 56, 480-3 (1952).

ⁱⁱ H.T. Hall, *J. Phys. Chem.* 59, 1144 (1955).

ⁱⁱⁱ L. Coes, Jr., *Science* 118, 131-2 (1953).

^{iv} P.W. Bridgman, *Proc. Am. Acad. Arts & Sci.* 81, (4) 165-251 (1952). See page 193.