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Theoretically Interesting Aspects of High Pressure Phenomena

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I. INTRODUCTION

THE invitation of the Editors of *Reviews of Modern Physics* to write some account of the theoretical aspects of high pressure phenomena was one which I was glad to accept because it seems to me that the time is now approaching when theoretical physics may hope to investigate the problems of this field with good prospects of success. Until very recently the condensed phases of matter, solid and liquid, have appeared too complicated to make it worth while to spend much effort in acquiring an understanding of them, particularly as long as the much more profitable field of the investigation of matter in its rarefied condition, as in vacuum tube phenomena of all sorts, had not yet been fully exploited. But now our understanding of the atomic, as distinguished from nuclear, phenomena presented by matter in its rarefied states is rapidly becoming satisfactory, and in a sense exhausted, so that an attack on the problem of the condensed states is obviously next on the program. Indeed already a very considerable degree of success has rewarded theoretical attack in this field, as, for example, in our rapidly growing theory of the metallic state in general and of the electrical properties of solid conductors in particular. The condensed state, *par excellence*, is obviously presented by matter under high pressure, so that, to say the least, our understanding of the condensed state cannot be regarded as satisfactory until we can give an account of the effect of pressure on every variety of physical phenomena. This we can at present do in very few cases indeed.

There are two aspects of theoretical concern with high pressure phenomena: a broader and a narrower aspect. From the broad point of view the eventual problem is to work out theoretical explanations of all known high pressure phenomena, and to predict the result of fresh extensions of experiment to pressures and groups of phenomena not yet reached. It must not be assumed too easily, I think, that this is a task of no particular interest, and that the problem is merely the problem of overcoming the complications of an analysis, the fundamentals of which are already completely understood. Such is without doubt the attitude of many theoretical physicists; in fact it seems to be a thesis of theoretical physics in its treatment of matter in bulk that there are no "emergent" properties, or in other words, that all the properties of aggregates of atoms can be found from an exhaustive knowledge of the properties of the isolated atoms. There is a sense in which this thesis may be regarded as a mere tautology, because I suppose no one would deny that it would be possible to put enough parameters into the equations for the individual atoms or electrons to reproduce by some more or less complicated kind of theory all the properties of combinations of atoms in bulk. But the thesis does have real content if one understands it to mean that it is possible by *experiments* on isolated atoms, or atoms in the rarefied condition, to determine all the parameters necessary to describe all the properties of condensed assemblages of atoms. No doubt the impulse of many would be to say that in experiments involving nuclear bombardment and breakdown we are dealing with individual atoms under conditions of much greater intensity of force than are ever encountered in condensed aggregates of atoms, so that there is no reason to think that such experiments will not give all the effective atomic parameters. But on the other hand it must be remembered that in highly condensed phases the character of the force to which the atom is subjected is different from that in collision experiments, the attack on the atom being now a more or less symmetrical and simultaneous attack from all sides, so that there may be a possibility of new kinds of effect. So far as I know no theoretical intimation was given, before the experimental evidence of astronomy, of the possibility of the existence of matter in conditions of density of the order of 100,000. Our persistent difficulty in understanding superconductivity of metals may also be significant. At any rate, I believe that it must be conceded as a matter of pure logic that the thesis of non-emergent characteristics cannot be securely established until at least the possibility of a theoretical deduction of all the properties of matter in the condensed condition has been established; what one's feeling will be as to the interest or profitableness of actually producing such detailed explanations will be largely a matter of taste and temperament.

The narrower aspect of the high pressure problem concerns the extent to which we can understand high pressure phenomena in terms of recent wave mechanics pictures of atomic behavior and interaction. This is the aspect of the problem which will serve as the background of our present discussion. It would have been desirable if this paper could have been written by someone who has made actual contributions to our understanding in terms of wave mechanics of the behavior of condensed phases, instead of by one whose qualification is merely an acquaintance with the nature of the experimental material. I shall have to content myself, therefore, with pointing out those aspects of the phenomena which are simplest and therefore where theoretical attack may most reasonably anticipate success, or those aspects which seem to me most suggestive and of intrinsic interest. I believe that our theoretical mastery in this field is not yet so far advanced but that a careful pondering of the qualitative significance of various general types of pressure phenomena will be profitable. I have this feeling because a number of years ago I had arrived at various qualitative pictures, as of the phenomena of electrical conduction or of polymorphic transition, which were somewhat at variance with the pictures common at the time, but which are becoming more and more justified by wave mechanics.

The experimental material which must form the basis of our present theorizing is almost entirely confined to the range from 10,000 to 20,000 kg/cm^2, although a few data have been obtained at somewhat higher pressures and there is the possibility of more in the future. These pressures are of the order of magnitude of the internal pressures which various theories have agreed in assigning to ordinary condensed phases;

such internal pressures vary from 3000 or 4000 kg/cm^2 for organic liquids and 10,000 or 20,000 for the more compressible metals, to a few hundred thousand for the most incompressible substances like iridium and diamond. Furthermore, the volume changes producible by pressures in the experimental range are materially greater than the volume changes due to temperature on cooling from room temperature to 0°K. One would appear to be justified therefore in anticipating that an adequate understanding of even the effects of pressure known at present would react beneficially on our general understanding of matter in the condensed state. By the application of pressure we have the tool, as it were, for producing artificially a great variety of new condensed states of matter.

In the following I shall not attempt to give more than the very briefest possible indication of the nature of the experimental material and refer the reader to my book *The Physics of High Pressure* published by Bell in England and Macmillan in this country, whenever he feels the need of more detailed acquaintance with the data.

II. Atomic Changes Under Pressure

Perhaps the first and most important question that confronts one on entering this field is whether it is legitimate to treat the atoms as fixed units, or whether pressures in the experimental range produce important changes in the atoms themselves. A rough answer is suggested to this question by means of an important theorem, which has been much neglected, originally due to Schottky[1] and proved on the basis of classical mechanics. Later Born, Heisenberg and Jordan[2] showed that essentially the same situation holds in wave mechanics, and the theorem has recently been re-emphasized and applied to some molecular problems by Slater.[2]

Schottky's theorem states that in any system controlled by internal electromagnetic forces, whether there are or are not in addition constraints imposed by quantum conditions, as for example, systems composed of molecules and atoms built of nuclei and surrounding electronic atmospheres, and on which in addition to the electromagnetic forces an external hydrostatic pressure, p, acts, the following relations hold:

$$dT = -dE + 3d(pv), \tag{1}$$

$$dV = 2dE - 3d(pv). \tag{2}$$

Here T is the average internal kinetic energy and V the average internal potential energy, the averages being taken over a time interval long enough to give constancy, E is the total energy of the system and v the volume.

By thermodynamics we have:

$$dE = \left[C_p - p\left(\frac{\partial v}{\partial \tau}\right)_p\right]d\tau - \left[\tau\left(\frac{\partial v}{\partial \tau}\right)_p + p\left(\frac{\partial v}{\partial p}\right)_\tau\right]dp.$$

Eliminating dE gives:

$$dT = \left[4p\left(\frac{\partial v}{\partial \tau}\right)_p - C_p\right]d\tau + \left[3v + \tau\left(\frac{\partial v}{\partial \tau}\right)_p + 4p\left(\frac{\partial v}{\partial p}\right)_\tau\right]dp, \tag{3}$$

$$dV = \left[2C_p - 5p\left(\frac{\partial v}{\partial \tau}\right)_p\right]d_\tau - \left[3v + 2\tau\left(\frac{\partial v}{\partial \tau}\right)_p + 5p\left(\frac{\partial v}{\partial p}\right)_\tau\right]dp. \tag{4}$$

Apply these equations to ordinary solid substances in the experimental range of pressure, and consider first the variation of T with pressure at constant temperature, paying attention only to orders of magnitude. $\tau(\partial v/\partial \tau)_p$ is evidently small compared with $3v$ and may be neglected. The most compressible solid metal is caesium; at 15,000 kg/cm^2 $4p(\partial v/\partial p)_\tau$ has the value 0.6 and $3v$ is equal to 2, so that $(\partial T/\partial p)_\tau = 1.4$ for Cs at 15,000. For lithium, on the other hand, the compressibility is much less, and $(\partial T/\partial p)_\tau$ at 15,000 has the value 2.4, the derivative referring in both cases to that quantity of matter which occupies 1 cm^3 at atmospheric pressure. Most solids are much less compressible even than this, so that we would not be making an error on the average much more than 10 or 15 percent if we set $\partial T/\partial p \approx 3$ in the experimental range of pressure. Hence at 20,000 kg/cm^2 we have at once $T_{20,000} - T_0 \approx 60,000$ kg/cm $\approx 3.5 \times 10^{22}$ electron volts. Expressed per atom, this becomes $3.5 \times 10^{22} \times 1.66 \times 10^{-24}$ $\times$at. wt./dens. ≈ 0.06 at. wt./dens., or

$$T_{20,000} - T_0 \approx 0.06 \times \text{at. vol. in electron volts per atom.} \quad (5)$$

For elements of high atomic volume this approximation is in general less good than for elements of low atomic volume, because compressibility is highest for high atomic volumes, and the actual value is less than the approximate value by a term proportional to the compressibility. In the ordinary range of temperature the specific heat of a solid is given approximately by Dulong and Petit's law, which ascribes three degrees of freedom to the kinetic energy of translational motion of the atom as a whole, and three degrees to the potential energy of position. Hence to this degree of approximation the kinetic energy of translation of the atoms is constant, independent of pressure, at constant temperature, and the change of kinetic energy with pressure which is given by Eq. (5) is change of internal kinetic energy of motion of the electrons inside the atoms. For lithium at 20,000 this is 0.8 e.v. per atom, for bismuth 1.3, for aluminum 0.6, and for iron 0.4. These energy changes are thus considerably smaller than the ionization energies of the atoms, but they are nevertheless of the same order of magnitude, being 18 percent for bismuth, and lead to the conclusion, I believe, that one should at least entertain the idea that appreciable internal changes may be produced by experimental pressures in the outer electron orbits of the atoms.

It is to be noticed that an increase of the internal kinetic energy of the electrons in their orbits such as we have just found means a shrinkage of the orbits, that is, a compression of the atom, assuming the same relation to hold in the condensed phase between atomic radius and electronic energy as holds for the isolated atom. The orbital shrinkage is evidently the theoretical version of the "compressible atom" first insisted upon by Richards and which has seemed to me to be demanded by many qualitative aspects of my measurements of compressibility.

The order of magnitude of the changes of internal kinetic energy just calculated shows that in the range of pressure at present realizable no very drastic rearrangements in the structure of the atom are to be anticipated, unless perhaps there may be a few cases in which the atom is already near some critical configuration. Drastic changes may, however, perhaps be expected at pressures of the order of 100,000 kg/cm^2. Consideration of what the nature of these effects may be will be postponed until the end of the paper; in the meantime we shall be concerned with the present experimental range in which changes in the atom itself may be expected to be small, although appreciable.

III. VOLUME CHANGES AND THE "LAW OF FORCE"

Doubtless the simplest of all the effects produced by hydrostatic pressure is the uniform change of volume of a fluid or an isotropic solid, and it is natural that theory should first attack this problem. The simplest of all condensed phases from the theoretical point of view is an ionic lattice of the NaCl type, and as is well known, theoretical attack on this problem, largely at the hands of Born,[3] has been successful up to a certain point. The ionic lattice is held together by the electrostatic attractions of the ions and prevented from collapsing by a repulsive force due to ionic interpenetration. The attractive force can be completely dealt with in terms of the known lattice structure and the known magnitudes of the ionic charges. The repulsive force is more difficult. In Born's original discussion an attempt was made to give some account of the repulsive forces in terms of the structure of the atom as pictured at that time by Bohr's theory, but this was unsatisfactory because it gave stability only for certain relative orientations of the atoms. The final result was that the repulsive force had to be treated from an almost purely empirical point of view, and a repulsive force acting as some unknown inverse power of the distance between atomic centers was assumed, with an unknown coefficient of proportionality. Two conditions, one on the size of the lattice at 0°K and the other on the compressibility, permitted a determination of the two parameters of the empirical law of repulsion. For most of the alkali halides the repulsive force turned out to be approximately as the inverse ninth power of the distance between atoms. The complete law of force thus having been assumed and its parameters determined, it was possible to carry the computation further and find how the compressibility should vary with pressure. It was calculated in this way that the compressibility decreases with increasing pressure, and to this extent there was agreement with experiment, but numerically the agreement was so far from satisfactory that it was obvious that a repulsive force of the form assumed could serve as an approximation over only a very narrow range when this type of phenomenon was concerned. The wave mechanics picture of the atom gives a more satisfactory basis than did Bohr's theory for calculating the repulsive force in terms of the mutual action of interpenetrating electron atmospheres, and Born, in recent revisions of his theory, has given the repulsive force an exponential form, which is the form that results most simply from the mathematics of the wave mechanics picture. But even this modification does not give the correct change of compressibility with pressure, so that again we have a comparatively short range approximation.

Experimentally, the compressibilities of all the alkali halides except RbF, which does not crystallize properly, have been determined up to 12,000 kg/cm^2. In this range the relation between pressure and volume may be represented by a two power expression in the pressure, the two parameters determining the initial compressibility and the variation of compressibility with pressure. In the case of such substances theory would at present have the task merely of reproducing these two parameters. There are, however, many substances for which the volume change in this pressure range is very definitely not representable by a two power series in the pressure, or even by a three or four power series, as for example, the alkali metals, and there are even substances whose compressibility increases with increasing pressure instead of decreasing. For such substances theory will eventually have to reproduce a considerable number of parameters, or discover some type of function better adapted to reproducing the volume than a power series.

In addition to the work of Born and others on the compressibility of ionic lattices there have recently been several calculations of the compressibility of the simplest metals, particularly the alkali metals.[4] Here again it has been found possible to reproduce the initial compressibility with some success, but the variations of compressibility with pressure are very wide of the mark.

One aspect of the method of treatment followed by Born is conventional in practically all derivations of an equation of state, whether or not intended to be applicable to high pressures and condensed phases, namely the assumption of a "law of force" between atoms, a function only of the distance of separation of atomic centers. In view of the failure of all attempts to reproduce more than the first derivative of volume with respect to pressure the question presents itself as to how far the action between atoms in condensed phases under variations of temperature and pressure can be represented by "a law of force." In assuming a law of force of the form, for example, $-a/r^2+b/r^n$, we are evidently maintaining that the behavior of the entire assemblage of atoms can be found by postulating that each atom of every pair of atoms acts on the other with the force given, irrespective of the presence of other atoms, in all orientations (orientation is not a factor for the type of ions just considered, which by wave mechanics have spherical symmetry), and at all distances. The assumption of a law of force of the form given certainly corresponds to the facts from the point of view of one very important first approximation. For two atoms acting on each other with a force of this character may be brought indefinitely close together by the action of sufficiently large forces, that is, such atoms are not rigid but are effectively deformable, as is demanded by many lines of experimental evidence. But the question is, how much further is the approximation represented by such a law valid. One may imagine oneself carrying through the detailed solution of the wave-mechanical problem of the NaCl crystal, for example, finding the complete ψ function, splitting this up into parts corresponding to p, s, d, etc., electrons associated with the different atoms, and then coalescing the results into a final law of force. Into this law of force will certainly enter the distribution of the electrons within the atoms. The law of force may remain good as long as the distribution of electrons remains fixed or as long as the electron distribution depends uniquely on the distance r, as when pressure is changed at constant temperature. But if the electron distribution is not fixed uniquely by r, a possibility which we must recognize if both pressure and temperature are allowed to vary, then we must be prepared to find that the interaction cannot be described in terms of constants and r only, that is, we must be prepared to find that there is no "law of force." Doubtless in a sufficiently narrow range the assumption of a law of force is a valid approximation. We have to consider whether it is a valid approximation in the range of pressure and temperature now open to experiment. We can obtain a qualitative answer to this question by means of Schottky's theorem.

In Eqs. (3) and (4) write as an approximation that the total kinetic energy T is the sum of two parts: one, mass motion of the atom as a whole (T_{at}) and the other kinetic energy of the electrons inside the atom (T_{el}), so that $T = T_{\text{at}} + T_{\text{el}}$. We could in the same way put $V = V_{\text{at}} + V_{\text{el}}$, where V_{at} is the part of the potential energy given by the "law of force" as in the discussion above, and V_{el} is the internal potential energy of the electrons inside the atom. This resolution into two parts should be a fairly good approximation for a simple ionic lattice; for complicated molecular lattices the resolution would be more questionable. We assume further that the substance under consideration approximately satisfies Dulong and Petit's law, which means that $(\partial T_{\text{at}}/\partial p)_\tau = 0$, $(\partial T_{\text{at}}/\partial \tau)_p = C_p/2$, neglecting the difference between C_p and C_v, which is legitimate for condensed phases. At high pressure it is highly probable that the specific heat becomes somewhat less because of the stiffening of the atomic constraints, so that more exactly, $(\partial T_{\text{at}}/\partial p)_\tau < 0$. This will have as a result that the conclusions to follow are in the nature of an understatement rather than an overstatement of the effect of pressure on T_{el}. Combining these results with (3) and (4) now gives at once

$$\left(\frac{\partial T_{\text{el}}}{\partial v}\right)_p = 4p - \frac{3}{2} C_p \Big/ \left(\frac{\partial v}{\partial \tau}\right)_p, \qquad (6)$$

$$\left(\frac{\partial T_{\text{el}}}{\partial v}\right)_\tau = 4p + \left[3v + \tau\left(\frac{\partial v}{\partial \tau}\right)_p\right] \Big/ \left(\frac{\partial v}{\partial p}\right)_\tau. \qquad (7)$$

Let us compare these two derivatives at low pressures, that is, compare $-(3/2)C_p/(\partial v/\partial \tau)_p$ with $[3v + \tau(\partial v/\partial \tau)_p]/(\partial v/\partial p)_\tau$. For NaCl we have the numerical values: $C_p = 0.219$ g cal./g, $(\partial v/\partial \tau)_p = 0.00012$, and $(\partial v/\partial p)_\tau = 42 \times 10^{-7}$, in kg/cm^2 units. Reducing everything to kg/cm^2 units, the two derivatives become, respectively, 2.5×10^5 and 7×10^5. That is, the change of electronic energy internal to the atom is nearly three times as great when a definite change of volume is brought about by a change of pressure as when brought about by a change of temperature. The internal electronic energy may be taken as a rough measure of the internal condition of the atom, and the force with which one atom acts on another depends on its internal condition. It follows therefore that the force between atoms changes differently when the mean distance of separation is changed by a definite amount by the application of pressure and when the distance is changed the same amount by a change of temperature, and that therefore the assumption of a "law of force" to be used in writing out an equation of state, or in writing out an expression for the virial, can be only an approximation. To find just how good an approximation it is to assume a law of force might well be one of the first tasks of a serious attempt to derive an equation of state valid for high pressures. The numerical values for NaCl show that the approximation is less good for changes of pressure than for changes of temperature. Furthermore, the formulas show that the approximation becomes poorer as pressure increases in virtue of the $4p$ term, which has an opposite sign from the other. However, even at 20,000 kg/cm^2 the $4p$ term has become only 33 percent of $(3/2)C_p/(\partial v/\partial \tau)_p$, assuming constancy of $C_p/(\partial v/\partial \tau)_p$. Both $(\partial v/\partial \tau)_p$ and $(\partial v/\partial p)_\tau$ vary importantly with pressure, however, so that actually the variation in the other terms is the important effect at high pressures. As a matter of experiment $(\partial v/\partial p)_\tau$ generally drops off with increasing pressure much more rapidly than $(\partial v/\partial \tau)_p$, so that for this reason also the assumption of a "law of force" is a less valid approximation at high pressures than at low pressures.

The important role played by the shrinkage of the atoms under some conditions is well brought out by another line of argument. Consider the change of total energy brought about by a change of pressure at constant temperature

$$dE_\tau = -\left[\tau\left(\frac{\partial v}{\partial \tau}\right)_p + p\left(\frac{\partial v}{\partial p}\right)_\tau\right]dp.$$

The two terms in this expression are of opposite signs. The term $p(\partial v/\partial p)_\tau$ starts with the value zero, so that at low pressures the sign of dE is determined by $(\partial v/\partial \tau)_p$. That is, the internal energy of all normal substances at first decreases as pressure is applied isothermally, more energy flowing out in the form of heat to counteract for the rise of temperature produced by the compression than is put in in the form of mechanical work by the external pressure. But at high pressures it is a matter of experiment that the term $p(\partial v/\partial p)_\tau$ preponderates, so that at high enough pressures the energy increases as pressure increases, the increase obviously being accounted for mainly by the work done against the repulsive forces of the atoms. The volume at which dE vanishes is the volume at which the attractive and repulsive forces balance. At 0°K the lattice is in equilibrium with all the lattice points at rest (neglecting zero point energy), so that the volume of 0°K at atmospheric pressure should be the volume at which the two sets of forces balance. This is indeed the case, because of 0°K $(\partial v/\partial \tau)_p = 0$ and $dE = -p(\partial v/\partial p)_\tau dp$ for the isothermal at 0°. That is E is a minimum at 0°K at 0 pressure, and with increasing pressure continually increases due to the action of the repulsive forces. If now we assume that the mutual potential energy is a function of volume only, independent of temperature, or amplitude of atomic vibration, which is obviously an approximation, and if we also assume that the translational kinetic energy is a function of temperature only, we would expect that at higher temperature $(dE)_\tau$ would become zero when the pressure had increased sufficiently to reduce the volume to the volume at 0°K at atmospheric pressure. The pressure at which this occurs is obviously $-\tau(\partial v/\partial \tau)_p/(\partial v/\partial p)_\tau$. This pressure I have computed for a number of solids at room temperature, and it is of the order of 10,000 or 20,000 kg/cm^2 for ordinary metals such as silver and iron. The volume corresponding to this pressure is approximately the same as that at 0°K and atmospheric pressure, although somewhat less. For helium, on the other hand, the relative changes of $(\partial v/\partial \tau)_p$ and $(\partial v/\partial p)_\tau$ under pressure are different, $\partial v/\partial p$ approaching 0 much faster relatively to $\partial v/\partial \tau$ than it does for solids, with the result that at room temperature the pressure at which $\partial E/\partial p = 0$ is higher than yet reached experimentally, that is, greater than 15,000 kg/cm^2. But at room temperature at 15,000 the volume of helium is only one-half the volume at 0°K at atmospheric pressure. In other words, the volume at which the attractive and repulsive forces are in balance at 15,000 at room temperature is less than half the volume at which they are in balance at 0°K. So large a discrepancy surely cannot all be attributed to departures of the forces from linearity, but there must be a change in the structure of the atom itself, resulting from some sort of rearrangement of the electron distribution. Under such conditions a "law of force," using as the only parameter the distance of separation of the atomic centers, must be inadequate. It is interesting to notice that the direction of the discrepancy with ordinary metals is the same as with helium, only it is less extreme. That is, at room temperature the volume at which $\partial E/\partial p$ vanishes is less, in either case, than the volume at 0°K at atmospheric pressure. In either case the internal kinetic energy of the atom increases with increasing pressure, accompanied by a shrinkage in the effective size of the atom, so that the sign of the effect is what would be expected.

A crude calculation of the effective change of size of the atom under pressure may be of interest. We have approximately at low pressure $1/v(\partial T_{el}/\partial v)_\tau \approx 3/(\partial v/\partial p)_\tau$. For NaCl this gives the numerical value 1.4×10^{-11} erg per atom per kg/cm^2 external pressure. Making now the crudest kind of an approximation, taking an atom of 14 electrons as the average of Na and Cl, supposing the 14 electrons to rotate in a single orbit about the nucleus with a radius of 1.35×10^{-8} cm with such a kinetic energy that the radial acceleration is held in equilibrium by the electrostatic force of attraction of the nucleus, one may calculate the change in radial distance when the kinetic energy in the orbit increases by 1.4×10^{-11}. The change of radius for this change of energy turns out to be of the order of only 1/100th of the change of distance between atomic centers brought about by the external pressure of 1 kg/cm^2. That is, the change in size of the atom when external pressure is applied probably accounts for only a small fraction of the total change of volume.

It is interesting to apply Schottky's theorem to a monatomic gas instead of to a solid as hitherto. Dulong and Petit's law does not apply to a gas, and we now have $(\partial T_{\rm at}/\partial p)_\tau=0$ and $(\partial T_{\rm at}/\partial\tau)_p=C_p-R$ to replace the former relations. Substitution in 3 will now give

$$(\partial T_{\rm el}/\partial p)_\tau=3v+\tau(\partial v/\partial\tau)_p+4p(\partial v/\partial p)_\tau,$$

as before, and

$$(\partial T_{\rm el}/\partial\tau)_p=4p(\partial v/\partial\tau)_p-2C_p+R.$$

For a perfect monatomic gas $\tau(\partial v/\partial\tau)_p=v$, $p(\partial v/\partial p)_\tau=-v$, and $C_p=5R/2$, so that $(\partial T_{\rm el}/\partial p)_\tau=0$, and $(\partial T_{\rm el}/\partial\tau)_p=0$, and there is no change in the internal structure of the atom for changes of either pressure or temperature. No gas remains approximately perfect, however, beyond a few hundreds of kg/cm^2, and under a few thousand kg/cm^2 all distinction between a gas and an ordinary liquid is lost. In this pressure range a little consideration shows that the change of $T_{\rm el}$ is of the same order of magnitude as it is for substances originally in the condensed condition (for example, for nitrogen pv rises from unity at atmospheric pressure to 16.5 at 15,000 kg/cm^2), and that therefore the internal distortion of the atoms of a gas is not different from that of other substances.

One might anticipate that it would be a simpler task for theory to calculate the variation with pressure of the volume of a substance like gaseous hydrogen or helium than of a solid like NaCl. This has not proved to be the case, however, and we have as yet no theoretical derivation of an equation of state for any gas at high pressures.

IV. Thermal Expansion and Entropy at Infinite Pressure

The most successful of the theoretical attacks on problems presented by the equation of state of solid bodies has been on the problem of compressibility at constant temperature; success has not been so great in dealing with thermal expansion. In nearly all cases thermal expansion decreases with an increase of pressure; this of course is the same thing as an increase of compressibility with rising temperature. As a general rule, the decrease of thermal expansion for a given increase of pressure is by a factor considerably smaller than the decrease of compressibility. It has been known for some time that thermal expansion involves a departure from linearity of the restoring forces on the atoms. At first glance, therefore, the decrease of thermal expansion with increasing pressure (decreasing volume) is paradoxical, because the repulsive forces between atoms are ordinarily represented as increasing very rapidly at small distances of separation, so that the smaller the volume, the greater would one expect the deviation from linearity to be, and therefore the greater the expansion. But the paradox is to a certain extent resolved if one considers the state of affairs at large volumes in the perfect gas. Here the restoring force on a molecule is zero during free flight, and it abruptly rises to a very large value during the collision that terminates free flight. This sort of thing is the extreme in the way of departure from linearity, so that a large thermal expansion may be expected, as is indeed the case. This collisional aspect of the interaction between atoms must be responsible for a large part of the thermal expansion of actual solids and liquids, and the fact that this aspect is becoming less and less important at high pressures is doubtless the main factor responsible for the decrease of thermal expansion with increasing pressure. It is not perfectly clear what to expect at exceedingly high pressures, beyond reach of present experiment. To the extent to which the "law of force" point of view is justified, one might perhaps expect that eventually the rapid increase of repulsive forces would bring about a reversal, so that at very high pressures thermal expansion might begin to rise again. The subject is an important one, but very difficult experimentally; I have made repeated attempts to get good values of the thermal expansion of some of the more interesting substances, but without much success. Quite recently, however, results have been obtained for the alkali metals, and the results are in process of publication in *The Proceedings of the National Academy of Sciences*.

Consideration of the thermal expansion suggests another interesting line of speculation on the probable limiting behavior of substances at very high pressures connected with the third law of thermodynamics. In some respects an increase of pressure is equivalent to a decrease of temperature, the volume effects are the same and there is also a stiffening of the constraints to which the atoms are subjected, resulting in an increase of the characteristic temperature with a displacement of specific heat, thermal expansion and similar properties to lower values, corresponding effectively to lower temperatures. This is very probably an important factor in the decrease of thermal expansion of solids with increasing pressure. Now at 0°K entropy vanishes in most cases according to the third law, and this led Lewis[4′] to suggest that it is plausible to expect that along an isothermal at higher temperatures the entropy will approach zero at infinite pressure. Since $(\partial S/\partial p)_\tau = -(\partial v/\partial \tau)_p$, integration gives

$$S_{p,\,\tau} - S_{0,\,\tau} = -\int_0^p (\partial v/\partial \tau)_p dp.$$

If we assume that $S_{0,\,0}=0$ by the third law, it is obvious that the thermal expansion must go to zero at infinite pressure, for if $(\partial v/\partial \tau)_p$ remained finite $S_{p,\,\tau}$ would decrease without limit as pressure increases indefinitely. It can be seen at once that if $\int (\partial v/\partial \tau)_p dp$ is to remain finite, $\partial v/\partial \tau$ must decrease with increasing pressure at least as rapidly as $1/p$. In the experimental range of pressure this condition is very definitely not met, either by ordinary solids, metals* or ionic crystals, or by the gases nitrogen and argon, the expansion in no case decreasing as rapidly as $1/p$. If then the condition $\lim_{p=\infty} S=0$ holds[8] there must be a reversal in the trend of $\partial v/\partial \tau$ at pressures beyond those yet reached. It is to be seriously considered, however, whether the expectation that the entropy at infinite pressure must vanish is a necessary one. In the argument which represents the third law as resulting from the complete vanishing of all randomness at 0° abs., the atom is treated as the inviolable unit with respect to which randomness is calculated. But at infinite pressure the atom certainly is not inviolate, for there are all sorts of penetration effects and interactions between electrons. If the electron or some other subgroup in the atom begins to acquire individuality at high pressures, there would seem to be no reason why entropy should not have negative values with respect to a system in which the atom is the unit. This is perhaps merely another way of saying that a system under very high pressures is one of those exceptional cases to which Fowler and Sterne have shown that the third law does not apply.

V. *P–V–T* RELATIONS IN LIQUIDS

1. Compressibility

Thus far we have considered mainly the effect of pressure on the volume of solids, and have also briefly considered gases. Theory has had some partial success in these fields, but has up to the present been almost powerless when confronted by the complications of an ordinary liquid. All that I can do here is to make some qualitative observations suggested by the behavior of liquids at high pressures. The experimental material is fairly extensive, including measurements up to 12,000 kg/cm² in the temperature range between 0 and 100°C on some 60 liquids, all of them organic except water and mercury. Mercury is in a class by itself, its compressibility being about one-tenth that of water, and of the same order magnitude as that of the solid metals, 50 percent more compressible than lead, for example, and much less compressible than the alkali metals. It would be interesting to know the compressibility of other liquid metals, but there is no reason to anticipate anything very striking. The other liquids fall roughly into three groups with regard to the total compression under 12,000 kg/cm²: Glycerine is in a group by itself with a total volume decre-

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* The recently completed experiments on the alkali metals indicate that they are exceptional in that they have a very large decrease of thermal expansion at high pressure.

ment of 14.5 percent; in the second group is water, C_6H_5Br, C_6H_5Cl and a number of the glycols with a volume decrement varying from 18 to 20 percent, and in the third group are all the others with a volume decrement of the order of 30 percent. The division into groups is rough and probably to a certain extent fortuitous. Doubtless it would be possible to find liquids fitting into all the gaps.

The order of magnitude of the compression is not particularly characteristic of the liquid as distinguished from the solid phase, but is rather a characteristic of the chemical nature of the material, for a number of organic solids have compressions of 15 percent at 12,000. The notable characteristic of the compressibility of liquids as distinguished from that of solids seems to be the relatively large decrease of compressibility at high pressure; the compressibility at 12,000 kg/cm^2 is in many cases only 1/15th of that at atmospheric pressure. Organic solids do not show the stage of very rapid decrease of compressibility at low pressures shown by the liquids. The decrease of compressibility of liquids is not uniform with pressure, but is by far the most rapid at low pressures; for many substances the relative decrease in the first 1000 kg of the range is as much as the relative decrease in the last 6000. Qualitatively an adequate picture is that at low pressures there is a large amount of "slack" between the molecules; increasing pressure removes this slack rapidly, and during this process the compressibility is high. When the slack has been removed there remains the compression of the molecules themselves, part of which may arise from a closer atomic grouping within the molecule, and part from a shrinkage of the atoms, as demanded by Schottky's theorem. A large part of the high initial compressibility of ordinary liquids is connected with the nearness of the critical point liquid-gas, for compressibility in the gas phase is high and at the critical point itself compressibility is infinite.

The persistence of the compressibility of the molecules at high pressures is a factor which has seldom been adequately taken into account in the various theories of liquids which have been proposed. Most of these theories have been more or less empirical in character and many of them have agreed in assigning a finite limiting volume to the liquid at infinite pressure. This limiting volume, extrapolated from measurements made in a range of 3000 or 4000 kg/cm^2, is sometimes higher than the volume actually reached at 12,000, and in any event the equations almost always give too small a compressibility at high pressures. Another aspect of this same phenomenon is that compressibility varies very much less from liquid to liquid at high pressures than it does at low pressures; among the liquids measured there is a tenfold variation of compressibility at atmospheric pressure, whereas at 12,000 the factor of variation is only 1.8.

2. Compressibility and chemical composition

There are various rough connections of the kind that might be expected between the compressibility and chemical composition. Thus at high pressures the volume of isomers tends more nearly to equality than at lower pressures, provided the volumes at low pressures are markedly different. That is, at high pressures the tendency is for structural differences to become obliterated and for the volume to approach more nearly to the sum of the volumes of the component atoms. An example is ether and *n*-butyl alcohol, both of which have the same composition, $C_4H_{10}O$, but which structurally are so different in character that the chemist often does not think of them as isomers. The ratio of the volumes of equal weights of these two substances at atmospheric pressure is 1.096 and is 1.037 at 12,000. On the other hand, if the isomers are not greatly different in structure, as *n*- and *i*-butyl alcohols, then the tendency to greater equality of volume at high pressures is not so marked, and there may even be slight changes in the opposite direction, 12,000 kg/cm^2 not being a sufficiently great force to assume complete control in these cases of slight difference.

If the molecule is bound together by intense forces, the compressibility is small. The $-OH$ group appears to exert such a consolidating effect on the molecule; the abnormally low compressibility of glycerine is to be attributed to the fact that the molecule contains three $-OH$ groups. The comparatively low compressibility of the glycols and of water is evidently due to an effect of the same sort. In general the addition of links of the hydrocarbon chain, CH_2, seems to favor high compressibility, and the presence of an oxygen atom anywhere in the molecule low compressibility.

3. Thermal expansion

The thermal expansion of liquids is much easier to measure than that of solids, and it is possible to obtain both the variation of expansion with pressure at constant temperature and the variation with temperature at constant pressure. The effect of increasing pressure at constant temperature is to decrease the thermal expansion, as is also the case for solids, but by a much larger factor. The variation with temperature is interesting. Normally, at atmospheric pressure, thermal expansion increases with increase of temperature, or $(\partial^2 v/\partial\tau^2)_p > 0$. At a pressure between 3000 and 4000 kg/cm^2, however, this effect reverses for nearly all organic liquids, so that at pressures higher than this $\partial^2 v/\partial\tau^2 < 0$. An apparent explanation suggests itself in terms of the failure of linearity of the restoring forces. At lower temperature at constant pressure the volume is less, and therefore the non-linearity in the restoring forces arising from the intense repulsive forces is greater and so the thermal expansion is greater. This suggestion I have published in several papers, but it evidently cannot be right, for the same argument would demand that the expansion increase with increasing pressure at constant temperature, which is not the case. It appears to me now that a possible factor in the situation is the Schottky change of dimensions of the molecules already discussed. We have seen that the molecules increase in size as temperature increases at constant pressure. At small volumes (high pressures) this may mean an important curtailment of the free flight aspect of molecular motion, an increasing degree of linearity, and therefore a decreasing thermal expansion. An exact working out of what is to be expected here obviously demands a careful balancing against each other of several factors; it is an interesting and important problem for theoretical attack.

Since $(\partial C_p/\partial p)_\tau = -\tau(\partial^2 v/\partial\tau^2)_p$, the fact that $\partial^2 v/\partial\tau^2$ becomes negative between 3000 and 4000 kg/cm^2 means that C_p increases with pressure beyond this point. As a rough average, C_p decreases to about 0.9 its initial value at 3000 or 4000, increasing from here on at such a rate that at 12,000 it has not quite recovered its initial value. The increase in C_p is not what one might at first expect, since part of the effect of pressure is to increase the stiffness of the constraints, increasing the characteristic temperature, and displacing the effective temperature to lower values and so decreasing the specific heat. But it must be remembered that the reversal of $\partial^2 v/\partial\tau^2$ has been established experimentally only for organic substances with rather complicated molecules. Under ordinary conditions the specific heat of such substances is known to be considerably less than that corresponding to the full number of internal degrees of freedom of the molecule. If the effect of pressure is to make the atom rather than the molecule the individual unit of structure, an increase of specific heat would be expected. Such a tendency is consistent with the increasing approach to equality of isomers at high pressures. If these considerations are correct, one would expect that metals and simple ionic lattices would not show the reversal in sign of $\partial^2 v/\partial\tau^2$; it is unfortunate that $\partial v/\partial\tau$ cannot at present be measured accurately enough for these substances to permit an evaluation of $\partial^2 v/\partial\tau^2$.

4. The pressure coefficient and the mechanism of pressure

The ratio $(\partial v/\partial\tau)_p/(\partial v/\partial p)_\tau$, which is mathematically identical to $-(\partial p/\partial\tau)_v$, has played an important part in various theories of liquids. It has received the name "pressure coefficient" and obviously gives the rise of pressure for one degree rise of temperature at constant volume. Various arguments have been advanced for supposing that the pressure coefficient is a function of volume only, and equations of state have been deduced on this basis. The physical meaning of this assumption is easy to see. If we put $(\partial p/\partial\tau)_v = f(v)$, integration gives at once for the equation of state

$$p = \tau f(v) + \varphi(v),$$

where φ is an arbitrary function of integration. The perfect gas equation and van der Waals equation are both special cases of this general form. The physical meaning of such an equation is obviously that the pressure exerted by the substance can be regarded as arising from two different effects, each acting independently of the other. The part given by $\varphi(v)$ is the same at all temperatures as at 0°K and obviously arises from the forces between molecules, as for example the force in Born's analysis for ionic crystals. The part $\tau f(v)$ is proportional to the temperature, and is evidently the part arising from kinetic bombardment against the walls. An elementary argument of kinetic theory shows that the kinetic pressure is of this form if we assume that the size of the molecules is independent of temperature and that the kinetic energy of temperature agitation is proportional to temperature, as in classical statistics.

When we make comparison with experiment, we find that in many cases $(\partial p/\partial \tau)_v$ fails to be a function of volume only by an amount far beyond experimental error. In general the tendency is for $\partial p/\partial \tau$ to decrease with increasing temperature at constant volume. The general reason for the discrepancy is clear; if the molecules are deformed by changes of pressure and temperature, as we have seen they must be, then the two mechanisms by which pressure is exerted do not act independently, but there must be interactions between them. Furthermore, there is always a contribution to the $\varphi(v)$ term arising from terms of higher order when the amplitude of vibration increases; just how important this is compared with the other effect is a question for detailed theory.

The change of internal energy of liquids under pressure presents the same general features as that for solids, that is, at low pressures it decreases with increasing pressure and then at higher pressures there is a reversal. The physical interpretation is also doubtless the same; at low pressures and large volumes the attractive forces preponderate, whereas at higher pressures and smaller volumes the repulsive forces preponderate. The pressure at which reversal occurs is markedly lower in the case of organic liquids than for solids, being in the neighborhood of 7000 kg/cm^2. This is what would be expected on the most general grounds, pressure being in general more effective in changing the properties of a liquid than of a solid.

5. Small scale irregularities

So far we have been concerned with comparatively large scale effects in which all organic liquids are more or less alike. Superposed on these large scale phenomena there is a bewildering amount of small scale behavior or fine structure, which varies with the individual liquid. Examples can be found of nearly every conceivable type of abnormal behavior. Thus the compressibility may increase with rising pressure or decrease with rising temperature, and thermal expansion may increase with increasing pressure and increase or decrease with rising temperature. Such a variety of behavior must mean that the individual differences of the different kinds of molecule are coming into play and becoming accentuated at high pressure, as is indeed most natural when one considers how the molecules are pushed into more intimate contact by pressure and forced to conform to each others' irregularities. The picture of the molecule that wave mechanics is developing seems to provide the possibility of just the sorts of complication that are required, valencies directed in space giving the possibility of shapes much more complicated than spherical, and regions in the outer parts of the atoms pulled together by the pairing of electrons of opposite spins giving the possibility of local centers of attractive force—in fact just the sort of complication that seemed demanded by qualitative considerations before the development of wave mechanics. The complications involved in the detailed working out of the possibilities will doubtless be prohibitive for a while, so that probably at first theory will confine itself to the broad features common to all liquids, where the possibilities are interesting enough.

From the existence of the great amount of individual detail one may draw the conclusion that there is no such thing as "an" equation of state, as has been tacitly assumed so often. It would obviously be hopeless to attempt to reproduce in a single type of equation with variable parameters all the possibilities of all types of molecule. The most that can be meant by "an" equation of state is a description of a general method, not a general result.

VI. Periodic Relations

One of the tasks of theory in dealing with the compressibility of the elements is to reproduce the strikingly periodic character of the compressibility, a feature first emphasized by Richards.[5] In Fig. 1 is plotted the logarithm to the base 10 plus 7 of the cubic compressibility of all known elements against the atomic number. There is good reason to think that the maximum positions in the figure would be occupied by the condensed phases of the rare gases, which have not yet been measured. This might be expected on general grounds, because of the nature of the forces holding the rare gases together, namely van der Waals forces, which are the weakest of the various recognized types of atomic force. Passing to the alkali metals, their high compressibility is evidently to be correlated with the single electron in the outer shell, making for a very deformable atom.

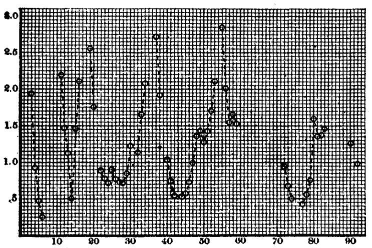

Fig. 1. The logarithm to the base 10, plus 7, of the compressibility of the elements plotted as ordinate against the atomic number as abscissa.

VII. Compressibility of Single Crystals

Theory must ultimately account for the difference of compressibility in different directions of single crystals of the non-cubic substances. The differences in different directions are often very marked; thus zinc is eight times more compressible along the axis than at right angles to it, and tellurium actually has a negative compressibility in one direction. Qualitatively the behavior is roughly as one would expect, the compressibility being greatest in the direction of greatest atomic separation, and in the case of tellurium there has been some success in connecting the behavior qualitatively with the filamentary structure of spirally arranged atoms in the direction of the axis. But quantitatively, practically nothing has been done, and one can hardly expect much before the more fundamental problem is solved of reproducing the lattice structure itself with its difference of spacing in different directions.

VIII. Two Phase Equilibrium

We now pass from consideration of the effect of pressure on a single condensed phase, solid or liquid, and consider the change in the equilibrium between two condensed phases, either solid and liquid or two solids, produced by pressure. The fundamental equation governing the phase equilibrium is of course the equation of Clapeyron

$$d\tau/dp = \tau\Delta v/L,$$

where Δv is the change of volume during the transition and L is the latent heat.

1. The melting curve

Clapeyron's equation applies to any kind of two phase equilibrium. With regard to the melting equilibrium between solid and liquid the problem which has attracted the most attention is that of the shape of the melting curve. Clapeyron's equation obviously allows $d\tau/dp$ to be any function of pressure, if only Δv and L have appropriate values, and in fact thermodynamics in general has no restriction to place on the shape of the melting curve. The question reduces to one of experiment, therefore. Expectation has been to a large extent controlled by the corresponding situation with regard to equilibrium between a liquid and its vapor. Here it has been established that all sorts of substances show the same sort of behavior; there is a critical point at which the distinction between liquid and vapor ceases, which means that it is possible by proper manipulation of pressure and temperature to pass around the critical point, and thus pass without discontinuity from the vapor to the liquid state. This general result seems to have been often taken over for the solid-liquid equilibrium without any very self-conscious realization that a special assumption was being made, for it has been generally assumed that there is such a thing as "*a*" melting curve, the same in general character for all substances, whether the substance is held together by van der Waals forces as in an inert gas, or by ionic forces as in a salt, or by exchange forces as in a metal or by valence forces as in some molecular compounds. This assumption did not appear to be so serious before the existence of these different sorts of force was clearly recognized, but now it would appear that to assume that there is such a thing as "*a*" melting curve is of itself considerable of an assumption.

Assuming that there is such a thing, there have been various expectations as to the character of the melting curve. The earliest was that there would be a critical point just as in the case of liquid-vapor, at which liquid and solid would become identical. Other expectations have been that the melting curve would rise to a maximum and then fall again (Tammann), that it would rise to an asymptotic temperature at infinite pressure (Schames), or merely that it would continue to rise indefinitely with pressure and temperature. In the experimental range of pressure neither of the first two expectations have been realized, while obviously the last two demand an infinite pressure range. The question has to be settled then on the basis of some sort of an extrapolation. Such an extrapolation can be made in terms of the behavior of Δv and L in Clapeyron's equation. Thus if there is a critical point, Δv and L must both tend to vanish at the same pressure (and temperature); if there is a maximum, Δv must tend to vanish at some finite pressure (and temperature) and L must tend to a finite value at the same pressure, etc. It is not necessary to go into greater detail here because the question has been freshly discussed in a recent paper in the *Physical Review*.[6] It seems to me personally that all the present experimental evidence is unequivocally in favor of the expectation that the melting curve rises indefinitely; this holds for substances as diverse as argon, nitrogen, liquid metals, and many organic compounds. This conclusion is, of course, restricted to a pressure range in which nothing occurs drastically new, like an atomic breakdown, and definitely does not apply to the extreme pressures considered in the Section XVI of this article.

The tacit assumption of "*a*" melting curve therefore seems to be justified. The explanation of it must rest on some broad general property of solid and liquid and not depend on the particular type of force binding the molecules together. Such a broad feature is obviously the regular arrangement of the crystal as opposed to the haphazard arrangement of the liquid. A melting curve which rises indefinitely merely means that no matter how high the temperature, it is possible to apply to any substance enough pressure to make it assume the regular arrangement of the crystal which it has at some lower temperature (except for polymorphic changes). Such a behavior appears most natural and quite in line with the experimental fact of the universality of the existence of the crystalline state of aggregation. But theoretically the explanation has not yet been given for the necessity of the existence of a crystalline phase. It is doubtless our inability as yet to understand theoretically this fundamental fact that is responsible for the persistence with which a number of physicists still maintain, as it seems to me against the experimental evidence, the idea that the melting curve will end in a critical point if only pressure can be carried high enough. It would be surprising if the universal tendency to crystallize could be suppressed by pressure, particularly in view of the fact that many substances are already in their natural state under a very high internal pressure.

Some theoretical discussions have been given of melting, mostly from a roughly empirical point of view, as, for example, that of Lindemann,[7] who postulates that melting occurs when the amplitude of atomic vibration has become about 10 percent of the distance of separation of atomic centers at 0°K. One characteristic of this argument of Lindemann has been common to most of the other arguments also, namely that the solid will melt when some critical condition is reached in the solid phase, irrespective of the nature of the liquid, as if melting were like the falling over of a row of dominoes. This of course, is not the case, but the melting point, which is the point at which solid and liquid are in equilibrium, is that point at which there is a certain relation between the properties of solid and liquid, as is shown by the thermodynamic formulation in terms of the equality of the thermodynamic potentials of liquid and solid. Any valid theory of melting must properly consider this aspect of the situation. The complete theory of melting must also take into account the still more detailed consideration of the precise crystal system of the solid.

There is room for the collection of considerably more experimental material which would be of value in formulating a theory of melting. It so happens that in spite of the large number of liquids whose properties have been studied under pressure, very few are liquids whose melting curves have also been investigated. The reason for this is connected almost entirely with questions of technique; thus the sylphon with which the compressibility of a large number of liquids has been measured is likely to be ruined if the liquid is allowed to freeze in it, so that liquids have mostly been picked out for measurement that do not freeze in the experimental range. The result is that we have entirely inadequate experimental knowledge of how the properties of liquid and solid vary together along the melting line. For example, the following simple questions cannot at present be answered: does the volume of the liquid in general increase or decrease along the melting line; or, does the energy content of the liquid in general increase or decrease along the melting line?

The normal melting curve rises to higher temperature with rising pressure, a consequence, according to Clapeyron's equation, of the facts that in nearly all cases the volume of the solid phase is less than that of the liquid, and the latent heat of transition from the low to the high temperature phase is of necessity positive. The only known exceptions have been water, bismuth and gallium. The abnormal falling melting curve of water is, however, only a temporary episode, for beyond 2200 kg/cm^2 a new modification of ice, denser than the liquid, replaces ordinary ice, and from here on the melting curve of water rises, as is normal. The expectation would be that this must also be the eventual state of affairs for bismuth and gallium, and a number of attempts have been made to find a new modification of bismuth. I have recently been successful at last in finding the second modification of bismuth,[8] the transition taking place at 25,000 kg at room temperature. It has not been actually shown experimentally that the melting curve of this new modification rises, but the magnitude of the change of volume leaves no doubt of it. One suspects that the new bismuth will prove not to have many of the abnormal properties of ordinary bismuth and that the general effect of the action of pressure on bismuth is to force it into normality, as is known to be the case with water. No serious attempt has been made to find a new modification of gallium beyond 12,000 kg; the slight departure of the melting curve of gallium from linearity leads one to be prepared to find that the high pressure modification of gallium occurs at higher pressure than that of bismuth. But with the example of bismuth freshly before us, I think that theory need have no hesitation in proceeding on the assumption that the rising melting curve is entirely normal.

There is another universal feature which all melting curves have in common that theory must ultimately explain, namely they are all concave downward, or $d^2\tau/dp^2<0$, whether they rise or fall.

Two remarks of a negative character can be made with regard to a theory of melting. In the first place, if melting temperature is plotted as a function of the atomic number of the elements, very much greater irregularities will be found than for such atomic properties as atomic volume or compressibility or electrical conduction; there are even places of unexpected reversal, as for example mercury between gold and thallium, and gallium between zinc and germanium. These abnormalities cannot be explained by the natural assumption that there may be missing modifications of the solid, which might be forced to appear by high enough pressure, like the new modification of bismuth. For these abnormal melting points are already too low, and the melting point of any as yet undiscovered high pressure modification would be even lower. The situation could be saved only by a new high pressure phase of the liquid, and two liquid phases are not known for any pure substance, unless one wants to count liquid crystals.

The second remark is that the melting of different sorts of substance is not governed by a law of corresponding states like the vaporization of the liquid phase. If there were such a law of corresponding states, then the temperature at which the difference of volume between liquid and solid phase has fallen to a definite fraction of its value at the normal melting point would bear a definite ratio to the normal melting temperature, the same for all substances. This is very definitely not the case. There may, however, be something corresponding to the law of corresponding states for restricted groups of substances. Thus the alkali metals, sodium, potassium, rubidium, and caesium, satisfy very approximately the condition just described on the volume differences.

The alkali metals show another interesting phenomenon with regard to melting; the melting curves of sodium and potassium cross in the neighborhood of 9000 kg/cm^2, and the slope of the other melting curves in the experimental range is such that it seems probable that below perhaps 30,000 kg/cm^2 there will be a complete reversal of the normal order of melting of all the alkali metals, lithium becoming the lowest and caesium the highest melting. A phenomenon like this I believe is very plausibly associated with the modification in the internal structure of the atom which we have already discussed with the help of Schottky's theorem. Caesium obviously has much greater latent possibility of internal readjustment than lithium, because the electronic structure of its atom is so much more complicated.

Schottky's theorem demands a special internal change in the atom on melting apart from the pressure and temperature effects in the homogeneous phase. Written for melting, Eq. (1) becomes:

$$\Delta T = -\Delta E + 3p\Delta v.$$

But $\Delta E = L - p\Delta v$. Hence

$$\Delta T = -L + 4p\Delta v.$$

To the degree of approximation that the kinetic energy of mass motion of the molecules is the same in the liquid and solid phase, this equation means that at low pressures (neglecting the $p\Delta v$ term) the internal kinetic energy of the molecule is less by the latent heat in the liquid phase than in the solid, which would indicate a swelling of the molecule in the liquid phase. But at high pressures this is counteracted by the $4p\Delta v$ term, so that at high pressures the internal structure of the molecules of liquid and solid tends to become more nearly equal. In fact, it will be found that for most of the liquids whose melting curve has been studied $4p\Delta v$ becomes greater than L at pressures below 12,000, so that there is a reversal. Of course in order to get a precise characterization of what occurs, some precise way of dealing with the kinetic energy of mass motion in the two phases must be devised, but at any rate it is indicated that at high pressures there may be important differences as compared with low pressures.

2. Polymorphic transitions between solids

Thermodynamically, as far as the application of Clapeyron's equation and of Schottky's theorem goes, there is no difference between a liquid and a solid (crystalline) transition and a transition between two solid phases. As a matter of experiment, however, the transition phenomena between two solid phases are very much richer and more varied than between a liquid and a solid. Melting phenomena all conform to one simple pattern; the melting curve rises with downward concavity, the difference of volume between liquid and solid decreases with rising temperature along the melting curve, and the compressibility of the liquid phase is always greater than that of the solid even in the abnormal case of ordinary ice. Transition curves between solids, however, may either rise or fall with either upward or downward curvature, the volume difference may either increase or decrease along the curve, and the compressibility of the phase of larger volume may be either greater or less than the compressibility of the phase of smaller volume. Not only may solid-solid transitions show very great variability with regard to the behavior of the thermodynamic parameters of the transition, but there may be the greatest variation with regard to the dynamic characteristics. The transition may run rapidly or slowly; the speed of the transition may be unsymmetrically affected by small displacements of pressure and temperature, positively or negatively, away from the equilibrium values; the transition may support subcooling only or superheating only or both or neither; the new modification may have a definite orientation with regard to the original orientation, or it may be at random; and finally the transition may run only when the parent form is a single crystal in a state of high purity and under other circumstances be entirely suppressed.

Thus far there appears to be only one generalization applicable to a solid-solid transition curve, namely that it never ends in a critical point. This of course means that one type of crystal lattice never changes continuously into another type. Such a continuous change is not impossible as a matter of pure geometry; thus a cubic lattice might change continuously into a tetragonal lattice by a gradual preferential expansion along one of the cubic axes. But such a change would involve a distinction between the cubic axes, and if the structure was originally truly cubic there can be no such distinction. Certainly from a physical point of view continuous transition from one type of lattice to another must seem highly improbable, and the fact that it is never found is a gratifying check on the validity of our picture of the constitution of a crystal, at least in this respect.

But beyond the impossibility of a critical point, apparently any type of behavior which might at first strike one as abnormal is possible. The mere existence of certain types of transition is significant. Thus there are transition lines which run vertically, which means that there is no latent heat. There is however in such cases a change of internal energy of amount $p\Delta v$ at the transition. If the transition takes place at comparatively low pressures, where the forces in both phases are on the average attractive, this means that although the atomic or molecular centers are pushed closer together the attractive forces receive work. This is not understandable if the centers of attractive force coincide with the geometrical centers of the molecules, but it does become understandable if the attractive centers are situated on what are effectively projections on the molecules. If the low pressure phase is one in which the projections on the different molecules are in register, held together by the attractive forces, it is easy to see that these projecting centers may be pulled out of register by high pressure, thus doing work against the attractions, but at the same time the volume may become less, the projections slipping past each other and interlocking in the high pressure modification. Such a picture is quite in accord with the possibilities now allowed by wave mechanics.

The change in the internal structure of the atom at such a transition demanded by Schottky's theorem may be considerable. Since $L=0$ for such a transition, we have $\Delta T=4p\Delta v$. Consider the high pressure transition of bismuth, which takes place at 25,000 kg/cm^2 with a volume change of 8 percent. $\Delta T=4\times 25{,}000\times 0.08=8000$ kg cm per cm^3. There are 2.8×10^{22} atoms of bismuth per cm^3 and 1 electron volt$=1.62\times 10^{-18}$ kg cm. Hence $\Delta T = 8000 \times 10^{18}/2.8 \times 10^{22}\times 1.62=0.18$ electron volt per atom. The sign of ΔT is such that the high pressure atom has the smaller internal kinetic energy. This under normal conditions would mean an expansion of the atom. This result is so highly paradoxical that obviously one of the first tasks of an exact theory is to examine to what extent our fundamental assumptions are valid, namely that the kinetic energy of atomic motion as a whole is the same in the two phases (that is, kinetic energy constant at constant temperature), and that the same simple connection approximately holds between internal kinetic energy and mean atomic radius for highly compressed atoms that holds for the free atoms of elementary theory.

At a vertical tangent the transition line in general is not perfectly straight, but has perceptible curvature. It can be shown by a simple thermodynamic consideration that this means that under the point of vertical tangency the phase which is stable at the lower temperature has the higher specific heat, an abnormal state of affairs.

An example has been found of a transition with maximum temperature, and it is probable that there is at least one example of a transition with a minimum temperature, which however could be realized in practise only with extreme difficulty because of the viscous resistance to the transition at low temperatures. At a maximum point the transition runs with no change of volume, but with a nonvanishing latent heat. On the transition curve, to the high pressure side of such a maximum point, the phase with the smaller volume has the higher compressibility, again a paradoxical result. It turns out, however, that more than half the solid transitions for which the measurements have been made are paradoxical in this respect, namely that the phase of smaller volume has the higher compressibility. Such a state of affairs is not inconsistent with the picture presented above, namely that in many crystals the attractive centers are effectively located on projections and are not situated at the geometrical centers of the molecules. A phase in which the attractive centers are so lined up as to be in register, that is, the phase of higher volume, would be expected to have a higher rigidity or a smaller compressibility, than a phase in which they are out of register, that is, a phase of smaller volume.

Chemical similarity of different substances is very much less likely to result in similarity of transition phenomena than in similarity of nearly every other physical property, and there are very few examples of chemically related groups which are polymorphically similar. One of the best examples of such a group is NH_4Cl, NH_4Br and NH_4I, all of which have a body centered and a face centered modification, the transition line running very nearly vertically, at pressures below 1000 kg/cm^2, and with very little latent heat. Furthermore, the pressure of the transition varies systematically in the series. RbCl, RbBr and RbI are another similar family, which is very similar to the family of the ammonium halides, there being also body centered and face centered modifications with nearly vertical transition lines, and a systematic variation of pressure through the series, which, however, is in the opposite direction from that in the ammonium family. The mean pressure of the transition for the rubidium family is in the neighborhood of 5000 kg/cm^2. Very recently I have found that the potassium family shows the transition in the neighborhood of 20,000, whereas in the sodium family the transition cannot occur much below 50,000.

The nitrates of the alkali metals are a family in which polymorphism is very common, and there are a certain number of resemblances in the behavior of members of the family, but there are also marked divergences. But there are also other examples in which there is no resemblance in the polymorphic behavior in spite of the closest chemical resemblance, as CCl_4 and CBr_4.

Theory has not advanced very far as yet in understanding the reasons for polymorphic transition, much less is it able to predict when a transition may be expected and to calculate the thermodynamic parameters of the transition. In fact, one cannot expect very much in this direction as long as the fundamental problem of understanding why a substance crystallizes into a lattice is not solved. One cannot discuss the problem of polymorphic transition until the problem not only of understanding why the lattice exists is solved, but one should also be able to calculate the lattice type. However, certain aspects of the problem of polymorphic transition have been subjected to theoretical attack. The difference between the body centered and the face centered lattices has been put on the basis of differences of minimum energy, and Hund[9] has attempted to show that when the exponent of the repulsive forces passes a certain critical value the type of lattice changes, and to explain in this way the difference of crystal system between the caesium halides and the other alkali halides. However, the attempt was not particularly successful, because the critical value for the exponent occurred at values very much higher than allowed by the compressibility. Hund's method of attack has been modified by Born and Mayer,[10] who have considered in addition to the attractive and repulsive forces the van der Waals forces arising from the polarization of the ions. The NaCl type of lattice proves to be the more stable, but if the van der Waals forces are doubled, a procedure which at first was purely empirical but which was later given theoretical support by Mayer, the CsCl type of structure turns out to be the more stable for the caesium halides (except the fluoride), and furthermore the difference of energy between the two types of lattice in the case of the rubidium salts proves to be of the same order of magnitude as the values actually found for the transition under pressure. Additional considerations, however, would seem to be necessary to show why the heat of transition is approximately zero, although the energy change is appreciable. For the potassium salts the energy values of Born and Mayer would lead to the expectation that it should be possible to force the transition of these salts also from the NaCl to the CsCl type of structure by pressures within the experimental range and indeed I have just found the transition near 20,000.

Even this simplest of all possible cases, the transition of the alkali halides from the NaCl to the CsCl type of structure, is affected by complications. RbCl undergoes a transition with very small volume change[11] at a pressure of about 2000 kg, half the pressure necessary to force the principal transition from what is supposedly the NaCl to the CsCl type. There seems no place for such a transition, and the nature of the new lattice is entirely in doubt. It seems to me probable that the lattice type does not change in this transition, but that there may be within the atom some comparatively minor readjustment in the energy levels of the electrons.

A knowledge of the lattice structure of the high pressure modifications would be most helpful in formulating a theory. Unfortunately no experimental determinations have as yet been made by x-rays while the material is actually under pressure, so that our knowledge of the structure of the high pressure forms is restricted to those cases in which the high pressure form can be realized at atmospheric pressure under proper conditions of temperature. Fortunately a number of such structures are known. The result is somewhat paradoxical in that in more than half the cases the form stable at higher pressure, that is, the form which has the smaller volume, is the form with lower symmetry. The crystal forms with highest symmetry are the close packed arrangements of spheres; one would expect the form of smaller volume, that is, the form stable at the higher pressure, to be a close packed arrangement, and therefore a form of higher symmetry. The conclusion must be that at high pressures the atoms or molecules do not on the average have spherical symmetry; spherical symmetry is a property of the atom at low pressures, where it has more free space at its disposal, but when the available space is less it is forced into less symmetrical form. In the case of such phenomena as directed valence in the water molecule, for example, the detailed proof has been given that wave mechanics demands a spherically unsymmetrical solution.

Any theory of polymorphic transition must take proper account of one very important respect in which a transition between solids may differ from the transition liquid-solid. If a solid and a liquid phase are in contact with each other at equilibrium, and the equilibrium is disturbed by a displacement of pressure or temperature, equilibrium is always exactly restored by an automatic change in the system, produced either by melting or freezing. That is, the system comes of itself to a sharply defined equilibrium point, the same from whichever direction it is approached, provided the two phases are in contact. The ordinary explanation is that equilibrium is a dynamic affair, that there are always molecules leaving the liquid phase and crystallizing into the solid, and also always molecules leaving the solid and melting to the liquid. At equilibrium the velocity of the two streams in opposite directions is the same; when equilibrium is disturbed the velocity of one or the other stream preponderates, and this excess acts in such a direction that equilibrium is presently restored automatically. In the case of two solids, on the other hand, the state of affairs may be quite different, in that it is often possible to displace the temperature or pressure on two solid phases which are in contact and in equilibrium with no resulting reaction at all. If, however, pressure or temperature is sufficiently displaced, the transition will run in such a direction as to tend to restore the initial condition. That is, solids may show the phenomenon of a "region of indifference." The extent of this region of indifference may be measured with some precision, and will be found to vary with pressure and temperature. There are no obvious regularities of behavior, but the fact of the existence of a region of indifference, and the manner of its variation with pressure and temperature are entirely independent matters, depending on the particular substance. In those cases where a region of indifference exists, it is evident that equilibrium between two phases cannot be a dynamic affair of the equality of two velocities in opposite directions, but the mechanism must be more static in character; probably there is something of the nature of a hill of potential between the two phases which can be surmounted only when the condition of equilibrium is violated by a sufficient amount. It is evident, I think, that in these cases, whatever it is that passes from one potential valley to the other over the intervening hill, cannot be endowed with a Maxwellian distribution of velocities, for if this were so there would always be some molecules with velocity sufficiently greater than the average to leap the potential barrier.

The very great variety in polymorphic transitions found experimentally is understandable now that the very great variety of theoretical possibilities is becoming appreciated. Thus it is recognized that there are lattices held together by various types of forces: ionic lattices, lattices held together by valence forces, or by van der Waals forces, layer lattices, and molecular lattices. Furthermore, the distinction between the types just enumerated is not always clean cut. Polymorphic transitions may be expected corresponding to the change from one to another of these types of lattice, or to partial changes in type. In addition we may be prepared for transitions involving internal electron rearrangements in the atoms; such changes might be expected particularly in those atoms with incompleted inner shells of electrons. Perhaps the transitions under pressure of cadmium and cerium are of this type.

The ultimate theory of polymorphic transition and of crystallization in general will doubtless incorporate one consideration which has received little attention up to date. It seems to me that broad considerations, such as for example the condition of minimum energy, are not enough here, but one must be sure in every special case that it is possible to actually realize the detailed steps necessary to build up the crystal. This sort of consideration has proved not to be necessary in treating certain classes of phenomena, since our experience has been that nature will often somehow find a way to adjust itself to the requirements of broad principles, as for example, in systems in which there is a Maxwellian distribution of velocities there are always some molecules which are able to settle down into a position of minimum energy even though an intermediate stage may be necessary in which the molecule is moving toward higher energy. That this sort of thing plays a definite role in polymorphic transitions is shown by the phenomenon of the "band of indifference" already considered. There is an analogous consideration with regard to the building up of the crystal from the liquid or vapor phase or from solution. Only recently have physicists been considering the details of the way in which the crystal grows. It appears that on the surfaces of deposition there are conditions of reversibility and growth to be satisfied quite different from the conditions at interior points. These growth conditions, as well as conditions on the completed structure, must obviously be met if the crystal is to exist. The thermodynamic conditions, expressed perhaps in terms of the equality of two thermodynamic potentials, are only a small part of the story.

IX. Irreversible Transitions

The transitions thus far considered have all been reversible thermodynamically and mechanically. There is one irreversible transition produced by high pressure, that from white to black phosphorus, which I think contains possibilities of great theoretical interest. This transition is remarkable for the very large increase of density, 46 percent, and for the very great change of properties, from a good insulator to a fairly good conductor of electricity, and for the details of the way in which the transition takes place. The transition cannot be hastened in the usual way by inoculating with a nucleus of the other modification, but some preliminary process of preparation is necessary which apparently takes place homogeneously throughout the volume with slight increase of density, and which proceeds at an accelerated pace for perhaps ten or fifteen minutes until some critical condition is reached which causes the entire system to collapse suddenly into the black modification. Just what this process of preparation may consist in seems at present quite obscure. It would be surprising if phosphorus were the only element, ordinarily non-metallic, which was capable of assuming irreversibly a metallic form. I have searched for a similar transition of sulfur, which stands next to phosphorus in the periodic table, but without success. A pressure of 50,000 $\mathrm{kg/cm^2}$ was applied at room temperature; it would be desirable to much increase the pressure range for investigations of this character.

Ag_2O affords an example of a transition intermediate between the completely irreversible transition of white to black phosphorus, and the clean cut perfectly reversible transition of many substances. If the volume of Ag_2O is determined as a function of pressure, increasing pressure uniformly to a maximum and then decreasing it to its initial value, a very broad hysteresis loop will be found, similar in shape to the magnetization loop of many ferromagnetic substances. Small amounts of hysteresis in solid-solid transitions are not uncommon, and would be expected if there are impurities forming solid solutions, so that phenomena of diffusion in the solid state are involved, but this seems to be something different, and the explanation does not yet appear.

X. DISCONTINUITIES—TRANSITIONS OF THE SECOND KIND, ETC.

The phase changes thus far considered, to which the conventional Clapeyron's equation applies, have involved discontinuities in the volume and the energy content. Recently another type of change has begun to attract attention, in which there are discontinuities in the derivatives of volume and energy content, that is, discontinuities in thermal expansion and compressibility and specific heat. This sort of phenomenon was first recognized at low temperatures, and perhaps the best known example is the case of NH_4Cl investigated by Simon,[12] who found that there is a region only a few degrees wide centering around −30°C in which there are enormous variations in the specific heat and the thermal expansion. Somewhat later at Leyden, Keesom[13] found that anomalous effects which he had previously discovered in liquid helium at low temperatures and which he had been at first inclined to explain as showing two modifications of the liquid, actually involved discontinuities in only the derivatives of volume and energy, the locus of these discontinuities being a curve in the $p-t$ plane. Ehrenfest[14] published a paper on the thermodynamic aspects, and proposed that such discontinuities should be called "transitions of the second kind," a name which has apparently been accepted.

Some time before the paper of Ehrenfest I had made an experimental study of the effect of pressure[15] on the anomalies of NH_4Cl and NH_4Br found by Simon. For NH_4Cl it appeared that the anomaly manifests itself by a change of direction, abrupt within experimental error, of the pressure-volume isotherm, which of course means a discontinuity in compressibility and thermal expansion. The pressure of this discontinuity was displaced toward higher values at higher temperatures, just like the displacement of an ordinary transition, and in fact at 9500 kg/cm² the temperature of the discontinuity is +30°C. I showed that there is a purely geometrical relation connecting the discontinuity in compressibility and thermal expansion with the slope of the line on which the discontinuity occurs, namely

$$d\tau/dp = -\Delta(\partial v/\partial p)_\tau/\Delta(\partial v/\partial \tau)_p$$

as indicated in Fig. 2. By utilizing the thermodynamic relation

$$(\partial Q/\partial p)_\tau = -\tau(\partial v/\partial \tau)_p$$

this can be thrown into a form exactly analogous to Clapeyron's equation, namely

$$d\tau/dp = \tau dv/dQ,$$

where dv/dQ is the ratio of volume change to heat absorbed in making the change corresponding to AB of the figure. Ehrenfest used also the equivalent relation

$$d\tau/dp = -\tau\Delta\partial v/\partial\tau/\Delta C_p.$$

The behavior of NH_4Br was unlike that of NH_4Cl in several respects. The volume anomaly is of the opposite sign, so that at high pressures it is displaced to lower temperatures instead of to higher. Because of the inconvenience of pressure manipulations at low temperatures, the anomaly was studied only at −72°, at which it occurs at 1600 kg/cm². Furthermore, the anomaly is much

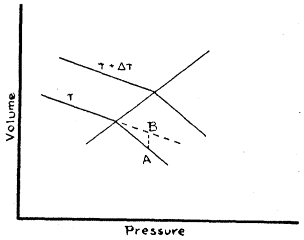

FIG. 2. Indicates the geometrical relations satisfied by a discontinuity of the derivatives of volume which experiences a temperature displacement when pressure is displaced.

more abrupt than for NH_4Cl, so that within experimental error it appeared like a discontinuity of the volume itself rather than of the derivative, and therefore had the characteristics of an ordinary transition.

Later I found a large number of anomalies[16] in the behavior of solid substances in the temperature interval between 0° and 100°C and up to 12,000 kg/cm^2. A number of these are, within experimental error, sharp and reversible discontinuities in the first derivatives, and would therefore be described as "transitions of the second kind." Phenomena of this sort are common among certain classes of alloys. There are also examples in which the discontinuities are not perfectly reversible, but there are hysteresis effects. There are also cases in which the anomaly has no sharply defined edges, but there is a region of anomalous curvature, which is displaced to other pressures when the temperature is changed. An example of this sort of anomaly is also afforded by NH_4Cl, this anomaly having apparently no connection with the one already discussed; another very striking example is afforded by metallic chromium in a state of high purity.

The great variety of phenomena offered by these small scale anomalies shows that a classification of transitions into "first, second, third" etc. kinds (for obviously Ehrenfest's scheme of classification and nomenclature can be continued indefinitely) is to a certain extent at present a matter of convenience, reflecting more or less closely the experimental accuracy. NH_4Br is a case in point; in Simon's measurements there appeared only very rapid variations in the thermal expansion, but under pressure, at a temperature 40° lower, the anomaly had been so sharpened that it appeared as a discontinuity in the volume itself. What may appear to rough measurements as a discontinuity in the first derivative may appear as a discontinuity in the second derivative to more refined measurements. It is to be remembered furthermore that an ordinary phase change would not appear to be perfectly discontinuous if measurements could be made accurately enough to detect the effect of the varying ratio of surface energy to volume energy as the transition progresses. It would appear to me that the physical value of the concept of the transition of the "second kind" will depend on the discovery of some characteristic physical process corresponding to such a transition, analogous to the change from one lattice to another which may characterize an ordinary transition. As far as I know this has not yet been done, but I can see no reason why it should not be done, or why the transition of the second kind should not be found to correspond to some significant type of physical process. In fact there may be several such kinds of significant process, just as we know that a transition of the first kind may mean a change from one amorphous phase to another or a change from an amorphous to a crystalline phase, or a change from one crystalline phase to another. It is, I believe, very probable that we already understand the mechanism of at least one type of process corresponding to a transition of the second kind; when certain of the gold-copper system of alloys are warmed there occurs a change from a type of lattice in which gold and copper atoms are arranged regularly to a lattice in which they are scattered about in haphazard positions, and the change from one to the other type of lattice seems to be initiated with a definite break in the derivative, according to the work of Bragg and Williams.[17]

Some progress has been made toward the explanation of these anomalies; probably the best known is that of Pauling[18] for the anomalies of NH_4Cl. Pauling's explanation is that there is a temperature range in which the molecules rapidly acquire rotational motion. This is a process which to a certain extent catalyzes itself, since the attaining of a small amount of rotational motion opens up the structure and makes the attaining of additional rotational energy increasingly easy. A similar element of autocatalysis is contained in the explanation of Bragg for the change in the gold-copper system, and it may be that this is an important characteristic of the transition of the second kind. But the details of Pauling's explanation have not been worked out; it does not appear whether there is a sharp break in a derivative or whether the transition is initiated more or less gradually, and the explanation of the difference in sign of the volume effects in NH_4Cl and NH_4Br has not been given in detail, although there would appear to be no unsurmountable difficulty here. In general, one may anticipate a number of different types of thing that might give rise to these anomalies, just as we have already seen that there must be different types of polymorphic change. Particularly does the number of possibilities appear very large when one reflects that the solid is not merely built up of a number of independent atoms, but that the whole solid is one structure, with an enormous number of energy levels and different types of wave function, much more complicated than the interior of a single atom.

XI. Electrical Resistance

We next consider the effect of pressure on electrical resistance, and in particular the resistance of metals. Theory has not yet been particularly successful in dealing with this phenomenon, and in fact the only attempt which endeavors to base the explanation on the most recent pictures of the conduction process and which can be regarded as promising is that of Kroll.[19] The reason for this comparative failure of theory can be appreciated when it is realized that wave mechanics treatments of electrical conductivity in metals give an expression for the conductivity itself only as a third approximation in the method of calculation,* and we are here concerned with the effect of pressure on the factors in this third approximation. The difficulties are suggested by a consideration of the simple formula for electrical conductivity given by the elementary Sommerfeld theory, in which the electrons are approximately treated as a gas obeying the Fermi statistics:

$$\sigma = e^2 ln/m\bar{v}$$

where l is the mean free path, $\bar{v}$ the limiting velocity of the Fermi distribution, and the other letters have conventional meanings. The elementary theory sets $1/\bar{v}$ proportional to the mean distance of separation of atomic centers, so that from this point of view the effect of pressure on $1/\bar{v}$ should be proportional to the compressibility. But we know from Schottky's theorem that the average kinetic energy of the electrons increases with pressure by a factor which is not simply related to the compressibility, so that from this point of view it is not probable that the connection between pressure and $1/\bar{v}$ can be as simple as the elementary theory would suggest. The calculation of the variation of l with pressure would obviously be very complicated, since it has to be left unknown in the elementary Sommerfeld theory, and can be computed only inversely by assuming the formula and substituting numerical values for all the other factors. l will obviously depend in a complicated way on the amplitude of atomic vibration, and the distance of separation of the atoms and on the frequency, that is, the stiffness of the restoring forces. The situation with regard to the pressure coefficient is even more complicated if one considers the expression for the conductivity given by the more exact theory, as in Bethe's article in the *Handbuch* on page 523. This contains four or five factors which may vary with pressure and which are not simple.

In spite of the lack of perspicuousness of the present theoretical picture with regard to the pressure effects, I believe that the experimental phenomena themselves are important enough so that we must demand that theory eventually give a satisfactory account of them. For the effects are not small; they are almost always greater by a factor of several fold than the changes of volume. Thus the volume of potassium under 15,000 kg/cm^2 is about 70 percent of its initial value, while its resistance is only 25 percent of its initial value; the resistance of strontium under 12,000 kg is 84 percent greater than initially whereas its volume is only 9 percent less. Among the nonmetallic elements there are even more extreme examples; the conductivity of black phosphorus at 18,000 is 100 times its initial value, that of tellurium at 20,000 is 100 times initial, and Ag_2S at 3000 is about 20 times as good a conductor as initially.

Confining ourselves now to the metals it would appear at first glance that there are great varieties of behavior. Most of the common metals decrease in resistance under pressure, and the rate of decrease becomes less at high pressures. However, the resistance of something like

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* The first approximation treats the atomic nuclei as stationary, the second approximation is that the atoms execute elastic vibrations independent of the electrons, and the third approximation is that the coupling between atomic vibrations and the motion of the electrons results in electrical resistance. See Bethe, *Handbuch d. Physik*, Vol. XXIV, 2, 2nd Ed., p. 369.

one-fifth of all the metals investigated increases under pressure; included here are bismuth and antimony, which would be expected to be abnormal, but there are other metals which one is less likely to think of as abnormal such as lithium and strontium. There seems to be no significant correlation between position in the periodic table of the elements and a positive coefficient. The pressure coefficient of resistance of all metals with positive coefficient increases with increasing pressure, that is, the plot of resistance against pressure is convex toward the pressure axis. Finally there are a few metals whose resistance at first decreases, but then passes through a minimum, and increases at higher pressures; these are caesium with a minimum at 4000 kg/cm^2, rubidium with minimum at 17,800, and barium with minimum at 9000. According to the present pictures of metallic conduction, a decrease of resistance with increasing pressure would seem to be the effect naturally to be expected. For electrical resistance is thought to arise essentially from interference with the electron waves by departures of the atomic lattice from perfect periodicity, and these departures are simply connected with the amplitude of atomic vibration. At high pressures the amplitude of atomic vibration becomes less because of increased stiffness of the forces of constraint and increase of the characteristic temperature, and hence the scattering of the electron waves becomes less and the resistance less. This wave mechanics picture is in some respects much like the "gap" theory of electrical resistance to which I was led by my pressure experiments, in which resistance to electron motion was pictured to arise from the gaps between atoms produced by temperature agitation. The existence of positive coefficients for some metals, however, would seem to demand a second type of mechanism; in the theory of Kroll such a second mechanism is provided by the effect of the distance of separation of atomic centers. By a sort of scattering effect the resistance becomes greater if the distance of separation becomes less, any inequalities in the structure becoming relatively accentuated at small distances. This gives Kroll a term proportional to the compressibility, tending to increase resistance with pressure.* In my gap theory I was similarly drawn to provide a second mechanism to account for some of the abnormal cases, particularly the phenomena of tension coefficient of resistance when combined with pressure coefficient. The second mechanism which I imagined was that some of the electrons pass through open channels between the atoms, and that these channels become contracted when the atoms are pushed together by hydrostatic pressure. This sort of thing was therefore very much like the second mechanism of Kroll. By thus providing two different mechanisms, opposite signs for the pressure effect can be provided for in different metals, and also the reversal of sign and the minimum of resistance, if we suppose that at first one of the effects preponderates and at higher pressures the other becomes larger. In this way Kroll provides qualitatively for the minimum of resistance of caesium; quantitatively, however, his results are rather wide of the mark in many cases.

Consideration of the complete body of experimental evidence, many features of which have been discovered since I last worked on my own theory ten years ago, makes me much less satisfied with this picture of two different mechanisms, one or the other of which may preponderate. The reason is that the effect of pressure on the resistance of nearly all metals (elements) yet measured can be described qualitatively in terms of a single family of curves, shown in Fig. 3. Here the resistance of any metal at constant temperature as a function of pressure has a minimum with respect to pressure, the minimum occurring at higher pressures as the temperature rises. The location of the origin of pressure in the diagram depends on the metal; for metals normally having a positive pressure coefficient of resistance the pressure origin must be taken beyond the minimum, so that for such metals a negative coefficient would be anticipated if high enough negative pressures could be

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* Kroll also has a term involving the variation with pressure of Poisson's ratio, which he ignored because he had no experimental values for it. I may remark parenthetically that I have determined the effect of pressure on rigidity,[20] and the change of Poisson's ratio under pressure may be calculated from this and the effect of pressure on compressibility. In general Poisson's ratio increases by about the same percentage amount as the incompressibility.

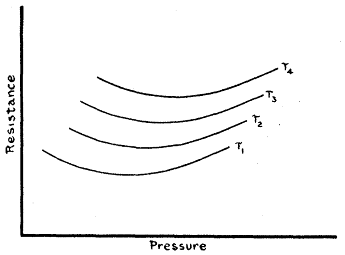

FIG. 3. The resistance of all metals as a function of pressure and temperature is consistent with a family of curves of this character. The curves are arranged in order of increasing temperature, that is, $\tau_2 > \tau_1$, etc.

realized. For normal metals, on the other hand, the pressure origin is as shown, and the pressure of the minimum is beyond the present experimental range. For only a few metals is the minimum within the range of experimentally realizable pressures. This diagram suggests that metals with positive and with negative coefficients both display aspects of essentially one phenomenon. Furthermore, the ultimate state of affairs with all metals would thus appear to be one in which resistance increases with pressure. What is still more significant, the curvature of resistance against pressure is always upward. Many phenomena vary with pressure in the opposite way, becoming less affected by equal increments of pressure at higher pressures; this is what might naturally be expected by a sort of law of diminishing returns. The fact that the curvature is like that shown suggests that there is no limit to the possible resistance of a metal, and that the tendency is to become a perfect insulator at infinite pressure. This would suggest that possibly as the atomic centers are pushed indefinitely close together a new type of solution of the wave equation will appear, by which the outer electrons, which are normally free and provide for the conduction, will become bound in the same way that the inner electrons are normally bound, the entire metal becoming as it were a single complicated nucleus.

It would be most important if the minimum of resistance could be established by actual experiment for elements of all situations in the periodic table. It has actually been established only for caesium, rubidium and barium, and indicated with high probability by a short extrapolation for potassium and sodium. Extrapolation for other metals does not give much hope of actually realizing the minimum for them, the probable pressure of the minimum being in all cases higher than 40,000 kg/cm^2. However, the existence of a minimum is made more probable in these cases if one plots log R against pressure instead of R. The reason is that the curve of resistance against pressure of those metals with a negative coefficient must almost inevitably be convex toward the pressure axis since the resistance can not become less than zero, and convexity has little significance, but log R on the other hand may go to minus infinity, there is no such restriction on the curvature, and convexity is significant. As a matter of fact, log R of all metals with a negative coefficient is convex toward the pressure axis, which is the direction of curvature demanded by the existence of a minimum.

It is an experimental fact that the pressure coefficient of resistance is little affected by temperature, or what is the same thing, the temperature coefficient of resistance is little affected by pressure. What slight change there is is consistent with Fig. 3. One would expect the temperature coefficient to be little affected by pressure because the temperature coefficient of all metals is roughly the same, $1/\tau$, and the same metal under pressure would not be expected to differ more from the same metal not under pressure than two different metals. The temperature coefficient $1/\tau$ is accounted for by the present theory, so that this aspect of pressure phenomena will be taken care of automatically in a theory of pressure effects based on present pictures.

There are a few abnormal metals which do not fit into the scheme of Fig. 3. But bismuth, which might be expected to be abnormal, does fit into the scheme. This may to a certain extent be accidental. It is highly probable that the abnormalities of bismuth are connected with its crystal structure, because the pressure effects of liquid bismuth are quite normal. This view with regard to bismuth becomes more plausible in the light of the recent discovery of the high pressure modification of bismuth, with normal volume relations to the liquid. It would be of great interest to determine the sign of the pressure coefficient of resistance of this high pressure modification of bismuth.

There have been comparatively few measurements of the effect of pressure on the resistance of liquid metals, and the theory of the resistance of liquid metals has been little considered. It seems to me that an attack on the problem of the resistance of liquid metals should not be too long deferred. Qualitatively, liquid metals show many of the same phenomena as solids, particularly with regard to the order of magnitude of the resistance itself. The present theory of electrical resistance, on the other hand, starts from the assumption of the lattice, and this assumption enters essentially into all the discussion. But resistance phenomena in liquids make it appear that these assumptions are not necessary to some of the conclusions, which could probably be deduced on more general grounds. In this connection, one pressure phenomenon is probably of significance. The resistance of the liquid phase seems to bear an approximately constant ratio to the resistance of the solid phase at the reversible freezing point, irrespective of whether freezing takes place at low temperature and low pressure or is displaced to higher temperature by high pressure. Thus the ratio of the resistance of liquid to solid potassium is 1.56 at the normal freezing point at 62.5° at atmospheric pressure, and is 1.55 at the reversible freezing point at 165° at 9700 kg.

It is probable that an ultimate increase of resistance with pressure is as characteristic of liquids as of solids. In the case of caesium extrapolation makes it highly probable, although the actual measurements could not be carried out, that the resistance of the liquid will pass through a minimum at about the same pressure as the resistance of the solid. Lithium in the liquid state has a positive pressure coefficient of resistance, and the plot of resistance against pressure is convex toward the pressure axis, as it is for solids. Liquid bismuth, on the other hand, has a negative coefficient, although the coefficient of the solid is positive. It may be, therefore, that there are special mechanisms capable of giving a positive pressure coefficient at low pressure as well as the universal mechanism giving the ultimate positive coefficient of all metals at extremely high pressures.

The effect of pressure on the resistance of non-metallic substances is of interest. A non-metallic conductor or a semiconductor is supposed to differ from a metallic conductor in that the allowed energy bands in some semiconductors are separated by wider intervals than in metallic conductors. One would expect that the effect of pressure might be to crowd the energy bands more closely together, giving the semiconductor more the characteristics of a metal. The few semiconductors that have been measured do have enormously large negative coefficients of resistance, so that at high pressures their resistance does as a fact approach that of a metal. Tellurium is a substance which is ordinarily classed as only partially metallic in character. Under 20,000 kg/cm^2 its resistance drops to one percent of its initial value; the plot of log R against pressure is convex toward the pressure axis, so that a minimum of resistance at considerably higher pressure would be consistent with the effect in the experimental range. Black phosphorus is, of course, more like the metals than ordinary yellow or red phosphorus, because it does conduct electricity appreciably whereas yellow and red phosphorus are complete insulators, but black phosphorus would be said to be much less metallic than tellurium. A non-metallic characteristic of black phosphorus is that its temperature coefficient of resistance is negative. The effect of pressure on the resistance of black phosphorus is also very large. Initially log R is concave toward the pressure axis, which means an increasingly rapid approach to the metallic condition as pressure increases; this is not unnatural because black phosphorus at atmospheric pressure is further from the metallic condition than tellurium. In the neighborhood of 12,000 kg/cm^2, however, the curvature of log R of black phosphorus reverses, becoming convex toward the pressure axis above 12,000, which means that at high pressure black phosphorus has become metallic in character at least to this extent. Furthermore, between 15,000 and 20,000 the sign of the temperature coefficient reverses, so that in this respect also black phosphorus becomes like the metals at high pressure.

One of the successful features of the new theories of conduction, which has been made much of, is the account which it gives of the resistance of alloys. When the effective free path is long, as it is in the wave mechanics picture, a single misfit atom may obviously have a great effect in introducing resistance. This picture is consistent with a generalization which may be made from all measurements to date, without exception, on the resistance of alloys: this is that the initial effect of adding a foreign substance to a pure metal is to make the pressure coefficient of resistance more positive (algebraically). The reason for this is purely geometrical; the relative misfit of a foreign atom which is a little too large, let us say, becomes greater the closer together the atomic centers of the other atoms of the lattice. But increasing misfit means increasing resistance, and increasing pressure pushes the atoms closer together. Hence pressure in such substances tends to increase the resistance more rapidly than in the pure substance, or the pressure coefficient of resistance is displaced in the positive direction.

Phenomena in single crystals of non-cubic metals have not as yet received much theoretical attention. There are, however, important phenomena to be considered here, and one may expect that this may be one of the next problems attacked. Such uniformities as, for example, that the resistance in a crystal is almost always greatest in the direction of greatest atomic separation, which is also the direction of greatest compressibility, must be significant. There are also uniformities in the behavior under pressure which must be significant. Thus the effect of pressure on the three "normal" non-cubic metals, zinc, cadmium and tin, is to make the crystal more nearly isotropic with respect to resistance, which is also the effect on the lattice spacing. The effect on the two abnormal metals bismuth and antimony is the opposite, however, pressure here makes the lattice spacing more nearly equal in different directions, but accentuates the non-isotropy of resistance.

Theory can usually derive some profit from considering the abnormal cases, which play somewhat the same role as pathological cases in medicine. Bismuth and antimony have already been mentioned, in which the pressure effect on resistance is probably accounted for by a different mechanism from that responsible in more normal metals such as lithium and calcium. There is another highly abnormal metal which I have recently found in a place in the periodic table where one would little expect it, namely, chromium. The resistance of chromium at atmospheric pressure is an abnormal function of temperature; there is a minimum of resistance at 10° and a maximum at 0°C, the shape of the curve being much like that of the curve for the volume of water as a function of temperature. As a function of pressure the resistance is highly abnormal; the coefficient is throughout negative, but the curvature of an isothermal of resistance against pressure may be of either sign, or there may be a reversal of sign on the same isothermal with a point of inflection. The resistance isotherms cross and recross in a complicated way, which means both positive and negative temperature coefficients at constant pressure. Not only is the resistance abnormal, but the relation between pressure and volume is also abnormal; there is, however, no obvious correlation between the abnormalities of resistance and volume.

Another abnormal metal is arsenic; this shows abnormalities only when very pure and only when in the single crystal condition, and the abnormalities are almost entirely connected with those directions in the crystal perpendicular to the principal axis. The abnormality seems to consist in definite pressure ranges within which the relation between pressure and resistance is linear, but with different coefficients in the different ranges, and no discontinuity of resistance itself from one range to the next. That is, there is a sort of transition of "the second kind" in the resistance. There are also some very unusual seasoning effects in single crystal arsenic.*

XII. Thermoelectric Phenomena

Another group of electrical phenomena is that of thermoelectricity. The rigorous theory of these effects is complicated; the simple Sommerfeld theory, in which the electrons are treated as free, gives acceptable results only for the alkali metals, for other metals there being discrepancies even of sign. The more rigorous theory takes specific account of the way in which the electrons are distributed among the allowed energy bands, and finds different signs for the Thomson effect

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* Since this paper was written, a very promising theory of the effects of pressure on resistance of the metals has been made by N. H. Frank, and submitted for publication in the *Physical Review*. This theory accounts for the minimum resistance of the alkali metals.

according as the bands are almost empty or almost full. As far as I know, no attempt has been made to deduce the effect of pressure on thermoelectromotive force according to the more rigorous theory, although Houston[21] has given an expression on the basis of the simple Sommerfeld theory which fails in the case of copper by a factor of ten. One would expect that the results of the more rigorous theory would be complicated. This expectation agrees with the experimental findings, for the effects of pressure on thermal e.m.f. are perhaps the most complicated of any pressure effect; there are great departures from linearity, curvature in both directions, points of infection, maxima and minima, crossing of the curves and reversals of sign. As a rough average for the some twenty metals examined, the sign of the effect is such that in more cases than not the electrons absorb heat in flowing from compressed to uncompressed metal. In this respect the electron gas is like an ordinary gas which also absorbs heat on expanding. There are so many exceptions to this rule, however, that the general result must not be given much significance. It is, however, significant that the magnitude of the effect is large; the Peltier heat when an electron flows from a metal compressed to 12,000 kg/cm^2 to the same metal under no pressure is on the average of the same order of magnitude as when an electron flows from one to another different metal. In view of the theoretical suggestion that the thermal e.m.f. depends importantly on the way in which the electrons are distributed in an energy band it would therefore appear that pressures in the experimental range are capable of affecting important redistributions within the energy bands. Hence in spite of, or rather because of, the complications, it may well be that a careful theoretical study of the effects of pressure on thermoelectric effects will give a deeper insight into the details of the electron distribution than other simple phenomena.

XIII. THERMAL CONDUCTION

Thermal conduction of metals also receives a treatment in the new theories, and in fact one of the most important results of Sommerfeld's simplified theory was that it still provided an explanation for the Wiedemann-Franz ratio, which had been the most important result of the classical theory of Drude and Lorentz, while meeting the specific heat difficulty which the classical theory could not avoid. But the new theory applies only to the part of the conduction performed by the electrons; so far as I know the relatively small part played by the atoms in conducting heat has not yet been fitted into the picture. Experimentally, of course, the contributions of the two agencies are not separated, so that a measurement of the pressure coefficient of thermal conductivity is a measurement of the pressure coefficient of both mechanisms. It turns out that there is no uniformity from metal to metal; for example, the thermal conductivity of lead and tin increases under pressure, while that of copper, silver and nickel decreases. Furthermore, in all cases except lead and tin the change of thermal conductivity under pressure is less than the change of electrical conductivity, so that except for lead and tin the pressure coefficient of the Wiedemann-Franz ratio is negative. The experiments are difficult; it was not possible to measure the more compressible metals for which large effects would be expected, and in practically every case it was not possible to find in which way the effect departs from linearity. Theoretically one would be prepared to find a zero coefficient for the Wiedemann-Franz ratio by the argument used before for the variation of temperature coefficient of resistance with pressure, namely that the Wiedemann-Franz ratio of all metals is nearly the same, and since in general a metal under high pressure would be expected to be more like itself under zero pressure than another metal, one would expect the effect of pressure on the Wiedemann-Franz ratio to be small. It is to be remembered, however, that for a single metal the variation with temperature of the Wiedemann-Franz ratio is in many cases not exactly that demanded by theory, and pressure doubtless affects the characteristic temperature of a metal. In view of the smallness of the effect in the metals which could be subjected to measurement it is obvious that a comparatively small shift in the parts played by electronic and atomic conduction could account for the experimental results. Furthermore, this shift may be a small range effect and be reversed at high pressures as far as any evidence goes which we have at present. An explanation of the pressure effects must therefore wait for the completion of the theory of the atomic part of thermal conduction; such a theory must be prepared to explain why in many cases atomic conduction becomes poorer at high pressures. It is perhaps not hopeless to anticipate that such an effect will be found in view of the fact that thermal conduction involves the scattering of elastic waves, and that any lack of perfect fit, which is conducive to scattering, may be accentuated by high pressure. But it must be a somewhat difficult point to show why it is that in the majority of cases pressure diminishes the scattering of electron waves but increases the scattering of elastic waves.

The effect of pressure on the thermal conductivity of non-metallic solids or of liquids is much easier to measure, and there is considerable experimental material of much greater accuracy than for the metals. The thermal conductivity of organic liquids increases under pressure by an amount which to a first approximation is the same for all liquids, the increase under 12,000 kg/cm^2 being roughly by a factor of two. The curve of conductivity against pressure is concave toward the pressure axis, so that the effect of equal increments of pressure diminishes at high pressures, as is usual. It turned out from the measurements that there is a rather close correlation between the effect of pressure on the velocity of sound, which can be calculated in terms of the compressibility, and the effect on thermal conductivity. This correlation suggested a very simple expression for the thermal conductivity of a liquid, namely

$$K = 2\alpha v \delta^{-2},$$

where K is thermal conductivity, α the gas constant, 2.02×10^{-16}, v is the velocity of sound, and δ is the average distance between centers of molecules, calculated approximately by assuming the liquid piled up with the molecules in simple cubical array as in a simple cubic crystal. One can derive this expression in an elementary way by supposing that the mean difference of thermal energy in the direction of the thermal gradient between adjacent molecules, which is $2\alpha\delta d\tau/dx$ (τ is temperature) gets handed along in the direction of the gradient with the velocity of sound. Jeffreys[22] has shown that a better way of arriving at the same result is to suppose that in a liquid the molecular irregularity is so great that the energy of an elastic wave is completely scattered in the minimum possible distance, the distance between centers of molecules. The derivation suggests that the formula should also be applicable to amorphous solids, and in fact it is known to be applicable to hard rubber and to some glasses.

The very simple expression $2\alpha v\delta^{-2}$ is applicable with an error of 10 or 15 percent to normal organic liquids, and is also applicable to water, the thermal conductivity of which is four times greater than that of the normal organic liquid. It is therefore somewhat surprising that the formula does not give very accurately the pressure coefficient of thermal conductivity; it would predict an increase of thermal conductivity at 12,000 between three and fourfold on the average, whereas the actual increase is only by twofold. Any lining up of the molecules of the liquid under high pressure by which the distance of complete scattering becomes greater would increase the thermal conductivity by a new factor and would therefore increase the discrepancy. On the other hand, if there is a tendency for the atom to become the unit of structure at high pressure instead of the molecule, which is consistent with the known tendency of the specific heats, centers of scattering would develop inside the molecule, and the too small pressure coefficient would be accounted for. The exact analysis of any such effect is obviously complicated; this much is at least evident, that an adequate theory of the effect of pressure on thermal conductivity in liquids will have to wait until a theory is developed competent to account at least for the simple volume relations.

In working out a more exact theory of thermal conduction in liquids a significant point to be kept in mind is that the temperature coefficient of thermal conductivity of nearly all liquids reverses at high pressures; at atmospheric pressure the liquid is a poorer conductor at high temperatures (greater elastic scattering) but at high pressures the liquid conducts better at higher temperatures. The pressure of reversal is roughly the same as the pressure of reversal of the sign of $\partial^2 v/\partial \tau^2$.

The effect of pressure on the thermal conductivity of simple crystals has been measured only for NaCl; there is room here for much more experimental work.

XIV. Viscosity of Liquids

There is extensive experimental material for the effect of pressure on the viscosity of liquids, mostly organic. The general characteristic of this phenomenon is the great magnitude of the effect, which is much larger than that of any other pressure effect. Thus eugenol increases in viscosity at 12,000 by a factor of 10^7-fold. At high pressures the increase of viscosity is roughly exponential, the plot of log (viscosity) against pressure being approximately linear; at the low pressure end this plot usually shows curvature which may be in either direction. There is a very marked correlation between the pressure effect and the size of the molecule; for monatomic mercury the increase of viscosity at 12,000 is only 33 percent against the 10^7 already mentioned for eugenol. There is no theory of the viscosity of liquids which adequately reproduces the effects of pressure. There have been elementary theories which demand that viscosity be a function of volume only; this was a fairly good approximation for the range of pressure experiments at that time available, which reached to only 3000 kg/cm^2, but over the extended range up to 12,000 the relation fails by a very large factor. An improved theory of Brillouin recognizes that viscosity need not be a function of volume only, but gives for the temperature coefficient of viscosity at constant volume a numerical result which is in error by a factor of 5000. By far the most successful theory of the viscosity of liquids is the recent one of Andrade.[23] This gives the temperature coefficient of viscosity at atmospheric pressure with considerable success, and also in most cases gives a fair account of the variations with pressure up to a few thousand kilograms, but at higher pressures it goes badly wrong. Andrade remarks that the pressure at which the theory begins to go wrong is also the pressure at which $\partial^2 v/\partial \tau^2$ reverses sign; apparently at this pressure some important reconstruction begins to take place in the structure of the liquid. From a qualitative point of view it has seemed to me that these high pressure effects are to be understood only in terms of an effective interlocking of the molecules; from this point of view the very large effects, particularly with the complicated molecules, and the failure of viscosity to be a pure function of volume, are understandable. Such interlocking effects demand that in any mass motion of the liquid such as is encountered in measuring viscosity the molecules retain their individuality, for one can hardly conceive that the forces required to tear the molecules apart would not be very much greater than are involved in even the high viscosity at high pressure. The hypothetical loss of individuality by the molecule at high pressure which we have discussed in connection with other phenomena is a less drastic thing, for these other phenomena have involved only pure volume compressions. The less drastic sort of loss of individuality may perhaps correspond to an internal quivering of the atoms in the molecule, with more relative freedom than they possess at lower pressures—the sort of thing that would result in a higher specific heat.

XV. Conditions of Rupture

We now consider a topic connected with high pressure effects a little more remotely than those which we have discussed hitherto. In the very extensive discussions of the last few years with regard to the so-called "structure sensitive" and "structure insensitive" properties of crystals, considerable attention has been paid to the tensile strength. It is well known that the actual strength is always very much less than the calculated strength, and discrepancies by a factor of 100 are not unusual. The "calculated" strength is found in terms of the assumed law of force between the molecules. The method always adopted is to find the distance of separation at which the total cohesive force is a maximum, and then to postulate that rupture occurs when the extension under external force becomes great enough to result in this amount of separation. There are complications because the lateral contraction and longitudinal extension are different, but this does not alter the main argument. The fact that rupture occurs in practise long before the extension reaches the calculated value is put down to internal imperfections.

Entirely apart from the question of whether there are or are not internal imperfections which might result in premature rupture, I do not believe that a correct criterion of rupture has been adopted in the theoretical calculation, and I believe that a simple effect observed at high pressure makes this absolutely certain. If a ring of hard rubber is provided with a closely fitting steel core, and if the whole assembly is then immersed in a liquid and subjected to hydrostatic pressure, the hard rubber ring will be found to split at a pressure of a few thousand kilograms, just as if a conical wedge has been driven into it. In fact, this is actually the nature of the effect. For if there had been no steel core the rubber ring would have shrunk by a very appreciable amount because of the high compressibility of hard rubber, but the steel core, the compressibility of which is very small, prevents the natural contraction of the rubber under pressure, so that we have effectively a steel wedge forced into the contracted ring. A simple calculation shows that although the rubber ring at the rupture point is larger than it would have been without the steel core, it is nevertheless smaller than it was initially under no pressure. In fact every strain in the hard rubber ring is a strain of compression, but nevertheless a clean tensile rupture takes place. It is therefore obvious that the critical distance of separation criterion of rupture cannot possibly be correct under these conditions. A little consideration shows, I believe, that the requirement that the molecular cohesive forces be a maximum at the critical extension is simply not pertinent, this being a criterion taken over rather uncritically from the method of function of a special type of testing machine. One may grant that the maximum force gives a sufficient condition for rupture, but not a necessary one. It seems to me that a stability criterion is much more pertinent; rupture certainly takes place when such an extension has been reached that the structure is unstable. The stability condition must also be a sufficient condition, and it would seem to be close to a necessary condition. A suggestion of this character has been made by Born on pages 768–769 of his *Handbuch* article, but this is the only suggestion I have seen in print that the conventional criterion of rupture may not be correct. Conditions of stability are notoriously difficult to formulate, and in fact the ordinary theory of ionic crystals does not yet deal satisfactorily with this fundamental point, but can show only that the lattice is stable for certain restricted types of displacement. It would probably therefore not be easy to work out exactly the criterion of rupture demanded by the stability condition, but it is easy to see qualitatively, I think, that the critical deformation would be less than that demanded by the maximum force criterion, for this latter is also a stability condition for a distortion uniform in every direction, which is itself a very unstable kind of distortion. The stability condition for uniform distortion doubtless sets only an upper limit. In view of the complexity of a general condition of stability, I do not believe that a rigorous application of the condition would result in any such simple condition of rupture as is often assumed in practise, such as a maximum extension, or maximum tensile stress, or maximum shearing strain criterion. This expectation also agrees with experiment, for there are types of rupture characteristic of high pressure which show that none of these criteria can in general be valid; further details will be found in *The Physics of High Pressure.*

XVI. SPECULATIONS

Finally we may indulge in a few perfectly frank speculations as to what sorts of effects may be expected at pressures very much higher than those yet reached in the laboratory. There is no natural upper limit to pressure, nor is there any limit to the amount of energy which can be imparted to a substance by compressing it; in the stars there are perfectly stupendous pressures of the order of billions of atmospheres, and we know that sometimes under such conditions matter is consolidated to densities of the order of 100,000—the field thus offered for speculation is a fascinating one.

A remark must first be made by way of correction. A number of years ago I published speculations on this topic in two papers.[24] Some aspects of the argument of the first paper were based to a certain extent on the experimental values of the compressibilities of the alkali metals, and in particular on the abnormal persistence of the compressibility of potassium at high pressures. I have recently found that there was a serious error in the reduction of linear to cubic compressibility; the abnormalities now disappear, and part of the argument of the first paper is thereby vitiated. The corrected details will be given in a forthcoming paper, in which the pressure range is extended from 12,000 to 20,000. Furthermore, the principal point of those two papers was that at high pressures the solid may be expected to break down into a gas of electrons and nuclei; the argument was made both from thermodynamics and from Schottky's theorem. However, no account could be taken at that time of the exclusion principle of Pauli, and it now appears that such a breakdown is probably inconsistent with the exclusion principle, for it is difficult to see how an increase of pressure would increase the number of energy levels in the neighborhood of $\frac{1}{2}\kappa\tau$ sufficiently to allow all the electrons to find places with this mean energy. It is therefore probable that the idea of a decomposition into a perfect electron gas at high pressures must be abandoned, although it is perhaps still legitimate to ask whether the quantum relations must necessarily hold under such extreme conditions.

Intimations as to possible behavior at very high pressure have appeared incidentally from time to time in the course of this paper. Thus there has been the suggestion that the smaller units in the structure may come to play more important parts at high pressure; the compressibility of isomers and the variation of the specific heat with pressure suggests that in liquids at high pressures the atom may come to play part of the role of the molecule at lower pressures, and in metals the behavior of thermal expansion at high pressures and the consequent dilemma with respect to entropy at infinite pressure suggests that the electron may be assuming some of the rôle of the atom. In semiconductors the very large increase of electrical conductivity under pressure means essentially a freeing of the electrons, which is the same sort of thing. On the other hand, the probable ultimate increase of resistance of all metals means a closer binding of the electrons.

The irreversible change from yellow to black phosphorus raises the question of whether there may not be many other such changes possible if the pressure is only raised high enough. Could heavy matter of density 100,000 continue to exist at atmospheric pressure if it had once been forced into existence by stupendously high pressure? One property of such heavy matter is indicated by the uncertainty principle, which suggests that such matter cannot exist in the condition of a regular space lattice. The reason is very much the same as the reason why hydrogen cannot exist as a lattice of the NaCl type composed of electrons and protons. The mass of the electron is so small that the uncertainty principle does not allow to it the definiteness of location that would be demanded by a lattice of the density of solid hydrogen. As mass increases the possible definiteness of location increases, so that ordinary atoms can assume positions in space lattices of the ordinary density, but if the density is very high, the mass of the ordinary atom may impose restrictions. For example, consider the case of sodium, and suppose it exists in a simple cubic lattice of density 100,000. The distance between atomic centers would be 7.3×10^{-10} cm. Assuming for the energy of temperature agitation the classical value, $mv^2/2=(3/2)\kappa\tau$ the uncertainty in position demanded by the uncertainty principle is $\Delta l\approx h/(3\kappa m\tau)^{\frac{1}{2}}\approx3.0\times10^{-9}$, at ordinary temperatures, and is thus four times greater than the lattice spacing. If instead of assuming classical energy one assumes that, because of the enormous restoring forces and high characteristic temperature at these high densities, the atoms are completely in the condition of a Fermi degenerate gas with an upper kinetic energy limit given by the Sommerfeld expression,

$$V_0=\frac{3}{10}\frac{h^2}{m}\left(\frac{3n}{4\pi}\right)^{\frac{2}{3}},$$

it will be found that the uncertainty in position demanded by an uncoordinated motion of this amount is 2.1 times the lattice spacing. It is therefore meaningless to attempt to describe the atoms as situated on a lattice, and the state of aggregation must be a more or less amorphous jelly. Matter at such extreme densities must be effectively in a new state, as different from ordinary matter, as for example, an ordinary gas is different from the "fourth state of matter" of Crookes. One may suspect "emergent" properties.

The value for Δl given by the uncertainty principle is seen to become smaller at higher temperatures. The pressure state of matter is, then, characteristic of low temperatures. There is therefore still some plausibility in one feature of the suggestion in my previous paper, namely that the extended pressure-temperature plane is crossed by a diagonal band, rising from low temperatures and low pressures to high temperatures and high pressures. Within this band matter exists in the state ordinarily known; on the high temperature side of the band it dissociates to a gas of electrons and nuclei according to ideas first emphasized by Saha, and on the high pressure side we now see that it collapses to a "pressure-squash." Whether quantum principles in their present form apply to this "pressure-squash" can be told better when it is found to what extent they apply to the interior of the nucleus. Furthermore, the possibility must be recognized that the pressure-squash is composed of neutrons, electrons and protons being forced to form closely coupled pairs by the extreme pressure. Such a system would be an electrical insulator, and in this respect would fulfil the tendency found in metals in the experimental range.

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