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Recent Work in the Field of High Pressures

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INTRODUCTION

THE purpose of this review is to summarize work in the field of high pressures which has been published in accessible form between the writing of my book, *The Physics of High Pressure*, in 1930 and June, 1945. Activity in this field, as in so many other fields of physics, is accelerating; the number of literature references in the last fifteen years is equal to the total in the entire previous history of the subject. Activity is increasing at both ends of the range. At the low pressure end industrial applications, such for example as the cracking of oil to produce gasoline, have stimulated intensive investigation of the properties of gaseous mixtures and of gaseous reactions up to pressures of a few hundred atmospheres. At the other end, quantitative measurements are being made up to 100,000 atmospheres, five times the range open to quantitative measurement fifteen years ago.

Any division of pressure phenomena into those of "low" or of "high" pressure must be to a certain extent arbitrary. We shall obviously not be concerned with vacuum tube phenomena; a possible definition would be that "high" pressure is to mean any pressure higher than atmospheric. We shall, however, restrict ourselves to phenomena which can be successfully investigated only by self-conscious attention to matters of technique, which in general means the use of fairly heavy metal containers and care in preventing leak. In other words, we are beyond the region of a sealing-wax and glass capillary technique. Roughly this may be characterized by pressures measured in thousands of atmospheres; this limitation means that we shall not be greatly concerned with such phenomena as critical phenomena, which for most substances play themselves out in a few hundred atmospheres. On the other hand, there are certain phenomena whose total arena may extend to thousands of atmospheres, which for one reason or another have up to now been investigated to only a few hundred atmospheres; these we shall regard as in our province.

In spite of accelerated activity in the field of high pressures, work is still confined to a comparatively small number of foci, and the average laboratory does not have the simple special equipment usually necessary. In the last fifteen years several new foci of high pressure work have appeared. The laboratory of C. Michels in Amsterdam, which in 1930 was still comparatively fresh in the field, has turned out a large amount of work with the cooperation of many students. The range of this work has been a few thousand kg/cm^2; its most notable characteristic has been its high precision and the development of ingenious instrumentation. Some fifty titles have appeared from the laboratory of James Basset in Paris, only two of which are prior to 1930. This work is not at all well known to physicists in this country; many of the papers are short, and the great majority emphasize the qualitative rather than the quantitative aspect. Basset's work has always had a more or less industrial slant; apparently the original object of the work was to effect the diamond synthesis; it seems to have had industrial support because of this, and a number of his papers deal with this subject. Basset has also been interested in the manufacture of apparatus and has issued catalogs of apparatus which he is in a position to supply for high pressure research. In addition, some 14 papers, mostly with collaborators, deal qualitatively with various biological effects. The most striking characteristic of Basset's work is the magnitude of the pressure range that has concerned him; one of his most recent titles describes an apparatus with which 100,000 kg/cm^2 may be reached. There is a brochure, issued without date, presumably a private publication of Basset, summarizing all his publications into 1942. It was printed by Imprimerie Moderne de Dreux, 9, Grande-Rue-Dreux (Paris?), and bears the title page: "Notice sur le Laboratoire pour la Recherche Scientifique aux Ultra-Pressions jusqu'a 100,000 kg/cm^2 et Résumés des Travaux Scientifiques de James Basset."

Activity in the field of high pressure in Russia is obviously high, but it is difficult to find the details. It is known that there is a laboratory devoted primarily to high pressure work, and a number of articles in the Russian journals have reached this country, but there is no reason to think that our present information is by any means complete. There is no present indication that material progress has been made beyond the possibilities open to the techniques described in my book in 1931.

In England, Imperial Chemical Industries has taken up seriously the investigation of chemical reactions under pressure and has published the results of many such investigations up to pressures of 12,000 kg/cm^2.

In this country the most notable new work has been the program of geophysical investigation at Harvard sponsored by its Geophysical Committee and directed for the first few years by W. A. Zisman and since 1933 by Francis Birch. This program has been concerned with, among other things, the application of pressures up to 12,000 kg/cm^2 in combination with high temperatures to problems of geophysical interest and has resulted in some 25 papers dealing with various pressure effects. The work of David Griggs at Harvard, some of it under the auspices of the Geophysical Committee, has also been to a considerable extent concerned with the application of high pressures to geophysical problems. At Pennsylvania State College, R. B. Dow has founded a high pressure laboratory which has produced some 20 papers dealing with the effects of pressure up to 5000 kg/cm^2, mostly on volumetric effects and changes of viscosity of various hydrocarbons and oils of industrial importance. On the west coast an extensive program at Pasadena, sponsored by the American Petroleum Institute, and associated chiefly with the names of B. H. Sage, H. H. Reamer, R. H. Olds, and W. N. Lacey, is being carried out on the volume and viscosity properties up to a few hundred kg/cm^2 of various hydrocarbons of industrial importance, and particularly on their mixtures. The high pressure field is attracting the attention of industry, and several commercial laboratories are beginning work, but it is probably too early to specify this in further detail.

Of the laboratories which were active in 1930, the Geophysical Laboratory in Washington; the work at Massachusetts Institute of Technology, principally in the laboratory of F. G. Keyes; and my own work at Harvard continue.

Of the workers who were prominent in the period up to 1930, Tammann, who contributed so much, reached the end of his productive period, contributing only a few papers since 1930, and died toward the end of the period of this review. Similarly Ernst Cohen at Utrecht reached the end of his labors and contributed only three titles in the present period. T. C. Poulter, who was active and did important work in this field at the end of the last period and in the first few years of the present period, has been diverted to other projects during the major part of the period, although there are indications that during the last few years he is returning to the field.

The order of presentation in the following will be essentially the same as in my book. We shall first be concerned with questions of technique, then with mechanical effects of pressure, of which the volumetric effects are most important because most simple, including here phase changes, then thermal, electrical, magnetic, and optical effects, proceeding finally to chemical and

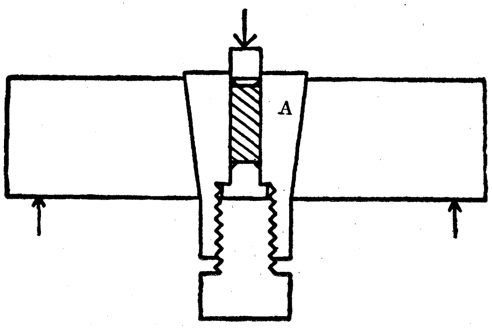

FIG. 1. Schematic representation of method of automatically subjecting the pressure vessel to external pressure.

biological effects. The bibliography will be given at the end of the respective sections.

TECHNIQUE

We shall here be concerned only with questions of general technique, leaving to the appropriate sections descriptions of apparatus for special purposes.

1. Extension of the Pressure Range

Perhaps the problem that first presents itself with regard to technique is extension of the range. The obvious and direct method of extending the range is by the use of stronger materials. There have been two important developments here. Steels are now available for the construction of pressure vessels with a tensile strength of some 350,000 p.s.i. and an elongation of several percent, as contrasted with tensile strengths of the order of 250,000 p.s.i. formerly available. For the pistons of pressure apparatus Carboloy is now available, with crushing strengths under ordinary atmospheric conditions which I have measured up to 67,000 kg/cm^2, and which Basset reports may reach 75,000 kg/cm^2. This is somewhat more than twice the compression that steel will support without undue plastic distortion. A further most important advantage of Carboloy is its very low elastic deformability, the elastic constants being about three times those of steel. Carboloy is, however, under ordinary conditions not as strong as steel in tension, and furthermore is excessively brittle. It can be used for pressure vessels, as contrasted with pistons, only by special devices, by which it may be made markedly superior to steel.

The pressures which can at present be reached are attained by a combination of the best materials, as indicated above, with special methods of construction. The conventional methods of special construction have been by the methods of shrinking on supporting rings or by wire winding, or by cold working (autofrettage). These methods are set forth in considerable detail in three English books, by Macrae,[1] Tongue,[2] and Newitt.[3] By such methods something of the order of double the normal strength of a vessel may be attained; the limit is set by reaching the flow point in compression of the inner wall of the container under the stress imposed by the external constraint. A more advantageous method of external support is to increase the external support in proportion as the internal pressure increases, instead of applying the maximum external support when the internal pressure is zero. A simple method of doing this is to make the external surface of the pressure vessel conical and to push the whole vessel into an external conical supporting sleeve. The simplest method of doing this is to let the thrust on the pressure generating piston itself push the vessel into the sleeve as shown in Fig. 1; by this method I[4] have reached pressures of 50,000 kg/cm^2 in apparatus with a 0.25-inch inside diameter, and have measured a number of volumetric effects. However, there are geometrical limitations to this simple method of producing the thrust, and it is usually better to produce the thrust that generates the external pressure by means independent of that which produces the thrust on the piston. I have two schemes for doing this; in one[5] the direction of thrust for external pressure is opposed to that of the thrust for internal pressure. With this apparatus pressures of 30,000 kg/cm^2 can be reached in volumes 0.5 inch in diameter and 6 inches long, and electrical leads may be taken into the chamber and complicated electrical measurements carried out. In the other,[6] the two thrusts are in the same direction, the external supporting arrangement is multiple for greater strength, and volumetric measurements have been made to 50,000 kg/cm^2 with much longer life for the apparatus and much less plastic distortion than when the piston generates the thrust for the external pressure. 50,000 kg/cm^2 is about the limit that can be reached by this method of support; the steel vessel is on the point of failing by fracture on planes perpendicular to the axis because of extrusion effects as well as on radial planes because of ordinary rupture due to internal pressure.

To reach still higher pressures a more complete external support must be supplied; this I have done[7] by immersing the entire pressure apparatus, both piston and cylinder, in a fluid bearing a hydrostatic pressure which may be pushed as high as 30,000 kg/cm^2. The gain by this method of support is materially greater than the mere increase of hydrostatic pressure, because the physical properties of the steel and Carboloy of which the apparatus is constructed are enhanced by the action of hydrostatic pressure. The most important effect is on the Carboloy. Under pressures of the order of 20,000 to 30,000 kg/cm^2, Carboloy loses its brittleness,[8] will tolerate plastic deformation in compression, and will also support the tension inherent in a pressure vessel, so that the pressure vessel as well as the piston may be made of Carboloy under these conditions. Carboloy under these conditions is much superior to steel for the pressure vessel both because of its greater strength and because of its much smaller elastic distortion. With apparatus of this sort, which is shown in Fig. 2, many volumetric measurements have been made up to 100,000 kg/cm^2. Higher pressures may be reached, but it is difficult to make accurate volume measurements because of slow creep of the pistons.

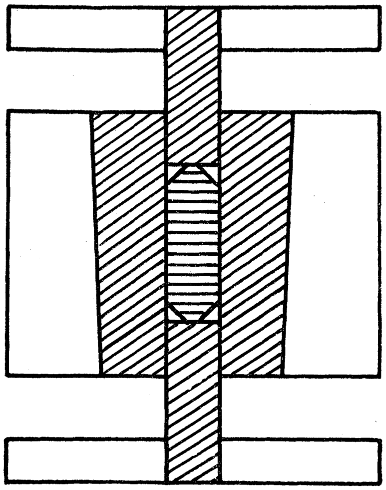

FIG. 2. The piezometer for volume measurements to 100,000 kg/cm^2. The diagonally shaded regions are Carboloy, the horizontally shaded region is the charge whose compression is to be measured, and the unshaded regions are steel.

There was an independent development parallel to this at the Geophysical Laboratory under Goranson[9] which was interrupted by the war. Goranson also supported his pressure vessel in an external fluid under hydrostatic pressure. Only preliminary reports of this work have been published. His supporting pressures were lower than mine, not over 20,000, and he reports reaching a pressure of 200,000 kg/cm^2. Until this work has been confirmed, I think the presumption is that 200,000 is considerably too high. In the early stages of my own work I had estimated my pressures as too high. The difficulty was occasioned by friction, which is hard to correct for and obscures the results. Goranson was to a certain extent predisposed to his high estimate of his pressure by his theory of the effect of confining pressure on the compressive strength of his pistons. According to his theory strength in compression increases at a much accelerated rate beyond a few thousand kg/cm^2, becoming infinite at a pressure indicated in one of his diagrams[10] as less than 15,000 kg/cm^2. Direct measurements of mine[8] up to pressures of 30,000 did not disclose this sort of behavior, but the increase of compressive strength remained approximately linear with the confining pressure over the entire range, with a maximum increase of strength of the order of 25 percent. The same qualitative behavior was found with some of the stronger minerals, such as quartz, sapphire, tourmaline, and diamond. These direct measurements of compressive strength under true hydrostatic confining pressure also negative some early observations of Griggs, who thought he had established the accelerated rise of strength expected by Goranson. Indeed, I thought in my own preliminary observations to have confirmed the conclusion of Griggs. The explanation in all cases is probably the obscuring effect of friction. The principal reason that pressures of 100,000 and more can be reached in Carboloy containers is probably not the actual increase of strength under the confining pressure, but rather the loss of brittleness and increase of ductility, an effect produced by high pressure on a number of materials.

In this same field Basset[11] has published the description of an apparatus for reaching 100,000 kg/cm^2. He does not utilize the support afforded by confining pressure, but instead cools the whole apparatus in liquid air, where he finds that the compressive strength of his Carboloy piston has risen from 75,000 to 100,000 kg/cm^2. Basset's pressure vessel is of Carboloy with shrunk-on steel jackets. No results have been published with this apparatus; the field of application would seem to be somewhat limited.

At these very high pressures the stresses are only approximately hydrostatic, because practically every liquid or even gas has frozen solid, and stress differences of the order of the plastic shearing strength of the solid would be expected. The shearing strength of metals like tin or indium is, however, only a few hundred kg/cm^2 even under high pressures, so that stresses sufficiently close to hydrostatic for purposes of measurement can be reached.

By suitable design it is possible to reach much higher stresses of compression in very small areas which are supported by massive surrounding regions less strongly stressed, and by interposing minute pieces of a plastic metal between the opposing parts higher approximately hydrostatic pressures may be reached. With a short Carboloy truncated cone pressed against a massive Carboloy block and supported by a fluid confining pressure of 30,000 kg/cm^2, I[8] have reached pressures of 425,000 kg/cm^2 in small bits of such substances as graphite or sulfur. Only qualitative permanent changes can be looked for under these conditions, and the results thus far have been negative.

It has appeared for some time that the domain of high pressure phenomena at very low temperatures would be exceedingly difficult of access for the reason indicated above, namely the freezing of any transmitting substance. Lasarew and Kan[12] have, however, indicated a method by which at least some results can be obtained in this region. They froze water in a closed container at temperatures of $-30°$ or $-40°$C, where the maximum pressure is about 2000 kg/cm^2, determined by the transition between ice I and ice II. At liquid air temperature the transition ceases to run, but they found that on cooling the apparatus to hydrogen temperatures most of the pressure attained at the higher temperature is retained. The pressure was determined from the elastic increase of the external dimensions of the pressure vessel. In this way they were able to measure the effect of a pressure of 1700 kg/cm^2 on the superconducting point of tin and indium wires embedded in the ice. The method is obviously limited to such effects as do not involve any large change of volume. The authors suggest that by utilizing the phase changes of bismuth it may be possible to reach pressures of the order of 10,000 kg/cm^2 in this domain.

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2. The Measurement of Pressure

The fundamental method of measuring pressure, to which other methods must ultimately make reference, remains the measurement of the thrust on a piston of known area. The instrument *par excellence* here is the free piston gauge. In the range up to a few thousand kg/cm^2 a number of elaborate studies have been made. The fundamental problem is to correct for the distortion of cross section brought about by the pressure itself. For precision of the order of $\frac{1}{10}$ percent or even better it is sufficient to take the effective area as the mean of the area of piston and cylinder and calculate the distortions of piston and cylinder approximately from elasticity theory. A rigorously accurate calculation of the distortion is not possible, however, because of the indetermination in the external stresses arising from the liquid escaping between piston and cylinder, and some method of at least checking the calculation becomes necessary.

Very extensive use has been made of the free piston gauge in the laboratory of Keyes at Massachusetts Institute of Technology, some fifty gauges having been used over a period of twenty years. These are described in papers of Keyes,[13, 14] and a careful study has been made by Beattie and Edel[15] and by Beattie and Bridgeman[16] of the effect of pressure on the gauge constant, on secular changes in the gauge constant because of shifting internal equilibrium in the steel, and the effect of viscosity in the oil. Their type of construction is such that there is no change in the gauge constant up to 600 kg/cm^2. Secular changes in the constant of as much as $\frac{1}{10}$ percent were found in a ten-year interval, dropping to one-fifth as much in the second ten years. No effect of oil viscosity could be detected. Michels[17] has utilized a mercury column giving 40 kg/cm^2 in his calibration, and has attained a reproducibility of 1/50,000 and a sensitiveness of 0.5 g on 300-kg total load. Ebert[18] has determined the functional cross section of a free piston gauge up to 3000 kg/cm^2 by comparison step-wise in steps of 500 kg against a multiplying arrangement which was packed, so that the correction for distortion of the multiplier was given simply by the change of its internal diameter. The functional cross section of Ebert's gauge increased 2 parts in 10^{-6} per kg/cm^2.

There has been no new determination of any fixed pressure point by the free piston gauge above 5000, and my fundamental value of 7640 kg/cm^2 for the freezing point of mercury at 0°C remains without confirmation by other observers. In Russia, Vereschagin and Alexandrov[19] essentially reproduced my free piston gauge and used it up to 10,000 kg/cm^2, but instead of making with it an independent determination of the mercury point, they used my value 7640 to obtain the effective cross section.

It still seems to me that there will be serious technical difficulties in using the free piston gauge to pressures materially higher than those of my original calibrations, 13,000 kg/cm^2. Precise pressures in the region above this will probably demand the use of a packed piston, so designed as to minimize friction. This may be done by refinement of mechanical construction, in particular reducing the thickness of the packing to a minimum. In this way I[20] have determined the parameters of the transition between bismuth I and II at 30°, which is suitable for a pressure fixed point. The difference between readings with increasing and decreasing pressure, that is, twice the width of the frictional band, was 3 percent; the mean should have a much higher accuracy. As the mean of five determinations, varying from 25,380 to 25,465, I have adopted for the pressure of transition between bismuth I and II at 30° the value 25,420 kg/cm^2. The accuracy should be of the order of $\frac{1}{10}$ percent. In making this determination it is necessary to correct for the distortion of the pressure cylinder by the internal pressure. This was directly determined by measuring the change of internal diameter while under pressure with a sliding wire arrangement, instead of calculating it by elasticity theory, which would have been hazardous.

The pressure fixed points having been established by a free piston gauge or its equivalent, secondary gauges may be constructed which will avoid the leak inherent in the free piston gauge and be otherwise more convenient. The change of resistance of manganin remains the most convenient and commonly used secondary effect. A little systematic work has been done in searching for other alloys better suited to this use; Schulze[21] suggests the use of a 15.9 percent Mn–84.1 percent Ag alloy as having a materially higher pressure coefficient and low temperature coefficient, but apparently it has not been seriously tried. There have been a number of investigations of the best details for the construction of the manganin gauge, particularly how to secure stability of zero. Michels and Lenssen[22] have studied the manganin gauge up to 3000; their coils were wound loosely in grooves on a porcelain cylinder. Results consistent to 0.05 kg/cm^2 can be obtained in the range up to 1000 kg/cm^2, consistent to 0.1 between 1000 and 1500, and consistent to 0.2 between 1500 and 2500. A slight pressure hysteresis can be eliminated by seasoning to a pressure 25 percent higher than that of subsequent use. The resistance of their manganin was sensibly not linear in pressure, the coefficient changing 0.25 percent per 1000 kg/cm^2. Adams, Goranson, and Gibson[23] have compared the manganin gauge against a free piston gauge up to 1300 kg/cm^2 and studied its behavior after exposures to 12,000. Freedom from constraint in the winding is essential; apparent departures of constancy of the coefficient of as much as 2.5 percent for 1000 kg/cm^2 may occur with improper winding. Their coil was sensibly linear over their range. If the coil is exposed to accidental changes of temperature of as little as 60° after stabilizing, permanent changes in the pressure coefficient may result of as much as 0.4 percent. Alexandrov and Vereschagin[24] have studied the manganin gauge up to 10,000; they find that the constraint imposed by coating the wire with a light coat of insulating enamel in addition to the conventional loose silk insulation is not harmful and facilitates construction. In my own work I have been using the manganin gauge for some ten years now up to pressures of 30,000 kg/cm^2. I find that under these conditions of use the zero is much more stable than it was formerly when used over the range of 12,000. The reason is probably a combination of the greater effectiveness of the seasoning afforded by the higher pressure, and also of a modified seasoning procedure with respect to temperature, the coil now being held alternately at 140° and −80° during the seasoning process, which extends over several days. In extending the range from 12,000 to 30,000 the most important consideration is the linearity over the enhanced range. I had already found indications, from the manner in which the electrical resistances of a number of different metals extrapolate consistently into the high pressure region against manganin, that any deviation from linearity would not be important. This could be quantitatively checked with the help of the pressure fixed point for the bismuth transition, and it was found[20] that the pressure obtained by linear extrapolation of results obtained at 7640 was not in error by more than one percent at 30,000. Calibration of the manganin gauge at two points is therefore sufficient to determine its behavior within experimental accuracy up to 30,000. The second degree term varies from coil to coil, even when cut from contiguous parts of the same spool, so that separate calibration of each coil is necessary. It is to be emphasized that this very favorable result is established only for my particular grade of manganin; it may be that manganin from other sources may show greater departures from linearity, as suggested by the result of Michels in a low pressure range. The deviation from linearity of my manganin was in an unexpected direction, the extrapolated pressures being too low.

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3. Miscellaneous Technique

In addition to these more fundamental developments there have been a large number of suggestions or developments of more special range of application. Ramsauer[25,26] has discussed quantitatively the possibility of reaching very high pressures for short intervals by the impulsive resistance to a projectile shot into a tightly fitting cylindrical hole. The calculations indicate very high figures, but the attempts to realize the method experimentally indicated that it would be very difficult to control, and nothing was obtained either useful or measurable. Adams[27] has described a comparatively simple equipment for pressures up to 12,000 or higher which makes use of Poulter's inverted rubber stopper packing on the end of the piston. This method of packing doubtless has a very real field of use. Boyd[28] and Schmidt[29] have described methods of measuring small pressure differences under high mean pressure. These devices are essentially U tubes with mercury with suitable arrangements of contacts for determining the difference of height in the two branches. Poulter and collaborators[30–33] have contributed several papers giving further details of his method of mounting windows without packing, which was already described in my book. The puzzling inconsistencies in the behavior of these windows now seem to be cleared up, and arose from water or other similar liquids such as alcohol which might be in contact with the window being forced by the pressure into solution in the glass. This might result in rupture under suitable conditions, whereas there is no such solvent action if the pressure medium is oil, and much higher pressures can be reached with oil. This, however, often has the disadvantage of freezing. In order to avoid this solvent action Poulter proposed and constructed a diamond window which has successfully withstood 21,000 kg/cm^2 transmitted by water and alcohol. Roebuck and Miller[34] have proposed and used transparent tubes of Bakelite suitably mounted for visual inspection of the interior of pressure vessels up to 400 kg/cm^2.

With regard to general technique the books of Tongue and Newitt, already mentioned, should be consulted. There have also been a number of articles dealing with special aspects of technique. Krase[35] in 1930 wrote an article entitled "High-Pressure High-Temperature Technology," dealing with industrial applications in very large vessels weighing up to 200 tons for pressures up to 1000 kg/cm^2. Berthelot[36] in 1941 wrote on the design of high pressure autoclaves, also for industrial use in the same pressure range. He was mainly concerned with creep effects at temperatures up to 500°C. Basset's trade catalog of undesignated date, but known to be not later than 1937,[37] gives many photographs of his high pressure equipment. The same author[38] in 1934 described laboratory equipment for pressures up to 25,000 kg/cm^2 before the Congress for Industrial Chemistry. Keyes[13] has contributed an article on "High-Pressure Technic," describing mainly the apparatus used in his laboratory up to 1000 kg/cm^2, notably in investigating the properties of steam. Korndorf[39] has a review article on the apparatus of a modern high pressure laboratory, describing some of the Russian developments.

In addition to these there are a considerable number of other papers dealing with matters related to technique that do not demand such extended description; these will be referred to chronologically. Tongue[40] describes the high pressure chemical engineering equipment of the chemical research laboratory, Teddington; the apparatus is used for handling gases and liquids to pressures of 1000 kg/cm^2. Basset[41] described apparatus for experimenting with gases up to 6000 kg/cm^2; this is more or less superceded by some of his later papers. Adkins[42] describes apparatus for studying reactions in the liquid phase up to pressures of 400 atmos. and to 250°. von Wartenberg[43] and four collaborators found that the resistance of glass tubes to internal pressure is practically as high up to the transformation temperature as at room temperature. Washburn[44] described a twin-bomb method for the accurate determination of pressure-volume-temperature data and a simple method for the accurate measurement of high pressure without accurate pressure gauges, which is limited to pressures for which the deviations from the perfect gas law are not important. Wertheim[45] has a review article describing methods of making leak-tight joints from 600 to 550,000 p.s.i. Welbergen[46] described a method of getting electrically insulated leads into a pressure chamber with a conical Pyrex glass sleeve, ground accurately to shape and assembled hot, which is good to 3000 atmos. and 200°. Beattie[47] outlines the apparatus used in measuring the compressibility of gases to 500 atmos. and to 325°. Frevel[48] describes a method for the x-ray examination of powders through the walls of a glass tube good to 1000 kg/cm². Burnett[49] describes a method of making accurate determination of compressibility without measurements of volume, which involves the expansion of a gas from one chamber to another. It demands accurate pressure measurements with a free piston gauge, and is good up to 125 atmos. Cohen and Lieshout[50] describe a dilatometer for use under pressure, in which the volume is determined by the varying resistance of a platinum wire in a capillary with rising mercury, and apply it to study the transition of tin up to 200 atmos. Roebuck and Cram[51] describe a multiple tube mercury manometer with a range of 200 atmos. and with an accuracy of 0.0014 percent. Cousen[52] has investigated with a special machine the bursting strength of glass bottles under static and rapidly applied internal pressures up to 700 p.s.i. *The Journal of Scientific Instruments*[53] describes an apparatus for sale by Kipf en Zonen for generating pressures up to 1000 kg/cm² by warming receptacles into which one of the permanent gases has been condensed at liquid air temperature. Morey and Ingerson[54] describe the construction of a bomb of stainless steel for experiments up to several hundred atmos. and 700°. Sage and Lacey[55] describe the apparatus used in connection with the program of the American Petroleum Institute for the study of pressure-volume-temperature relations in gases and liquids up to 10,000 p.s.i. and 600°F. A noteworthy feature is the elaborate method for controlling and changing the weights on the free piston gauge. Bohmshtein[56] discusses the construction of locks to be used up to 900 atmos. Aristov[57] describes a high pressure differential manometer with magnetic transmission. Ipatieff and Munroe[58] describe an apparatus which is rotatable to insure mixing of the contents, which they have used in determining the solubilities of gases in liquids up to 75 atmos. H. von Wintsch[59] gives elaborate calculations, based on the mathematical theory of plasticity, for the design of autofrettaged and built-up vessels to carry up to 10,000 kg/cm². Krupp[60] patents an alloy containing Cr between 2 and 4.5 percent, Mo 0.15 to 0.7 percent, C not more than 0.3 percent, balance iron, said to be especially adapted to the construction of high pressure vessels, particularly in the chemical industry.

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MECHANICAL EFFECTS OF HIGH PRESSURE

1. Volumetric Effects in Gases

Of necessity most of the work on this subject has been confined to a few hundred kg/cm^2, and is therefore outside our main interest; the nature of the work will be only briefly indicated. The principal foci of activity have been the laboratory of A. Michels at Amsterdam, Keyes and collaborators at Massachusetts Institute of Technology, the Fixed Nitrogen Laboratory in Washington, and the group in Pasadena engaged on the program of the American Petroleum Institute. High precision is obtainable in this field and different laboratories can obtain results consistent with each other. Of particular interest is a cooperative investigation of the isotherms of nitrogen up to 400 kg/cm^2 by Otto of the Reichsanstalt and Michels and Wouters in Amsterdam in which agreement was reached for the values of pv out to one in the fourth decimal place.[61]

By far the most active have been Michels and his collaborators, who have contributed some 17 titles.[62–78] The range of this work has been 0° to 150°C and up to 3000 kg/cm^2. In this range complete data have been obtained for the p-v-t relations of hydrogen, deuterium, nitrogen, carbon dioxide, and ethylene. In addition methane has been investigated to 400 kg/cm^2. Elaborate power series representations of the results are given, with six or seven disposable coefficients, calculated by least squares to six significant figures. Michels and Nederbragt have also measured methane-ethane mixtures up to 60 kg/cm^2.

The range of the work at Massachusetts Institute of Technology[79–87] has usually been 0° to 200° and up to 1000 kg/cm^2. Keyes has published data for ammonia, and Beattie and numerous collaborators have measured various hydrocarbons: ethane, propane, normal and *iso*-butane, heptane, and mixtures of ethane and *n*-butane. A good deal of this material extends into the two-phase region or into the region of the liquid. In the gaseous region the equations of state of Keyes and of Beattie reproduce the results well, and the constants for these equations are given in many instances.

The contributions from the Fixed Nitrogen Laboratory[88–92] mostly appeared near the beginning of our period. The usual range was from −70° to 200°, although 300° was reached on occasion, and up to 1000 kg/cm². Data have been published for hydrogen, helium, nitrogen, carbon monoxide, methane, and hydrogen-nitrogen mixtures.

The group at Pasadena,[93–99] comprising Lacey, Olds, Reamer, and Sage, have been mainly interested in the industrial hydrocarbons. Their range has been 250° and 700 kg/cm². They have published on methane, ethane, *n*-butane, and mixtures of methane with water, ethane with water, methane with *n*-pentane, methane with carbon dioxide, methane with decane, and *n*-butane with water. The data extend through the two-phase region and above the critical point.

There have been a number of papers from Russia, from several laboratories, chiefly concerned with gases of industrial interest. Kazarnovskii[100] has measured ammonia to 1600 kg/cm² and to 300°, and has written on the equation of state for mixtures of gases. The Russian work has been largely concerned with ternary mixtures: Krichevskii and Markov[101] with both binary and ternary mixtures of hydrogen, nitrogen, and carbon dioxide to 500 kg/cm² and 200°; Bolshakov and Lebedeva[102] with ammonia-methane-nitrogen mixtures from −20° to 50° and up to 560 kg/cm²; Kazarnovskii, Simonov, and Aristov[103] with nitrogen-hydrogen-ammonia mixtures up to 1640 kg/cm² and to 300°, and Bolshakov and Etherman[104] with hydrogen-nitrogen-methane mixtures from −30° to 250° and up to 800 kg/cm².

Buchmann,[105] in Simon's laboratory, has determined the isotherms of helium at 13.5° and 20.4°K up to the freezing pressure, about 2000 kg/cm². Three papers by Maron and Turnbull[106–108] may be mentioned dealing with equations of state in terms of the critical constants which can reproduce the data summarized here up to 1000 kg/cm².

Finally there have been two publications to somewhat higher pressures. Basset and Dupinay[109] measured the volumes at 0°C to 5000 kg/cm² of hydrogen and nitrogen. Benedict,[110] in my laboratory, determined the volume of nitrogen from −175° to 200° and up to 5800 kg/cm². Benedict's results are doubtless much more accurate than my own values published in my book; the discrepancy in the volumes is of order of 1 percent. Benedict derived an equation of state that fits his results with an error of 0.14 percent. Except for this work of Benedict there has been no check or repetition of my measurements in 1923 on five permanent gases to 15,000 kg/cm², except some work of my own.[111] In the course of measurements of the melting parameters of nitrogen and argon, I made certain redeterminations, and also some new determinations of fiducial data which previously had to be assumed, which made it possible to give the volumes of gaseous nitrogen up to 6000 kg/cm² and at temperatures between −140° and 23.5°, and also to combine with previous measurements on argon to obtain the absolute volumes, whereas formerly only differential volumes had been possible, in the range up to 15,000 kg/cm².

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2. Volumetric Effects in Liquids

A. Pure Liquids

Comparatively little new work, except some of my own, has been done here. There have been a number of acoustical measurements of the velocity of sound, which permit the calculation of the compressibility, but because these in general apply only at atmospheric pressure, we shall not consider them, although this is a very good method of getting the initial adiabatic compressibility.

In the following summary of other work than my own the arrangement is chronological. Jessup[112] measured the volume relations of 14 petroleum oils between 0° and 300° up to 50 kg/cm^2. The compressibility for different oils of the same initial density may vary by 30 percent; however, compressibility is a nearly unique function of initial density and viscosity taken together. Tammann and Ruhenbeck[113] measured volumes of water between 20° and 650° and of ethyl ether and ethyl alcohol to 400°, up to 2500 kg/cm^2 by a piston displacement method. They verified the maximum in the thermal expansion with temperature at constant pressure at high pressures found by me. Ruzicka[114] and collaborators determined the compressibility of four multi-membered ring compounds. Smith and Keyes[115] measured the compressibility of liquid mercury from 30° to 300° between 50 and 350 kg/cm^2. Dow[116] measured, in my laboratory and by my sylphon method to be described later, the volumes of six oils up to 4000 kg/cm^2 between 25° and 75°. The same method was applied by Dow and Fenske[117] to a study of the effect of fractionating the oil on its compressibility. Talbott[118] applied an acoustical method to get the adiabatic compressibilities and an adaptation of the piezometer of T. W. Richards to get the isothermal compressibility of a number of oils between 0° and 80°C up to 400 kg/cm^2. Macleod[119] made a theoretical study of my measurements for liquids up to 12,000, and by applying the van der Waals equation to the molecules themselves reports that he has a three-constant formula which will reproduce my results. Tammann[120] gives a theoretical explanation of the abnormal behavior of liquid water in terms of two different kinds of water molecules. Russell and Hottel[121] have measured the volume of liquid naphthalene up to its critical temperature, 425°C, and to 400 kg/cm^2. Under these conditions there is no decomposition. Biquard[122, 123] has an elaborate study of the propagation of acoustic waves up to 1000 kg/cm^2 in an apparatus constructed by Basset with fourteen windows which permitted observation of the standing wave system of fringes. He measured water and four organic liquids. The acoustical absorption at 500 kg/cm^2 was twice as great as was expected from theoretical considerations involving the effect of pressure on viscosity. Kelso and Felsin[124] have made measurements on *n*-hexane and 2-methylpentane up to the critical points. Dow and

Fink[125] summarize the measurements on oils at the pressures already indicated, and represent the results analytically. Felsing and Watson[126] give the compressibility of liquid *n*-octane up to 300 kg/cm^2 at 25° intervals between 100° and 275°. In a later paper[127] the same authors give similar data for 2,2,4-trimethylpentane.

The next section on the compressibility of solutions should also be consulted for the incidental determination by Gibson of the compressibility of a number of pure liquids to 1000 kg/cm^2.

My own work on the compressibility of liquids divides into two parts. There is in the first place the development of a new technique for measurements up to 12,000 kg/cm^2, and there is in the second place the extension to pressures as high as 50,000.

The method of the sylphon or metallic bellows was developed for measurements to 12,000. This has already been described in my book, but the development came at the end of the period and had not been published elsewhere at that time, so that a description of it legitimately falls here.[128] My previous method for measuring compressibility was a simple piston displacement method, which has the merit of great simplicity, but suffers certain disadvantages. The corrections for the transmitting medium may be larger than the total effect to be measured. In particular, measurements of thermal expansion have to be corrected for the change of volume of the transmitting medium when passing from a vessel at one temperature to one at another. In the new method the corrections are small, the pertinent part of the apparatus is all at one temperature, and, a very important consideration, the pressure gauge can be always maintained at room temperature, thus eliminating any effect of changing temperature on the gauge constant and zero. Furthermore, the method has the advantage of greater convenience and speed. It is my opinion that the method is as good as the piston displacement method, but Goranson in his summary of the properties of water for the *Handbook of Physical Constants* of the Geological Society of America prefers my earlier values for water, suspecting some distortion in the sylphon. In the most unfavorable case different determinations on the same liquid by the two methods have differed by 0.003 on the volume. With this apparatus I have determined the volumes between 0° and 95° and up to 12,000 kg/cm^2 (or up to the freezing pressure) of some 45 liquids.[128–131] These liquids are: normal and *iso*-pentane, *n*-hexane, 2-methylpentane, 3-methylpentane, 2-2-dimethylbutane, 2-3-dimethylbutane, *n*-heptane, *n*-octane, *n*-decane, benzene, monochlorobenzene, monobromobenzene, carbon tetrachloride, bromoform, *i*-propyl alcohol, *n*-butyl alcohol, *n*-hexyl alcohol, ether, water, glycerine and water mixture, ethylene glycol, trimethylene glycol, propylene glycol, dimethylene glycol, glycerine, tri-o-cresyl-phosphate, tri-acetin, ethyldibenzylmalonate, methyloleate, tri-caproin, *n*-butylphthlate, eugenol, *i*-octane, isoprene, triethanolamine, the propyl, butyl, and amyl normal chlorides, bromides, and iodides, octanol-3, 2-methylheptanol-3, 2-methylheptanol-5, 3-methylheptanol-1, 3-methylheptanol-4, and heavy water. These new measurements confirmed two of the most important results of the previous measurements, namely the reversal of sign of $(\partial^2 v/\partial \tau^2)_p$ with increasing temperature at constant pressure at a pressure of a few thousand kg/cm^2, and the fact that $(\partial p/\partial \tau)_v$ is not a function of volume only.

The experimental material is extensive enough to permit detailed study of the effect of many sorts of molecular substitution. The original papers must be referred to for this discussion. The following more important points may be mentioned here. The volume difference between isomers has a tendency to be wiped out by pressures of 12,000, but the tendency is not universal, and there are even examples where the volume difference becomes accentuated, showing that details of molecular structure remain effective up to pressures of this magnitude. Glycerine is notably the least compressible organic compound studied. Its low compressibility may be ascribed to the three OH groups. In general, the larger the number of OH groups in the molecule, the smaller the compressibility. An oxygen in the molecule also in general has a similar, although smaller, effect in depressing compressibility. The replacement of a hydrogen by a halogen, as in monochloro- and monobromobenzene, is accompanied by a notable depression of compressibility. With regard to ordinary and heavy water, the molecular volume of heavy water is greater than that of ordinary water at all pressures and temperatures, the excess tending to become less at high temperatures and high pressures. There are small scale fluctuations which appear beyond experimental error. In general, all these liquids have given evidence of small scale local irregularities, characteristic of the individual liquid, as did also my previous measurements. Less attention was paid to this matter, however, in these more recent measurements. The temperature intervals were chosen larger, and often small scale irregularities which appeared beyond experimental error were deliberately smoothed out in reporting the results. When the theory of liquids is more fully developed, this subject must be reopened and consistent experimental values obtained for the fine structure of the volumetric behavior of liquids; this will obviously demand much more experimental effort than has yet been devoted to the subject.

Passing now to my measurements[132] to 50,000 kg/cm^2, I made these by the piston displacement method in the conical externally supported container already described in the section on technique. Measurements were made at 25° intervals from 25° to 175° on the following twenty-one substances: methyl-, ethyl-, *n*-propyl, *i*-propyl-, *n*-butyl-, and *n*-amyl alcohols, ethyl-, *n*-propyl-, and *n*-butyl bromides, ethyl acetate, *n*-amyl ether, chloroform, carbon bisulfide, benzene, chlorobenzene, methylene chloride, ethylene bromide, cyclohexane, methylcyclohexane, *p*-xylene, and water. Under the experimental conditions the usual packing of the piston was not possible, and these liquids were handled by sealing into lead capsules. In nearly all cases freezing was encountered in part of the pressure-temperature field, and a complete study was made of both liquid and solid phases and the parameters of melting. The data involving the solid phase and melting will be referred to later. The most striking result for the liquid phase was the close approach to a uniform behavior shown by all the liquids in the upper pressure range. The maximum variation in the volume decrements between 25,000 and 50,000 kg/cm^2 was from 0.054, for methyl alcohol, to 0.070 for *n*-butyl-bromide, the volume under standard conditions being taken as unity. Variations of as much as 10 percent in the compressibility at the upper end of the pressure range are not common. Roughly the compressibility varies inversely as the pressure, which means that the volume can be represented approximately by the formula $v_0 - v = c \log (p/p_0)$, where p_0 is in the neighborhood of 10,000. It will be noticed that this formula is very much like the Tait formula which Gibson has found so satisfactory. Incidentally neither this formula nor that of Tait can have indefinite validity, because both demand negative volumes at sufficiently high pressures. However, the pressure of the reversal of sign of volume is, for my formula, of the order of 10^7 kg/cm^2, so that no essential limitation is imposed in the experimental range. The precision of the measurements to 50,000 is naturally not as high as in lower pressure ranges, so that a number of interesting questions cannot as yet be answered. It appears certain, however, that the thermal expansion continues to decrease over the pressure range, but by an amount markedly less than the decrease of compressibility; the same qualitative behavior was found in the lower pressure ranges. The behavior of the thermal expansion has an obvious connection with the entropy at infinite pressure.

Finally, mention may be made of a recent development in the technique of measuring compressions of liquids, which I have not yet published, which permits the very rapid measurement of compressions in the range up to 5000 kg/cm^2 with accuracy sufficient for many purposes. The compression is measured by piston displacement, the piston being packed with the minimum packing and so mounted as to be rotatable so that friction is minimized. The piston is driven by a larger piston, also with similarly minimized friction, which in turn is direct connected to a free piston gauge. The entire pressure vessel is filled with the liquid to be measured, and the corrections are small.

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B. Mixtures of Liquids and Solutions

A completely satisfactory scheme of classification for systems with more than one component is not easy. In multi-component systems we have complicated phenomena of separation into discrete phases, which may be solid or liquid. If the phase that separates is solid, the phenomenon may be described as one of solubility limits from the point of view of the one component or as one of the melting point from the point of view of the other component. The scheme of classification will have to be dictated somewhat by the interest and emphasis of the experimenter. If the principal interest is in the homogeneous liquid phase, the subject will be treated here; if the interest is in the details of separation of various discrete phases, it will be treated later, after phenomena of melting and polymorphic transition in one component systems.

By far the most extensive work on the volumetric relations in homogeneous solutions, both of solids, including salts, and of liquids in other liquids, has been done at the Geophysical Laboratory in Washington, largely by Gibson and Gibson and Loeffler.[133–142] The pressure range of most of this work has been 1000 kg/cm². Up to 1938 nearly all the measurements were made at 25°; since then the temperature range has been extended to above 100°. The technique has been greatly improved. The method is essentially the mercury injection piezometer of Richards. This has been constructed of fused quartz, thus eliminating irregularities due to strains in the glass; the injection arrangement has been transferred to the bottom, thus removing the necessity for a strictly monotonic increase of pressure; the injection capillary has been made smaller; and the final stages of the injection process are controlled visually with the help of suitably mounted windows, thus eliminating irregularities due to capricious variation in the size of the hanging droplet of mercury. With this apparatus the volume decrement may be determined to one part in a thousand. In connection with the replacement of glass by quartz for the piezometer, Gibson reports that the absolute volume compressibility of glass is a function of its thermal treatment. The experimental material is very extensive. In 1938 Gibson stated that some 250 solutions had been measured, mostly aqueous solutions of electrolytes; since then a large amount of material has been collected for various organic solvents. Incidentally the compressions have been determined of a number of pure organic liquids: water, carbon tetrachloride, ethylene glycol, methanol, aniline, nitrobenzene, bromobenzene, and chlorobenzene. The original papers must be consulted for extensive discussions of the theoretical significance of the results. There are perhaps two outstanding results of the theoretical discussion. The first is the wide applicability of Tait's equation for the volume of a liquid as a function of pressure, $v=v_0-c \log [(B+P)/B]$. This equation is shown not only to reproduce Gibson's results on solutions up to 1000 kg/cm^2, but also to apply to other measurements on pure liquids up to at least 10,000 kg/cm^2. The constants in the equation are shown to have theoretical significance. There is a connection with the internal repulsive and attractive pressure; it is shown that the internal attractive pressure is a function of volume only. Furthermore, there are simple connections between the constants of the Tait equation for the solution and for the simple components. The second point is that the thesis of Tammann is sustained, practically without modification for aqueous solutions and with simple changes for non-aqueous solutions. This thesis is that in the solution the solvent makes a contribution to the total behavior determined by the behavior of the pure solvent under an external pressure higher than the pressure on the solution by a characteristic amount. The difference between these two pressures is the so-called "Binnendruck" of the solution.

The arrangement of the following summary of work other than that from the Geophysical Laboratory is mainly chronological.

Perman and Urry[143] measured up to 200 kg/cm^2 and to 80°C solutions of sucrose, urea, KCl, $CaCl_2$ in water up to nearly saturation concentrations. A formula of Gilbault applies, and the Debye-Hückel theory is confirmed. Gucker[144, 145] has two papers on the compressibility of solutions which are often quoted. These are review papers, with no new experimental material; the discussion is confined to the effect of pressures below 200 kg/cm^2. It is found that the apparent molal compressibility is a linear function of the square root of the concentration, and also approximately linear in the molality. Thomas and Perman[146] present measurements at 30° up to 100 kg/cm^2 of aqueous solutions of KCl, KBr, KI, $CaBr_2$, $SrBr_2$, $BaBr_2$, AcOH, and HCHO. Debye[147] has a theoretical paper in which the decrease of compressibility of solutions is correlated with the great concentration of water in the neighborhood of the ion by the electrostatic forces. The effective pressure in the water in the ionic neighborhood is estimated to be as high as 50,000 kg/cm^2. Scott, Obenhaus, and Wilson[148] have made measurements up to 300 kg/cm^2 by the method of Richards on aqueous solutions of the chlorides and bromides of Li, Na, K, and the iodides of Na and K, in half a dozen concentrations each, and Scott and Wilson[149] have discussed the theoretical significance of the results; there are deviations from linearity, lithium in the opposite direction from the other alkalis. They find their results not inconsistent with the idea that the limit of solubility is reached when the compressibility of the solute in solution becomes equal to that of the crystalline salt. Lanman and Mair[150] measured at 25° by the method of Richards up to 300 kg/cm^2 three concentrations each of LiCl, NaCl, KCl, LiOH, NaOH, KOH, HCl, acetic acid, and potassium acetate. They also determined the compressibility of glacial acetic acid. They verified the result of Gucker of a linear relation between apparent molal compressibility and square root of concentration. Bridgman and Dow[151] measured by the sylphon method up to 8000 kg/cm^2 the compressibility of aqueous solutions of the three amino acids, glycine, α-amino butyric acid, and ϵ-amino caproic acid, at five concentrations up to $2.5N$ at 25° and 75°. The pressure limit of 8000 was imposed by the solubility limits. These measurements apparently constitute the only ones on this type of substance. There are notable departures from linearity. The most striking result was that at low pressures the apparent compressibility of the acid in solution is positive, whereas in all other known cases the apparent compressibility is negative. Expressed in terms of Tammann's thesis this would mean that in solutions of these acids the water behaves like pure water under a negative pressure. Brander[152, 153] gives two theoretical discussions, utilizing mostly Tammann's earlier data up to 3000 kg/cm². A connection is found between the coefficients in the equations for the solution and for pure water, and Tammann's thesis is confirmed. Scott and Bridger[154, 155] have two papers on aqueous solutions of LiCl, LiBr, and $Ca(NO_3)_2$ at concentrations reaching into the supersaturated region at 35° and up to 300 kg/cm². The lithium salts display certain irregularities. Certain results proposed by Masson and by Redlich and Rosenfeld do not apply. Sage and Lacey,[156] as part of the program of the American Petroleum Institute, have measured liquid mixtures of butane and crystal oil up to 200 kg/cm² and between 20° and 100°C and have calculated a number of the thermodynamic parameters which are determined by the volumetric data. Kritschewsky[157] has a theoretical discussion in which a formula is derived from a result of Born for the dependence of partial molal volume on pressure and applied to infinitely dilute aqueous solutions of NaCl and K_2SO_4 up to 3000 kg/cm².

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3. Volumetric Effects on Solids

The only sustained work on this subject, represented by more than one or two titles, has been from the Geophysical Laboratory in Washington, the geophysical work at Harvard at first by Zisman and for the major part of the period by Birch, and my own work. In general comment, it is necessary to employ pressures of the order of thousands of atmospheres to obtain acceptable accuracy here, instead of the hundreds that are adequate for gases and liquids. In the following the scattered work will be described first.

Only one radical innovation in the technique of measurement has appeared. In 1939 Jacobs[158] measured the lattice constant by x-rays of copper and aluminum while exposed to a hydrostatic pressure of 4500 kg/cm^2 and thus was able to get the cubic compressibility. The measurements were made by the Debye-Scherrer method; the miniature camera was entirely mounted in the pressure chamber and bathed with the pressure transmitting medium, which was gaseous helium, the absorption of which even at such high pressures proved not to be prohibitive. The x-rays were led into the chamber through a beryllium window. For the mean compressibility over his pressure range Jacobs obtained for copper a value lower by 0.26×10^{-7} than my value obtained by bulk methods on multi-granular material, and for aluminum a value 0.46×10^{-7} lower. The former is within possible experimental error of the method, but the latter not. Jacobs thinks the difference is real in both cases and is probably to be explained by a difference of compressibility between the crystal grains and the intercrystalline cement, the compressibility of the latter being higher. Jacobs developed and first applied his x-ray technique to the investigation of polymorphic transitions under pressure, and the matter will be referred to again. Müller[159] in 1941 made x-ray measurements on a series of normal hydrocarbons while exposed to pressures up to 1500 kg/cm^2. The material was mounted in thin-walled containers, either of steel or of beryllium, fashioned by the methods of powder metallurgy, and the x-rays were transmitted through the walls of the container. By this method it was possible to get the linear compressibilities parallel and perpendicular to the carbon chain. In the direction perpendicular to the chain the linear compressibility was found to vary from 3 to 12 $\times10^{-12}$ cm^2/dyne, but in the direction of the chain to be less than 3×10^{-13}. In 1935 Frevel[160] described a technique for x-ray study of materials under pressure, in which the material was sealed with a liquid in a heavy walled glass capillary and pressure developed thermally by heating. Frevel did not measure compressibilities by this method, but inverted the procedure, estimating the pressure generated from the displacement of the lines and the known compressibility; his estimated pressure was slightly less than 1000 kg/cm^2. The x-ray method in its present state of development is not capable of reaching very high pressures or of giving sufficient accuracy to answer such questions as to the variation of compressibility with pressure, but it would seem to have possibilities and further work should be done with it.

Turning now to the other scattered papers, Tammann and Jellinghuas[161] measured the volumes of the glasses selenium, salicin, and colophony in their softening ranges between 10° and 70° up to 2000 kg/cm^2. At pressures somewhat above 1000 the isotherms were found to cross, which means that above this pressure the volume at first decreases with rising temperature, passing through a flat minimum. In speculating on the significance of the results the conclusion is drawn that the volume of a glass may depend on the pressure under which it was solidified. One is reminded of the finding of Gibson that the compressibility of the glass of his piezometers depended on their thermal treatment. Scott,[162] at the Bureau of Standards, measured the compressibility and volume expansion between 10° and 85° up to 800 kg/cm^2 of a number of rubber-sulfur compounds of from 3 to 31 percent sulfur. The method was by visual observation of the change of length through Poulter windows. The compressibility decreases with increasing sulfur content, the range being from 21×10^{-6} to 66 $\times10^{-6}$ in kg/cm^2 units. Large variations of compressibility were found with pressure, considerably larger than had been previously found by Adams.

The most important of the scattered work is that of Ebert[163] on the absolute determination of the linear compressibility of a number of metals up to 5000 kg/cm². The method was observation with a microscope through windows of the change of length. As a preliminary to this work the investigation was made of the free piston gauge already described in the section on technique. The accuracy was high enough to give the second degree term in change of volume as a function of pressure, and the determination of this term was one of the principal objects of the investigation. Measurements were made on single crystals of the cubic metals, iron, aluminum, gold, lead, and silver, and of the hexagonal magnesium in three orientations and on polycrystalline copper, manganin, and steel. In general his absolute compressibilities for the single crystals are slightly lower than mine and also his second degree term. For polycrystalline copper there is exact agreement in both terms. Ebert is inclined to see a real difference between single and polycrystalline material, as did Jacobs later, and to believe that except for this factor there is essential agreement between his work and mine, both in the first and second degree terms. It is to be remarked, however, that I have recently revised my second degree terms, so that the agreement is probably not as close as it might appear.

Megaw and Simon[164] have determined the compressibility of solid hydrogen and deuterium at 4.2°K up to 100 kg/cm². The average compressibility of the former is $(5.0\pm0.5)\times10^{-4}$ and of the latter $(3.3\pm0.7)\times10^{-4}$, in kg/cm² units. There is a very rapid change of compressibility with pressure, the initial value being twice the average. Bartholomé[165] has determined the compressibility of solid hydrogen and deuterium at their triple points; the former is 2.3-fold larger than the latter. Lyman and Parks[166] have determined the compressibility of glucose glass at 24° up to 25 atmos. to be 18.8×10^{-6} in atmos. units. Basset[167] has measured the compressibility of graphite up to 20,000 kg/cm² at intervals of 5000, obtaining the mean compressibility 4.41 $\times10^{-6}$ in the interval 1–5000 and 1.90×10^{-6} in the interval 15,000–20,000. Compared with values of my own his absolute compressibilities are materially higher and the falling off with increasing pressure more rapid.

At the Geophysical Laboratory in Washington Adams and Gibson[168] measured by the piston displacement the compression of one sample of hard rubber and two of soft up to 12,000 kg/cm². They found total volume decrements varying from 16 to 20 percent. The variation of compressibility with pressure is high, there being a rapid drop of compressibility in the first part of the range. On the whole the volumetric behavior of rubber was found to be much like that of a liquid. Adams[169] has discussed the application to geophysical questions of the most probable values for the compressibility of fayalite and its variation with pressure up to 15,000 kg/cm². Adams and Gibson[170] have measured up to 12,000 the compressions of Pyrex, quartz glass, obsidian, duralumin, NH_4NO_3, K_2SO_4, Na_2SO_4, and *n*-butyl ether. Goranson[171] has discussed the elastic properties of rocks under pressure, dealing principally with the results of Zisman. He concludes that the method of linear compressibility for materials like rocks is not as good as the measurement of over-all volume compressibility as it is given by the method of piston displacement, which is the method used almost exclusively at the Geophysical Laboratory.

The work at Harvard in connection with the geophysical program has been mostly done by the method of linear compressibility, using a sliding wire and its change of resistance determined with a potentiometer as I had done in my earlier work. The first measurements were by Zisman[172–174] on some fifteen representative rocks at room temperature up to 1000 kg/cm². Large initial compressibilities were found, rapidly dropping to an asymptotic behavior. Very great differences were found, particularly for the more porous rocks, according as the pressure transmitting medium was allowed to freely permeate the pores or acted only on the surface, that is, according as the specimen was "covered" or "uncovered." Later Birch cleared up the question of the proper way to measure the compressibility of rocks for geophysical purposes (they should be "covered" and the linear method gives satisfactory results if the rocks are sufficiently fine grained) and much extended the technique. He has developed apparatus for reaching pressures of 10,000 kg/cm² with the whole pressure cylinder at 500°C. If the furnace is mounted inside the pressure apparatus much higher temperatures may be reached with the same pressures, as indeed had been done at the Geophysical Laboratory some time ago. Birch developed means for measuring linear compressibility under the conditions just mentioned, the specimen being mounted in the heated cylinder and the change of length under pressure taken out by rigid members through the transmitting pipe to another vessel at room temperature, where the motion is measured. The transmitting medium for these high temperature experiments is nitrogen. Birch and Law[175] have determined the average compressibility up to 10,000 kg/cm^2 of lead in the range up to 200°, of aluminum up to 435°, of silica glass up to 283°, and diabase glass up to 300°. My results for the metals are approximately verified, both absolute value and temperature coefficient in my much narrower range. For silica glass they found the same abnormal sign of the second degree term in the pressure that I had found. The diabase glass has a maximum compressibility with temperature near 150°. Birch and Dow[176] measured six artificial glasses, Solenhofen limestone and Vinal Haven diabase to 10,000 kg/cm^2 and temperatures of 300° or 400°. The abnormal decrease of compressibility with rising temperature of the glasses reverses at temperatures in the neighborhood of 200°, so that above this the sign of the temperature variation of compressibility is normal, except silica glass, which remains abnormal over the entire range up to 400°. There are indications that silica glass also will become normal at some higher temperature. Geophysical applications are made in a discussion of the probable velocity of seismic waves to a depth of 40 km in the crust of the earth.

My own work on this subject has several phases. In the first part of the period, up to 1935, measurements up to 12,000 kg/cm^2 and at 30° and 75° by the linear compressibility method described in my book were extended to a considerable number of new materials and new types of material. In 1931[177] such measurements were presented for: NaF, BaF_2, SrF_2, CdF_2, AlSb, CdTe, HgTe, TiN, TiC, and single crystal Mg. The compression of NaF falls into line with what would be expected from that of the other alkali halides, the data for which are herewith complete. In the series of the halides of Ca, Sr, and Ba the same regular progressions do not occur, however. The compressibility of the other compounds is low in general, much less than would be calculated from the compression of the constituents by the rule of mixtures. Also in 1931[178] I studied the effect of pressure on the well-known volume anomalies of NH_4Cl and NH_4Br, and as part of the study determine the volumes of the former over the pressure range to 12,000 kg/cm^2 at temperatures from 0° to 75°, and the volume of the latter at temperatures from $-72°$ to 75°. In 1932[179] I studied the volumetric relations of Ag_2O over the regular pressure and temperature range. There is a very sluggish transition, smeared out over the entire pressure range. Also in 1932[180] were published results for 18 cubic compounds: CaS, SrS, BaS, MgO, CaO, Cu_2O, As_2O_3, $Sr(NO_3)_2$, CuCl, CuBr, CuI, LiI, NaI, RbCl, CsF, CsCl, CsBr, and CsI. The specimens for a number of these measurements were made in the form of compressed powders because of the difficulty of getting the material in other form. The powders were compressed by 20,000 kg/cm^2 at a temperature of 450° and appeared homogenous and compact to casual examination. I have since found, however, that it is practically impossible to consolidate some powders to give the same compression as perfectly homogeneous (single crystal) material. The magnitude of the effect depends on the material; for a substance like NaI it is impossible to detect any difference between the compression of a compressed powder and a single crystal, but for MgO, which was later obtained in single crystal form, the best compressed powder that I could make showed a compression roughly twice that of the single crystal. I have found the effect important for even so innocent appearing a substance as lead. In 1933[181] I published results in the same range for the elements Cb, Rh, Ru, Cr, As, and Be, the compounds gulonic lactose (single crystal, three directions), rhamnose (single crystal, three directions), sucrose (single crystal, four directions), $MnCl_2$, $ZnCl_2$, Al_2O_3, and Cu_5Cd_8, three gold-silver alloys, three iron-tungsten alloys, three tungsten-cobalt alloys, and a ternary alloy of iron, tungsten, and cobalt. A number of these materials, particularly the alloys, are known to show various phenomena associated with shifting internal equilibrium when temperature changes, and it might be expected that pressure would produce similar effects. In fact a number of the materials enumerated did show irregularities of various types; some of these were reversible, of the kind usually referred to as transitions of the second or higher kinds, and some showed hysteresis. The subject matter thus opened for investigation is obviously enormous, and when theory is further advanced more extensive and systematic data must be collected: I myself have not found occasion to return to the matter. Among the other materials of this paper the element chromium deserves especial mention. There are marked volume anomalies; below 0° the compressibility increases with increasing pressure, an unusual effect shown among other substances most strikingly by quartz glass. The anomaly appears only in chromium of high purity. My last work in the 12,000 range was published in 1935[182] and was concerned chiefly with intermetallic compounds of which the following were measured: Ag_5Cd_8, Ag_5Zn_8, Cu_5Cd_8, Cu_5Zn_8, $Cu_{31}Sn_8$, CuZn, AgCd, AuZn, AgZn, Cu_5Sn, Ag_2Al, Mg_3Al_2, Mg_xAl_y, Mg_2Pb, $MgZn_2$, SbSn, $AuSb_2$, Sb_2Tl_7. In addition were investigated: germanium, LiF, Ag_2S, PbSe, PbTe, $Ag_2SO_4 \cdot 4NH_3$, and basalt glass. The results for the intermetallic compounds in many cases show pressure hysteresis, and also other small irregularities and discontinuities, and sometimes creep. The compressibility is in almost all cases markedly less than would be calculated by the law of mixtures from the constituents. This points to a high internal pressure arising from chemical affinity. In this paper are given corrections for certain compressibilities published before 1925 arising from an error just discovered in calculating the second degree term on passing from linear to cubic compressibility.

In 1935[183] were published the results of my first serious attempt to materially extend the pressure range beyond my customary 12,000 kg/cm². This first attempt involved no radical change in technique; stronger grades of steel which had come on the market were employed, and the apparatus was simplified by being made in one piece, with only a single straight hole down the axis of the cylinder. After much experimenting with this type of apparatus it became obvious that it did not permit sufficient extension of range to justify the frequent and capricious fractures, with consequent destruction of the internal apparatus, which seemed unavoidable. Some results were obtained with this apparatus, however. The electrical resistance of certain materials which seemed likely to be especially interesting at higher pressures was measured, to be referred to later, and the volume of the three alkali metals, lithium, sodium, and potassium was determined as a function of pressure and temperature in the range from 0° to 95° and up to 20,000 kg/cm². The especial interest in the measurements was the behavior of thermal expansion at high pressure. Two significant variations from the usual behavior of thermal expansion were found for these three alkalies. In the first place, the drop of thermal expansion with increasing pressure is greater than the drop of compressibility, the reverse of the usual behavior. In the second place, the curves of expansion cross with increasing pressure, so that at high pressure potassium is the least and lithium the most expansible. This reversal of expansion is similar to the reversal in order of the melting points already described in my book, and may well be connected with it. The drop of thermal expansion for these alkalies is so great that any vanishing of entropy at infinite pressures, which has been often suspected on theoretical grounds, would seem to be very questionable. Even assuming the rate of drop of entropy with increasing pressure to be maintained constant at all higher pressures at the value which it has at 20,000, the entropy of potassium, for example, would not vanish below 450,000 kg/cm². As a matter of fact the rate of drop of entropy with pressure is, at 20,000, itself dropping rapidly with increasing pressure.

My next attempts to reach high pressures adopted more radical changes of technique, external support of the pressure vessel which increased as pressure increased. This support might be given in one of two ways; a partial support on the external cylindrical surface, most simply applied by making the vessel slightly conical instead of truly cylindrical, and complete external support by immersing the vessel in a liquid carrying hydrostatic pressure. Two types of extension of the previous measurements to

12,000 are possible. One type of apparatus permits as accurate and as elaborate measurements to 30,000 as were formerly made to 12,000; with other types of apparatus, measurements of less accuracy are possible over a considerably wider range, these measurements at present being volumetric almost exclusively. The first compressibility measurements using the new technique were published in 1938;[184] these comprised measurements of the compression of a number of the more compressible solids at room temperature up to 45,000 kg/cm². The substances were: Li, Na, K, Rb, Cs, Ca, Sr, Ba, In, Sn, Pb, S, NaCl, and CO_2 (at −80° and 0° and to 35,000). The method was the piston displacement method in a conical vessel with a single stage of external support. The compressions of the alkali metals were in good agreement with values deduced theoretically by wave mechanics, to be referred to again later, and in all cases fairly good extrapolation could be made from 20,000 to 45,000 by a semi-empirical formula just developed by Murnaghan.

The next volumetric measurements were published in 1940;[185] these attempted to lay the basis for an extension of accurate measurements into the 30,000 range. The important question here is the change of compressibility with pressure. The accuracy of an experimental determination of this is proportional, other things being equal, to the square of the pressure range. Theory was in a position to calculate the pressure variation of compressibility with pressure, and the theoretical physicists were dissatisfied with my measurements of this quantity, which they thought were too large, particularly for the more incompressible substances. For substances like iron my second degree term was thought to be from 10 to 100 times too large. The compression of most substances was measured differentially against iron, so that the first step in a re-examination of the matter was a determination of the absolute compression of iron in the range to 30,000. This involved in the first place the establishment of pressure fixed points and a determination of the deviations of the manganin gauge from linearity, which have already been described. The determination of the absolute compression of iron involved a measurement of the shortening of an iron rod relative to the pressure vessel, and a measurement of the absolute distortion of the pressure vessel. The former was done with my conventional sliding contact device; the latter was done by means of probe rods reaching in through small drilled holes into close proximity to the vital parts of the pressure vessel. The result of some four hundred measurements, smoothed by least squares, was a formula for the volume decrement of iron in which the first degree term was nearly the same as before, but the second degree term was smaller by a factor of three. There seemed no possibility of a reduction of the second degree term by as much as 10 or 100. Recently it has developed that there was an error in the theoretical calculations, and experiment and theory now seem to be in agreement, even for the more incompressible substances. Since the matter is of extensive applicability, I reproduce the result for the change of volume of pure iron at 24° in the range up to 30,000:

$$-\Delta V/V_0 = 5.826\times 10^{-7}p - 0.80\times 10^{-12}p^2, \quad p \text{ in kg/cm}^2.$$

At 75°, the best value for the temperature coefficient gives an increase of the first degree term of 0.066×10^{-7} and no perceptible change of the second degree term.

The new value for iron will affect all compressibilities which were differentially determined with respect to iron. I give here the formulas, which have not been previously published, for correcting my previously published values to the new value of iron. The volume decrement is given by a second degree expression:

$$-\Delta V/V_0 = a_{\text{new}}p - b_{\text{new}}p^2.$$

Then:

$$a_{\text{new}} = a_{\text{old}} - 0.033\times 10^{-7},$$
$$b_{\text{new}} = b_{\text{old}} - 1.56\times 10^{-12} - a_{\text{old}}\times 0.022\times 10^{-7}.$$

Pressure is measured in kg/cm². The corrections are sensibly the same at 30° and 75°.

The program of accurate measurements of compressions relative to iron up to 30,000 is now just beginning: I have unpublished results for copper, aluminum, and lead.

In 1940 measurements were published[186] on the compressions of 46 substances up to 50,000 kg/cm² at −80° and room temperature. These

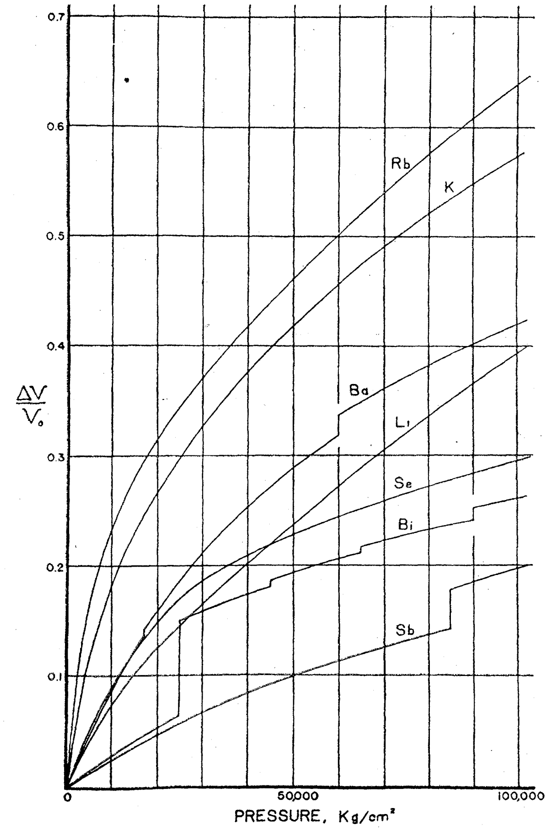

FIG. 3. The volume compressions of several elements to 100,000 kg/cm². The breaks in some of the curves indicate polymorphic transitions.

measurements were made in an apparatus improved over that in which the previous measurements to 45,000 had been obtained. The principal improvement consisted in providing two stages of external support, which considerably reduced the distortion in the containing vessel and increased its life, and decreased the magnitude of the corrections. These 46 substances embraced the 21 halogen compounds of Na, K, Rb, Cs, NH_4, Ag, and Tl; the 18 sulfides, selenides, and tellurides of Ca, Sr, Ba, Pb, Zn, and Hg; and In, S, Se, Te, Sb, Bi, and rubber. The principal results are that the compressibility at 50,000 averages from 30 to 50 percent less than initially, and that the thermal expansion is roughly one-half the initial value. The smaller relative decrease of compressibility with pressure accompanies the smaller absolute compressibility, as was already known in general.

In 1942 the measurements of the compressions of 21 liquids to 50,000 already referred[132] to included the compressions of the solid phases of these substances above the melting pressures. These substances, all of them organic except water, approach an even greater uniformity of behavior at high pressures in the solid phase than they do in the liquid. The volume decrement between 25,000 and 50,000 varied from a minimum of 0.045 to a maximum of 0.059.

In 1941[187] were published the first compressions to 100,000 kg/cm²—for the 17 elements Li, Na, K, Rb, Ca, Sr, Ba, Zn, Cd, In, Tl, Sn, As, Sb, Bi, Se, and Te, all at room temperature. Some of these results are shown in Fig. 3. This was followed in 1945,[188] many of the measurements having been made, however, before December, 1941, by the compressions in the same range of the 21 halogen compounds previously measured to 50,000, the nitrates of Na, K, Rb, Cs, Ag, Tl, and NH_4, and $AgBrO_3$, Pb, In, and S. For the elements, the relative drop in compression on doubling the pressure range from 25,000 to 50,000 is greater than the drop on further doubling it from 50,000 to 100,000. Something like this would be expected merely as a geometrical consequence of the fact that the volume cannot become negative at any pressure. On the whole, however, the compressibility did not drop off as rapidly in the new pressure range as had been anticipated, or in other words these elements remained more compressible than expected. The various compounds exhibited much the same qualitative behavior as the elements. The compounds in general retain their original volume order, and there are only a few examples of crossing of the volume curves above 50,000. On the whole there is a tendency for the compounds with the greater number of atoms to the molecule to have the greatest relative decrease of compressibility with rising pressure. In general, the accuracy of these measurements to 100,000 is not as high as in lower ranges of pressure, and the apparatus is not yet sufficiently developed to make it profitable to attempt volume measurements on substances materially less compressible than the least compressible of those measured above. The chief source of error is in the measurement of piston displacement, which is obtained by measurements external to the supporting pressure chamber of the displacement of the piston with which the supporting pressure is generated. A number of corrections have to be applied, some of which involve friction and hysteresis. A new form of apparatus is now under construction in which the piston displacement is measured from inside the supporting chamber, and it is hoped that measurements of the compressions of the more incompressible substances will thereby be made feasible in the range to 100,000.

In 1945[189] was also published another method of getting compressions of solids to high pressures, which is at present restricted to room temperature, but has the advantage of great convenience and speed of operation, and a greater accuracy in the determination of the second degree term than any of the other methods used above 30,000. The material is in the form of a thin disk, with thickness one-half its diameter to minimize friction, compressed between Carboloy pistons in a Carboloy cylinder mounted in a conical steel supporting cylinder of such proportions that there is no change of cross section under internal pressure, thus minimizing the corrections. Measurements have been published with this to 25,000 kg/cm^2, but it has lately been applied with equal success up to 40,000. With this apparatus the compressions of some 61 substances were determined: the elements Tl, As, Cd, In, Pb, and graphite; NaCl, the nitrates of Na, K, Rb, Cs, Ag, Tl, and NH_4; the chlorates of Na, K, and Cs; the bromates of Na, and Ag; the iodates of Na, K, and NH_4; the perchlorates of Li, Na, K, Rb, Cs, NH_4; the periodates of Na, K, Rb, and NH_4; levulose; dextrose; dextrin; starch; menthol; naphthalene; anthracene; triphenylmethane; thymol; succinic acid; anthroquinone; benzophenone; *o*-, *m*-, and *p*-aminobenzoic acid; and 14 synthetic and natural rubbers. Among the organic solids mentioned, the compressibilities at high pressure lie very nearly on a single curve when plotted against initial density. The volume compression of the rubbers at 25,000 kg/cm^2 varies from 0.146 to 0.212. A number of these rubbers show a more or less pronounced transition of the second kind in the general neighborhood of 4000, which can be described as a smeared-out freezing. In virtue of this there tends to be volume hysteresis at higher pressures.

It would be beyond the scope of this review to attempt to summarize the many theoretical discussions of the change of volume with pressure, but it will not be out of place to mention a few that have been especially concerned with some of the new experimental material. Bardeen,[190] developing the method of Wigner and Seitz, gives two formulas for the volume of sodium and lithium as a function of pressure. One of these is semi-empirical in that it contains one disposable constant; with this formula almost perfect agreement is obtained with my data up to 45,000 (the later data to 100,000 had not then appeared). The other formula has no disposable constants; with it the volume of sodium may be reproduced, but there is a 15 percent discrepancy for lithium. Herring[191] has discussed the matter and indicated the nature of the assumption which may be responsible for the discrepancy of lithium. Fürth has papers which were published in 1941[192] and 1944[193] applying formulas originating in Born's theory of crystal lattices, which have been elaborated in great detail by Born and his pupils so as to apply explicitly to lattices of different types, and obtains approximate agreement with my experimental results for the salts to 50,000 and the metals to 100,000.

Of a different order are a number of theoretical discussions of the pressure volume relations at astronomical or superastronomical pressures, sufficient to produce atomic breakdown. Among these are papers by Hund,[194] Cernuschi,[195] and Auluck.[196] Hund carries the computation to pressures of 10^{23} kg/cm^2 where matter breaks down into a neutron gas which is degenerate at temperatures lower than 10^{10} degrees. Of more immediate pertinence to the experimental material is a paper by Jensen,[197] in which the Thomas-Fermi model with the Pauli exclusion principle are used in calculations up to 10^{15} kg/cm^2, where all matter has broken down into a perfect electron gas. Under these conditions the curves for volume as a function of pressure are entirely different in character from those of ordinary matter, which in the ordinary range show no hint that they will ever extrapolate at high pressures to the theoretical shape. Jensen has used my new data for Cs and Ba up to 50,000, plotted log volume against log pressure, and found that in the neighborhood of 20,000 the curves begin to curve upward as demanded by the theoretical extrapolation.

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4. Phase Changes under Pressure in One Component Systems

A. Vaporization

We do not consider ordinary vaporization or critical point phenomena as in our field, but will mention one measurement because of its intrinsic interest and the magnitude of the pressure. Basset[198] has established the triple point of graphite to be at 4000°K and 105 kg/cm^2. Pressure was transmitted by argon and the method was a visual one through windows. Above the triple point the method was not accurate enough to establish the numerical magnitude of $d\tau/dp$ for the solidification of the solid from the amorphous phase, but it was accurate enough to establish that the sign was positive, thus contradicting and correcting an earlier result of Basset that the solidification curve of graphite falls with rising pressure. The pressures in this experiment were pushed to 11,500 kg/cm^2; in all cases the graphite phase separated out from the amorphous phase.

B. Melting

It will not be possible to make an absolutely sharp separation between the discussion of melting, which is the main topic of this section, and polymorphic transition, which is the topic of the next section, because in a number of instances one polymorphic form gives place to another along the melting line. Many of the papers dealing with melting are directed to the question as to the character of the melting curve, about which there is even yet no unanimity of opinion. The question at issue is whether the melting curve ends in a critical point, rises to a maximum and then falls, rises to an asymptotic temperature with increasing pressure, or rises indefinitely with increasing temperature and pressure.

At the end of the period covered by my book there was important work by Simon and collaborators[199] on the melting curves of a number of the permanent gases at pressures as high as 6000. Simon and Glatzel[200] proposed an analytical expression for the equation of the melting curve, namely $\log (a+p) = C \log \tau + b$, which has proved capable of representing the melting curve over a wide range and has assumed considerable importance. The form of the equation demands an indefinite rise of pressure and temperature. It was the opinion of Simon that, nevertheless, the melting curve probably ends in a critical point; in order to establish this the shape of the melting curve is not sufficient, but other thermodynamic parameters must be determined. To this end Simon and Steckel[201] early in the period attempted direct measurements of the latent heat of melting of helium along the melting curve. The experimental difficulties were serious and only preliminary results were obtained. These indicated an initial rise of latent heat, and then a slight fall, which Simon pointed out was not inconsistent with the eventual fall to be expected if there is a critical point. The experiments were inconclusive, and Simon has not returned to the matter.

There are a half-dozen papers from Leiden by Keesom[202–207] and collaborators in which the melting of some of the permanent gases has been determined over a much lower pressure range than Simon but with a higher accuracy. These measurements were on the melting of hydrogen to 610 kg/cm^2, on neon to 200 kg/cm^2, oxygen to 170 kg/cm^2 and nitrogen to 200 kg/cm^2. The formula of Simon and Glatzel was applicable and the constants were determined. In comparison with the results of Simon, Ruhemann, and Edwards, the temperatures of Keesom were inclined to be higher; this might be explained by insufficient purity in Simon's material, but there is another more probable source of error which I pointed out in comparing Simon's results for nitrogen with my own. The method of both Simon and Keesom was the method of the plugged capillary. In this method the material under investigation is contained in two vessels connected by a capillary, the temperature of which is lowered until an increment of pressure applied at one vessel fails to be transmitted to the other because of solidification in the capillary. The solidified plug in the capillary must obviously be subjected to some shearing stress, and it is known that the effect of shearing stress is to lower the melting point, thus simulating the effect of impurity. If the possibility of the error is recognized it can be minimized by appropriate manipulation, but Simon apparently did not recognize it and it may have introduced appreciable error in his measurements. In the last paper of the series of Keesom, that on oxygen in 1935, comment is made on this criticism of mine and the promise made to investigate in a later paper whether the error might have been important under Keesom's conditions, but apparently this investigation was never made. Later Michels and collaborators[208] in Amsterdam employed the same method to investigate the melting curve of CO_2 to 2800 kg/cm^2 and of mercury to 3000.[209] They were fully cognizant of the possibility of error, and by appropriate manipulation of temperature were able to reduce the difference of pressure on the two sides of the plug when the stoppage was detected to less than one atmosphere, so that error from this source must have been negligible. Michels results agree with mine within my experimental irregularity. He was able to represent his results over his entire range by the formula of Simon and Glatzel. Neither the measurements of Keesom nor of Michels are competent to distinguish between a critical point and indefinite rise because the other necessary parameters were not determined.

A result of Keesom and Clusius[202] will be mentioned here, although not dealing with a melting proper, because the phenomenon is unique and is outside our general scheme of classification. Helium is the only substance with two liquid amorphous phases; the transition temperature is a function of pressure. Keesom and Clusius determined the coordinates of the transition line; it is very short, being terminated by the solidification line. The line is retrograde, and was found to run from 2.19° and 0.050 atmos. to 1.86° and 23.6 atmos.

Returning now to the melting curve, there has been much activity in the laboratory of Timmermans,[210–214] much of it by Deffet. This work has been confined to a pressure range of 1000 kg/cm^2; its special feature has been the careful purification of the materials. Deffet's first method[210] was a modification of the well-known temperature arrest point so extensively used at atmospheric pressure. In Deffet's method the pressure vessel was maintained at constant temperature and pressure released from a value so high that the material was completely solidified. On crossing the melting line there was melting with automatic recovery of pressure. A limitation of the method is that it does not give the volume change, and if the amount of impurity is appreciable would require elaborate manipulation to give the proper corrections. With this apparatus the melting curves of some 40 substances were followed up to 1000 kg/cm^2. These were: carbon terachloride, nitromethane, pentachlorethane, ethylene bromide, tertiary butyl alcohol, tertiary amyl alcohol, formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthylic acid, caprilic acid, formamide, cyclohexane, benzene, nitrobenzene, *p*-nitrotoluene, *o*-xylene, *p*-xylene, phenol, *m*-cresol, benzophenone, methyl benzoate, benzonitril, aniline, dimethyl aniline, *p*-toluidine, piperidine, cetyl alcohol (fusion and transition) dotriacontane (*f.* and *t.*), methyl cyclopentanol (*f.* and *t.*), acetophenone (*f.* and *t.*), cetyl iodide (stable and unstable forms), *o*-nitrotoluene (*s.* and *uns.*), *o*-toluidine (*s.* and *uns.*), salol (stable and two unstable forms), and methylene iodide. The latter has a new stable form under pressure, and also a totally unstable form, the existence of which was not previously known. The totally unstable form is capable of entering into reversible transition with the new stable form; it is this that explains the many strange features in the phase diagram which Tammann had obtained for this substance. In comparison with the work of others, Deffet's melting curves are inclined on the whole to show somewhat less curvature. Deffet discusses his results from the point of view of chemical regularities, and also combines his slope of the melting curve with those latent heats which are otherwise known to obtain the change of volume on melting. His range is hardly sufficient to give any significant information as to the ultimate character of the melting curve; he is apparently inclined to the opinion that an indefinite rise is as probable as anything.

Timmermans and Deffet[211] followed the melting curve of heavy water to 1051 kg/cm^2 and $-5.00°$; they found it to run nearly parallel to the melting curve of ordinary water. In 1940 Deffet[213] modified his method so as to give changes of volume on melting, still in the same pressure range of 1000. He published results for the freezing pressure as a function of pressure, the volume change, the latent heat, and the slope of the melting line for the following substances: gallium, succinonitrile, fenchyl alcohol, bromobenzene, *m*-cresol, benzyl alcohol, alpha-bromonaphthalene, bibenzyl, ethylstearate (stable and unstable), cyclohexanol (also a transition), *p*-dichlorobenzene (also a transition), *p*-dibromobenzene (also a transition), *o*-cresol (also a transition), and veratrole (stable and unstable forms). Deffet and Vlérick in 1942[214] published similar data for benzene, *p*-xylene and naphthalene. In 1938 Robberecht,[212] with the same apparatus, followed the ordinary melting line and the transition line between the isotropic and non-isotropic liquid (liquid crystal) for: the formate, acetate, propionate, *n*-butyrate, *n*-caproate and *n*-valerate of cholesterol and cholesteryl chloride; the methyl, ethyl, and propyl carbonates of cholesteral and *p*-azoxyanisol; and the ethyl carbonates of *p*-azoxyphenol, *p*-azophenol, and *p*-azoxybenzoate. It was found that the transition line of all these substances rises at approximately the same rate, 50° per 1000 kg/cm². This is in all cases more rapid than the rise of the melting line of the non-isotropic phase, so that the domain of existence of the liquid crystal becomes more extensive with increasing pressure.

Basset[215–218] has contributed several papers on the fusion of graphite, already referred to, and has also followed the melting curve of tetrahydronaphthalene[219, 220] to 11,000 kg/cm², and speculates as to the existence of a critical point, apparently without complete familiarity with the literature.

Swallow and R. O. Gibson[221] determined by a visual method the effect of pressure up to 2000 kg/cm² on the melting points of *o*-, *m*-, and *p*-xylene. Their results are in fair agreement with those of Tammann and my own. Dow and Hibsham[222] studied the melting to 4000 kg/cm² of *o*-, *m*-, and *p*-mononitrophenol. They compared two methods; the first was the regular piston displacement method. The second method maintained the pressure vessel at constant temperature in a bath, lowered the pressure across the melting curve, and detected the beginning of melting by the temperature reaction of a thermocouple embedded in the material. Substantial agreement was obtained between the two methods. Clusius and Weigand[223] followed the melting curves from the triple point up to 200 atmos. of the gases: A, Kr, Xe, CH_4, CH_3D, CD_4, C_2H_4, C_2H_6, COS, and PH_3. The results were reproduced by a second degree expression in the pressure.

Several theoretical papers have appeared on the character of the melting curve. In 1932 van Laar[224] abandoned his earlier point of view that the melting curve rises to an asymptotic temperature and adopted the view that it rises indefinitely. He derived theoretically the formula for the melting curve:

$$p+a=B\tau+C\tau^{1+\epsilon},$$

where the coefficients are related to the properties of the pure phases. This is very much like the empirical formula of Simon and Glatzel, which for purposes of comparison may be written in the form: $p+a=C\tau^b$. Jänecke about this time had two papers;[225] the first showed how a formula could be written for the melting curve featuring van Laar's asymptotic temperature, and in the second paper the formula was withdrawn when van Laar altered his opinion. In 1934 Tammann and Moritz[226] published a paper on the character of the melting curve. Tammann was still unwilling to give up his maximum temperature, although the temperature of any possible maximum gets continually higher with every experimental extension of range. In this paper he points out that my experimental results for the change of volume on melting up to 12,000 can be represented within experimental error by the formula: $\Delta v=a-b\log(c+p)$. This formula demands the vanishing of Δv at some finite pressure, which is the pressure of the maximum. This would be at 40,000 kg/cm² for CO_2 and at 67,000 for nitrobenzene. The formula of Simon and Glatzel for the melting curve is repudiated because it does not admit a maximum. Rice[227, 228] has two theoretical papers on the liquid-solid equilibrium in argon. Theoretical considerations yield certain expressions for some of the thermodynamic parameters of liquid and solid phases separately, from which the equation of the melting line may be found. His equation reproduces my experimental results to 10,000 kg/cm^2. Rice is apparently of the opinion that a critical point is by no means to be ruled out.

Several papers on this topic have come from my laboratory. In 1934[111] I followed the melting curves of nitrogen and argon to 5000 kg/cm^2, and pointed out that the conclusions to be drawn from these new data over a considerably greater range of reduced parameters than any of my previous data for liquids up to 12,000 were the same as the conclusions to be drawn from my previous work, namely that there is no indication of anything other than an indefinite rise of the melting curve. My melting temperatures were higher than those of Simon, and I indicated the possible source of error already discussed. Later, Benedict[110] improved my apparatus and got more accurate coordinates for the melting curve. In particular, he was not able to substantiate an irregularity which I had found at the low pressure end of the curve, which I had thought to indicate a possible new polymorphic modification of nitrogen. In 1935[131] I determined the melting curves of D_2O up to 9000 kg/cm^2 and 20°; this involved the melting curves of four different modifications. In general, the melting curves for heavy water run closely parallel to the melting curves for ordinary water. The entire phase diagram was determined at the same time as the melting curves, and the matter will be discussed again. In 1937[229] the melting curve of a newly discovered high pressure form of ice, ice VII, was followed to 190° and 40,000 kg/cm^2. The difference of density between the liquid and the solid phase is surprisingly large, considering that there have already been freezings to four other modifications of ice at lower pressures. At the triple point between liquid, ice VI, and ice VII, the change of volume is 0.09 cm^3/g. The change of volume and the curvature of the new melting line follow the accustomed pattern. On the other hand, a new feature appears in the behavior of the latent heat. Usually it remains approximately constant along the melting line; here it increases with increasing pressure and temperature and at a rate more than sufficient to compensate for the increase of temperature, so that the entropy difference between liquid and solid increases with rising temperature and pressure along the melting line. This is the first pronounced instance of such behavior; it hardly needs to be emphasized that this is compatible with neither a maximum nor a critical point. Finally, there are my measurements to 50,000 kg/cm^2 of the volumetric behavior of both liquid and solid phases which have already been discussed[132] in connection with compression of liquid and of solid, which included the melting phenomena of the following substances: ethyl alcohol, *n*-butyl alcohol, ethylbromide, *n*-propylbromide, chloroform, carbon bisulfide, chlorobenzene, methylene chloride, and water. The range of pressure was about 40,000 kg/cm^2 and of temperature to 200°; it is usually difficult to follow the melting phenomena completely out to the end of the possible pressure range, 50,000, because of subcooling phenomena, and also frequently because the temperature would have run out of the range. The measurements were by the piston displacement method, permitting a determination of all the parameters. The general character of the results remains the same as in the lower pressure range, and no parameter behaves either singly or in combination in a way to suggest that the ultimate course of the melting curve is different from an indefinite rise with temperature and pressure. The curve rises with decreasing curvature, the volume difference decreases with convexity toward the pressure (or temperature) axis, and the latent heat does not decrease. In fact, the latent heat displays a new tendency in the new pressure range; on the whole it formerly remained constant. Now it tends to increase; in all cases there is at least a slight increase, and there are three cases of an increase so marked that the entropy difference between liquid and solid increases along the curve. These are: water, already mentioned; ethyl alcohol; and *n*-butyl alcohol. Two other substances show a less marked increase of entropy. In summary, in my opinion these results over a greatly increased pressure range only confirm the conclusion which I had drawn from all my other measurements, namely that there is no experimental reason to expect anything else than an indefinite rise of the melting curve. This does not necessarily mean, however, as might naturally be supposed, that any substance, no matter how high its temperature, can be brought to freeze by the application of a pressure sufficiently high. A new effect enters at high pressures, namely greatly increased viscosity which makes for greater sluggishness of all internal changes, and which may result in an indefinitely great subcooling. It is consistent with other experience that the tendency to the formation of a nucleus of a new phase passes through a maximum as pressure is displaced at constant temperature beyond the equilibrium point, so that if the liquid is not brought to freeze by pressures of the present range the probability is that no pressure will suffice. In the above work four substances were found that could not be forced to freeze, although the thermodynamic conditions were favorable. The geophysical implications of this state of affairs are obvious. Other regularities discovered in the high pressure range connected with melting phenomena were: the absolute volumes of both liquid and solid tend to become smaller along the melting line, the effect of pressure being dominant over that of temperature; the compressibility of the solid at the melting point is never greater than that of the liquid at the melting point and is usually less, but by not a great amount, of the order of 25 percent; the internal energy of both liquid and solid in general probably increase along the melting curve. The fact that the entropy difference between liquid and solid tends to increase means, among other things, that the tendency of the specific heat of the liquid to be greater than that of the solid is accentuated at high pressures.

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C. Polymorphic Transitions

Two papers have been published by Goranson and Kracek from the Geophysical Laboratory on the transitions of $K_2Si_4O_9$[230] and sodium tungstate.[231] These measurements were made in an apparatus in which an electrically heated furnace was mounted inside the pressure chamber, forced water cooling was provided through channels cut in the heavy shrunk-on supporting rings, the closure was made through two covers pressed home between the plattens of a hydraulic press, the pressure of which could be raised to keep pace with the increase of internal pressure, and the running of the transition was detected by the temperature arrest method with thermocouples let into the pressure chamber. The measurements on $K_2Si_4O_9$ were made to a maximum pressure of 3000 kg/cm^2 and a temperature of 775°, just above the melting temperature. The melting curve of modification I drops with rising pressure from 765° (this is an example of an ice type melting which is practically never quoted), and the transition curve between I and II rises from 592° to a triple point near 650° and 2250 bars. Above 140 bars the substance decomposes into quartz and water, so that the transitions described above refer to the prolongation of the curves into the region of thermodynamic instability. The melting curve of sodium tungstate was followed for 1000 bars, beginning at 695°. There are three solid modifications. II has a very restricted region of stability, almost at once giving place to III, the transition curve of which with I was followed to 1000. The transition between I and II is abnormal in that it runs with no volume change, which means that the temperature of transition is independent of pressure. The unstable prolongation of the transition line was followed for 600 bars.

In 1931 Tammann and Kohlhaas[232] described a device essentially an anticipation of one which I used independently later in some of my preliminary explorations. The material is in the form of a cylindrical button of thickness less than the diameter, in order to minimize friction, enclosed in a massive steel collar, and compressed from two ends simultaneously by two pistons forced together by a hydraulic press. The chief advantage is the extension of pressure range that it permits. With this apparatus they redetermined some of the transition parameters for phenol and AgI, obtaining values for the volume decrements which agreed with my published values better than with their own former values obtained by another method. They studied the transitions of FeS, which has a transition falling from 130° at atmospheric to 10° at 3000; there are irreversible effects with this substance and the density depends on the previous pressure history. They also examined a transition of borneol and the transition from white to gray tin. The principal object of the new apparatus, however, was to discover the suspected high pressure modification of bismuth analogous to the high pressure ices. They were not successful in this; it turned out later that their maximum pressure, 19,000 kg/cm^2, was not high enough.

Jacobs[233] in my laboratory has published several papers. His first investigation was of the transformation of black phosphorus, the particular object being to find the explanation for the anomalous reaction rates which I had previously found. His range was up to 230° and 15,000 kg/cm^2; the method was a piston displacement method, together with quenching and examination at atmospheric pressure. Jacobs found a new variety of black phosphorus which is formed in a region of the pressure-temperature diagram contained under the line running from 17,000 and 180° to 11,000 and 230°. Above this there is a band of the pressure-temperature plane such that if the initial compression is started in this region, the anomalous transition rates occur which I found, with eventual transformation into the old and denser form. Still above this there is a region such that if the initial compression starts here, there is immediate and complete transformation to the old form. The explanation of my anomalous effects was that the less dense form was first formed under my conditions, and that progress of the transition developed enough heat to eventually bring the temperature of the interior of the apparatus to the temperature of immediate formation of the dense form. Calorimetric measurements indicated that the order of stability is: black crystalline (the old dense form), red, black amorphous (the new less dense form), and yellow. Jacob's amorphous less dense black form of phosphorus is probably the same as the second form of black phosphorus found by Hultgren, Gingrich, and Warren[234] in the course of their x-ray analysis of a sample of black phosphorus supplied by me. Jacobs[235–237] next developed the method already referred to[158] of taking x-ray diagrams of substances while under pressure, and applied it to a determination of some of the unknown crystal systems of such new forms as could be reached by the available pressure of 5000 kg/cm^2. He first demonstrated that the high pressure form of AgI has NaCl structure. From the spacing of the lines he calculated that the change of volume at the transition is 0.0288 cm^3/g, which is considerably higher than the value 0.0239 which I had found. He suggested that the discrepancy might be due to an incomplete transformation of my material; this was in the form of compressed powder and a suppression of the transition in the finer grains would not be unnatural. I later checked his explanation; on pre-compressing the AgI beyond 20,000, considerably higher than the pressure of my first measurements, I found a change of volume on releasing pressure which exactly checked Jacob's x-ray measurements. Jacobs in the same paper obtained the x-ray photographs for the high pressure modification of CsClO$_4$, but the pattern was too complicated to permit a determination of the crystal system. It was not until his second paper that he was able to measure the transition of RbI. This proved especially sensitive to subcooling and suppression of the transition, effects which were only avoided by exceedingly high purity. The high pressure form was found to be body-centered cubic; this by implication may be taken to be the structure of the other alkali halides whose transition pressure is beyond the reach of this apparatus, and puts a more secure foundation under various theoretical speculations which have had to assume the high pressure structure. Jacobs found a volume change for the transition 30 percent greater than mine; the explanation is probably that already given. In the same paper a theory is given of these transitions; the energy relations are such that it is probable that the sodium halides will not be stable in the body-centered form at any pressure, no matter how high. This checks with my recent observations up to 100,000. On the other hand, the theory indicates that the NaCl form of AgI may have a transition to the body-centered form in the neighborhood of 50,000, and none has been found to 100,000.

In this connection determinations should be mentioned by McFarlan[238] of the crystal structure of some of the high pressure ices, although these measurements were not made under pressure. At liquid air temperature the transitions of these ices are so sluggish that they do not run with appreciable velocity at atmospheric pressure, so that once the ices have been formed at higher temperatures under pressure, the apparatus may be cooled and opened, the ice removed, and its crystal structure determined in an x-ray camera maintained at liquid air temperature. In this way McFarlan found the structure of ice II to be side-centered ortho-rhombic; all the crystal parameters were determined. Less complete information, not all of which was published, was obtained for ices III, V, and VI.

Clusius and Weigand[239] determined the effect of pressure up to 250 kg/cm^2 and at low temperatures on the I–III transitions of solid H_2S and D_2S. The volume changes for the deuterium compound are about 20 percent less than for the hydrogen compound.

T. C. Wilson[240] has studied the effect of pressures up to 10,000 kg/cm^2 and temperatures up to 426° on the order-disorder transformations in the alloys CuAu, Cu_3Au, CuZn, and Cu_3Zn. The work was done at Yale under the direction of McKeehan. The method was a study of the discontinuities in the curve of electrical resistance *versus* pressure. The general pressure technique was very similar to mine, and in fact parts of the apparatus were loaned by me. The entire chamber containing the sample was heated to the required temperature, and the leads for measuring resistance were taken out through the connecting pipe. The critical points of CuAu and Cu_3Au were raised by pressure, the general effect of which seems to be a slight increase in the degree of ordering of the constituents. Among the results obtained were detailed data for the effect of pressure and temperature on resistance through an unusually wide temperature range. With regard to the general subject of order-disorder transitions reference may be made again to some of my anomalous volumetric relations for this class of substance.

Barth[241] has determined by x-ray methods the structure of the high pressure modification of KNO_3 III. The method is similar in principle, although entirely different in detail, from that of McFarlan. By suitable manipulation, the high pressure form may be realized at atmospheric pressure and its structure determined. It is found to belong to the ditrigonal-pyramidal class of Groth, space group C_{3v}^5.

Dow[242] has studied the effect of pressure on that internal change in rubber which corresponds to freezing. At 8000 there is an enormous retardation of the transition, which under his conditions did not run appreciably in 14 days. At a lower pressure, 1270 kg/cm^2 and 77°, it ran to completion, the coordinates of the transition point agreeing with those calculated by Clapeyron's equation.

Prosvirin[243] has found that a simple compressive stress of 12,500 kg/cm^2 (not a hydrostatic pressure) has a very marked stabilizing effect on the internal transformations which often run spontaneously in high speed steel.

Gunther, Geselle, and Rebentisch[244] have made a serious but unsuccessful attempt to effect the transformation from graphite to diamond by exceeding the pressure of the thermodynamically reversible transition at temperatures high enough so that the transition velocity might be expected to be appreciable. In estimating the probably necessary conditions they used the calculations of Simon that at 2000° the pressure of reversible transition is 45,000 kg/cm^2. Their apparatus was constructed of steel, of a shrunk-together construction for maximum strength. Pressures were generated by air pressures acting on a hydraulic press with large piston. Air was admitted until pressure built up sufficiently to rupture two members with which the ram of the press was restrained; the rupture permitted an impulsive advance of the ram, which drove a piston, which swept before it a piece of graphite electrically heated into a containing vessel. The initial pressure is impulsive and was calculated from the deformation of calibrated steel plattens; the final pressure was determined by the air pressure acting on the ram. The graphite was heated initially to 3000°; the initial pressures were stated to have reached 120,000 kg/cm^2 and the final pressure 100,000. No certain transformation was ever accomplished, and the authors regard their results as negative, and explain it by the short times, which were insufficient for sensible progress of the transition. It seems to me probable, however, that their estimates of both temperature and pressure were too high. The piece of graphite was small and had to be carried a distance of some centimeters before it was finally driven home in its mold; there must have been an appreciable drop of temperature. It is hard to believe that steel under their conditions of support would tolerate such high stresses; this is almost certainly the case with their estimated final static pressure of 100,000. No allowance was made for friction of the steel piston on the sides of the mold, which under the conditions may have been excessive. They state that under their conditions a graphite was produced with a density of 2.355, against the figure 2.25 for normal single crystal graphite, with a contraction of the normal atomic spacing along the *c* axis of 0.07A. The same authors[245] applied the same apparatus to a study of the conditions of formation of black phosphorus. Exposure of yellow phosphorus for five minutes to 60,000 kg/cm^2 yielded a blackish gray mass, mostly soluble in CS_2. Exposure to 100,000 impulsively yielded a black product not soluble in CS_2, a conductor of electricity, and with practically the same density as my black crystalline phosphorus. They observed a partial transformation back to yellow on sealing in a glass tube for six months; the origin of the black so treated was not stated. They draw the conclusion that black is unstable with respect to yellow, and all the more with respect to red. They also make the point that they have produced black directly from the modification I of yellow phosphorus at room temperature, instead of from yellow phosphorus II, as I had done. They overlooked the fact, however, that their modification I had to be carried through the region of II before the conditions of transformation to black were reached. It seems to me probable that they produced under their conditions both Jacob's amorphous black variety and my crystalline variety. They were not acquainted with the work of Jacobs[233] nor my own work in 1935[246] in which violet phosphorus was transformed to black.

My own work on polymorphic transitions in this period started in 1931 with a study to 12,000 kg/cm^2 already referred to[178] of the volume anomalies of NH_4Cl and NH_4Br. At atmospheric pressure these anomalies are ordinarily described as transitions of the second kind. With increasing pressure the temperature of the anomaly of NH_4Cl is raised and the abruptness of the discontinuity of thermal expansion is smeared out. With NH_4Br, on the other hand, the temperature of the anomaly is depressed with rising pressure and the discontinuity becomes more abrupt, changing into something experimentally indistinguishable from a discontinuity in the volume itself, that is, changing from a transition of the second kind to a transition of the first kind with increasing pressure. Actually, of course, no true discontinuity can ever be established experimentally, and the description of the data in terms of discontinuities of one kind or another is only a matter of approximation and convenience. In 1932 an investigation up to 12,000 was made of a much smeared out transition of Ag_2O, already referred to.[179] In 1934 I made the first measurements in the new materially higher pressure range.[247] With the double piston apparatus, already used by Tammann, I found the anticipated transition of bismuth at 25,000 kg/cm^2, and transformed white phosphorus to black at room temperature at 35,000. It is highly probable that this black phosphorus contained at least a considerable fraction of Jacob's amorphous black variety; there were indications at the time that it was not the former crystalline variety. In 1935[131] the complete phase diagram of heavy water was worked out up to 9000 kg/cm^2. The transition lines between the various modifications run nearly parallel to the corresponding lines in the diagram of ordinary water, the temperatures being from 2.5° to 4° higher. In the course of the work the existence of an absolutely unstable form of ice was discovered; this usually appears in preference to the stable form V in the domain of stability of V. The thermodynamic parameters of the reversible melting of IV, the designation proposed for the new ice, and of the reversible transition between IV and VI were established. After the existence of this new form had been established for heavy water, I re-examined my original data for ordinary water, and found that the existence of the same instable ice had been encountered and some of the parameters measured; at the time the results were discarded as owing to experimental error. In fine detail, there are failures of complete parallelism between the phase diagrams for the two waters which must be taken into account in any final and complete theory, and which show that the entire phenomena are not explicable in terms merely of a difference of zero-point energy.

In 1935 4(a) I published the first results with the new technique of external support applied to conical vessels. The first measurements were on the elements, in the pressure range up to 50,000 kg/cm^2, and at temperatures from $-80°$ to 200°. The method was the piston displacement method at constant temperature, permitting the determination of all the thermodynamic parameters of the transition. Three high pressure modifications were found for bismuth, one for mercury, one for thallium, two for tellurium, one of these being probably the same as a form already known at high temperatures at atmospheric pressure, two new forms for gallium, one being totally unstable, and one new form for iodine. New forms were also found for the three potassium halides at pressures ranging from 18,000 to 20,000 kg/cm^2; these were anticipated in analogy with the rubidium salts, but previous attempts had not yielded them. In 1937 4(b) and (c) I applied the same technique in the same range of pressure and temperature to a determination of the phase diagrams and the thermodynamic parameters of the transitions of some 35 compounds as follows (in the following, a number after a compound indicates the number of new high pressure forms in excess of 1): Cu_2I_2, AgCl, AgBr, Ag_2S, $ZnBr_2$, $HgCl_2$, $HgBr_2$ (3), HgI_2 (2), GeI_2, PbI_2 (2), Cr_2O_3, KCN (3), AgCN, $NaNO_2$, $AgNO_2$, $RbNO_3$, $CsNO_3$, $AgNO_3$ (3), $NaClO_3$ (3), $NaBrO_3$, $NaClO_4$ (2), $NaIO_4$, $KClO_3$, KIO_4, $RbClO_4$, $AgIO_3$, $AgClO_4$, $CsClO_4$, $CsIO_4$, $TlClO_4$, NH_4ClO_4, Na_2SO_4 (2), $KMnO_4 \cdot CsMnO_4$ (2), and $Pb(C_2H_3O_2)_2$ (3). A statistical study of these new transitions compared with those previously studied in the range up to 12,000 shows a marked increase in the proportional number of so-called abnormal transitions of the ice type, with negative $d\tau/dp$ and a volume of the high temperature phase less than that of the low temperature phase. In the former range up to 12,000, 24 percent of the transitions were of the ice type; in the new range 43 percent are of this type. The abnormal ice type of melting is one which is wiped out by high pressure in all known cases; the same type of relation between polymorphic forms does not seem to imply any essential instability and there is no tendency for it to be wiped out by pressure, but the reverse. At these high pressures the changes of thermal energy on passing through the transition tend to become unimportant, the energy difference between the phases becoming mainly the difference of mechanical energy generated by the pressure acting through the volume change. A study of the relation between phase diagram and chemical composition confirms the conclusion reached in the lower range that chemical similarity does not predispose to similarity of phase diagram in general, although there are some contrary examples.

In 1937[229] the new apparatus was applied to extending the phase diagram of water from 22,000 to 40,000 kg/cm^2. A new modification of the solid, ice VII, was found just beyond the pressure range of the previous work. In 1938,[184] incidentally in the course of volumetric measurements, a transition of barium was found in the neighborhood of 17,000 and one of CO_2 in the neighborhood of 25,000. In 1938[248] was published a study of the transitions of some 25 organic compounds with the apparatus for 50,000 between the former temperature limits. These substances were: carbon tetrabromide (3), iodoform (3), cyanamide, urea (5), thiourea, ammonium thiocyanate, nitroguanidine, ammonium formate (2), urea nitrate, methylamine hydrochloride (4), semi-carbazide hydrochloride, dichloroacetamide, iodoacetic acid (2), oxamide (?), acetamide (3), guanidine sulfate (4), quinone, *p*-dichlorobenzene, dichlorophenol, hydroquinone, *p*-toluidine (2), naphthalene, *d*-camphor (10), menthol (3), and aniline sulfate. In comparison with inorganic compounds polymorphism seems to be a much more common phenomenon among the organic compounds. On the other hand, the transitions are less clean cut, the volume changes are smaller, phenomena of subcooling or total suppression of a transition are much more common, and on the whole the subject is more difficult and less satisfactory to investigate. This is probably as would be expected from the greater complexity of the organic molecule.

One paradoxical phenomenon shown by CBr_4 is worth special comment. Below 160° the transition phenomena of this substance exhibit an unusual combination of delay and retardation effects combined with preliminary initiation effects. The result is that at low temperatures the transition, which thermodynamically should occur at about 13,000, does not appear at any pressure up to 50,000, irrespective of the period of waiting. Some process of initiation apparently occurs at this high pressure, so that if pressure is maintained at 50,000 for a while and then lowered back into a region where internal viscosity is less, the transition may run at say 20,000 as a result of decreasing pressure, with *decrease* of volume, a phenomenon thermodynamically impossible if the transition is reversible and often mistakenly thought to be physically impossible under any conditions. Comment should also be made on the 11 probable different modifications of *d*-camphor, by a considerable margin the largest number of forms shown by any substance.

In 1939[249] in studying the behavior of certain minerals two new high pressure forms were found for calcite in the pressure range 15,000 to 25,000 and the phase diagram established.

What amounts to a transition of the second kind for quartz glass was also investigated. At low pressures the compressibility of quartz glass anomalously increases with rising pressure. This phenomenon persists at room temperature up to 35,000, where it ceases so abruptly as to result in a cusp on the volume isothermal, or a transition of the second kind.

In a study of the compressions of a number of new compounds up to 50,000 in 1940 already referred 4(c) to new high pressure forms were found for BaTe, PbS, PbSe, PbTe, ZnSe, ZnTe, HgSe, and HgTe, and the volume changes measured at −80° and room temperature. In addition to its reversible pressure transition, HgTe presents the phenomenon not previously observed of a pure pressure decomposition. HgTe is one of the few compounds that is formed from the elements with increase of volume; at pressures above 15,000 it is slowly decomposed at room temperature into the elements. The decomposition runs so slowly that the reversible transition superposed on it could be approximately studied.

In the course of the volume measurements on liquids 132(b), a new form of CS_2 was found, very much like black phosphorus in appearance. At pressures above 40,000 kg/cm^2 and temperatures above 175°, CS_2 is transformed slowly and irreversibly into a black solid, stable indefinitely in the air at room temperature. The density is about 4 percent greater than that of the elements constituting it. It may be heated in the air without effect to approximately 175°, above which it decomposes quietly to sulfur and carbon. The structure is too fine to permit x-ray analysis up to the present, and the other physical properties have not been determined; it is natural to think that the structure may be similar to that of SiO_2.

Finally, on extending the pressure range from 50,000 to 100,000 kg/cm^2 a number of new high pressure forms have been found.[187, 188] The measurements to 100,000 have been made only at room temperature, so that for these transitions it has not been possible to determine the phase diagram or to obtain the thermal parameters of the transition; it is possible, however, to determine the volume change at this temperature. The new transitions in the range 50,000 to 100,000 are for calcium, strontium, barium, antimony (doubtless analogous to the lowest transition of bismuth), two for bismuth, making six modifications in all for bismuth, tellurium, silver chloride, silver bromide, and sodium nitrate. Also a new transition has been found[189] with Carboloy apparatus for rapid measurements up to 40,000 for lithium perchlorate at 16,000 at room temperature.

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5. Phase Changes under Pressure in Multi-Component Systems

The complete phenomena of phase change in multi-component systems are complicated and do not lend themselves to any one dimensional scheme of classification. The phenomenon which has attracted principal attention is that of the solubility limits, or the separation of the solute from the solvent with increasing concentration. We will discuss the solubility phenomena first and then others, such as the displacement of the eutectic point by pressure.

A. Solubility of Gases in Liquids

The simplest solubility phenomena are those of gases in liquids; we shall give only cursory attention to it because the pressure range is below that of our main interest. At low pressures Henry's law, which states that the amount of gas absorbed is proportional to the gas pressure, approximately holds. The chief interest of much of the work on gas solubility has been to determine quantitatively the departures from Henry's law. Because of the industrial importance there are many titles here. The arrangement of the following summary is in the main chronological.

Frolich, Tauch, Hogan, and Peer[250] measured the solubility to 200 atmos. of H_2, N_2, O_2, and CH_4 in sixteen organic solvents and water. Henry's law is followed if account is taken of the deviation of the gases from the perfect gas laws. For these gases Henry's law seems to be followed up to two-thirds the saturation point. Goodman and Krase[251] measured the solubility of nitrogen in water up to 300 atmos. at temperatures from 0° to 169°. Wiebe, Gaddy, and Heins[252] measured the solubility of nitrogen in water at 25° up to 1000 atmos. Wiebe and Tremearne[253] determined the solubility of hydrogen in liquid ammonia between 25° and 100° and up to 1000 atmos. The relations are linear over most of the range; in the initial region there is some crossing of the solubility curves. Krichevsky and Kasarnovsky[254] gave a theoretical discussion of the solubility of nitrogen and hydrogen in water up to 1000 atmos., obtaining approximate agreement with experiment and clearing up some misconceptions in previous theoretical discussions. Kritschewsky, Shaworonkoff, and Aepelbaum[255] have determined the solubility of various mixtures of gases in water up to 30 atmos. Wiebe and Gaddy[256] measured the solubility of 3 to 1 mixture of hydrogen and nitrogen in water at 25° up to 1000 atmos. The solubility of the mixture can be calculated within a few percent from that of the pure components. The same authors[257] determined the solubility of helium in water between 0° and 75° and up to 1000 atmos. The solubility passes through a minimum at 30°, and the solubility at high pressures cannot be calculated from that at low. Ipatieff and Levina[258] measured the solubility of hydrogen in hydrocarbons of the aromatic and naphthenic series. Henry's law is followed up to 100° and 100 kg/cm^2; beyond this there are departures, the solubility coefficient increasing with increasing pressure. The solubility is less in the aromatic compounds. Michels, Gerver, and Bijl[259] determined the solubility of methane in water and aqueous solutions of six halogen salts, sugar, glucose, and formaldehyde up to 450 atmos., at temperatures which occasionally reached 150°. A somewhat complicated analytical formula reproduces the results. Basset and Dode[260] determined the solubility of nitrogen in water at room temperature up to 4500 kg/cm^2. Under the higher pressures we are here dealing with approximately two liquids. The surprising result is found that the solubility, measured as cm^3 of nitrogen in one cm^3 of water, passes through a maximum near 3000. They find that the system water-nitrogen does not tend toward complete miscibility at much higher pressures, but water remains denser than nitrogen up to 15,000 kg/cm^2. Krichevskii and Kazarnovskii[261] contribute another theoretical paper in which they successfully compute the solubility of the 3 to 1 hydrogen-nitrogen mixture in water up to 1000 atmos. Krichevskii, Zhavoronkov, and Tsiklis[262] determine the solubility of hydrogen and carbon monoxide and their mixtures in methanol up to 300 atmos. and to 140°. The solubility increases with increasing temperature, and there is a crossing of solubility isotherms of CO. Krichevskii[263] gives a theoretical explanation of the maximum in the nitrogen-water solubility found by Basset and Dode. Wiebe and Gaddy[264] determine the solubility of hydrogen and nitrogen in liquid ammonia up to 100° and 1000 atmos. and investigate the critical phenomena in the ammonia-nitrogen system; they find the critical pressure to be 600 atmos. at 90° and 400 atmos. at 100°. Ipatieff and Levina[265] determined in the range up to 200° and 200 atmos. the solubility of hydrogen, nitrogen, carbon monoxide, carbon dioxide, and methane in shale gasoline and kerosene. Bykov[266] determined the solubility in the range up to 240° and 100 atmos. of air, oxygen, nitrogen, and hydrogen in three aqueous solutions of KCl. Solubility passes through a sharp minimum with rising temperature; hydrogen obeys Henry's law better than nitrogen and oxygen. Zel'venskii[267] determined the solubility of carbon dioxide in water up to 100 atmos. and between 0° and 100°; Henry's law is followed. Gonikberg, Fastovskii, and Gurvich[268] measured the solubility of hydrogen in liquid nitrogen at temperatures between 79° and 109°K up to 190 atmos. and found good agreement between experiment and calculation. Gonikberg and Fastovskii[269] determined the solubility of helium in liquid nitrogen over the same temperature range and up to 295 atmos. The system obeys the laws for ideal solutions. Gerver[270] contributes a general review article. Dodge and Newton[271] have a theoretical paper on liquid-vapor equilibrium in binary systems in which they compute the solubility of nitrogen in water up to 1000 kg/cm^2 from the experimental data up to 300. Levina and Stsibarovskaya[272] determined the solubility of air, oxygen, and nitrogen in aqueous solutions of NaOH of three concentrations up to 100 atmos. and between 0° and 240°. They find a solubility minimum of nitrogen and oxygen in pure water at 75°, the temperature of the minimum being displaced to lower values on increasing the NaOH concentration. Zel'venskii[273] has studied up to 300 atmos. the solubility of gaseous mixtures of carbon dioxide with nitrogen and with hydrogen. In general, the presence of one gas decreases the solubility of the one present in excess. Wiebe and Gaddy[274] determined the solubility of carbon dioxide in water between 50° and 100° and up to 700 atmos. Their results agree with the theory of dilute solutions. A criticism of one aspect of this paper of Wiebe and Gaddy is made by Katz.[275] Fastovskii and Gonikberg[276] determined the solubility of hydrogen in liquid methane at temperatures between 90° and 127°K and up to 230 atmos. The behavior is in agreement with the theoretical equation of Krichevskii. Krichevskii, in a paper entitled "Limited Mutual Solubility of Gases at High Pressures,"[277] finds that at 140° and 5000 kg/cm^2 a mixture of 67.6 percent NH_3 and 32.4 percent N_2 splits into two gaseous phases containing 76.6 and 33.1 percent NH_3, respectively. This is an interesting result in a range of pressure much higher than most of the rest of the work at present under review. The pressure is so far beyond the critical pressure, however, that the densities are approximately those of ordinary liquid phases, and the designation "liquid" would be more appropriate than "gas." The phenomena of limited miscibility in liquid phases are known to be of not infrequent occurrence. Wiebe and Gaddy[278] measured the solubility of carbon dioxide in water in the temperature range from 12° to 40° up to 500 atmos. The existence of a solid cryohydrate, CO_26H_2O, was established in the higher pressure range. Sattler[279] found that the solubility of hydrogen in hexane, cyclohexane, benzene, and *m*-xylene is a linear function of pressure up to 150 atmos. Schoch, Hoffmann, and Mayfield[280] determined the solubility of methane in cyclohexane up to the critical pressures and at temperatures from 100° to 220°F. They also give values for the volume and compressibility of the liquid phase. In a second paper[281] the same authors determine the solubility of methane in hexane over the same range. Gonikberg and Fastovskii[282] have determined the solubility of helium in liquid methane between 90° and 106°K and up to 160 atmos.; a complete copy of this paper has apparently not yet reached this country. Krichevskii and Tsiklis[283] have extended the pressure range of the former work of Krichevskii from 4500 to 9500 and find limited solubility phenomena in the systems methane-ammonia, methane-nitrogen-ammonia, and nitrogen-hydrogen-ammonia. Again the title refers to the phenomenon as of limited solubility in *gases*.

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B. Solubility of Solids in Liquids and Related Phenomena

Our knowledge of phenomena in this field has been notably enlarged in the period under review, to a large extent by the work at the Geophysical Laboratory. The pressure range of that part of the work limited to the ordinary temperature range was 12,000 kg/cm^2; Goranson has made measurements to 1000°C or higher, and the pressure range of this part of the work was 4000 kg/cm^2.

In the early part of the period there are three papers by Adams and Gibson,[284] Adams and Hall,[285] and Adams[286] on the system NaCl-water. In this work both direct and indirect methods were used; in general the indirect methods proved more convenient and the direct methods were mostly used merely by way of check. The indirect methods rest on the fact that the solubility limits are set by the equality of the partial potentials of the components in the various phases. The partial potentials under pressure can be obtained from the known partial potentials at atmospheric pressure and their pressure derivatives. The pressure derivatives depend on the partial volumes. Experimentally the method reduces to a determination of the partial volumes, which means an accurate determination of the compression of solutions of various concentrations as a function of pressure. Fortunately the methods for measuring compression are now of sufficient precision to give the necessary accuracy in the partial potentials. At low pressures up to 1000 the method of measuring compression was the modified mercury injection method already referred to,[133] and between 1000 and 12,000 the piston displacement method. The first paper, by Adams and Gibson, deals with the melting of the little known dihydrate $NaCl\cdot 2H_2O$. At atmospheric pressure this hydrate melts incongruently, forming solid NaCl and the saturated aqueous solution of NaCl. The temperature of incongruent melting rises with increasing pressure. The curve of incongruent melting was found to pass through a maximum at 25.8° and 9500 bars pressure, the second known example of this phenomenon, the first being $Na_2SO_4\cdot 10H_2O$ discovered by Tammann. Thermodynamically the existence of a maximum means that the volume change of the transition passes through zero. This means that on an isothermal below the temperature of the maximum, on increasing pressure the saturated solution plus NaCl may be made to crystallize to solid $NaCl\cdot 2H_2O$ with decreasing volume, and on further increase of pressure the solid $NaCl\cdot 2H_2O$ may be made to melt with further decrease of volume. This was checked experimentally. It was also found that in the neighborhood of the maximum an impressed increase of pressure was followed by an anomalous secondary reaction in the direction of a further increase of pressure; this occurs only for finite pressure changes. For infinitesimal pressure changes thermodynamics apparently demands the opposite sign. In the paper by Adams and Hall an electrical conductivity method was applied to determine the solubility of NaCl in water at 30° and up to 4000 bars, with agreement with results obtained by other methods. Finally Adams worked out the complete phase diagram for the system water-NaCl at 25°, up to 12,000 experimentally, and by calculation up to beyond 16,000. This is reproduced in Fig. 4. At this temperature the phase diagram splits into eight regions. Two isolated regions of existence of NaCl solution should be noticed; this is a consequence of the existence of a maximum temperature on the curve of incongruent melting of the dihydrate. Also to be noted is the pressure eutectic of NaCl solution, ice VI+solution, and ice VI+NaCl. This means that if any mixture of NaCl and water is compressed at 25°, the pressure passes through an arrest point on reaching 16,700 bars until any solution remaining has completely solidified to NaCl+ice VI.

Adams[287] applied the same technique to an investigation of the system K_2SO_4 at 25° and found a complicated phase diagram. Again a pressure eutectic involving ice VI was found, this time at 10,750 bars at 25°. As is the case with NaCl, it was found that the fictive volume of the salt in solution *increases* with increasing pressure; this means that the solution becomes more ideal. Adams and Gibson[288] investigated the solubility of ammonium nitrate in water at 25° up to 10,000 bars. The partial volume of NH_4NO_3 in general decreases with increasing pressure; above 15 percent concentration it is independent of concentration and the partial compressibility differs only slightly from that of solid NH_4NO_3. The solubility curves of ice VI and NH_4NO_3 IV were calculated and a pressure eutectic found at 12,100 bars at 25.3 percent nitrate by weight. Later Adams[289] contributed a paper, mostly theoretical, working out the details of the indirect thermodynamic methods of determining the phase diagrams of hydrates, and systematizing the various types of phase diagram that are to be expected.

Gibson[290] discusses methods of calculating solubilities under pressure, showing how, by an application of the equation of Tait and the hypothesis of Tammann, already discussed, solubilities may be calculated up to 10,000 kg/cm^2 from experimental data up to 1,000 only, checks this against experiment for the already known cases of NaCl, K_2SO_4, and NH_4NO_3, and contributes new experimental material for KI, which also checks. These four salts give solubility curves of different types, so that the presumption is that any other salt can be treated by the same methods. In a later paper Gibson[291] gives a general discussion of the effect of pressure on the solubility of solids in liquids. Only in exceptional cases is the solubility of a solid in a liquid increased by pressure. The exceptional cases include aqueous solutions of carbonates, sulfates, sulfides, fluorides, and hydrides of some of the alkalies, alkali earths, and heavy metals. He thinks it unlikely that in the geophysical field there are significant cases of increase of solubility brought about by pressure. New experimental material is presented for the solubility of CsBr in water up to 1500, and the partial volumes of NaCl up to 1,000 bars and at temperatures up to 95°, the previous temperatures having been not higher than 30°. In 1938[292] he wrote a popular and summarizing article on "The Nature of Solutions and their Behavior under High Pressures." To be mentioned in this connection is also Gibson's[293] summary in the *Handbook of Physical Constants* issued by the Geological Society of America.

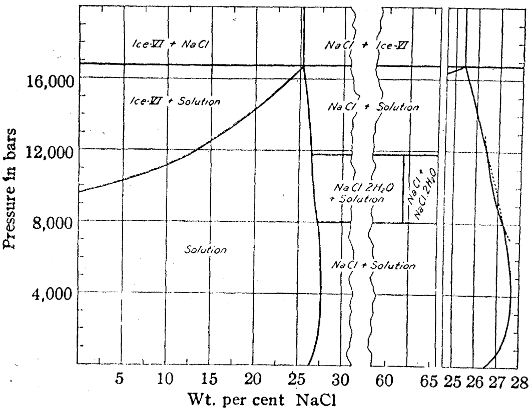

FIG. 4. Adams' equilibrium diagram for the system $NaCl-H_2O$ under pressure at 25°. The freezing pressure curve and the solubility curve intersect at a pressure eutectic. On the right the solubility curve is shown on an enlarged scale.

The work of Goranson at the Geophysical Laboratory on the present topic has been mostly concerned with temperatures of the order of 1000° with apparatus already described. In 1936[294] he determined the solubility of water in Albite-melt between 900° and 1200° and up to 3000 or 4000 bars. At any fixed temperature the amount of dissolved water could be represented by a formula of the type $x=p/(a+bp)$. The constants a and b in this formula both increase with increasing temperature. The solution of water is accompanied by evolution of heat; this heat increases with temperature and decreases with pressure. In 1938[295] Goranson published on phase equilibria in the $NaAlSi_3O_8$-water and $KAlSi_3O_8$-water systems over the same range of pressure and temperature. Complete evaluation of some of the results awaits a determination of the constants of pure water in this region. It was established that during the process of crystallization in these systems sufficient pressures might be developed to be a factor in vulcanism.

Passing now to the more scattered work in this field. Swallow and R. O. Gibson[221] in the course of their measurements of the effect of pressure on the melting of the xylenes already referred to observed the binary system composed of 30 percent para- and 70 percent orthoxylene. The point of first crystallization was $-16.3°$ at 445 kg/cm^2

and 11.6° at 1605 kg/cm^2; the eutectic temperature was displaced from 1135 kg/cm^2 at $-11.5°$ to 2180 kg/cm^2 at 10.0°. In both cases the relation between temperature and pressure was linear; their results agreed with those obtained by Nakatsuchi in 1929. McKay and Higman[296] give a theoretical thermodynamic discussion of the relations at the eutectic point, finding previous analyses unsatisfactory in certain respects. They derive formulas which are not inconsistent with the experimental results of Puschin and Grebenschtschikov, referred to in my book, for the displacement of the eutectic point by pressure. Poppe[297] has investigated in the laboratory of Timmermans up to 1000 kg/cm^2 the solubility phenomena in some thirty binary systems both of whose components are liquid, mostly organic liquids, but embracing three systems with ordinary water as one component and four with heavy water. The object of particular interest, and the systems were chosen from this point of view, was the mapping out of the limits of the regions of complete immiscibility. In general the results confirmed previous work of Timmermans. Heavy water, as compared with ordinary water, was found in all cases to notably enlarge the domain of unmixing in all directions. Deffet[298, 299] studied various binary mixtures up to 1000 kg/cm^2 with the same apparatus already described in connection with his determination of the melting of simple substances. In the system benzene-naphthalene the eutectic composition is independent of pressure; the temperature of the eutectic rises 23° for 1000 kg/cm^2. In the benzene-urethane system the eutectic becomes richer in urethane with increasing pressure. In the system $Na_2CO_3 \cdot 10H_2O$ a discontinuity in the slope of the melting curve was found at 51 kg/cm^2. Pressure was found to have little effect on the *form* of the melting point curves (that is, the entire curve is lifted bodily by pressure) in the systems: *p*-dichlorobenzene-*p*-dibromobenzene, aniline-phenol, and *o*-cresol-*m*-cresol. In the systems cyclohexane-aniline and hexane-nitrobenzene there is a composition range in which two liquid phases are in equilibrium with the solid; the extent of this range decreases with rising pressure.

Kean,[300] in my laboratory, has worked out the phase diagram of the alloys of sodium and potassium up to 10,000 kg/cm^2 and 165°. The method was an electrical one; the resistance of specimens of alloys of a range of compositions was measured as a function of pressure and temperature. The discontinuities in the resistance curves indicated the beginning of the separation of new phases. The phase diagram has two eutectics: liquid with Na_2K and K, and liquid with Na_2K and Na. The effect of pressure is not linear. Incidentally, the method yielded results for the effect of pressure on resistance which will be referred to later.

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6. Effects of Pressure on Viscosity

A. The Viscosity of Gases

Boyd[301] determined the viscosity at 30°, 50°, and 70° up to 240 atmos. of nitrogen, hydrogen, and a mixture of the two. The method was a transpiration method, that is, of flow under a small differential head. A theory is proposed based on an anology between kinetic pressure and viscosity, using an equation of state of the Lorentz type. Agreement is obtained with experiment. It is said that this theory offers the first direct proof of the justifiability of treating separately the kinetic and cohesive pressures in the equation of state. Michels and R. O. Gibson[302] measured the viscosity of nitrogen to 1000 atmos. at 25°, 50°, and 75°; the method was a transpiration method with a driving head of about 1 atmos. The isotherms of viscosity as a function of pressure cross in the neighborhood of 400 atmos.; below this pressure the viscosity is less at low temperatures and above it less at high temperature. A minimum in the quotient of viscosity by density predicted by the theory of Enskog is found, and in general there is good agreement with theory. Nasini and Pastonesi[303] measured the viscosity of air at 14° up to 200 atmos. by an efflux method; the viscosity increases by 26 percent in this pressure range over its atmospheric value. R. O. Gibson in 1933[304] published his doctor thesis done in Michel's laboratory on the viscosity of gases at high pressures. Besides the measurements on nitrogen already published with Michels, data are presented for hydrogen at 25° up to 300 atmos. There is general agreement with the theory of Enskog. Sage and Lacey[305] have made measurements up to 220° and 200 atmos. on the viscosity of air, methane, and a lean and a rich natural gas. Viscosity always increases with increasing pressure; the rate of increase with pressure is greater at the lower temperatures. The viscosity isotherms intersect in the general neighborhood of 35 atmos. Golubev[306] described a new form of capillary viscosimeter adapted to measurements with gases up to 5000 atmos. and applied it to the measurement of air up to 300 atmos. between 0° and 100°. Sage, Yale, and Lacey[307] have measured the viscosity of butane and *iso*-butane in both the liquid and the gaseous regions between 100° and 200°F up to 150 kg/cm^2. Comings, Mayland, and Egly[308] and Comings and Egly[309] have made measurements by a falling mercury drop method up to 170 atmos. and 105°C on CO_2, C_2H_4, CH_4, and C_3H_6.

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B. The Viscosity of Liquids

A good deal of the work on liquids has been concerned with lubricating oils because of the importance of the pressure coefficient of viscosity in determining the lubricating properties, particularly under heavy loads. The most sustained work here has been done by Dow, either alone, or with various collaborators; the work was begun at Harvard with my apparatus and continued at Penn State. Dow's thesis,[310] published in 1935, contained a study of the viscosity of six pairs of liquids over their entire concentration range at 30° and 75° up to 12,000 kg/cm^2. The method was the falling weight method and the apparatus the same as that already described in my book. The pairs of liquids were: *n*-hexane-CS_2, *n*-hexane-diethylether, *n*-hexane-*n*-decane, *n*-hexane-chlorobenzene, *n*-pentane-benzene, and eugenol-CS_2. Pure *n*-decane was also measured. The mixtures of *n*-hexane with CS_2 and with *n*-decane are found to follow the Arrhenius rule of mixtures, the logarithm of the viscosity being a linear function of the composition. For the other mixtures there are complicated departures from the Arrhenius rule; the anomalies are sometimes situated at the ends of the concentration range and sometimes in the middle. The effects are ascribed to interlocking effects due to the complicated shapes of the molecules. In 1935 Dow[311] published a theoretical discussion of data of Kleinschmidt and Dow on the viscosity of lard, sperm, and Pennsylvania oils in which it was shown that Batschinski's theory is not applicable because the viscosity is far from being a function of volume only. In 1936[312] he published results by the rolling ball viscosimeter method up to 4000 kg/cm^2 on a Pennsylvania, an Oklahoma, and a California oil. These were "matched" oils, that is, they were so blended that their initial viscosities were the same. The pressure effects were quite different; at 2000 kg/cm^2 the increase of viscosity of the California oil was four times as great as for the Pennsylvania oil. In 1937[313] this study was extended on the same oils to include the temperature range 100° to 210°F. In 1937 Dow, Fenske, and Morgan[314] studied the viscosity, by the same method and over the same range, of three oils and two chlorinated diphenyls "Aroclors." They observed the greatest pressure effect yet recorded on one of the latter which showed an increase of viscosity of 15-fold for a pressure of only 250 kg/cm^2. Morgan and Dow[315] measured the viscosity by the same method up to 100°C and 4000 kg/cm^2 of the ortho-, meta-, and paraforms of toluene and its mono substitution products with the bromine, nitro, and iodo groups. The pressure coefficient of viscosity may be either increased or decreased by a systematic change in the position of the substitution group. As the atomic weight of the substitution group increases the pressure coefficient of viscosity increases in the ortho- and meta-positions, but decreases in the para-position. Dibert, Dow, and Fink[316] in 1939 measured over the same range the viscosity of six different Pennsylvania oils. The pressure coefficient of viscosity tends to increase with increasing molecular weight, but the correlation is exact only in a narrow boiling range for a single oil. The temperature coefficient of viscosity at constant pressure increases with increasing molecular weight at all pressures for all oils. In 1939 Dow[317] reviewed some of his early work and presented new data for the viscosity of six mixtures of CS_2 and CCl_4 at 30° and 75° up to 10,000 kg/cm^2. In 1939 Thomas, Ham, and Dow[318] described a new apparatus with which absolute determinations of viscosity may be made under pressure. This consists of a cylinder rotated at known speed inside another concentric cylinder, which is elastically tethered; the displacement from the equilibrium position gives a measure of the viscous drag and so of the viscosity. The entire apparatus, motor and all, is mounted inside the pressure vessel. The method is not as well adapted to determine pressure coefficients as the rolling ball method, which is relative instead of absolute. Within the limits of error, checks were obtained on the pressure coefficient by the two methods on several representative oils. In 1941 Dow, McCartney, and Fink[319] measured the viscosity of Russian and Rumanian oils over their usual range. The effect of pressure is greater on these oils than on the American oils, which is doubtless connected with their chemical structure in terms of naphthenes, or aromatic hydrocarbons instead of paraffines. The variation of the viscosity is represented by an exponential expression in the density.

Turning now to the more scattered work Suga[320] measured 20 oils up to 1000 kg/cm^2 and compared the effect of pressure on mineral, vegetable, and animal oils. A linear relation was found between pressure and the logarithm of viscosity. Hersey and Snyder[321] gave a careful theoretical discussion of the total efflux viscosimeter, and showed how to calculate the pressure coefficient of viscosity at any pressure from the curve of total efflux against pressure.

Measurements were made by this method on a heavy and a light grease and on castor oil up to 3000 kg/cm^2, and in the case of castor oil fair agreement was obtained with previous measurements by other methods. Talbott, in connection with his volumetric measurements on liquids already referred to,[115] measured the viscosity of an oil by a falling weight method up to 400 atmos. and 210°F, finding the typical effects. Ebbecke and Haubrich[322] determined the effect of pressure up to 800 atmos. on the viscosity of different organic liquids. Pressure was found to have a very small effect on the viscosity of protein solutions; a "slight" effect on carbohydrates; a "definite" effect on egg yolk, starch, and honey; and a very large effect on all oils. Versluys, Michels, and Gerver[323] applied a falling weight method to the measurement of the viscosity of an oil saturated with methane in the pressure range up to 218 atmos. and between 25° and 100°. The saturation concentration of the methane increases so rapidly with pressure as to over-compensate the normal increase of viscosity with pressure, leaving as net effect a decrease of viscosity with increasing pressure amounting to about sevenfold over the entire pressure range. Sage, Inman, and Lacey[324] determined the viscosity up to 200 atmos. of the liquid phase of 18 mixtures of methane and propane with crystal oil. Bradford and Vandergrift[325] give a theoretical discussion of the importance of a high pressure coefficient of viscosity in ensuring satisfactory performance of an oil in bearings, and indicate desirable relations between the temperature and pressure coefficients. Hersey and Hopkins[326] summarize work done on the fatty oils by Hyde, Kieskalt, and Suge in connection with the lubrication study program of the A.S.M.E. Different types of apparatus have been used, and essential agreement has been reached. Dane and Birch[327] contribute a study in a different range of experimental conditions of the effect of pressure on the viscosity of boric anhydride glass. The paper was inspired by the importance for geophysics of a knowledge of the effect of pressure on the viscosity of glass, which certain lines of argument indicated would be very large. Boric anhydride is the only glass which seemed to be accessible to present technique in a range of temperature sufficiently close to terrestrial conditions to give significance to the results. The method was a total efflux method; the pressure range 2000 kg/cm^2 and the temperatures 359° and 516°C. At constant temperature the relation between viscosity and pressure is exponential, $\eta=\eta_0 e^{\alpha p}$. At the higher temperature $\alpha=4.64\times10^{-4}$ cm^2/kg, and at the lower $\alpha=15\times10^{-4}$ cm^2/kg. The variation of the pressure coefficient with temperature is much greater than would be given by Andrade's theory of viscosity. Needs[328] has discussed the performance in bearings, as connected with the pressure coefficient of viscosity, of castor oil, a paraffinic mineral oil and glycerol up to a bearing pressure of 1500 atmos. The effective coefficient of friction passes through a minimum at high pressure. Ebbecke and Haubrich[329] have studied the effect of pressures up to 800 atmos. on solutions containing round molecules (glycogen) and long molecules (starch). The pressure effect is very much greater on the starch solutions, which is ascribed to the molecular shape. Volarovich[330] described a modified method with falling sphere and magnetically operated counterweight with which he has determined the viscosity up to 1000 kg/cm^2 and 100° of various aviation and machine oils, colophony, and sugar solutions in glycerol. The effect is least for the sugar solution, threefold, and greatest for colophony, 22.3-fold. From a later paper of Volarovich[331] it appears that the oils in the paper just described were saturated with nitrogen, so as to correspond to the conditions in the cylinders of compressors or internal combustion engines. Swearingen and Redding[332] have determined the effect of pressures up to 250 atmos. on saturated solutions of natural gas in various oils; the viscosity drops with increasing pressure under these conditions.

There have been a number of theoretical papers on the theory of viscosity of liquids in general and of the effect of pressure in particular. The weakness of most of the earlier theories of the viscosity of liquids was that they demanded that viscosity should be a function of volume only, which is definitely not true for the liquids which I measured up to 12,000. van Wijk and Seeder in two papers[333, 334] proposed a theory in which liquids were divided into two classes, configurational and non-configurational liquids.

In the former there are temperature effects on viscosity apart from the pure volume effects. An exponential formula in the temperature is derived with a coefficient which involves the co-volume, with which my results can be reproduced, both for organic liquids and mercury, in which the effect is very small, up to pressures of about 7000 for the organic liquids; above that there are deviations, the viscosity increasing with pressure faster than the theory indicates. Bingham, Adams, and McCauslin[335] have made an elaborate theoretical study based on my measurements of viscosity to 12,000 kg/cm^2. They introduce the concept of a minimal molecular volume for the fluidity.

The Princeton school of physical chemists has contributed several theoretical papers. The fundamental idea is that there is a similarity between the molecular process by which momentum is transferred from one layer to another in a liquid moving viscously and an ordinary chemical reaction. The molecule which moves along the velocity gradient receives or delivers energy and in passing from a position in one layer to that in the next is thought of as passing over a potential barrier before it can settle down into its new position, just as a molecule taking part in a chemical reaction has to pass over a potential barrier before it finds its position of greater stability. The same sort of an exponential formula governs the velocity of either process, with an activation energy. The activation energy for viscous flow can be calculated from the kinetics of the liquid and is in general considerably smaller than the energy of vaporization. Ewell and Eyring[336] and Ewell[337, 338] develop this point of view in three papers, and among other things obtain expressions for the effect of pressure on viscosity which agreed with my data up to 2000 kg/cm^2 in the early paper and which were later improved to give agreement up to 7000. This was followed by two papers by Eyring and his collaborators Frisch, Kincaid, and Stearn[339, 340] in which the concept of a maneuver space was introduced, which had to be available to the molecule if it is to slip past its neighbor into a position of greater stability with respect to the viscous motion, and this maneuver space is connected with various thermodynamic parameters. The authors find that with a theory of this kind they can reproduce with only small error the viscosity of any liquid up to 10,000 kg/cm^2. Auluck and Kothari[341] have applied the "hole" theory of liquids in which a physical substantiality is attributed to the vacant spaces in a liquid and are able to give a qualitatively correct account of the variation of viscosity with pressure.

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7. The Effect of Pressure on Elastic Constants

This is obviously a topic of much interest for geophysics because the velocity of seismic waves at depths in the crust of the earth will depend on the effect of pressure on the elastic constants. Practically the only experimental work on this topic in the present period has been done by Birch and by Birch and Bancroft[342–346] in connection with the geophysical program at Harvard. There have also been a couple of theoretical discussions. Some of the early discussions, in particular that of Green and much later that of Brillouin led to the improbable result that the velocity of distorional disturbances would decrease with increasing pressure. In 1932 Hencky[347] proposed a theory for finite strains which was formally plausible and led to an expression for the velocity of a compressional wave which increased with pressure, as is otherwise plausible. Murnaghan in 1937[348] proposed a theory of finite strain of intrinsic formal plausibility and mathematical naturalness. Murnaghan in his discussions has applied his formulas especially to my experimental determinations of the variation of compressibility with pressure with striking success. Birch[344] has extended the analysis and has obtained expressions for the effect of pressure on the elastic constants of isotropic solids, on the whole with good agreement with experiment. There seems to be some difference of opinion as to whether the success of Murnaghan's formula is largely formal and empirical or whether there is some deeper significance. My personal opinion is that the theory is chiefly formal, and primarily owes its success to the adoption of a mathematical expression for volume as a function of pressure which formally leads to zero volume at infinite pressure. With our present knowledge of the structure of the atom this is the limiting volume to be expected; most of the early theories assumed a finite limiting volume, and these theories all failed when pressure was pushed materially beyond the former experimental limits. I think the formal character of Murnaghan's analysis is made more evident by his most recent paper[349] in which he modifies some of his former analysis in the light of my measurements to 100,000. He now puts the conventional elastic constant $\lambda+\frac{2}{3}\mu$ a linear function of pressure, and comes out with a formula for the change of volume as a function of pressure containing two empirical constants, with which my data can be reproduced.

Birch's first experimental paper[342] dealt with the method, which was a dynamic method in which torsional vibrations were excited electromagnetically in a cylindrical specimen exposed to pressure. Various questions with regard to the method had to be examined, such for example as the effect of viscosity of the transmitting medium, which was nitrogen. It was found that the effect of the transmitting medium could be neglected for torsional vibrations, but the disturbances were prohibitive if the attempt were made to determine Young's modulus by exciting longitudinal waves. The method was applied to a number of homogeneous substances, metals and glass. The modulus of rigidity was found to increase with increasing pressure for metals and to diminish for quartz and Pyrex glasses. The agreement with my previous results obtained by a static method was gratifyingly good. The range of this first work of Birch was 4000 kg/cm^2 at room temperature. Birch and Bancroft in two subsequent papers[343, 345] and Birch in a final paper[346] successively extended the range until finally measurements were made up to 600° and 9000 kg/cm^2, and determined the elastic constants of a number of rocks. The difference in behavior of "covered" and "uncovered" rocks was carefully examined and an adequate understanding of the complicated phenomena acquired. In general the initial effect of hydrostatic pressure is to produce large increases in the elastic constants, which later approach asymptotically a much slower rate of increase as the effect of initial porosity in the rock is wiped out. Geophysical application of the results is made, with a discussion of such topics as the probable constitution of the crust in depth as suggested by a comparison of the measured velocity of seismic waves with the velocities calculated with the help of the pressure coefficients of elasticity.

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8. The Effect of Pressure on Plastic Flow and Similar Phenomena

Most of the work on this topic in the period has been done at Harvard, at first by me and later by Griggs. The subject is not so well adapted to exact measurement as many of our other topics, and many of the results are qualitative in character.

The apparatus with which my measurements were made is described in my 1937 paper.[350] Two cylindrical blocks of steel, *B* in Fig. 5, have very short cylindrical bosses machined on them; these bosses are pushed from opposite sides by a hydraulic press against a rectangular steel block, *C*. The region of contact between the boss and the block is a region of high stress concentration. Because this region of stress concentration is highly localized in the midst of a surrounding mass of comparatively little stressed steel, much higher stresses can be reached locally without fracture than would be possible if the stress were homogeneously distributed. With suitably treated tool steels mean compressive stresses of well over 50,000 kg/cm^2 can be reached between the boss and the block without fracture, whereas under normal conditions pistons of this same steel will not support 30,000 kg/cm^2 compressive stress. If a thin disk of some plastic material is placed between boss and block at *A* and pressure applied, the plastic material will be squeezed out laterally until a certain limiting thickness is reached depending on the pressure and the plastic strength. Indefinite extrusion is resisted by friction on the flat faces of the disk; it is evident on consideration that a finite friction will retain any pressure, no matter how high, if the disk only becomes thin enough. In practice there is deformation of the

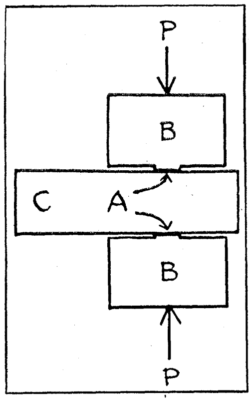

FIG. 5. Schematic representation of the apparatus for combining hydrostatic pressure and shearing stress.

steel parts, and the disk becomes lens shaped, thin at the edges. The effective friction resisting expulsion is confined to a narrow annular region at the outer edge, and the greater part of the interior of the plastic material is exposed to a stress approximately hydraulic. The experiment consists in rotating the steel block around the axis of the two bosses while pressure is maintained on the thin disk. A photograph of the actual set-up is shown in Fig. 6. At low pressures there is surface slip between steel and substance; when pressure has reached such a value that the frictional drag on the surface equals the internal plastic flow strength, surface slip ceases, and from here on there is internal flow inside the disk, each plane perpendicular to the axis shearing as a rigid whole over the planes below and above it. From a measurement of the torque required to turn the block, the shearing stress necessary to produce internal plastic flow may be calculated.

The experiment, briefly described, consists in measuring the torque as a function of normal pressure on the bosses, and calculating from the torque the shearing strength as a function of pressure. In the ordinary range of stresses and under ordinary conditions the effect of pressure on flow stress is small, and for the usual engineering purposes it is customary to neglect it. With this apparatus a domain of pressures can be reached high enough to produce marked effects on flow stress. Perhaps the most important use of the method is to determine the effect of pressure on flow stress; in practically every case flow stress increases with pressure, sometimes by large amounts. A typical example is shown in Fig. 7. The essential difference between plastic flow in a solid and viscous flow in a liquid appears at once with this apparatus, for whereas with a liquid the viscous drag is proportional to the velocity, the resistance to plastic flow in a solid is approximately independent of velocity, and the torque is accordingly also independent of speed.

The first use of the apparatus was for a different purpose than indicated above. If the material undergoes a polymorphic transition with increasing pressure, the flow strength of the new modification will in general be different from that of the one which it replaces, with the result that there will be breaks in the curve of torque *versus* pressure at the pressures of transition. Figure 8 shows the relations for bismuth. Since the manipulations with this apparatus were very easy and rapid, this affords a simple tool of exploration for finding new transitions in new substances. The method was at first used extensively for this purpose, and a number of new transitions were located in this way, for which the thermodynamic parameters were later determined in the piston displacement apparatus. Transitions with volume changes too small for the piston displacement method may be discovered with this apparatus under favorable conditions. Furthermore, transitions which would otherwise be suppressed because of viscous resistance to formation of new nuclei will run when shearing is combined with pressure at temperatures sometimes 100° to 200° lower than the temperature at which the transition ceases to run under pure hydrostatic pres-

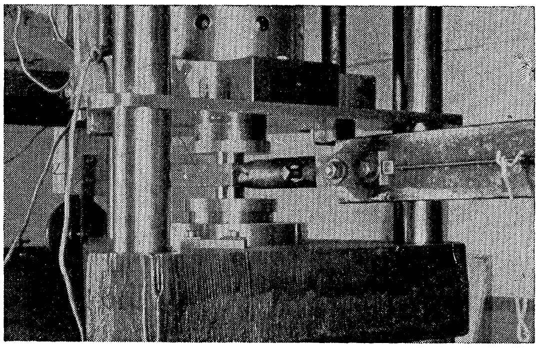

FIG. 6. Close-up of the shearing apparatus mounted in the hydraulic press together with the handle for rotation.

sure. It is also probable that there are certain reversible transitions which occur only under shearing stress, and will not occur at all with pure hydrostatic pressure; lithium is a probable example of one of these.

Some 300 substances have been investigated in all by this method; no attempt here will be made to more than indicate the nature of this very extensive material. Fifty-seven elements have been investigated; some 250 inorganic compounds and a number of organic compounds.[248] The rate of increase of plastic flow strength with pressure is characteristic of the substance; usually the curve of flow strength against pressure is concave toward the pressure axis and the total rise under 50,000 kg/cm^2 for most elements and inorganic compounds is by not more than a factor of two, with a number of substances showing very small increases. With organic substances, on the other hand, the rise of shearing strength may be exponential in character, with increases of thousands of fold at the maximum pressure (paraffin is an example). By continued rotation of the steel block between the bosses it is evidently possible to build up an indefinitely great shearing distortion. At the beginning of the rotation there are various transient effects, the pattern of which varies with the substance, but after a rotation of 20° or 30° a steady state was usually reached. The total rotation was seldom pushed beyond 60°; this corresponds to a shearing distortion of the outer layers of the disk of something of the order of 120 radians. Such very large distortions can seldom be reached under ordinary conditions because of termination of the experiment by fracture; here the geometry is such that fracture does not terminate the experiment. Under these extreme distortions most substances show a high degree of destruction of the original lattice structure, in many cases an x-ray analysis showing barely perceptible traces of the original lines. The nature of the flow when the steady state is reached varies with the substance; many substances flow smoothly with constant shearing force. For others, the flow is continually interrupted by snapping, that is, internal fracture, with self-healing under the high stresses, and then resumption of the cycle of limited flow and fracture. It is possible that the mechanism of deep seated earthquakes is connected with this effect. As a rule, flow is likely to be smooth in those substances which normally crystallize in the cubic system, which has many slip planes, and to be spasmodic, with internal fracture, if the crystal has none or few slip planes.

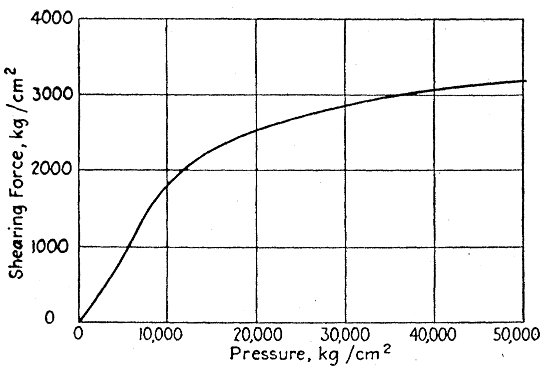

FIG. 7. Relation between shearing force and pressure for magnesium. At approximately the point with coordinates 10,000 and 2000 surface slip ceases and internal plastic shearing flow begins.

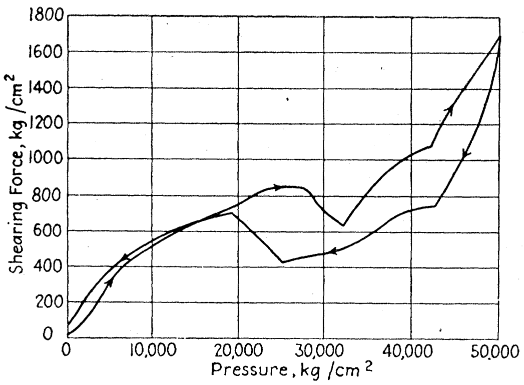

FIG. 8. Relation between shearing force and pressure for bismuth. The breaks in the curves are the result of polymorphic transitions.

Flow under these extreme conditions may be accompanied by various irreversible effects; transitions of certain minerals from forms thermodynamically unstable to the stable form may be effected—for instance wurtzite is changed to sphalerite, or red phosphorus may be changed to crystalline black, a transition which is not known to run under other conditions. Chemical changes may be produced, including synthesis of compounds from the elements, as of Cu_2S, decomposition, as of Bi_2O_3 into metallic bismuth, or change of valence, as of SnO_2 into SnO. In the cases just mentioned the chemical transformation was complete throughout the entire mass, and could be checked by x-ray analysis. There are a great many instances of only partial transformation, shown by color changes on the surface, but in which the amount of product is too small to analyze. It is evident that if the shearing strength of the new substance is less than that of the original the reaction may be self-limiting, plastic flow being confined to the thin surface film of transformed material which protects the interior of the substance from reaching an intensity of shearing stress necessary to effect the transition. Organic substances may show drastic changes of a nature not easy to specify, as, for example, rubber is transformed into a horny mass. In my earlier papers a number of examples were given of detonations produced under these conditions. The matter has not been finally cleared up, but it is probable that most of these cases of detonation were not pure stress effects, but required the cooperation of high temperature also. In some cases steel wedges may shear off the edges of the boss at the highest pressures, the expulsion of which would be accompanied by intense local heating effects. In some cases, if the original thickness of the disk is too great, a state of instability is reached with increasing pressure, when the bulk of the material of the disk is expelled laterally with great violence, accompanied by local heating.

There is immediate geophysical application of many of the results, the conditions of rock deformation at depth in the earth's crust being much like the experimental conditions, except for temperature. Larsen and Bridgman[351] studied the effect of shearing deformation combined with hydrostatic pressure on a number of minerals, either singly or in combination. They were not able to synthesize any of the so-called stress minerals, but other types of permanent change were observed. A number of cases were observed of the transformation of crystalline material into glass. Opal was transformed into quartz. Definite reorientations were produced in many cases, many of them agreeing with the geological observations of Sander.

An enormous amount of work remains to be done on these phenomena, particularly in establishing the nature of the chemical changes. The precision of the measurements of flow strength and the range of stress can be much increased by constructing the apparatus of carboloy instead of steel. I have constructed such an apparatus and have made preliminary measurements with it, in a number of cases essentially checking results with the steel apparatus. With this new apparatus I have reached pressures well over 100,000 kg/cm^2 combined with the shearing stress necessary to produce flow, with a life of the apparatus markedly superior to steel.

Recently Boyd and Robertson[352] have essentially duplicated this shearing apparatus, but with the provision of an automatic arrangement for drawing the torque-displacement curve, and have examined the friction properties of a number of lubricants at high pressures with a view to their practical use. They have qualitatively reproduced some of my results. They find stearic acid, tungsten disulphide, and molybdenum disulphide to be the best solid high pressure lubricants under their conditions.

The experiments of Griggs[353–356] in this field have been mostly directed to answering questions of immediate geophysical application. The experiments of F. D. Adams and von Kármán on this subject are well known, in which substances like marble or limestone were shown to be capable of marked distortion in compression if they were afforded lateral support. Griggs very much extended the range and sharpened the experimental conditions.[353] He constructed an improved apparatus in which the specimen under test was exposed to a true hydrostatic pressure exerted by a liquid, and in which an arbitrary simple compressive force could be superposed on the hydrostatic pressure. His pressure range was usually 10,000 but on occasion rose to 13,000 kg/cm^2. He observed shortenings of as much as 30 percent without fracture under one sided compression applied to limestone and marble, with increases of compressive strength. Beyond a hydrostatic pressure in the general neighborhood of 6000 kg/cm^2 the compressive strength accelerated with marked rapidity. It was found that the increase of compressive strength was much greater if the specimen was jacketed to prevent entrance of the transmitting liquid into the pores. A modification of the same apparatus permitted the application of tension to limestone while exposed to hydrostatic pressure; it was a surprise to find that the plasticity for compressive deformation does not extend to tension, but the specimens broke in tension under hydrostatic pressure just as brittlely as they do at atmospheric pressure. The effect was later traced to the shape of the tension specimen, permitting stress concentrations at the shoulders. Griggs[354] also studied the flow of single calcite crystals under hydrostatic confining pressure and found the effects qualitatively different from those in limestone, which is a haphazard aggregate of crystals. The ductility of the single crystal to compressive distortion is also increased by hydrostatic pressure, but it does not show the accelerated increase at the higher end of the range, remaining linear up to 10,000 kg/cm^2. In the lower end of the range the ductility of the single crystal is greater than that of the aggregate and in the upper end less. The mechanism of flow was studied.[355, 356] Griggs had not been able to produce plastic flow in quartz under these conditions. He addressed himself to this problem in a study with my apparatus for 50,000 kg/cm^2. He was not able to produce any measurable flow up to rupture in simple compression, but did observe very great increases of strength of an exponential character beyond 10,000 kg/cm^2 confining pressure. The conditions of these experiments were, however, exceedingly difficult of accurate control; pressure was transmitted by lead and the compressive stress was controlled by leakage of the lead through the annular space around a loosely fitting piston. In my later work, I repeated the measurements on the compressive strength of quartz under better conditions, with a true liquid to transmit pressure, and was able to find only a linear rise of compressive strength with increasing pressure. Griggs also observed the fracture of quartz under higher temperatures and lower pressures in the presence of water, and obtained results conforming to geological observations in the field.

With regard to plastic distortion of quartz in the cold under high stress, some unpublished early experiments of mine may be mentioned. In connection with experiments on the crumbling of cavities in rocks under external hydrostatic pressure, I had exposed some quartz crystals containing the well-known cavities partly filled with liquid CO_2, so-called "negative crystals," to an external pressure of 30,000 kg/cm^2 with no observable effect of any sort. The crystals were put away and by chance examined again some ten or fifteen years later. Fine fractures were now found radiating in every direction from all the cavities; there must have been some permanent distortion produced by the application of pressure, although too small to detect at the time, which slowly relaxed in the course of time, resulting in fracture. In 1940[355] Griggs discussed the application of his experiments to geological problems and came to the conclusion that other factors in addition to hydrostatic pressure are necessary to account for the deformation of rocks as observed in nature; perhaps the most important of the other factors is the presence of water in combination with temperature. Goranson[357] followed Griggs' paper with an analysis of the process of plastic flow from a thermodynamic standpoint, and among other things considered the effect of hydrostatic confining pressure on flow. The fundamental point of view is that a large part of plastic flow in the presence of water is a solubility and recrystallization phenomenon, the effect of hydrostatic pressure on which can be calculated by thermodynamic considerations. Goranson calculates that the effect of a hydrostatic confining pressure of 1000 kg/cm^2 on the velocity of flow of alabaster under compressive stress will be 1.5-fold greater than at atmospheric pressure, against the experimentally determined factor 1.6 by Griggs.

Griggs later redesigned and very much improved his apparatus for the study of tension under pressure. The tension specimens were in the form of simple uniform cylinders, so that the stresses were uniform, with no stress concentrations. The specimen was prolonged by a hardened steel plunger of the same diameter, passing out of the pressure chamber through a stuffing box. The specimen was jacketed with a thin tube of copper soldered to the steel plunger. By exposing the protruding part of the plunger to a variable compressive stress, stress systems could be produced in the specimen equivalent to a uniform hydrostatic pressure plus a superposed simple tension along the axis up to an intensity numerically equal to the intensity of the hydrostatic pressure. The apparatus was used only in a single investigation, by Balsley,[357a] of the deformation of marble in tension under pressure. Pressures were studied up to 10,000 kg/cm^2. Under these conditions marble exhibits marked ductility in tension, elongations as great as 25 percent having been obtained without fracture. At the lower pressures the phenomenon of necking is shown, like a metal. Tensile strengths of more than 5000 kg/cm^2 were found, of the order of 20 times the strength for simple compressive stress at atmospheric pressure. The geometrical description of the flow process remains to be worked out, whether by twinning or translation-gliding.

At the beginning of our period there are some little known qualitative experiments of Heide[358] on plastic flow. He embedded plates of single crystals of baryt, coelestin, and anglesite in clay, which he placed in a heavy walled steel cylindrical vessel, and applied pressure to the clay with a steel piston up to 20,000 kg/cm^2. Because of frictional drag of the clay on the walls, the deformation was not uniform, and the plates, which were perpendicular to the axis, were deformed into cups. This deformation, under the high confining pressure, took place without fracture. Heide studied the slip planes which accompany the bending. He found that deformation at a higher temperature, 400°, is accompanied by slip on more sets of crystallographic planes than at room temperature. A summarizing article by Volarovich[359] is also to be mentioned, in which many of the experiments just described are discussed with respect to their applications to geology and geophysics. Some experiments of Volarovich on the solubility of water in basalt glass at high pressures and temperature are referred to.

In the last few years I have made extensive observations of the effect of hydrostatic pressure on the plastic flow of metals. The experiments were made[360–364] in the apparatus for 30,000 kg/cm^2, the confining pressure was exerted by a true liquid, the pressure in which might rise to 30,000 kg/cm^2, and accurate measurements could be made of the deforming forces acting on the specimen by the same electrical device, employing the change of resistance produced by the stress, that had been used in measurements of compressions up to 100,000 kg/cm^2. The experiments were mostly on various grades of steel, although copper, aluminum, brass, and bronze were found to show the same qualitative effects. Figure 9 shows on the left a tension specimen of steel broken at atmospheric pressure with moderate reduction of area, and at the right the same steel pulled under pressure to a great reduction of area without fracture. The degree to which ductility is raised by pressure depends on the grade of steel, and in general is less the harder the steel or the higher the carbon content. A typical example is that of a 0.45 carbon steel which under atmospheric pressure breaks in tension with an elongation of two- or threefold; under a confining pressure of 25,000 kg/cm^2 an elongation of 300-fold has been observed without fracture. The quantitative relations are simple. If the "natural" strain is used to measure the deformation, that is the natural logarithm of the ratio of the initial area of cross section to the final area, which in virtue of the constancy of volume is the same as the ratio of the final length to the initial length (all taken at the neck of the tension specimen where the deformation is a maximum), then it will be found that the natural strain at fracture is very nearly a linear function of the hydrostatic confining pressure. The slope of the line is greater the softer the steel. This relation holds up to natural strains of 5, that is, up to elongations of 100-fold; at higher elongations the geometry begins to go bad because of the dominating effect of individual crystal grains and the measurements cannot be easily made. Accompanying the enormously increased strains there is a very notable strain hardening, the tensile stress required to produce plastic flow increasing with the strain. Here again the relations are simple; the stress required to produce plastic flow is a linear function of the natural strain, right up to the point of fracture. If a tension specimen is pulled under pressure but not to the fracture point, and the confining pressure is released and the specimen then pulled a second time at atmospheric pressure, it will be found that even though the stretching under pressure was pushed to an elongation far beyond the elongation at fracture for normal pulling at atmospheric pressure, a certain degree of further ductility will nevertheless be exhibited, and the

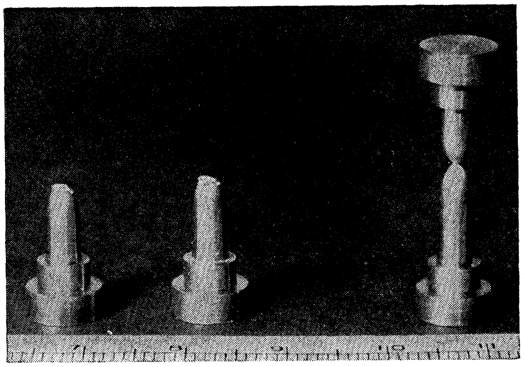

FIG. 9. Illustrating the effect of hydrostatic pressure on ductility in tension. On the left, a tension specimen broken at atmospheric pressure with a reduction of area of approximately 60 percent. On the right a specimen of the same steel pulled under a pressure of 25,000 kg/cm^2 to a very much greater reduction of area without fracture.

stress required to fracture may be much increased beyond the stress at fracture for normal atmospheric pulling. If the specimen is broken under confining pressure, it will be found that the character of the fracture is strongly dependent on the pressure. As pressure increases the phenomenon of tensile fracture by separation across the fibers parallel to the direction of pull becomes less prominent and eventually disappears, the fracture eventually becoming entirely shearing in character. The great increase of ductility of steel in tension also extends to other kinds of deformation; thus a punch may be pushed practically through a sheet of mild steel if it is bathed in a fluid carrying high hydrostatic pressure, with no breaking out of the punching or loss of cohesion. The experiments just described have not as yet been published in full detail in any of the regular scientific journals; they have, however, been described in several unclassified reports to the Watertown Arsenal.

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9. Miscellaneous Mechanical Effects of Hydrostatic Pressure

There have been a number of papers on penetration of gases or liquids into metals under pressure. Jellinek[365] observed that iron, palladium, and silver may be activated by heating in gases so that they become capable of reversibly absorbing or giving off hydrogen or nitrogen when exposed to these gases under pressure. The pressure range was 30 atmos.; the method was measurement of electrical resistance, the resistance being a function of the amount of gas absorbed. Ipatieff and Tikhomirov[366] studied the diffusion of hydrogen into water under pressures of 100 kg/cm^2; they observed no significant difference as compared with the diffusion under atmospheric conditions. Poulter and Wilson[367] studied the permeability of glass and fused quartz to various liquids at pressures up to 15,000 atmos. Water, alcohol, and ether under high pressure diffuse into quartz or glass and on release of pressure diffuse out again. This results in various sorts of fracture. If glass is exposed to water under pressure for some time, an appreciable amount of water is absorbed in the outer layers of the glass. If pressure is rapidly released, the water does not have time to diffuse out, and the glass fractures because of the expansion of the occluded water. If, on the other hand, pressure is released slowly, the water has time to diffuse, and there is no fracture. Consistent with this picture is the fact that if pressure is rapidly applied and then immediately released, there is no fracture, because the water does not have time to diffuse into the glass. There is apparently no penetration of glass by paraffin oil or by glycerine. I may add that I have made similar observations, unpublished. A heavy walled capillary of glass sealed at both ends and exposed to external hydrostatic pressure under water may, on release of pressure, separate into onion skin like layers. The effect is a strong function of the kind of glass. Poulter and Uffelman[368] in a special apparatus observed the penetration of hydrogen through steel under a pressure of 4000 atmos., an effect which I had already found extremely troublesome in attempting to determine the compressibility of hydrogen. Poulter and Uffelman found the degree of penetration to depend on the kind of steel. Inglis and Andrews[369] made an elaborate study of the effect of hydrogen on various steels up to 250 atmos. and 500°C for times extending up to 8000 hours. At first, for mild steel, there is a period of absorption, with impairment of physical properties, which may be recovered by heating. If exposure is more prolonged, the impairment is permanent and is accompanied by decarburization. The effects depend markedly on grain size, and are much less in some alloy steels, particularly those containing Ni, Cr, or Mo. Alekseev and Ostroumov[370] have studied the influence of hydrogen on steel up to 530° and 780 atmos. The impairment in mechanical properties is greater the higher the carbon content, and runs parallel with the amount of decarburization. Steel containing as much as 0.3 percent carbon cannot be exposed to pressures above 50 atmos. above 500° without danger. Maxwell[371] studied the action of hydrogen on various ferrous metals up to 400° and 250 atmos. There is marked decrease of elongation and reduction of area with moderate decrease in tensile strength; the cause of the embrittlement is attack of the grain boundaries. The addition of 2.25 to 3.0 percent Cr diminishes the rate of attack. Smithells and Ransley[372] studied the diffusion of oxygen through nickel up to 900° and at low pressures. The rate increases rapidly up to a pressure of 0.25 mm of mercury, beyond which it is constant. The explanation is in terms of a surface film which reaches saturation at this pressure. They also studied the diffusion of hydrogen through nickel up to 400° and 112 atmos. Over this range the rate of diffusion is proportional to pressure. It is thought that the molecules of hydrogen impinging on the surface penetrate through the surface film into the interior of the liquid, unlike the case with oxygen. Perminov and V'yunov[373] studied the diffusion of hydrogen through Armco iron up to 360° and 1700 atmos. Over most of this range the velocity of diffusion is proportional to the square root of the pressure. Diffusion takes place both through the grains and along the intergranular surfaces; it is greater along the latter. At high pressures the effect of grain size is relatively low. Welter and Mikolajczyk[374] tested the effect of the casting conditions on the permeability of castings to liquid pressures up to 1000 atmos. and gas pressures up to 150 atmos. Most of the castings were impermeable in this range. Smithells[375] studied the diffusion of hydrogen through iron, nickel, molybdenum, platinum, copper, and aluminum up to 1000°. There was great variation with the metal; at room temperature it is by far greatest for iron. The total amount of gas diffusing through is not much affected by increasing the wall thickness.

Another topic on which there have been several titles is the effect of pressure on adsorption. Frölich and White[376] studied the adsorption of methane and hydrogen on charcoal up to 150 atmos. and 100°C. The amount adsorbed at first increases rapidly with increase of pressure, reaching saturation in the neighborhood of 100 atmos. At 25° three times as much methane is adsorbed as hydrogen. In mixtures methane is adsorbed preferentially, to the practical exclusion of hydrogen. The amount of methane adsorbed is approximately the same as if it were present alone at the same partial pressure. Antropoff[377] measured the adsorption of nitrogen on charcoal up to 200 kg/cm^2 between $-160°$ and 150°. Pressure saturation was reached at the lower temperatures, and the saturation value is a marked function of temperature. The results were in agreement with the Langmuir adsorption isotherm. Coolidge[378, 379] contributed two papers on adsorption at high pressures. In the first paper he makes theoretical application of a theory of Polanyi, and in the second paper he checks it experimentally by measurements of the adsorption of CO_2, N_2O, and SiF_4 on charcoal up to 100 atmos. Krichevskii and Kalvarskaya[380] have made studies between −10 and 50° up to 600 atmos. of the adsorption of nitrogen and hydrogen on sugar charcoal with benzene and carbon tetrachloride. Maxima and minima were found. Rosen[381] measured the adsorption of acetic acid from aqueous solution by activated carbon at 25° at pressures of 1, 1000, and 2000 atmos. At all three pressures the adsorption isotherms were of the same type and did not conform to Freudlich's equation. The increment of adsorption against pressure gives straight lines for concentrations between 0.01 and 0.15*M*.

The remaining miscellaneous topics do not fall into considerable groups, and they will be presented chronologically. Welter[382] has studied the effect of casting a number of fairly low melting metals such as aluminum, and zinc with various of their alloys with each other and with copper up to pressures in most cases of about 12,000 atmos. Metal solidified under pressure was found to have notably better mechanical properties, having higher tensile strengths up to 25 percent, greater extension, and greater hardness. The structure is notably finer grained, and the density is higher. The effect is ascribed chiefly to the elimination of macroscopic flaws and voids. Annealing of solid castings made under normal conditions at atmospheric pressure under a pressure of 20,000 atmos. in lead resulted in no marked improvement in properties. Trzebiatowski[383] compressed gold and copper powders in an oxygen free atmosphere at temperatures up to 600° and at pressures up to 15,000 atmos. The density and hardness increase as the pressing temperature increases up to 200°. Between 200° and 400° the hardness drops, ascribed to an annealing process. The density, electrical resistance, and temperature coefficient of resistance of the massive metal are reached on pressing at 400°. Above 400° there is a still further softening caused by a recrystallization. van Wert[384] studied in my laboratory the effect of pressure on the age hardening of alloys. Duralumin, various other age hardening aluminum alloys, and an alloy of lead and calcium were studied at room temperature up to 12,000 kg/cm^2. In all cases a decrease in the rate of age hardening was produced by pressure, but the final equilibrium hardness was unaffected. The only exception was an alloy of iron with 0.07 percent nitrogen for which no effect on rate of hardening could be detected even under 20,000 kg/cm^2. In general the effect on rate was greatest for the most compressible substances; van Wert ascribed the effect to an increase of viscosity. In 1935[385] I established by measurements of the linear compressibility of highly purified zinc single crystals to 12,000 kg/cm^2 that the cubic compressibility is not sensitive to slight amounts of impurity. This work was suggested by measurements of Hanson, who measured some of the elastic constants and calculated the cubic compressibility, and who concluded that the cubic compressibility was probably sensitive to slight impurity. The result of Hanson was probably an effect of the high sensitivity of his elastic constants to internal strain. Incidentally, this paper[385] contains better values for the compressibility of zinc than my earlier values. Selisskii and Kuznetsov[386] found that at 150° the aging of duralumin proceeds more slowly under 10,000 kg/cm^2 than at atmospheric pressure. Tammann and Hartmann[387] studied the age hardening of Duralumin at room temperature at pressures of 1, 1500, and 3000 atmos. The rate is decreased by pressure; the effect of 3000 is more than twice that of 1500. Thiessen and Kirsch[388] found that crystallization may be induced in rubber at temperatures between 0° and 15° by pressures of 100 atmos. if the pressure is applied for periods extending up to three months. The crystallization produced was a permanent effect, and was detected by x-rays. Poulter[389] discussed the importance of extreme pressures in engineering applications. This is to a large extent a review of his own work. Poulter states in this paper that he has reached 100,000 atmos. in an apparatus apparently constructed of steel. However, he gives no details and has not followed it with later publications; it would seem probable that the true pressures were obscured by friction. One of the most important fields of application he thinks is in investigating the properties of lubricants under high pressures. In a previous paper[390] he had called attention to the fact that if there is any moisture in a lubricating oil, ice VI may separate from it under the stress conditions in a bearing, and this ice may have abrasive properties. Jones[391] discussed the possibilities of reaching very high pressures in the consolidation of powders in metallurgy by utilizing for the dies the same principle of external conical support that I had employed in reaching 50,000 kg/cm². There was a discussion of the paper by me, in which I mentioned the possibility of strengthening drawing or extrusion dies by the same construction. Efremov, Selisskii, and Georgievskii[392] studied the effect of quenching a eutectoid steel from 1000° under a simple compression (not a hydrostatic pressure) of 20,000 kg/cm². The quenched steel was martensitic; the authors explain this by a lowering of the A_1 point by the stress below the martensite point. Bochvar, I. P. Velichko, and Yu. A. Velichko[393] found that the mechanical properties of Si and Sn bronzes are improved by casting under pressures up to 10 atmos. There is not much improvement beyond 7 atmos., and the effect is ascribed to suppression of gas bubbles. Bochvar[394] in a later paper found that the improvement in properties produced by casting under pressure is confined to those alloys which ordinarily crystallize over a temperature range; under these conditions the alloy remains plastic during part of the solidification process and open flaws are prevented from forming. If the alloy is such that it crystallizes at a single temperature, extremely high pressures are necessary to eliminate flaws. Goranson[395] has a summarizing article dealing with many of the effects of pressure and including his method of reaching the highest pressures with "cascaded" apparatus, already referred to. Heilprin[396] gives a preliminary description of work done in my laboratory on the effect of pressure on surface tension. The differential rise of mercury in two capillaries of different diameters is observed through glass windows. Measurements up to 2500 kg/cm² indicate a decrease of the mercury-water interfacial surface tension. The completed work has not yet been published but is available in thesis form. Leipunskii and Frank[397] have found that the rate of setting of the thixotropic colloid of hydrated iron oxide is decreased by pressures of 2000 atmos. The effect is especially marked in fresh gels in low concentrations of electrolyte, and is ascribed to a change in the conditions of adsorption on the surfaces of the micelles.

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THERMAL EFFECTS OF HIGH PRESSURE

Any separation of thermal effects from mechanical effects is to a large extent arbitrary and a matter of convenience. In fact all the pressure-volume-temperature relations and the phase transitions described in the previous section on mechanical effects might with equal justice have been described as thermal. In this section a comparatively small number of papers will be reviewed in which the classification as a thermal effect is explicitly suggested by the form of the title.

1. The Effect of Pressure on Specific Heats

If the complete p-v-t relations are known, the variation of specific heats with pressure may be found thermodynamically by differentiation, and this is the most common method of attack. There have been, however, direct experimental measurements of specific heats under pressure; these are mostly for gases.

Hoxton[398] has discussed the specific heat of oxygen and air at 26° between 20 and 100 atmos., comparing the values calculated from the p-v-t values with those directly determined experimentally in new experiments. His conclusion is that the differentiations of the p-v-t values are so sensitive to the analytic methods of handling the data that the direct experimental determination is to be preferred. Workman[399] has described a new continuous flow method for measuring specific heat, and has applied it to oxygen at 26° up to 100 atmos. Krase and Mackey[400] describe a continuous flow method for the determination of the specific heat of gases up to 1000 atmos. and apply it for nitrogen up to 200. Newitt[401] derives values for the molecular heats of nitrogen, water, and carbon dioxide up to 3000°C from a study of the explosion data of mixtures of carbon monoxide and hydrogen with air at initial pressures varying up to 170 atmos. Workman[402] has determined by his continuous flow method the specific heat of oxygen, nitrogen, and hydrogen up to 60° and 130 kg/cm^2. At any constant temperature C_p increases approximately linearly with density, the increase being least for hydrogen (4 percent at the maximum pressure) and greatest for oxygen (20 percent). Godnev[403] gets close agreement between calculated and experimental values of C_v for oxygen up to 200 atmos. Workman[404] has determined experimentally C_p for carbon dioxide up to 65.3 kg/cm^2 and finds wide variations with temperature. C_p for helium does not vary perceptibly with pressure between 10 and 120 kg/cm^2. Golubev and Kul'chintskii[405] have determined the heat capacity of the gaseous mixture $3H_2+N_2$ up to several hundred atmos. between 25° and 100°. The heat capacity increases with pressure and by a larger amount at the lower temperatures. There is agreement between experiment and calculation up to 200 atmos. but divergence beyond. Zlunitzin[406] has determined the heat capacity of ammonium chloride and bromide up to 1425 kg/cm^2. The paper has been available to me only in abstract, and checking with the original appears desirable. The measurements of heat capacity are made up to within 0.01° of the point of discontinuity; the discontinuity is said to be finite, indicating a phase change. For NH_4Cl the temperature of the point of discontinuity is reported to have been depressed 14° by 1525 atmos. and for NH_4Br depressed 28° by 1430 atmos. This is exactly opposed to my own results; I found that the point of discontinuity was raised by pressure for the chloride, depressed for the bromide. It may be that the abstract has confused the discontinuity of the second kind which at atmospheric pressure occurs below 0°C with a conventional phase transition which occurs above 100°. In a second paper Zlunitzin[407] measures the specific heat of NH_4I between $-60°$ and 10° at four pressures up to 1550 kg/cm^2, and from the thermal data determines the displacement of the temperature of the "Curie point" (transition of the second kind?) and of the normal transition point with pressure. The former is depressed, the latter raised. For the latter his results are at least in qualitative agreement with my early results. Trapeznikova and Milyutin[408] have measured the specific heat of both CH_4 and CD_4 at pressures up to 2,000 kg/cm^2 and in the temperature range from 12° to 30°K, that is, on the solid phase. CH_4 has two anomalies; the first is displaced from 20.6°K to 30°K by 2000 kg/cm^2, and the second from 18.5° to 27° by the same pressure. CD_4 at 1 kg/cm^2 is equivalent to CH_4 at 1410 kg/cm^2 as far as the first anomaly is concerned. The thermal anomalies are associated with anomalies of density. Matveenko[409] has a theoretical paper giving a method of extrapolating the compressibility data of hydrogen, nitrogen, methane, and hydrogen-nitrogen mixtures to high temperatures and pressures and calculating the specific heats.

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2. Miscellaneous Thermal Effects of High Pressure

Saunders[410] has discussed natural convection at high pressures; by an application of dimensional analysis he shows how the convection in large systems can be obtained from model experiments on smaller systems by increasing the pressure of the medium (air). The results are calculated up to pressures of 700 atmos., using the data of Michels and Gibson for the viscosity of air as a function of pressure, but he thinks caution should be used in applying the results beyond 100 atmos. because of uncertainty arising from the as yet unmeasured thermal conductivity of air at higher pressures. Basset[411] has measured the energy input required to maintain a spiral heating element stretched along the axis of a cylindrical bomb at a temperature of 600°C in an atmosphere of hydrogen or of nitrogen at various pressures up to 6000 kg/cm^2. The energy input rises with pressure at a continually decreasing rate, perhaps asymptotically in the case of nitrogen, and at the maximum pressure is 62.5 percent greater for hydrogen than nitrogen. At the higher pressures Basset is of the opinion that the major part of the loss is caused by conduction; he points out that the loss is approximately proportional to the total mass of the medium. Gusak[412] has determined experimentally the enthalpy (total heat) diagram for nitrogen in the pressure range 60 to 200 atmos. and the temperature range 115° to 292°K. Up to 60 atmos. his results agree with those of the Bureau of Mines. Starr,[413] working in my laboratory, has determined the effect of pressures up to 12,000 kg/cm^2 at room temperature on the thermal conductivity of a number of metals. He was able to improve very materially on methods which I had previously used; I had used two methods, one for metals of low conductivity and another for those of high conductivity. My measurements by the latter method were never entirely satisfactory. Starr's improved method for metals of high conductivity eliminated several sources of uncertainty in my method and showed that my conclusion was erroneous, namely that for such metals the Wiedemann-Franz ratio between electrical and thermal conductivity might either increase or decrease under pressure. Starr found for copper, silver, and gold that the ratio of thermal to electrical conductivity increases approximately 1 percent for 10,000 kg/cm^2. Allen and Ganz[414] measured the influence of pressure on the thermal conductivity of Helium II; their pressures were by the nature of the case limited to 25 kg/cm^2. The apparent thermal conductivity is known to be a function of the temperature gradient. Operating at a constant gradient of about 0.001 degree per cm, they found that below 1.63°K the pressure coefficient of thermal conductivity is positive and above it negative. The explanation is complicated; it is connected in some way with a mass transfer of liquid. Budenholzer, Sage, and Lacey[415] have measured the Joule-Thomson coefficient in methane between 70° and 220°F and at six pressures between 20 and 105 kg/cm^2, and have given tables of various thermodynamic functions that may be calculated with the aid of the Joule-Thomson coefficient. The same authors[416] have also determined over the same range the Joule-Thomson coefficient of three mixtures of ethane and methane. Gilliland and Lukes[417] have developed an expansion method for the determination of enthalpy and have applied it to measurements on benzene up to 200 atmos. and to 290°C, which is 1.2 times the critical temperature. Volarovich[418] determined the effect of heating various rocks and minerals to 1100° at pressures of 1000 kg/cm^2. Igneous rocks show no change. Sedimentary rocks show changes of color and microstructure which are greater the higher the pressure. Rhodochrosite is oxidized and changed to pyrolusite. Budenholzer, Botkin, Sage, and Lacey[419] have measured the Joule-Thomson coefficient of three mixtures of methane and propane between 70° and 310°F up to 105 kg/cm^2, and have calculated the partial enthalpies of methane and propane in the mixtures.

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ELECTRICAL EFFECTS OF HIGH PRESSURE

1. The Effect of Pressure on the Electrical Resistance of Solids

There have been a number of theoretical papers in this field, in which wave mechanical methods have been used to explain the effect of pressure on resistance. However, these are outside the range that we have set for ourselves, and we will be little concerned with them except to give a brief summary at the end of this section. Except for my own work there has been comparatively little new experimental work in this field, most of it scattered. Of this scattered work, the most sustained has been from the laboratory of Michels. Michels and Lenssen[420] made a most elaborate study of the effect of annealing at various temperatures up to 400° on the effect produced by pressures up to 2000 kg/cm^2 on the electrical resistance of pure gold. This study was doubtless prompted by a desire to explore the suitability of the electrical resistance gauge as a tool for precise measurement. Toward the end of the period of my book Michels had a paper on the effect of pressure on electrical resistance, in which he emphasized the irregularities in the behavior of resistance under pressure which could be induced by appropriate manipulation; the implication at that time seemed to be that changes of resistance were not adapted to precise measurement. The spirit of approach of the paper of Michels and Lenssen is the opposite, namely, to find whether by suitable manipulations the behavior of resistance under pressure cannot be given sufficient regularity to make it suitable for precise measurement. Michels and Lennsen find changes in resistance up to 4 percent produced by annealing, and increases in the pressure coefficient up to 3 percent; on the first application of pressure after an anneal there is always noticeable pressure hysteresis in the resistance. The pressure effect was studied at four temperatures from 25° to 100°, and complete tables are given of the results. Much of this work on gold was later republished as Lenssen's doctor thesis[421] and in addition measurements were made on manganin up to 1000 kg/cm^2. An elaborate study was made of the best seasoning procedure, which was found to be a simultaneous exposure to changes of pressures and temperature; a stability of the zero corresponding to 1/20 kg/cm^2 was obtained for pressure cycles of 1000 kg/cm^2, and of $\frac{1}{10}$ for cycles of 2000. Michels and van Sante[422] measured the effect of pressure in their accustomed range on three alloys of nickel and iron between 25° and 125°; the pressure coefficient decreases by a factor of more than three with increasing temperature, and passes through a marked maximum with increasing nickel content at about 45 percent nickel.

Fischer[423] measured the change in the pressure coefficient of Pb, W, Mo, Cu, Fe, and constantan at temperatures down to liquid hydrogen temperatures. His pressure range was 150 kg/cm^2, obtained from the pressure in the compressed hydrogen supply bottle that provided the transmitting medium. In general he finds a marked increase of pressure coefficient with decreasing temperature, and surprisingly enough the increase is greatest for metals with the highest characteristic temperature; the coefficient of tungsten at 20°K is three times its value at room temperature. Later measurements of mine were not able to check his numerical values; I think his pressures were too low to give accurate results. The measurements are of extreme difficulty for as small changes of pressure as this. Braunbek[424] measured the electrical resistance of mercury under the pressure of its own vapor up to 600°. In the same year Birch[425] published his doctor thesis under me in which the resistance of liquid mercury was determined between 0° and 1200° and at pressures up to 4000 kg/cm^2. The mercury was contained in a quartz capillary, wound with a suitable heating unit, and mounted with suitable thermal insulation in the pressure vessel. Temperatures were measured with thermocouples let into the pressure vessel. Tables are given for the resistance, and the pressure and temperature coefficients of resistance over the range. These three quantities rise with increasing temperature and decrease with increasing pressure. At the upper end of the range values also were found for the resistance of the vapor. The critical point was found by extrapolation to be 1460±20°C and 1640±50 kg/cm^2. Basset[426] determined the resistance of a rod of zirconium oxide containing as impurity 10 percent thorium oxide and 10 percent yttrium oxide at a temperature of 900°C at pressures up to 4000 kg/cm^2.

The maximum pressure *increased* the resistance from 4300 ohms, its atmospheric value, to 1,500,000 ohms. Jost and Nehlep[427] measured the resistance of AgCl and AgBr at 300°C to 300 atmos. The resistance increases under pressure; the pressure coefficient of the chloride is 2.5×10^{-4} and of the bromide 3.5×10^{-4}. They give a theoretical expression agreeing within 25 percent with the experimental values. Holmes and Allen[428] measured the resistance of single crystals of selenium up to 700 kg/cm². For short applications of pressure there is marked hysteresis, which disappears if pressure is maintained for 30 minutes or longer. Under these conditions the resistance decreases linearly with pressure, the coefficient being -3.1×10^{-4}; this is said to be the largest pressure coefficient yet reported. Kean, in the paper already referred to[300] on the phase diagram of the binary alloys of sodium and potassium, gave data for the change of resistance up to 10,000 kg/cm² of the liquid sodium-potassium alloys of four representative compositions. These are "as measured" resistances, and involve the compressibility of the glass capillary. The resistance decreases with increasing pressure, and the coefficient is markedly less than for the pure components. Kean finds evidence that the liquid alloy rich in potassium (85.5 percent) may have a minimum in resistance at a pressure materially lower than 25,000, the pressure at which pure potassium has a minimum. Wilson, in connection with his measurements of the effect of pressure on the order-disorder transformation in alloys already referred to,[240] gives extensive graphical material for the resistance of his four alloys as a function of temperature and pressure up to 10,000 kg/cm². The alloys were: CuAu, Cu_3Au, CuZn, and Cu_3Zn. All alloys decrease in resistance under pressure. Except in the regions of internal change, resistance is approximately linear in pressure. In all cases the pressure coefficient increases with rising temperature, and at an accelerated rate (concave upward). In the case of CuAu and Cu_3Au, there is very accentuated acceleration of the increase above 250°. It will be recalled that for pure metals the pressure coefficient is approximately independent of temperature. Mints[429] measured the resistance of various carbon materials, artificial graphite, coke, petroleum coke, and anthracite between 20° and 2100° up to 350 kg/cm². High pressures diminish the effect of temperature. The results are said to depend on ionization in microscopic cracks. Lasarew and Kan,[430] by a method already described in the section on technique,[12] studied the effect of pressures up to 1750 kg/cm² on the transition to the superconducting state in tin and indium. The temperature of superconductivity of tin is lowered 0.095° by 1750 kg/cm²; the pressure coefficient to be deduced from this agrees with the value found by Keesom over a much lower pressure range, so the effect is apparently linear in pressure. Only preliminary values were found for indium. Mention should also be made here of two papers from Michels' laboratory,[488, 493] to be referred to in greater detail later in another connection, in which measurements of the effect of pressure on resistance were made incidentally as a means of finding the change of the Curie point. Full data will be found in these papers for the effect of pressure up to 2650 atmos. in the range of temperature embracing the Curie region on a 70-30 Ni-Cu alloy, and on a monel alloy containing Ni 68, Cu 29, Fe 1.6, Mn 1.0, Si 0.1, and C 0.15. The pressure coefficients are negative; there are various anomalies connected with the Curie point.

My own work in this field was confined in the early years of the period to my regular pressure range of 12,000 kg/cm², and in the later years was extended to 30,000. The technique has not yet been developed for measuring resistance to higher pressures; the difficulties are a suitable transmitting medium and electrically insulated leads that will stand the stress differentials incident to passing into the pressure chamber.

In 1931[177] I published measurements of the effect of pressure on the resistance of TiN and TiC; the resistances of both decrease under pressure and the decrease is unusually small and linear within error. In the same paper was determined the effect of pressure on the resistance of single crystal magnesium in different directions in the crystal. The resistance decreases under pressure and may be represented by the customary second degree expression in the pressure. The pressure coefficient is very nearly equal in the two crystallographic directions, being slightly greater perpendicular to the hexagonal axis. Approximate equality would be expected in the two directions because the crystal structure of magnesium is the close packed arrangement of *spheres*. However, the slight departures from isotropy are in the abnormal direction, the resistance being least across the cleavage planes, that is, parallel to the hexagonal axis.

In 1932[181] the effect of pressure was measured for the elements Cb, Rh, Ru, Cr, and As, and for three alloys of gold and silver. The first three elements exhibit the normal decrease of resistance with pressure, the magnitude of the pressure coefficient being in the range normal for high melting metals. Chromium has marked anomalies, shown only by highly purified metal; I had previously measured the resistance of chromium of an inferior grade of purity and found no abnormalities. The curve of resistance of pure chromium against temperature at atmospheric pressure is S shaped, with a minimum and maximum closely juxtaposed in the neighborhood of 0°C, strongly reminiscent of the curve of specific volume of water over the complete temperature domain into the heavily subcooled region. The resistance decreases at all temperatures with increasing pressure, but because of the character of the resistance curves at atmospheric pressure there is complicated crossing of the curves. The effect of pressure on resistance was measured between $-80°$ and $90°$. The pressure coefficient has a strong maximum at $-40°$, where it is about twice as high as at the highest temperatures. Arsenic was measured in the single crystal, three different orientations. The effects are very irregular and not reproducible. There are pronounced seasoning effects, sometimes so large that on the initial application of pressure the resistance may increase with pressure, instead of decrease, as it does after settling down to a more or less steady condition. The relation between resistance and pressure can be approximately represented by three linear ranges, with different slopes, as could also the relation between volume and pressure. The pressure effect on resistance is least for the orientation in which the hexagonal axis is at right angles to the direction of current flow. The effect of pressure on the resistance of the three gold-silver alloys presents no unusual features; the resistance decreases with pressure and may be reproduced by the usual second degree expression; The coefficient is less for the 50-50 composition than for those on either side. The resistance did not show the various small scale irregularities which had been found in measuring the effect of pressure on volume; in general such irregularities are less marked for resistance phenomena than for volume phenomena, in part because of the greater sensitivity of the latter sort of measurement.

In 1932[431] I published measurements of the effect of pressure up to 7000 kg/cm^2 at temperatures down to liquid oxygen temperature, 90°K, on the resistance of the following 15 metals: Pb, Mg, Al, Ag, Au, Cu, Ni, Fe, Pd, Cb, Pt, Rh, Mo, Ta, and W. Pressure was transmitted with helium, a choice made almost necessary by the freezing of other media at the pressures contemplated. There were very considerable difficulties of technique, chiefly connected with leak of helium due to mechanical imperfections in the steel. The leads to the resistance specimens were taken out through the connecting pipe to a block containing the insulating plugs at room temperature. In general the pressure coefficient of resistance increases at low temperature, but by an amount markedly less than found by Fischer,[423] with no agreement as to the detailed manner of variation from metal to metal. Fischer found the greatest increase for tungsten and tantalum, whereas I actually found decreases for these two metals. I have already indicated that I believe the explanation to be Fischer's low pressure range, combined with seasoning effects of pressure, which usually do not disappear below pressures several times Fischer's range. Two questions are of interest in respect to the effect of pressure on resistance at low temperatures: does pressure induce the supra-conducting state at higher temperatures than normal, and is there any evidence that the suspected minimum of resistance with pressure occurs at a lower pressure at low temperature? The evidence of the measurements was negative with regard to both questions.

The paper on the resistance at low temperatures of 15 metals, most of them cubic, was followed[432] by measurements of the resistance of seven non-cubic single crystals in different orientations over the same range of temperature and pressure. The single crystals were: Zn, Cd, Sn, Bi, Sb, As, and Te. With the exception of tellurium, which is non-metallic, the effect on the six metals is the same as that previously found: at low temperatures the pressure coefficient is greater *arithmetically*, whether it is intrinsically positive or negative, than at higher temperatures. With regard to the difference of effect in different orientations, it was already known that pressure at ordinary temperatures has the effect of equalizing the difference of resistance in different orientations for zinc, cadmium, and antimony, but it accentuates the differences for bismuth and tin. At low temperature the equalizing effect of pressure becomes less marked for the first three, but the unequalizing effect for the latter two becomes greater. The magnitude of the pressure effects on tellurium is very large, the resistance at 12,000 being of the order of one percent of that at atmospheric pressure. To a first approximation, the logarithm of resistance is linear in pressure; the rate of pressure decrease is very much less at −78° and −182° than at 0° and 95°. This demands a crossing of curves and a reversal of sign of the temperature coefficient with rising pressure. These effects in tellurium do not vary markedly with crystal orientation.

In 1935[183] I published my first measurements over a wider pressure range, up to 20,000 kg/cm². The apparatus did not differ radically from that with which measurements had been carried to 12,000; it was made of an ostensibly stronger steel, and was made in one piece, without connecting pipe or side inlets, for greater strength. The resistance of gold, silver, and iron was measured to 20,000 against the manganin gauge in order to obtain presumptive evidence as to the justifiability of extrapolating the latter from 12,000, the range of calibration, to 20,000. The four metals, gold, silver, iron, and manganin were found to extrapolate approximately together from 12,000 to 20,000, from which the conclusion was drawn that a linear extrapolation of the manganin was probably not in error at 20,000 by more than a fraction of a percent. Assuming the manganin gauge to be correct, the resistance of three other substances, black phosphorus, tellurium, and copper sulfide, was now measured. The pressure effects were known to be large for these substances and therefore any error in the manganin gauge would have a comparatively small effect. Both black phosphorus and tellurium approach the behavior of metals with regard to resistance; the temperature coefficient of resistance reverses sign at high pressure, and there is indication of the fairly close approach of a minimum of resistance at pressures beyond the range. Copper sulfide is the first semiconductor measured to high pressures. At 30° the resistance decreases about 10 percent at 20,000 kg/cm²; the effects are repeatable and reversible, and there is a sharp discontinuity in the tangent at 3000, the rate of decrease of resistance with pressure above 3000 being ten times less than below 30°. At 75°, the resistance also decreases, but here there are irreversible effects, with slow internal changes and creep.

In 1935[182] I also determined the effect of pressure up to 12,000 kg/cm² on the same list of intermetallic compounds that has been enumerated above in connection with measurements of compression, and also on germanium and silver sulfide. The resistance of all the intermetallic compounds, except those noted, decreases with increasing pressure, the coefficient being of the general order of magnitude of that for pure metals. The resistance of Mg_3Al_2 increases with pressure at both temperatures; the coefficient of Ag_5Zn_8 is unusually small numerically, and is negative at 30° and positive at 75°, whereas that of Ag_2Al is positive at 30° and negative at 75°. Most of the compounds show evidence of the same shifting internal equilibrium that was shown volumetrically; the resistance irregularities are in general less marked than the volume irregularities under the conditions of the experiments. The resistance of germanium increases under pressure, at a rate increasing at higher pressures, and with marked deviations from a second degree relation. The increase at 12,000 is of the order of 25 percent. The resistance of silver sulfide decreases drastically with increasing pressure, dropping to about 0.001 of its atmospheric value at 12,000. The logarithm of resistance against pressure is approximately linear.

In 1938[5] I published measurements of the effect of pressure up to 30,000 kg/cm² at 30° and 75° on the resistance of the following 19 metals: Cu, Ag, Au, Fe, Pb, Li, Na, K, Rb, Cs, Ca, Sr, Ba, Hg, Bi, Zn, Sn, Sb, and Te, the latter four for two orientations of the single crystal. The pressure was measured by linear extrapolation of the manganin gauge; since the deviations from linearity of the changes of resistance are large, any error in the extrapolation will be comparatively unimportant. The resistance of the comparatively hard metals Cu, Ag, Au, and Fe behaves about as would be expected from extrapolation from 12,000 kg/cm^2. The second degree relation is, however, significantly departed from, and in such a direction that if there is a minimum of resistance at high pressures it occurs at a pressure higher than would have been extrapolated from the second degree relation valid up to 12,000. For the other metals, extrapolation from 12,000 goes off so badly as to be hardly profitable. The expected minimum in the resistance of potassium was found at 25,400 kg/cm^2, about 2000 higher than had been anticipated by extrapolation. The minimum for sodium was not reached, although it had been anticipated at some pressure below 30,000 kg/cm^2; if it exists it would now appear that it is to be found above 40,000 kg/cm^2. The resistance of rubidium continues to increase beyond its previously found minimum, at an accelerated rate. The resistance of calcium, strontium, and barium continue to increase with upward curvature over the new pressure range, the rise for barium being punctuated by a slight drop in the neighborhood of 17,000 kg/cm^2 due to a transition, which was located also volumetrically. Caesium has a transition in the general neighborhood of 23,000 kg/cm^2; both before and after the transition the resistance increases with increasing pressure. The increase of resistance under pressure would therefore appear to be an effect probably not intimately connected with the lattice. The direction of discontinuous change of resistance at the transition is up, against the change of volume. This is a highly anomalous effect, and the first example of it found; usually the discontinuity in resistance follows the discontinuity in volume. A second example of the same anomaly was later found for bismuth. At the first bismuth transition between I and II the resistance drops, as is normal, but by an unusually large amount, by a factor of 6. At the second transition between II and III it jumps up, in the abnormal direction, by a factor of 2.5. Both modifications II and III are normal in having a negative pressure coefficient of resistance. The resistance of solid mercury decreases under pressure by an amount to be expected of a soft metal with its position in the periodic table. By good fortune the resistance measurements permitted an unusually precise determination of a point on the melting curve at nearly twice the previous pressure maximum. The melting curve of mercury is unusually straight, and may be extrapolated with more than usual accuracy. The accuracy of the extrapolation of the melting curve gave independent presumptive evidence as to the small error in extrapolating the manganin gauge. High pressure reverses the relation of resistance in different directions for single crystal zinc, the resistance along the hexagonal axis becoming less than that at right angles. In single crystal tin the resistance in both directions decreases smoothly over the entire pressure range, with practically no change in the ratio of resistance in different directions. Single crystal antimony is the only known example of a metal whose resistance passes through a maximum with increasing pressure; this maximum occurs at lower pressures the more nearly the axis is perpendicular to the length, and the pressure of the maximum is a strong function of temperature. Single crystal tellurium decreases in resistance at 30,000 by a factor of 600; it is probable that the temperature coefficient of resistance will reverse sign not far beyond 30,000.

In 1939[20] I communicated results, not published until a year later, establishing pressure fixed points in the new range (the transitions of bismuth), and accurately determined the change of resistance of manganin. It appears that by extrapolating from 7600 to 25,000 kg/cm^2, assuming linearity, a pressure will be obtained which is one or two percent too low. The precise amount of deviation varies with the specimen of manganin, and the coils have to be individually calibrated. It will be noticed that the deviation from linearity is in the abnormal direction and indicates that the curve of resistance *versus* pressure for manganin is concave toward the pressure axis, instead of convex as it is in all other known cases of a positive pressure coefficient.

Finally, mention may be made of an attempt made in conjunction with the shearing experiments[350] to extend the range of resistance measurements to 50,000. The method was to measure the resistance of the thin disk between the steel boss and the rectangular steel block. Only very rough qualitative results were obtained. It appears that in some cases, bismuth notably, there may be a very high skin resistance in the highly disorganized surface layer, of the order of thousands of times greater than the resistance of the massive disk proper. This surface film, in spite of its disorganization, is nevertheless capable of showing the discontinuities of resistance on passing through the polymorphic transitions. The resistance of the surface film notably decreases with increasing pressure, although that of the massive bismuth increases. On the other hand, other metals may have a much smaller surface film resistance; for instance the surface resistance of silver practically disappears above 40,000 kg/cm^2.

The following summary of theoretical explanations of the effect of pressure on electrical resistance makes no pretense to being complete and will attempt only to indicate the nature of the subject matter of the papers without reproducing the arguments. Honda, Nishina, and Hirone in 1932[433] and Honda and Hirone in 1938[434] wrote expressly on the pressure coefficient of resistance, checking their theory against my data. The method was by evaluating the effect of pressure on the various factors in Sommerfeld's expression for resistance. They state that they have secured fairly good agreement with experiment, but it would appear that such agreement as they obtain cannot be used as an argument for the presumptive validity of the fundamental idea, because the final mathematical expression contains two disposable empirical constants, one of which is so adjusted as to give the experimentally determined initial slope of the resistance-pressure curve. The difference between their calculated values and the experimental values increases at an accelerated rate at the higher pressures. Kroll,[435] assuming the Bloch-Peierls theory, derives an expression for resistance as a function of pressure involving grating space, compressibility, and Poisson's ratio. Neglecting the variation of Poisson's ratio with pressure, he derives values for the pressure coefficient of silver and gold which are not far from experiment, and also deduces the positive sign for lithium, but in general the agreement is not good in detail, and there may be failures by a factor of several fold. Frank[436] addressed himself to the problem of the pressure coefficient of the alkali metals, in particular the difference between sodium and lithium. He ascribes the difference to the difference in the shape of the curves of energy *versus* atomic distance for the $2p$ and the $2s$ electrons; for lithium, ΔE decreases with decreasing atomic distance; and for sodium, it increases. He reproduces the increase of resistance of lithium at 12,000 within 25 percent. The theory indicates an eventual reversal of sign of the pressure coefficient of sodium, which experiment suggests is probable, and also an infinite resistance for lithium at some finite pressure, for which there does not seem to be so much experimental evidence. Mott[437] develops a general theory of metallic resistance from the wave mechanics point of view and makes especial application to the pressure effects. His theory leads to practically taking over Grüneisen's expression, which gives fair agreement with experiment. The pressure coefficient of alloys would in general be expected to be less than that of pure metals, which checks with experiment. He gets good agreement with experiment for the effect of low temperatures on pressure coefficient (my data). The abnormal positive signs for calcium and strontium are explained on the basis of the special shapes of the Brillouin zones, but the positive sign for lithium proves difficult. Lenssen and Michels[438] have deduced expressions for the pressure effect on resistance based on Nordheim's wave mechanical theory of resistance. The effect of pressure on the thermal part of the resistance and the part residual at zero absolute are considered separately. As regards agreement with experiment, no very definite conclusions are reached, the final formulas having too many disposable constants. Saha[439, 440] has two papers dealing with the effect of pressure. In the first he bases his analysis on the rigid ionic model of Nordheim, using a screened Coulomb potential. He gets good agreement with experiment for silver, gold, and copper, and in general for metals with low compressibility. Comparison with the results of Kroll indicates that the present method of attack is to be preferred in general to one based on Fermi; neither method seems to work for the alkali metals. In his second paper Saha uses the deformable ionic model of Bloch; at ordinary temperatures he gets fairly good agreement with experiment for sodium, potassium, gold, silver, copper, nickel, lead, palladium, platinum, and molybdenum. At liquid air temperature he finds the pressure coefficient should be larger, which agrees qualitatively with the general trend of my results. The increase of resistance of lithium cannot be reconciled with the theory. Grüneisen[441] considers the application of his theory especially to my low temperature measurements. The residual resistance due to impurity introduces a complication which requires special discussion. For pure metals the theory indicates a pressure coefficient which is constant independent of temperature in a high range of temperature, a second pressure coefficient, much higher, and also independent of temperature in a low range of temperature, and an intermediate transition zone. This normal behavior is so modified by the residual resistance that on occasion the pressure coefficient may increase with rising temperature. Fairly good agreement is obtained with my low temperature data, and also with some of Fischer's. A positive pressure coefficient of resistance is outside the scope of the theory.

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2. The Effect of Pressure on the Electrical Resistance of Solutions

There are two papers from Tammann's laboratory which chronologically come at the end of the period of my book; they were not discussed there however, and therefore will be mentioned here. Tammann and Tofuate[442] measured solutions of six acids and of ammonia up to 3000 kg/cm^2 at 0°, 20°, and 40°. The pressure coefficient of the increase of conductivity, plotted as a function of concentration, reaches a maximum at concentrations which are higher for those acids which have the larger dissociation constants. The pressure coefficient of the degree of dissociation increases with concentration more slowly for ternary than for binary electrolytes. Pressure increases interionic friction, except for H and OH ions, for which it decreases. Tammann and Rohmann[443] measured up to 3000 kg/cm^2 at 20° and 40° the conductivity in several concentrations of solutions of NaOAc, KCN, $BaCl_2$, $CeCl_3$, $HgCl_2$, NH_4CN, NH_4OAc, and HCN. The pressure increase of conductivity passes through a maximum with increasing pressure for the strong electrolytes, the maximum being less pronounced the more concentrated the solution and the higher the temperature. $HgCl_2$ shows no maximum. When correction is made for the effect of pressure on viscosity, the conductivity becomes almost independent of pressure for the strong electrolytes, indicating complete dissociation. Adams and Hall[444] measured up to 4000 bars at 0°, 25°, and 30° the conductivity of dilute and concentrated NaCl solutions and dilute solutions of K_2SO_4 and KCl. Pressure decreases the conductivity of dilute NaCl solutions and increases that of concentrated ones. At high pressures, the conductivity of NaCl solutions passes through a maximum with increasing concentration. Monoszon and Pleskov[445] have measured the effect of pressure on the solutions in ammonia of $LiNO_3$, $NaNO_3$, and KNO_3. The paper has been available only in abstract and further details are not indicated. Brander[446] worked on solutions of: CO_2, $O_2NC_6H_4OH$, $(CHCO_2H)_2$, $NaHCO_3$, $O_2NC_6H_4ONa$, $(CHCO_2Na)_2$, K_2SO_4, and $MgSO_4$. For univalent salts R_p/R_0 is independent of concentration. The variation with pressure is slight for K_2SO_4 and greater for $MgSO_4$. The pressure effect on solutions of CO_2 is abnormally high. Zisman[447] has measured in my laboratory the conductivities up to 11,000 kg/cm^2 at 30° and 75° of $0.01N$ solutions in water of HCl, LiCl, NaCl, KCl, RbCl, CsCl, NaF, NaBr, NaI, Na_2SO_4, $NaC_2H_3O_2$, $CaCl_2$, $BaCl_2$, $ThCl_4$, $K_3Fe(CN)_6$, and $K_4Fe(CN)_6$. In many cases the conductivity has a flat maximum with pressure at low pressures; between 3000 and 8000 the conductivity in almost all cases decreases linearly with increasing pressure and at the same rate for all solutions. The behavior of HCl is exceptional. The maximum in conductivity cannot be entirely caused by a change in the degree of dissociation with pressure. The Debye-Hückel formula demands that there be a large change in ionic diameter with pressure. Edler and Zeier[448] measured the conductivity to 200 atmos. of pure transformer oil. Ohm's law is not followed; the deviation from Ohm's law is not affected by increase of pressure. At constant field the current decreases exponentially with increase of pressure. Fisher[449] contributes a review article, with fifteen references. Jost and Nehlep[450] have a theoretical calculation of the energies of disorderliness and swelling, in which they also discuss the effect of pressure on electrolytic conductivity.

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3. The Effect of Pressure on Dielectric Constant

The laboratories of Michels and of Keyes have contributed the most titles on this topic.

A. Michels and C. Michels[451] measured the dielectric constant of nitrogen up to 150 atmos. at 25°, 75°, and 125°; except at 1 and 25 atmos., where the experimental accuracy was too low, they found the Clausius-Mosotti expression $(\epsilon-1)/(\epsilon+2)\cdot(1/d)$ to be constant. The same authors[452] measured the dielectric constant of carbon dioxide up to 1000 atmos. between 25° and 150°; the range covers the critical region, and slightly above and below it. The Clausius-Mosotti expression was found to be independent of temperature and to have a tendency to decrease with increasing pressure. Michels, Jaspers, and Sanders[453] measured the dielectric constant of nitrogen to 1000 atmos. between 25° and 150°. In this range the Clausius-Mosotti expression is sensibly constant. Michels, Sanders, and Schipper[454] measured the dielectric constant of hydrogen up to 1425 atmos. between 25° and 100°; the Clausius-Mosotti expression is constant within error. Michels and Kleerekoper[455] measured the dielectric constant of carbon dioxide at 25°, 50°, and 100° up to 1700 atmos. This was in part a repetition of earlier measurements, with special emphasis on greater accuracy in the region of low densities. The Clausius-Mosotti function is found to have a well-marked maximum, in a total range of variation of the order of 2 percent, at pressures below 300 atmos.; the maximum is cusp-like at 50°, rounded at 100°.

Keyes and Kirkwood[456] measured the dielectric constant of carbon dioxide at 0°, 35°, 70°, and 100° up to 200 atmos. The Clausius-Mosotti expression is constant for variations of temperature, but not for variations of density, becoming larger asymptotically at higher densities. Keyes and Kirkwood[457] measured the dielectric constant of ammonia at 100°, 125°, 150°, and 175° up to 100 atmos. The Clausius-Mosotti function is far from constant, increasing with increasing pressure and decreasing with increasing temperature; the extreme variation in the range was from 36.49 to 43.05. Uhlig, Kirkwood, and Keyes[458] repeated and extended the previous measurements on carbon dioxide and ammonia, and added methane, hydrogen, and nitrogen. The range was 0° to 200° and up to 250 atmos. The Clausius-Mosotti expression is independent of density for methane, hydrogen, and nitrogen; it increases slowly with density for carbon dioxide, and more rapidly for ammonia. The molar polarization, P_0, is independent of temperature for all except ammonia, indicating no permanent dipole moment. P_0 for ammonia increases with temperature; the permanent dipole moment calculated from the temperature variation by extrapolation agrees with that of other observers. Keyes and Oncley[459] review the very considerable literature of the dielectric constant of compressed gases. They conclude that the Clausius-Mosotti function is independent of temperature and density for helium, hydrogen, and nitrogen, and a function of density for carbon dioxide, methane, and propane.

The following four papers deal also with the effect of pressure on the dielectric constant of gases. Broxon[460] measured the dielectric constant of air to 170 atmos.; he found that it varies nearly linearly with pressure. In a second paper Broxon[461] presented measurements for commercial nitrogen over the same range. $\epsilon-1$ varies linearly with pressure, at the rate of 556×10^{-6} per atmos. at 16.5°. McNabney, Moulton, and Beuschlein[462] determined the dielectric constants of air and hydrogen at 20° between 72 and 335 atmos. The Clausius-Mosotti function for air shows slight irregularities, but is probably constant within error; for hydrogen it decreases uniformly with pressure from 1.16 to 0.99. Kubo[463] has given an elaborate theory of the pressure effect in gases on the basis of Debye's theory of polarization, the particular feature being the method of integration over all orientations, both for polar and non-polar molecules. Satisfactory agreement is obtained with the experimental data of Keyes and Kirkwood, and of Michels.

The remaining papers dealing with this topic are concerned with the dielectric constant of liquids. There seem to be no measurements in this period on solids; the experimental difficulties are obviously greater than for gases or liquids. Trendelenburg[464] proposed a method for the measurement of rapidly varying pressures by measuring with an oscillograph the variations in the capacity of a condenser filled with a liquid. Benzene was suggested as a suitable liquid, and the paper contains calibration data for the dielectric constant of benzene as a function of pressure to 200 atmos. Measurable departures from linearity were found. An illustrative application of the method is given up to 300 atmos.

Danforth[465] in my laboratory measured the dielectric constant at several temperatures between 0° and 75° up to 12,000 kg/cm^2 of the following ten liquids: carbon disulphide, ethyl ether, *n*-pentane, chlorobenzene, bromobenzene, hexyl alcohol, ethyl alcohol, *i*-butyl alcohol, glycerin, and eugenol. Measurements were made at an audiofrequency and at 247,000 cycles. At the high frequency a marked decrease of dielectric constant at the higher pressures was exhibited by the liquids glycerin, *i*-butyl alcohol, and eugenol. These are precisely the three liquids for which pressure produces the largest increase of viscosity. The obvious explanation of the anomolous dispersion is the suppression of the ability of the molecules to rotate fast enough to follow the field because of too great viscosity. There was no trace of the anomoly at audiofrequency, which incidentally shows that the effect was not caused by freezing. The dielectric constant was found to continue the same trend in the pressure range above 3000 that Kyropoulos had previously found up to that limit. The Clausius-Mosotti function in general decreased with increasing pressure. Danforth found, however, that a simplification was introduced if the reciprocal of the Clausius-Mosotti function was plotted against density instead of against pressure; plotted in this way the curves for most of the liquids are nearly straight. The results are thought to demand a variation in both the polarizability of the molecules under pressure, and a variation of the "constant of the inner field," which is usually taken as $4\pi/3$. The two effects cannot be separated, however, without other data than the pressure effect on dielectric constant. In 1934 Chang[466] published the results of measurements that he had made in my laboratory several years before on dielectric constants of liquids up to 12,000. This work was described briefly in my book, and since it was done prior to Danforth's, no further abstract is necessary here. Scott[467] at the Bureau of Standards measured up to 700 atmos. the dielectric constant, power factor, and conductivity at 1000 cycles of a number of rubber-sulphur compounds, containing up to 32 percent sulphur. The effect of pressure varies markedly with the sulphur content; each of the three properties has a maximum with increasing sulphur content, and under pressure this maximum is displaced toward lower sulphur content. Up to 7.5 percent S the dielectric constant increases slightly with pressure and decreases beyond that. The power factor is independent of pressure up to 2 percent S, increases with pressure between 2 and 12 percent S, and diminishes beyond that. In the range 12 to 19 percent S the conductivity increases with increasing pressure; outside this range it diminishes with pressure. Bancroft[468] in my laboratory measured the effect of pressures up to 10,000 kg/cm^2 on the susceptibility of Rochelle salts in the temperature range −20° to 60°. At atmospheric pressure it is well known that Rochelle salt has a lower critical temperature at −18° and an upper critical point at 23.7°; between these two temperatures the dielectric constant is effectively infinite, and the behavior is the electric analog of a ferromagnetic substance. Bancroft found that both critical temperatures are raised by pressure, at an approximately linear rate; the upper point is raised 10.73° and the lower one 3.77° for 1000 kg/cm^2. Complete curves are given for the reciprocal susceptibility as a function of pressure at 10° intervals across the ferromagnetic region into the normal region on either side. No simple explanation on the basis of present theory appears possible. Owen and Brinkley[469] contribute a theoretical paper on the pressure effect in liquids in which they find that the dielectric constant satisfies an equation of exactly the same form as the Tait equation for density, already discussed in connection with the work of Gibson, the constants in the logarithmic part being the same in the two equations. The equations reproduce the experimental values of Francke, of Kyropoulos, and of Danforth. Böttcher[470] discusses theoretically the effect of pressure on the molecular polarization in dipole-free gases and liquids. A modified form of the Clausius-Mosotti function is deduced, involving the molecular polarizing factor and the molecular radius. With this formula the data of Danforth for CS_2 up to 12,000 kg/cm^2 can be reproduced. The formula demands that the molecular polarization should pass through a pressure maximum; there is experimental evidence for this in the case of CS_2 and CO_2.

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4. Miscellaneous Electrical Effects of Pressure

Poulter, Ritchey, Wilson, and Fulton[471] in 1929 published measurements of the effect of pressures up to 16,000 atmos. on the e.m.f. of a Weston standard cell. This was followed in 1932 by a paper on the same subject by Poulter and Ritchey,[472] in which more precise measurements were made up to 12,000 atmos. Two experimental arrangements were used. One, which was used to 8000, mounted the cell in an open container of glass or beeswax, the electrodes being brought in at the open top. The other, used to the maximum, mounted the cell in a completely enclosing rubber container, pressure being transmitted through the walls. The e.m.f. increases with pressure; the rate of increase for the first thousand atmos. agrees with results obtained previously by Cohen and Sinnige. Above the first few thousand atmospheres there are large deviations from linearity in the direction of a smaller rate of increase. The total range of e.m.f. in the pressure range is between 1.018 and 1.074 volts. The authors feel that there are too many unknown factors to justify the attempt to calculate thermodynamically what the pressure effect would be expected to be. Cohen and Sinnige had secured agreement between theory and experiment in their range, so that there must be new and unknown factors at high pressures. Skutta[473] measured the electrical resistance of tubes of nickel and steel exposed to high internal pressures exerted by hydrogen or nickel. The tubes were activated by a previous heating to red heat in hydrogen at a pressure exceeding that of subsequent use. The resistance increases with pressure for the system steel-hydrogen and decreases for nickel-hydrogen. With nitrogen there is a considerable increase of resistance for both metals. Skaupy and Kantorowicz[474] compressed 15 powdered metals dry up to 4000 atmos. and found the electrical resistance of the compacted pellet to vary from 1.1 times that of the massive metal for tin to 400-fold for tungsten. Bellia[475] found that the Hall coefficient increases under a pressure of 50 atmos.; this is apparently the only investigation ever made of this effect. Cassel and Krumbein[476] measured the effect of pressures up to 10 atmos. on overvoltages in the electrolysis of water. Some of their effects agreed with previous observers; others were considerably larger. Cohen and Piepenbroek[477] measured the effect of pressure up to 1500 kg/cm^2 on the e.m.f. of the concentration cell:

Tl-amalgam/TlCNS-KCNS/
KCl-TlCl/Tl-amalgam.

The e.m.f. was 0.00856 volt at atmospheric pressure and 0.01282 at 1500. There is agreement with the theoretical value calculated thermodynamically within 0.75 percent, better than could be expected in view of the error in the thermal parameters. Schischkin and Karnauch[478] found that 100 atmos. produce a slight decrease of both anode and cathode potentials of nickel electrodes used in the electrolysis of 5*N* NaOH solution. Iron electrodes show a similar but somewhat smaller effect. Sharavskii[479] applied pressures up to 8000 atmos. in a study of the effect on copper oxide rectifiers. The rectifying properties are improved up to 4000 to 5000 atmos.; above this there was impairment. No change in electrical conductivity of Cu_2O could be detected up to 8570 atmos. Michels, Michels-Veraart, and Bijl[480] have recalculated certain former results of theirs for the dielectric constant of CO_2, and find that the Clausius-Mosotti function decreases with increasing pressure and is nearly a single valued function of pressure but not of density. They think that the polarizability of the molecule must be a function of pressure. This is followed by a theoretical paper on the same topic by Michels, de Boer, and Bijl[481] utilizing their experimental values up to 3000 atmos. Trey[482] found that the rectifying action associated with the adsorbed layer on the surface of a pellet of compressed PbS powder disappears when the pellet is subjected to a pressure in excess of 4000 kg/cm^2. Birch[483] discussed the small corrections arising from the effect of pressure on thermo-electromotive force when thermocouples are used inside a pressure vessel for the measurement of temperature. Basset[484] described experiments in which he has succeeded in maintaining an arc between graphite terminals in an atmosphere of nitrogen or argon at pressures up to 9000 kg/cm^2. Voltages up to 600 volts and currents up to 10 amp. are necessary. The crater is very small and the rod burns very rapidly; the temperature of the crater is about 5000°. He has also maintained arcs between tungsten and tantalum electrodes under similar conditions.

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MAGNETIC EFFECTS OF HIGH PRESSURE

Comparatively little new work has been done in this field.

Adams and Green[485] measured the effect of pressure up to 3600 atmos. on the temperature of the magnetic inversion point in a 35 percent nickel steel, pure nickel, pure iron, a meteoric iron, and magnetite. The measurements were made by making the specimen one arm of a transformer mounted in the pressure vessel, which contained the miniature heating furnace. Their conclusion was that any effect of pressure on the inversion point of any of these materials is too small to be certainly measurable; if anything, the temperature may drop very slightly with increasing pressure. They infer that the crust of the earth is far above the temperature of any possible magnetization. Steinberger[486] in my laboratory studied the effect of pressures up to 12,500 kg/cm^2 on the magnetic flux density in a series of 11 iron-nickel alloys, in steps of nominally 10 percent nickel, including the pure metals. The specimens were in the form of anchor rings, with primary and secondary windings. The effect was studied both of varying the magnetic field at various constant pressures and of varying pressure at constant field. The effects are complicated; there are linear, non-linear, and hysteresis effects. The effect of applying pressure at constant field is usually to decrease the flux, often by relatively large amounts. The 30 percent nickel alloy is rendered nearly non-magnetic by a pressure of 12,000 kg/cm^2. Of the other alloys, pure iron shows the greatest and the 90 percent nickel the smallest change of flux with pressure. Ebert and Kussmann[487] studied the effect of pressures up to 3000 kg/cm^2 at room temperature on magnetic permeability through the entire range of field, but especially on the saturation intensity. Ballistic methods were used, with two different forms of apparatus for low and high fields. At high fields the pressure vessel was made of the non-magnetic beryllium copper, and was mounted on the axis of an electromagnet in such a way that it could be jerked bodily out of the field by longitudinal displacement along the axis of the electromagnet at the same time that another geometrically similar specimen not exposed to pressure was jerked into the field. Measurements were made on pure iron and pure nickel; on selected alloys of iron with nickel, cobalt, chromium, and platinum; on alloys of nickel with aluminum, chromium, cobalt, copper, and manganese; on an alloy of platinum with manganese, and on the ternary system iron-cobalt-chromium. In general the effect of pressure on saturation magnetism is very small, varying from 0.1 to 0.01 percent per 1000 kg/cm^2. There are, however, certain alloys in a critical range of composition in which the effect may be much larger, up to a decrease of 6.5 percent per 1000 kg/cm^2. The critical compositions are Fe 70-Ni 30, Pt 60-Fe 40, and one of the Fe-Co-Cr compositions. There seems to be a connection between these large coefficients and a marked temperature hysteresis between the α- and γ-phases. Michels, Jaspers, de Boer, and Strijland[488] determined the effect of pressure up to 2615 atmos. on the Curie temperature of a 70 Ni-30 Cu alloy. At atmospheric pressure the Curie region is smeared out between 10° and 40°. The method was to measure the electrical resistance and to determine how the region of anomaly in the resistance is displaced by pressure. Since the phenomena are so much smeared out, accurate results are difficult. They conclude that the anomaly is displaced in a way that would correspond to a raising of the fictive sharp Curie point which represents the mean of the anomaly by 6.5×10^{-5} degree for 1 atmos. Ebert and Kussmann[489] in a second paper determine the effect of pressures up to 4000 kg/cm^2 on the Curie temperature in the temperature range from $-100°$ to 220° on seven different alloys: Ni-Cu, Ni-Al, Ni-Fe-Mn (4), and Co-Fe-Cr. Magnetization decreases with rising pressure. The pressure effect on magnetization increases with increasing temperature and decreases with increasing pressure up to the Curie point; the rates of variation become accentuated in the neighborhood of the Curie point. It is inferred by extrapolation that the pressure-temperature-magnetization surface would become asymptotic to the p-t plane, so that ferromagnetism cannot be made to vanish by any finite pressure. This is equivalent to saying that the Curie temperature is not affected by pressure and is thus opposed to the findings of other investigators. Leipunskii[490] contributes a theoretical paper in which he calculates both from Clapeyron's equation and from Heisenberg's theory of ferromagnetism that the Curie point in nickel and iron should be displaced by pressure by quite recognizable amounts. He thinks the experiments have never been performed under the proper conditions. He calculates that the Curie point of iron or nickel in the interior of the earth is between 2000° and 4250°, which would not rule out a ferromagnetic core. Birch[491] studied the effect of pressures up to 4000 kg/cm^2 on the α-γ transformation in iron. Normally this runs at about 900°; the volume decreases on passing through the transition, so that the transition line is displaced to lower temperatures by rising pressure. The method was a thermal expansion method which permitted a determination of the displacement of the temperature of the volume discontinuity by pressure. The effect is linear in the pressure; the temperature is lowered 8.5° per 1000 kg/cm^2. It would appear then that the alpha-phase is of comparatively little importance in the problem of the magnetism of the earth, because it is wiped out by pressure under the conditions prevailing in the crust. Slater[492] contributes a theoretical discussion in which he shows by an application of Clapeyron's equation that in the iron-nickel series the initial effect of pressure beginning with pure iron is to raise the Curie temperature by 5×10^{-5} degree per atmos. This coefficient becomes less with increasing nickel content and should reverse sign at 70 percent nickel. He is of the opinion that no explanation of the magnetism of the earth in terms of ferromagnetism is plausible. Michels and Strijland[493] have determined the effect of pressure up to 2640 kg/cm^2 and between 0° and 99° on the electrical resistance of a monel alloy (Ni 68, Cu 29, Fe 1.6, Mn 1.0, Si 0.1, C 0.15) and from a study of the displacement of the region of anomalies in the resistance conclude that the Curie temperature is shifted toward higher values at the rate of 0.03° per thousand atmos. The pressure coefficient of resistance passes through a cusp-like maximum within the range.

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OPTICAL EFFECTS OF HIGH PRESSURE

1. The Effect of Pressure on Index of Refraction

Bennett[494] measured by an interference method and for three wave-lengths the dispersion and index of refraction of nitrogen up to 7 atmos. The Lorenz-Lorentz relation is followed, and the dispersion is a linear function of pressure. Poulter, Ritchey, and Benz[495] measured the index of refraction of a paraffin oil to 13,600 atmos. and of glycerine to 7200 atmos. The apparatus·consisted of a pressure chamber containing two Poulter windows mounted at an angle of 30° to each other, so that the space between them constituted a 30° prism. The index of the medium filling the pressure vessel was determined by a minimum deviation method, using the conventional formulas, and with no correction for the effect of pressure on the index of the windows. The Lorenz-Lorentz expression was found to be approximately constant for both liquids over the pressure range; the small variations in the L-L expression were irregular, and at the extreme, 2 parts in 300 for oil and 4 parts in 300 for glycerine. Poindexter and James[496] described an apparatus apparently much like Poulter's with which they measured the effect of pressure up to 1440 atmos. on the index of water at three wave-lengths. The Lorenz-Lorentz function is not constant, but at the maximum pressure decreases by an amount varying from 4 to 14 parts in 2000; the decrease is greater at the shorter wave-lengths. Poindexter and Rosen[497] measured the effect of pressures up to 1800 kg/cm^2 on the index of refraction of pure water and pure ethyl alcohol and five intermediate solutions. The measurements were made in a liquid prism of 51° angle. They represent the index by a four constant expression in the pressure. The behavior of the Lorenz-Lorentz function is not discussed; the change of the index of pure water under a given pressure change is only one-third the fractional change of density. Poindexter,[498] apparently with the same apparatus and over the same pressure range, determined the effect of pressure on the index of carbon disulfide. Measurements were made for three wave-lengths. The dispersion increases with pressure, but apparently is not linear, the rate of increase being higher at the lower pressures. John,[499] in Calcutta, discussed theoretically the effect of pressure on the refraction and dielectric constant of carbon dioxide, and was able to secure agreement with former experimental results of Phillips and of Michels and Michels. Michels and Hamers[500] measured the effect of pressure up to 2400 atmos. on the index of refraction of CO_2 at 25°, 32°, 50°, and 100° and for six wave-lengths between 4471 and 6678A. Elaborate tables and diagrams are given. The Lorenz-Lorentz function is not constant, but decreases with increasing pressure, the extreme decrease being 2.3 percent. Gibson and Kincaid[501] have measured up to 1250 bars and from 25° to 65° the volume and index of refraction of benzene. The index of refraction is measured by a novel method—noting the pressure of disappearance of fragments of optical glass of various indexes immersed in the liquid. The correction for change of index of the glass with pressure is only 2.5 percent. The Lorenz-Lorentz expression $[(n^2-1)/(n^2+2)]\cdot[1/d]=\text{const.}$, is badly out in one direction, and the Gladstone and Dale formula, $(n-1)/d=\text{const.}$, is out in the other direction. A formula of Eykman, purely empirical, $[(n^2-1)/(n+0.4)]\cdot[1/d]=\text{const.}$, reproduces the results within experimental error. The dispersion, that is, $n_{589}-n_{436}$, is increased seven percent by 1000 bars. Hayden,[502] with Poindexter's apparatus and under Poindexter's direction, as a thesis in 1933, measured the index of refraction and the dispersive power of glycerol at three wave-lengths and up to 2500 atmos. The dispersion was found to be a linear function of pressure, increasing with increasing pressure. The Lorenz-Lorentz relation was confirmed.

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2. Photographic Effects of High Pressure

A majority of the titles refer to a "pressure" effect, which turns out not to be an effect of hydrostatic pressure, but of simple compressive stress. There is doubtless some connection between the effects of the two kinds of stress, and I thought it worth while to mention all the titles here; unless there is an express statement to the contrary it is to be assumed that the "pressure" is a simple compression.

Schwarz and Urbach[503] have a paper on the photochemistry of the alkali metal halides and the photographic elementary process, which I have seen only in abstract. The abstract mentions that a remarkable effect is produced by the application of 100 to 200 kg/cm², but does not particularize further. Maring[504] investigated the effect of pressure on the formation of the latent image and on reversal in the region of solarization. Pressure reduces the density of the image, the reduction is greater at higher pressures and less with longer exposures. It is not a linear function of either pressure or exposure. In the region of solarization pressure produces a marked acceleration of reversal. Ny and Tsien[505] found that pressure always reduces sensitivity, both in the region of normal and of over-exposure. The pressure effect diminishes with increasing wave-length, and varies widely with the nature of the film. Ny and Lu[506] describe the apparatus for applying pressure to the plate, a solid quartz plate pressed against the photographic plate with a lever, and the variations of sensitivity. Reardon[507] applied pressures up to 1375 kg/cm^2 and studied the variation of the pressure effect with the method of development. Pressure reduces the density of the image for all methods of development; the reduction varied from 13 to 68 percent depending on the method of development. Poindexter, Reardon, and DeFoe[508] described a "new" pressure effect in photography. After exposure and before development the film was exposed to hydrostatic pressure in water up to 2500 atmos. for from 20 to 30 minutes. The developable image density is lowered; the reduction was 4 to 5 percent for an image density in the neighborhood of 0.7. Ny[509] found that pressure lowers the density of the image, the pressure effect increases with the wave-length of the incident light, and the relative lowering does not depend on the absolute value of the density. Jacobs,[236, 237] in two papers already referred to in connection with polymorphic transitions, described incidentally the behavior of photographic film under exposure to x-rays while subjected to a pressure up to 5000 kg/cm^2 exerted hydrostatically by helium gas. The effect of pressure on sensitivity, if any, was not greater than 10 or 15 percent. Various precautions have to be taken in applying and releasing pressure in order not to damage the film mechanically. The film after being subjected to pressure is stretched about 2 percent; this makes the use of fiducial wave-lengths necessary. Reardon[510] describes experiments in which the film is subjected to simple compressive stress by a glass block during exposure. In all cases pressure reduces the density of the image, by an amount depending on exposure and type of development. Lu, Chang, and Lu[511] investigated the effect of pressure on the sensitivity of a photographic plate to x-rays. It was already known that pressure diminishes the sensitivity to visible light, but increases it to γ radiation. Simple compressive stresses from 110 to 1180 kg/cm^2 were applied. The sign of the pressure effect for x-rays depends on the plate; sensitivity is decreased for Kodak and Agfa plates and increased for Ilfad. It is thought that there are two different mechanisms, one for visible and one for gamma-light; both of these mechanisms respond for x-rays, but in relative amounts depending on the plate. Lu, Chang, and Lu[512] give a systematic description of the effects of pressure up to 140 atmos. Choong[513] applied hydrostatic pressure with nitrogen up to 140 kg/cm^2. Various small effects were observed, which were the same for violet and yellow light.

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3. Miscellaneous Optical Effects of High Pressure

Przibram[514] investigated piezochromatism in natural minerals. Various powdered minerals were compressed to 20,000 kg/cm^2 and the changes of color investigated. There was little change in yellow and red fluorite, but green and blue fluorites change to violet, and light green ones to blue-green. Barites and tourmalines do not change. Yellow Joplin calcite becomes light bluish gray, a color not found in nature. The effects are only slightly affected by particle size. The changes in color are ascribed to a lattice distortion and neutralization of the partially or completely free ions by photoelectrically detached electrons. Poulter and McComb[515] observed through glass windows ZnS phosphorescent screens under pressures of 30,000 atmos. and found the intensity of phosphorescence reduced to one-half. There was no diminution in the number of scintillations produced on the screen by radioactive materials introduced into the pressure chamber. Bhagavantam[516] found that the discrete lines in the Raman spectrum of gases disappear above a certain pressure. A calculation yields results said to be in approximate agreement with experiment; the calculated pressure of disappearance varies from 450 atmos. for hydrogen to 5 atmos. for carbon dioxide; nine gases were investigated altogether. Eiseman and Harris[517, 518] contributed two papers from Keyes' laboratory on the absorption spectra at high pressures and low temperatures of argon, methane, and carbon dioxide. No absorption could be found, in either the gaseous or liquid phases at wave-lengths varying from 2130 to 6780A and at pressures up to a maximum of 400 atmos. Positive results which they had previously found for liquid carbon dioxide could not be reproduced, and are ascribed to some unknown impurity. These results are in disagreement with previous work of Harig, which the authors think was in error. Cohn[519] described various attempts, begun in my laboratory, and largely unsuccessful, to make x-ray investigations under high pressure. The x-rays were admitted into the pressure chamber through a beryllium window, and emerged through a glass window so arranged as to permit a large angle. Pressures were applied to 3000 atmos. The technique was later improved by Jacobs,[236, 237] who placed the camera inside the pressure chamber. Groot and Bol[520, 521] have studied the emission and absorption spectra of mercury vapor at pressures up to 300 atmos. There is a strong continuous spectrum from the ultraviolet to the infra-red. The superposed spectrum lines become very diffuse and drawn out on the red side. The optical absorption was utilized to determine the pressure instead of a pressure gauge in certain experiments, after the fundamental calibration had been established. Zinser[522, 523] used an apparatus with Poulter windows to investigate the effect of pressures up to 700 kg/cm^2 on the optical absorption of water and the rotation of sugar solutions. No satisfactory values for the absorption of water under pressure were obtained, the unknown disturbing effect of the pressure distortions of the window being too large. The optical rotation of a sugar solution is diminished by pressure; linearly up to 200, and then more slowly. Pressure exerts a strong inverting effect on the sugar solution; if pressure is maintained at 200 for several hours and then released, the rotation is much diminished, and sugar does not crystallize out of the solution on evaporating, but a jelly is formed. Gibson and Loeffler[524] measured the effect of pressures up to 1500 bars between 25° and 85° on the optical absorption of solutions of analine, dimethylaniline, diphenylamine, and triphenylamine in nitrobenzene, and a number of related solutions. The same apparatus was used as in measurements of the effect of pressure on index of refraction. The absorption is pushed significantly toward longer wave-lengths by increasing pressure, and also by an increase of temperature at constant volume, but the absorption may be displaced in either direction by an increase of temperature at constant pressure. The authors think that the effects are not caused by the formation of compounds in the solutions, but are an effect of the mutual polarizations of the different kinds of molecule. Deutsch[525] applied pressures from 560 to 11,300 kg/cm^2 to Rochelle salt powder and made Laue photographs. The powder was compacted to only 80 percent of the density of the single crystal; interference and asterism were very weak. Kuss and Stewart[526] determined the Kerr constant in nitrogen, carbon dioxide, methane, and ethylene up to 400 atmos. For carbon dioxide the Kerr constant varies smoothly through the critical point. The results are interpreted in terms of long and short range order. At high pressure there seems to be a fairly high degree of short distance order. Bobolev and

Leipunskii[527] found that under a pressure of 2500 atmos. and at 25° the rate of mutarotation of glucose is 3.4-fold greater than at atmospheric pressure. The energy of activation is 14.5 cal. against 17.5. Sander[528] studied the effect of pressure up to 600 atmos. on the inversion of sucrose and the mutarotation of glucose. The rate of inversion is not affected by pressure, but the speed of mutarotation is increased.

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CHEMICAL EFFECTS OF HIGH PRESSURES

No attempt will be made to classify the chemical effects under various subtopics. Most of the papers have to do with displacements of chemical equilibrium, or changes in the reaction rate, which is so closely connected as not to be separated with profit. The majority of the references are to reactions in gases and the interest is mainly industrial; these can be dismissed with only brief reference. The arrangement in the following is chronological.

Komatsu and Masumoto[529] studied the catalytic hydrogenation of ethers up to 100 atmos. Komatsu and Hagiwara[530] studied the catalytic action of reduced copper on phenols up to 122 atmos. and 220°. Hugel and Cohn[531] studied the effect of temperatures up to 300° and pressures up to 1000 kg/cm^2 on a hydrocarbon whose decomposition temperature is below its critical temperature and on another which normally decomposes above its critical temperature, Gillespie and Beattie[532] contribute a theoretical paper in which all the known data pertaining to the ammonia synthesis in the range from 352° to 952° and to 1000 atmos. are correlated with the compressibilities and heat capacities of the pure gases by means of an equation for the mass action function which involves only two adjustable constants. Njegovan[533] in a theoretical discussion applies the van der Waals equation to the Haber-Bosch ammonia process up to 1000 atmos., where the yield of NH_3 is greater than calculated. Ipatieff and Muromtzev[534] have investigated the displacement of metals and their oxides from solutions of their salts by hydrogen up to 300° and 250 atmos. This paper deals especially with metal nitrates. A second paper by Ipatieff, Razuvaev, and Malionovskii[535] considers, in the same range, especially the displacement of arsenic from its salts by hydrogen. Morgan[536] and collaborators discuss industrial applications of catalytic reactions under high pressures, with a consideration of modern theories. Bone[537] contributes a review article, dealing with high pressure gas reactions.

Komatsu and Mitsui[538] have studied the catalytic hydrogenation of benzoic acid to 225°

and 92 atmos. Tanaka and Amatatsu[539] studied the catalytic hydrogenation of safrole to 100 atmos. Lewon and Eyring[540] studied the reaction $N_2O_5 \rightleftarrows N_2O_4+\frac{1}{2}O_2$ by dissolving N_2O_5 and N_2O_4 in CCl_4 and exposing to pressure exerted by gaseous oxygen up to 1000 atmos. The reaction runs completely to the right. The value of ΔH was found to be not more than 1600 cal., against 2690 in the literature. Adkins, Cramer, and Connor[541] studied the rate of hydrogenation of five organic compounds over nickel as a catalyst at pressures between 27 and 350 atmos. Acetoacetic ester may be reduced at 30 atmos. but the rate is much increased at higher pressures, particularly between 120 and 350 atmos. Dehydroacetic acid was reduced more than twice as rapidly at 149 as at 108 atmos., and more than four times as rapidly at 323. Aniline is not affected in the 30 atmos. range; the rate is somewhat increased at the higher pressures, but not enough to make the reaction practical. The reduction of benzene and phenol proceeds well in the 30–40 atmos. range, but is much increased by further increases of pressure up to 330. Morgan[542] contributed a review article on organic syntheses facilitated by pressure, with many references to the patent literature. Tammann and Pape[543] studied the effect of pressure up to 3000 kg/cm^2 in the temperature range between 0° and 400° on the polymerization of styrene, isoprene, vinyl acetate, dimethyl butylene, and indene. There are large effects; at higher pressure polymerization will start at lower temperature. The behavior is like that of a monomolecular reaction. It is supposed that the polymerization is initiated by some controlling change in the individual molecules. Ipatieff and Tikhomirov[544] studied the displacement of antimony from solutions of its salts by hydrogen up to 150 atmos. Up to this pressure the effect is proportional to pressure; it is a first-order reaction. Ipatieff, Platonova, and Malinovskii[545] studied the displacement of arsenic from solutions of its salts by hydrogen. Up to 150 atmos. the amount of arsenic separated is proportional to pressure, and up to 250 atmos., for solutions no stronger than $1N$, the reaction is of the first order. Ipatieff, Molkentin, and Teodorovich[546] made a similar study for the displacement of bismuth. The rate of displacement varies markedly with the metal. In order to displace by hydrogen at 100 atmos. 1 percent of bismuth from a N $BiCl_3$ solution 37 years is necessary; for the similar displacement of 1 percent of antimony from N $SbCl_3$ solution, 160 years, and for 1 percent of arsenic from N $AsCl_3$ solution, 1140 years. A summarizing paper is contributed by Ipatieff and Teodorovich;[547] the difference of potential of these three metals in solution is not greater than 0.02 volt.

Tammann and Ruhenbeck[548] studied the behavior of several carbon compounds when heated to 650° at constant volume under an initial pressure of 1000 kg/cm^2. The rate of increase of pressure with temperature of a number of such compounds has a constant characteristic value up to 400° to 500°, and above this a more rapid rate due to decomposition. Brown and Souders,[549] and Brown, Souders, and Smith[550] describe high pressure equipment for a study of the properties of paraffin hydrocarbons. Leone and Vinti[551] studied the effect of pressures up to 150 atmos. on the saccharification of cellulose by H_2SO_4 both before and after boiling. There is no effect on the boiled material. In the unboiled material 30.4 percent of glucose is formed at atmospheric pressure and 35.6 percent under 150 atmos. Warren[552] has studied the effect of pressure on the pyrolysis of methane. The methane flows through a quartz tube at temperatures between 900° and 1120° at pressures up to 104 atmos. at varying rates of flow. Increase of pressure up to 10 atmos. decreases the yield of unsaturated hydrocarbons, but has little effect on the amount of hydrogen formed. At higher pressures the yield of hydrogen decreases. Hugel and Kohn[553] performed 22 experiments studying the decomposition of hexadecene at 300° and 400° at pressures up to 1000 kg/cm^2. Hugel and Friess[554] studied the hydrogenation of a few derivatives of coal tar under high pressures and temperature (presumably as in the last reference). The results were complicated; there was cracking at the higher temperatures. Conant and Peterson[555] contributed a final paper in the series on polymerization under high pressures; the two earlier papers in the series, by Bridgman and Conant and by Conant and Tongberg, were reviewed in my book. In this paper they study especially the mechanism of the reaction. They now think that the presence of oxygen is always necessary for polymerization, revising an opinion expressed in one of the earlier papers. The function of pressure in hastening the polymerization is to align the molecules into bundles so that long reaction chains are possible. They report a new substance polymerizable by pressure, cyclohexene oxide; the reaction runs very slowly. They have been unsuccessful in attempts to stabilize the polymeric aldehydes which are formed under pressure and which revert on release of pressure. The pressure range of the new experimental work was the usual 12,000 kg/cm^2.

Hugel and Kohn[556] give more detailed results on the 22 experiments referred to in the last paragraph. Several other hydrocarbons were added to the hexadecene, which was the main subject. Between 300° and 400° only polymerization occurs at pressures above 15 kg/cm^2. Above 400° cracking begins; between 400° and 450° decomposition occurs only in the vapor phase, but above 450° in the liquid phase also. Cohen and Piepenbroek[557] check the equation of Planck for the reaction constant

$$\left(\frac{\partial \log K}{\partial p}\right)_T = -\frac{\Delta V}{RT}$$

up to pressures of 1500 atmos. by measurements of the pressure effect on the e.m.f. of a cell with thallium amalgam electrodes. The experimental material is apparently the same as in the paper already referred to[477] on the effect of pressure on e.m.f.; it is simply that the calculation is cast in a different form.

Fawcett and R. O. Gibson[558] have studied 50 organic reactions up to 180° and 3000 kg/cm^2; the experimental study is preceded by a theoretical discussion of the various types of behavior that are to be expected. They find that reactions which run slowly at atmospheric pressure are accelerated by pressure; the effect of 3000 is an increase of velocity averaging from 5- to 10-fold. If the reaction does not run at all at atmospheric pressure in the absence of catalysts, it will not run at 3000 either. They find that the position of equilibrium in a tautomeric system may be shifted by pressure. In a second paper[559] the same authors studied the effect of pressure up to 3000 on the rate of formation of cetylpyridinium chloride and bromide. There is a very marked accelerating effect of pressure initially, but no effect on the final equilibrium, which was reached at atmospheric pressure in some 250 hours with a 75 percent yield. A few experiments at 6000 kg/cm^2 gave anomalous results, the yield being less than at 3000 kg/cm^2. Kassel[560] gives a theoretical discussion of unimolecular decomposition at high pressure, in which he reaches conclusions disagreeing with former conclusions of Coffin and Geddes. Starkweather[561] has studied polymerization between 20° and 74° and at pressures from 2000 to 9000 kg/cm^2. A large number of unsaturated organic compounds containing conjugated double bonds are polymerized under these conditions; they give first-order reaction constants with ΔE equal approximately 20,000 cal. Increasing pressure from 6000 to 7000 kg/cm^2 approximately doubles the rate of polymerization. Bushmakin, Frost, and Ruiskov[562] studied the effect of elevated temperatures and pressures up to 350 atmos. on the oxidation of yellow and red phosphorus, phosphorous acid, and phosphine. Wiezevich and Frolich[563] studied the oxidation by air or oxygen at pressures between 33 and 200 atmos. of several saturated hydrocarbons ranging from CH_4 to C_7H_{14} and natural gas. These were all in the gaseous phase except C_7H_{14}, which was liquid. Coffin and Geddes[564] discuss the decomposition of complex molecules at high pressures; they find that the velocity of homogeneous decomposition of gaseous paraldehyde slowly decreases as pressure increases, and suggest a possible mechanism which may apply to all first-order decompositions of complex molecules. Poulter and Frazer[565] investigated the action of H_2SO_4 on zinc up to 30,000 kg/cm^2. The velocity of attack is little affected up to 8900; above this chemical action practically stops, probably because of the formation of ice VI. An electrolytic cell having electrodes of zinc and hydrogen has its polarity reversed by a pressure sufficient to form ice VI. At 20° and 8900 atmos. the reaction $4H_2+H_2SO_4 \rightarrow H_2S+4H_2O$ runs to completion in the presence of platinized platinum. Basset and Dodé[566] studied the direct oxidation of iodine and iodides by pressure. Iodine and oxygen combine directly to form I_2O_5, but the yield is small, there being only a 2.3 percent yield in 2 hours at 325° and 1200 kg/cm^2 partial oxygen pressure (3600 total pressure). Increasing the oxygen pressure or adding platinum black did not increase the yield. KI under a partial pressure of oxygen of 1200 kg/cm^2 at 410° yields 40 percent KIO_3 in 1 hour and 90 percent in 5 to 6 hours. At higher temperature the action is more rapid, but there is more free iodine. Dodé and Basset[567] describe experiments, mostly a repetition of those just abstracted, but there is additional material on the behavior of $KClO_3$. This cannot be oxidized to $KClO_4$ by an oxygen pressure of 1200 kg/cm^2 at temperatures up to 475°; at higher temperatures rapid decomposition begins. Basset[568] has studied the synthesis of ammonia up to 4500 kg/cm^2 and at temperatures as high as 1200°C. The yield is insensitive to impurities such as H_2S and CO_2. At 850° and 4500 kg/cm^2 the yield is independent of the presence of any catalyst, and is practically total (97 percent). At 2000 kg/cm^2 at this temperature the yield is 40 percent and at 1000 only 3 percent. R. O. Gibson, Fawcett, and Perrin[569] have studied the effect of pressures up to 3000 kg/cm^2 on the reaction of sodium ethoxide and ethyl iodide in solution, and of pressures up to 8500 on pyridine and ethyl iodide. The k in the reaction equation $k=Ae^{-E/RT}$ increases with pressure, by a larger amount for a slow reaction. Both the A and the E of the equation are changed by pressure. Vollbrecht and Dittrich[570] studied the attack on two alloy steels by hydrogen and a mixture of hydrogen with H_2S between 200° and 300° by pressures up to 200 atmos. and for times extending to 20,000 hours. Hydrogen alone has a more deleterious effect; when H_2S is present a protective film of FeS is formed. Ipatieff and Freitag[571] heated $BaSO_4$ and Na_2CO_3 to 320° in an autoclave; when twice the equivalent amount of Na_2CO_3 was used there was 97 percent conversion of $BaSO_4$ to $BaCO_3$. Craft, Johnson, and Kirkpatrick[572] studied the effect of applying hydraulic pressures of 2000 p.s.i. to cement while setting. In general the compressive strength of the cement decreases with rise of temperature and increases with rise of pressure. Cement set at 180°F under a pressure of 2000 p.s.i. has a compressive strength greater by 1660 p.s.i. than when set at atmospheric pressure at the same temperature; when set at 205°F the corresponding increase of compressive strength is 3375 p.s.i.

Adams[573] has a theoretical paper on the variation with temperature and pressure of activity and related thermodynamic functions, the chief purpose of which is to get the relations into perspicuous form to permit ease of application to pressure experiments. Adams himself regards the old fashion thermodynamic potentials as the most convenient. Lewis[574] has a theoretical paper dealing chiefly with an application of thermodynamic data for gases to gas reactions of industrial interest. Komar and Ivanov[575] find that the rate of transformation of white tin into gray tin is decreased by pressures up to 160 atmos. The temperature of maximum velocity of transformation is shifted from $-33°$ at atmospheric pressure to $-38°$ at 90 atmos. Gillespie[576] discusses theoretically methods for the thermodynamic correlation of high pressure gas equilibria with the properties of the pure gases. He finds that the chief lack is thermodynamic data of the requisite accuracy for the pure gases. Williams, Perrin, and R. O. Gibson[577] extend the former work of Fawcett and Gibson to 12,000 kg/cm^2 on reactions in solutions. Organic reactions fall into three main classes. (1) Normal reactions: pressure has a small accelerating effect, falling off at the higher pressures; the increase of rate at 12,000 is of the order of fivefold. (2) "Slow" reactions: pressure has a much greater accelerating effect on these, tenfold at 5000 and 45-fold at 8500. (3) Unimolecular decompositions: the results are in agreement with those calculated by the transition state method of calculating reaction velocities. Hoffmann[578] found that a pressure of 2000 kg/cm^2 changes the color of Pb_2O to grayish blue, 3000 to gray; and at 12,000 it acquires a metallic luster, and coherent lead flakes can be removed from the surface. Pressure was without effect on Pb_3O_4. Steacie, Hatcher, and Rosenberg[579] have developed a more accurate method and have studied the decomposition of ethyl ether up to 260 atmos. and 426°. Their previous results are verified. The rate of reaction is still increasing at the highest pressures reached; the reaction is not a simple monomolecular change. Bone and Newitt[580] describe a reaction chamber for the study of reactions up to 5000 atmos. and apply it to a study of high pressure explosions in the system CO-N_2-O_2 and of the slow oxidation of hydrocarbons.

Newitt,[581] in a review article, discusses the oxidation of hydrocarbons at high pressure. Pressure exerts a well-defined effect on the combustion of aliphatic and aromatic hydrocarbons: it accelerates the rate of reaction, exerts a directive influence on the primary oxidation process, and partly determines the distribution of oxygen in the products. Newitt, Linstead, Shapiro, and Boorman[582] describe the design and construction of apparatuses to be used in a program of investigation of liquid-phase reactions up to pressures of 5000 and of 20,000 atmos. Preliminary experimental work is described on the hydrolysis of esters and the Knoevenagel reaction. Shapiro, Linstead, and Newitt,[583] in the second paper of the program just mentioned, investigated the polymerization of olefines up to 10,000 atmos. Pressure accelerates the polymerization, and also produces higher molecular weights. At higher temperatures the molecular weight of the polymer decreases. Perrin and Williams,[584] at the same laboratory as the three preceding references (Imperial Chemical Industries) investigated reactions between amines and alkyl halides in acetone solutions. The pressure range of most of the work was 3000 kg/cm², but the reaction of triethylamine and dimethylaniline in acetone solution was carried to 12,000. All of the reactions are classified as "slow" reactions under normal conditions, as described in previous communications from this same laboratory. They find that the present reactions are on the average increased tenfold in velocity by 3000 kg/cm² and 500-fold by 12,000 kg/cm². Zeise[585] contributes a theoretical paper in which he calculates from spectroscopic data the dissociation up to 100 atmos. and for temperatures between 1000° and 3000° of the following reactions: $H_2 \rightleftarrows 2H$; $O_2 \rightleftarrows 2O$; $H_2O \rightleftarrows H_2 + \frac{1}{2}O_2$; $H_2O \rightleftarrows H_2 + O$; $H_2O \rightleftarrows \frac{1}{2}H_2 + OH$; $H_2O \rightleftarrows H + OH$; $CO_2 \rightleftarrows CO + \frac{1}{2}O_2$. Wiederholt[586] studied the corrosion by mixtures of hydrogen and carbon dioxide up to pressure of 31 atmos. exerted for periods up to 3 days on polished specimens of the following metals: steel, brass, monel metal, nickel, copper, Duralumin, aluminum, lead, and zinc. Pure iron is most attacked of all the metals tried. Steels containing chromium and nickel-chromium are practically unattacked. In the case of mild steel the rapidity of attack is proportional to pressure up to 21 atmos.; beyond that the rate falls off. Waesar[587] contributes a summarizing article on apparatus and reactions at the highest pressures, dealing mostly with the work of Basset and the ammonia synthesis.

P'eng, Shapiro, Linstead, and Newitt,[588] from the laboratories of I.C.I., contribute a study of the esterification of acetic acid between 50° and 80° and up to 4000 atmos. A general discussion is given of the effect of pressure on the activation energy in the Arrhenius equation. It increases under pressure by different amounts for different substances; the largest observed increase is 40 percent for 4000 atmos. Shapiro and P'eng[589] continue from the same laboratory with a study of the effect of pressures up to 5000 atmos. on the autocondensation of cyclohexanone and its condensation with aniline; the effects observed are small. Perrin[590] from the same laboratory discusses before the Faraday Society twelve typical reactions in six different solvents at pressures up to 12,000 atmos. The pressure effect on the A and E of the rate equation ($k = Ae^{-E/RT}$) is found. The preferred classification of reactions is now presented as follows: (1) "normal" reactions, the rate of which increases under a pressure of 3000 by something of the order of 2, (2) "normal slow" reactions, whose rate increases tenfold at 3000, and (3) unimolecular reactions, whose rate decreases under pressure. Kato[591] investigated the thermal decomposition of waste rubber in the presence of heavy petroleum oil up to pressures of 200 atmos. The yield was a maximum at 180 atmos. and the product was suitable for aviation gasoline. Palfray and Sabetay[592] contribute a note on catalytic reduction at high pressure. Dintses, Korndorf, Lachinov, and Lel'chuk[593] describe the complete experimental technique for studying reactions up to 10,000 kg/cm², and study a large number of organic and inorganic reactions, particularly condensations, polymerizations, and hydrolyses. Elaborate tables are given of the results. Michel-Lévy and Wyart,[594–597] in a series of four papers running from 1938 to 1940 have studied the production of minerals by the high temperatures and pressures attained in the detonation of explosives. Powdered mixtures of various solids containing the elements from which minerals might be synthesized were placed in an explosion chamber with various detonating explosives, the quantity of which was so chosen as to give temperatures of the order of 4000° and pressures up to 12,000 kg/cm^2 at the detonation. After detonation the products were annealed for several days at pressures up to 3000 kg/cm^2 and temperatures up to 700°. Minute quantities of a great many minerals were formed, such as: zincite, willemite, graphite, quartz, cristobolite, all the minerals found in granite, anorthite, and sphalerite.

Trifonov and Toshev[598] exposed to 10,000 kg/cm^2 three different brown coals and six bituminous coals, and found marked changes in the extraction and distillation yields and other alterations. Morgan[599] reports on the synthesis under pressure of acetic acid from methanol and carbon monoxide, and of some of the higher aliphatic acids and alcohols. Raistrick, Shapiro, and Newitt,[600] from I.C.I. studied the polymerization of cyclopentadiene and α-dicyclopentadiene between 0° and 40° up to 5000 atmos. Three stages of the process are distinguished: (1) dimerization, (2) production of higher polymers, (3) an explosive decomposition, occurring within definite pressure limits at each temperature, accompanied by the formation of a carbonaceous residue and much gas. The constants of the bimolecular reaction were determined. The details of the explosive process are studied in the next paper of the series. Stupochenko[601] discusses theoretically a possible mechanism for the influence of pressure on chain gas reactions; the "crowding effect" should be detectable at high pressures, low rates of reaction, and low rates of diffusion. Muraour and Basset[602] exposed various solid explosives to gas pressures up to 12,000 kg/cm^2 exerted by nitrogen, argon, or hydrogen, and found essential modifications in the manner of decomposition, which tends to run without the accompaniment of mechanical effects. Nitroglycerine and picric acid burn without detonation under these conditions.

Holtermann[603] studied the oxidation by oxygen gas at pressures up to 300 atmos. of strontium, barium, lead, manganese, and cobalt. Hieber and Lagally[604] studied various metal carbonyls up to 760 atmos. Lachinov[605] discusses in detail industrial applications of high pressure to fuel gasification, and the manufacture of alcohols, aldehydes, ketones, acids, metal carbonyls, urea, and others. Ewell[606] has a theoretical paper on the calculation of chemical equilibria in gases at high pressures. Andreev[607] investigated the combustion of explosives under pressures up to a maximum of 700 kg/cm^2; pressure was prevented from exceeding this maximum by the fracture of lead disks or the bursting of tubes. Leipunskii and Reinov[608] describe micro-methods for studying reactions up to 450° and 12,000 atmos. Shatenshtein[609] describes an apparatus of glass and CrNi steel used at the Karpov Institute, Moscow, in the investigation of the chemical properties of solutions and reactions in liquified gases under pressure. Matui and Yasuda[610] investigate the oxidation of methane up to pressures of 100 atmos.

Adams[611] contributes from the Geophysical Laboratory a review article in which he summarizes the theory and cites experimental results up to several thousand kg/cm^2 and to above 1000°. Applications to refractories, petrology, and vulcanology are discussed. Gibson and Loeffler,[612] from the same laboratory, investigate the effect of pressure up to 1200 atmos. on acidity in water solutions. The dissociation constants of weak bases and weak acids increase with rise of pressure. Cresol red and bromophenol blue were used as indicators; the effect of pressure on the dissociation constants of the indicators was not determined. The results agree with those of Brander obtained by a conductivity method. Owen and Brinkley[613] contribute a theoretical paper on the effect of pressure on ionic equilibria in pure water and salt solutions based on the experimental work at the Geophysical Laboratory up to 1000 bars. The effect of pressure on the ionization of pure water is calculated. Gillespie[614] has a theoretical review article on thermodynamic methods of calculating pressure effects on gaseous reactions from the equation of state. The basic need is still better experimental data. Mention is made of an unpublished equation of state of Keyes that should permit improvement as far as this application is concerned. Trifonov and Phillipov[615] exposed six Bulgarian brown coals to 10,000 kg/cm^2 with the production of definite changes. The effect depends on the duration of the pressure. In general, pressure has the same effect on the distillation products as an increase in the temperature of distillation. Krichevskii and Bolshakov[616] studied the heterogeneous equilibrium in the ammonia-nitrogen system between 90° and 125° up to 5600 atmos. The critical curve has a temperature minimum between 85° and 90°, and there is a barotropic phenomenon. Kazarnovskii and Kharapet'yants[617] calculate theoretically the heat of formation of ammonia between 250° and 500° and up to 7000 atmos. by an improved method which they state indicates errors in previous values in the literature. At the highest temperature and pressure the heat of formation is about 20 percent greater than at atmospheric pressure.

Fuchs[618] calculates theoretically the effect of pressure on the equilibrium constant of ammonia, basing his calculations on the second virial coefficient. It is stated that the dipole character of NH_3 should not seriously affect the calculation. Good agreement is obtained with experiment up to 300 atmos., where divergence begins, attributed to an increase in the virial coefficients. Volarovich and Leont'eva[619] have studied the effect of pressure up to 500 kg/cm^2 on the linear rate of crystallization of melts containing 73.3 percent SiO_2 and 26.7 percent Na_2O. The rate of crystallization is increased eightfold by this pressure, and the temperature corresponding to the maximum rate of linear crystallization is changed from 260° to 740°. Dickey[620] gives a summarizing article on the use of pressure equipment in the synthesis of organic chemicals and lists 49 different reactions which can be materially facilitated by pressures in the range between 5 and 400 atmos.

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BIOLOGICAL EFFECTS OF PRESSURE

This field of pressure investigation is the one in which there has been the greatest proportional increase of activity; at the time of my book there were only a few references, whereas now there are some 45 new ones. Most of the work on biological effects has been done in four main centers: Basset and associates at Paris, Dow and associates at Pennsylvania State College, Brown, Marsland and associates mostly from Princeton, and Ebbecke, Haubring, and associates in Germany.

Basset and Macheboeuf[621] found that bacillus prodigiosus, staphylococcus aureus, and the bacillus of Koch are killed by 6000 kg/cm^2. The spores of bacillus subtilis are not destroyed by exposure to 17,500 kg/cm^2 for 45 minutes. Various diastases are sensitive to pressure; their activity is reduced approximately by one-third by 9000 kg/cm^2, and is completely destroyed by 15,000. The toxin of tetanus is destroyed by 13,500 kg/cm^2; the toxin of diphtheria retains 1 percent of its activity after 45 minutes under 17,500 kg/cm^2. Cobra venom and tuberculin are not damaged by exposure to 17,500 kg/cm^2 for 45 minutes. Basset and Macheboeuf[622] in a following paper found that tetanus toxin inactivated by pressure does not develop an anatoxin. The antitoxine of horse serum immunized against tetanus maintains a marked antitoxic activity after exposure to 13,500 kg/cm^2 for 45 minutes. Basset, Wollman, Macheboeuf, and Bardach[623] found that various bacteriophages are much more sensitive to pressure than the corresponding bacteria, a pressure of 3000 kg/cm^2 usually being sufficient to destroy the activity of the bacteriophage. In the presence of the corresponding bacteria, the resistance of the bacteriophage is enhanced. Basset, Lisbonne, and Macheboeuf[624] found that pressure entirely destroys the activity by acidification of pancreatic juice from the dog, but does not destroy the prokinase or the activity effect with calcium. Exposures were to 15,000 kg/cm^2 for 45 minutes. The pancreatic lipase is entirely destroyed under these conditions; the activity of the amylase was reduced to $\frac{2}{3}$ and of the trypsinogen to $\frac{1}{2}$. Basset and Macheboeuf[625] have summarized the results mentioned thus far in German. Basset, Macheboeuf, and Sandor[626] find that whole blood serum is coagulated by exposure to 6000 kg/cm^2 for 30 minutes at 18°C. The pure globulins, englobulins, and pseudoglobulins are coagulated by 15,000 kg/cm^2. Coagulation seems to be accompanied by no detectible chemical change. Macheboeuf, Basset, and Levy[627] study the action of pressure on diastases and toxins, adding to the variables previously considered a more detailed examination of the effect of varying the time of exposure and of changing the *p*H of the solution. Basset, Macheboeuf, and Perez[628] find that the anaphylactic specificity of serum is completely destroyed by pressures greater than 4000, and that the serum so treated has acquired a new antigenic specificity. Basset, Eugene Wollman, Elisabeth Wollman, and Macheboeuf[629] find that the spores of *Bacterium Subtilis*, contaminated by the corresponding bacteriophage, resist exposure to 13,500, whereas the bacteriophage, mixed with the simple culture and not with the spores, is completely inactivated by 7500. The bacteriophage of *Bacterium Megatherium* is inactivated by 6500; the lysogen from cultures of the spores of the same bacterium resists 9500. Basset, Wollman, Macheboeuf, and Bardach[630] find that the active principle of a number of tumors is highly sensitive, being completely inactivated by exposure to 1800 kg/cm^2. The active principle of the sarcoma of Rous has a resistivity of the same order as that of the bacteriophages. Basset, Nicolau, and Macheboeuf[631] experimented with five different viruses; they all resist 2000 kg/cm^2 and are inactivated by pressures varying from 3000 to 7000 kg/cm^2. Lépine, Basset, and Macheboeuf find that the virus of the avian pest[632] is destroyed by 30 minutes exposure to 4000 kg/cm^2; the virus thus inactivated has a weak immunizing power.

On the basis of the different responses to pressure it is emphasized that a distinction must be maintained between the nature of the viruses and the diastases. Macheboeuf and Basset[633] contribute a paper summarizing their biological work to date. Wollman, Macheboeuf, Bardach, and Basset[634] find that the principle of the papilloma of Shope resists pressures up to 4000 and is destroyed by 6000 kg/cm². The principle of the carcinoma of Brown-Pearce behaves like that of certain mouse tumors previously investigated; it resists 1000 but is destroyed by 1800 kg/cm²; these are the most sensitive substances yet found. Basset, Macheboeuf, and Wollman[635] summarize extensively all their work for the Institut Pasteur. This includes: description of apparatus and technique, action of pressure on both spored and non-spored bacteria, on diastases and on toxins, researches on immunity, on the ultra virus and filterable viruses, the immunizing power of viruses inactivated by pressure, and studies on bacteriophage and neoplasms. Basset, Gratia, Macheboeuf, and Manil[636] describe in an American journal experiments which show that there is a perceptible effect of pressures as low as 2000 on the tobacco virus; at 6000 kg/cm² it retains 58 percent of its virulence, and at 8000 it has lost all but 2 percent.

One general comment by way of warning seems to me to be justified with regard to all the work of Basset and his collaborators which will complicate the interpretation of any results obtained at pressures higher than 8000 kg/cm². The fact that water freezes to ice VI above this pressure was apparently never recognized nor commented on. Recent unpublished experiments by Dr. W. Boyd and myself, in which we approximated Basset's conditions, indicate not only that the water does freeze out of its biological solutions under such pressures, that is, that the presence of the biological material is not effective in retaining the liquid phase by subcooling, but also that the transition from liquid to ice is accompanied by discontinuities in the biological effects.

At Pennsylvania State College, River, Popp, and Dow[637] found that pressures of the order of several thousand atmos. hasten and improve the germination of those seeds having hard impermeable coats, but are not effective with those seeds having persistently dormant embryos. The effects are mechanical, caused by the entry of water or oxygen into the seed, hastening the physiological processes. Dow[638] describes the effect of pressures between 3000 and 7000 atmos. on various proteins. Hemoglobin, pepsin, renin, and insulin in aqueous solution are denaturized. Other effects are produced in urine, blood, and milk. Milk is sterilized by killing the lacto bacillus. Pressure disintegrates the erythrocytes in blood and coagulates it to a solid. Dow and Matthews[639] apply pressures up to 13,000 kg/cm². They get complete coagulation of blood and destruction of all erythrocytes and leucocytes by applications of 6 hours at 3500 or 3.5 hours at 13,000 kg/cm². The proteins of the red cells are more easily coagulated than the proteins of the plasma. They do not believe that the effects are mechanical in nature, that is, caused by rupture of the cell walls, for example, but are chemical. Dow,[640] in a popular article, described some of the details of the cooperation between the Physics Department and the Biology Department in these biological investigations. Dow, Matthews, and Thorp[641] find that the physiological activity of insulin is not impaired by prolonged exposure to 10,000 kg/cm², although it is coagulated. Matthews, Dow, and Anderson[642] find that the activity of renin and pepsin decreases with rising pressure and completely vanishes between 5000 and 6000 kg/cm². The effect is strongly dependent on temperature. There is no change in the amino-nitrogen content up to 10,000, indicating that no hydrolysis is caused by pressure. Both substances are heavily coagulated by 10,000; the product produced by pressure is the same as that produced by temperature. Since the energy relations are quite different on heating and exposing to pressure, the energy changes alone are not responsible for the effects. Grant, Dow, and Franks[643] dissolved 20 g of Merck powdered egg albumen in 500 cm³ of water and exposed to pressures from 1000 to 7500 kg/cm². Some coagulation was produced by all pressures, the amount being greater the higher the pressure. Lauffler and Dow[644] found that the tobacco virus is almost completely inactivated by 7500 kg/cm². A coagulum is also formed, which is a maximum in amount between 6000 and 8000. The coagulation at 7500 kg/cm² seems to follow the course of a first-order reaction. Inactivation at high pressure proceeds much more rapidly than coagulation, and the mechanisms are probably different.

The biological work associated with the names of Brown and Marsland begins with an isolated paper by Brown in 1934[645] on the effect of rapid changes in hydrostatic pressure on the contraction of skeletal muscle. Marsland's[646] first paper was in 1938 on the effects of pressure on cell division in arbacia eggs. Pressures between 1 and 333 atmos. retard the rate of intrusion of the cleavage furrow toward the axis of the spindle. Up to 450 atmos. furrows already formed recede. The effect is reversible if the cleavage is not suppressed for more than 15 minutes. There seems to be a close connection with the effect of pressure on viscosity. Marsland[647] found that under pressures up to 600 atmos. a jelly which is formed in the cell under normal circumstances undergoes progressively increasing liquefaction with increasing pressure. Marsland[648] found that up to 600 atmos. the rate of protoplasmic streaming in *Elodea canadensis* regularly diminishes with increasing pressure. Brown, Johnson, and Marsland[649] studied the effects of pressure up to 500 kg/cm^2 on the luminescence of three strains of bacteria. These bacteria have temperatures of optimum luminescence varying from 21° to 32°. Below the optimum temperature pressure decreases luminescence and above it increases it. The pressures were applied for less than 3 minutes, and the effects were strictly reversible. Luminescence is supposed to be caused by two different mechanisms acting in opposite directions; the optimum temperature is where the rates balance. The effect of pressure is explained by a slowing of both reactions, which are supposed to run normally with increase of volume. Johnson, Brown, and Marsland[650] in a following paper expand their conception of the mechanism responsible for the pressure effects on luminescence, which they think involve an enzyme equilibrium shifted by pressure. Johnson, Eyring, and Williams[651] discuss the nature of the enzyme inhibitions in bacterial luminescence produced by sulfanilamide and urethane and incidentally discuss the pressure effect. Johnson, Brown, and Marsland[652] find that the luminescence of photobacterium phosphoreum, which under normal conditions is inhibited by the action of certain narcotics, is restored by a pressure of 500 kg/cm^2. In these cases pressure alone without the narcotic has little effect on luminescence. On the other hand, there are certain narcotics whose inhibiting effect is not changed by pressure. The explanation is in terms of a pressure sensitive equilibrium between certain enzymes. Marsland and Brown[653] describe a pressure bomb with windows through which the time of fall of a ball in various protoplasmic gels may be observed. Myosin and methyl cellulose display an increasing degree of solution with increasing pressure; gelatin becomes progressively stiffer.

Ebbecke[654] found that Paramecia may be exposed to 800 atmos. without undergoing irreversible injury. Ebbecke and Hasenbring[655] applied pressure to various marine organisms and found diverse excitatory and paralytic phenomena. Haubrich[656] investigated the effect of time of exposure, temperature, and season of the year on the irreversible injury produced by pressure in the erythrocytes of the frog. Deuticke and Ebbecke[657] found that the contraction which is produced in muscle by the application of hydrostatic pressures up to 500 atmos. is accompanied by the same chemical changes as those which accompany normal muscular activity. Ebbecke and Haubrich[658] found that if the capacity of blood to coagulate has been lowered by the addition of certain substances, the capacity to coagulate may be totally suppressed by the application of from 200 to 800 atmos. Haubrich[659] found that up to pressures of 800 atmos. the inhibiting effects of pressure on retraction and on coagulation run parallel to each other. Ebbecke[660] in a paper dealing mostly with other topics discusses the mechanism of the effect of pressure on coagulation; pressure is supposed to exert a stabilizing effect on the coagulating system. Ebbecke and Zipf[661] find that the coagulation of blood compressed to 1000 or 2000 atmos. is delayed or prevented. On reduction of pressure the resulting clot is less rigid than normal and does not retract. Fibrinogen solutions show the same effect.

Turning now to the scattered papers on biological effects, Wilson and Poulter in 1929[662] published experiments in an inaccessible journal which did not get into my book. They found that pressures up to 12,000 atmos. are necessary to kill some bacteria; as the complexity of the bacterium increases the requisite pressure decreases. Hydra and planaria will survive 1300 atmos. The effect of pressure is thought to be to precipitate some of the colloidal constituents. The effect of pressure on the precipitation of other colloids was studied. These were: sulfur, silver, gold, ferric hydroxide, molybdenum blue, and prussian blue. Colloidal ferric hydroxide is completely precipitated by 100 atmos., while molybdenum blue is only slightly affected by 17,000. Lloyd and Moran[663] studied isoelectric gels up to 3200 atmos. Pure water is forced out of the gel by pressure; the concentration of the residual gel is a function of pressure. A thermodynamic equation of Katz for swelling is applied to the results. Moran[664] investigated the effect of pressure up to 2500 atmos. on the composition of various gelatin-NaCl gels, containing up to 15 percent gelatin and from 1 to 15 percent NaCl. The amount of NaCl remaining in the gel after exposure to pressure is a linear function of the original concentration. Increasing pressure reduces the amount of water remaining in the gel. Cattell[665] contributed a review article on the known physiological effects of pressure. Grundfest[666] found that the irritability of frog nerve increases up to 400 atmos., and then decreases to 700. Benthaus[667] found that the growth of tissue cultures is inhibited at pressures above 1000 atmos.; the growth of fibroblasts in cultures of chicken embryo heart is entirely suspended above 1850 atmos. Deuticke and Harren[668] studied enzymic reactions in muscle up to 800 atmos. The metabolic processes of muscle are accelerated, but injury to certain enzymes is indicated. The effects depend on the duration of the pressure. Glucolysis in blood is inhibited by 2000 but unaffected by 800 atmos. Deuticke and Hasenbring[669] studied the chemical processes in the isotonic and isometric contraction of muscle produced by pressures up to 500 atmos. Certain pressure effects reverse sign with the passage of time. Leipunskii[670] studied the coagulation of gelatin; the transition from sol to gel is accelerated by pressure. Viscosity measurements indicated that at 2000 atmos. the initial coagulation is increased from 2- to 2.5-fold. Kitching and Moser[671] found that exposure to 340 atmos. stopped all movement in ameboid eggs; there was complete recovery on release of pressure. No permanent bad effects were produced by exposures of several minutes to pressures as high as 680 atmos. Nakasima and Ikeda[672] studied the hydrolysis of soybean protein, caseinogen and gelatin at temperatures between 140° and 195° and pressures between 38 and 185 atmos. for times up to 4 to 5 hours. The complicated products were analyzed; the abstract does not indicate that unusual products were formed. Pease and Regnery[673] exposed the salivary chromosomes of drosophila to hydrostatic pressures of 1000 atmos. and could find no obvious changes, either of shape or of chromosome binding. Benthaus[674] found that the hydrolysis of starch by various diastases is accelerated by 1500 atmos. The activity of pancreatic lipase, proteinase, and pepsin was diminished by this pressure, but the activity returned to normal on release of pressure.

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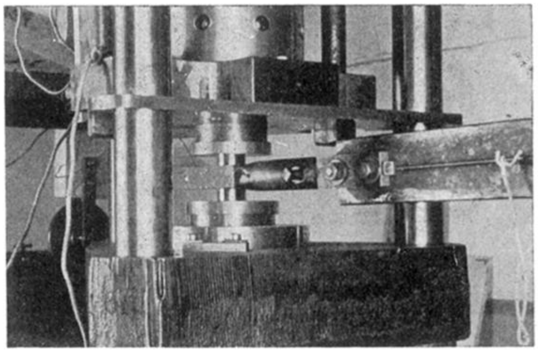

FIG. 6. Close-up of the shearing apparatus mounted in the hydraulic press together with the handle for rotation.

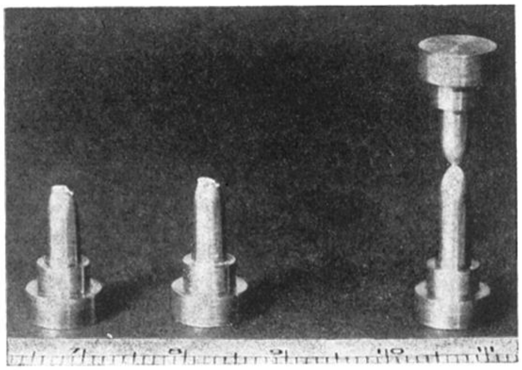

FIG. 9. Illustrating the effect of hydrostatic pressure on ductility in tension. On the left, a tension specimen broken at atmospheric pressure with a reduction of area of approximately 60 percent. On the right a specimen of the same steel pulled under a pressure of 25,000 kg/cm² to a very much greater reduction of area without fracture.