THE PHYSICS OF HIGH PRESSURE

BY

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PREFACE

THIS book is intended primarily as a summary of work in which I have been personally engaged in the last twenty-five years in the field of high pressure. It is also intended, however, that the book shall give a fairly complete survey of all the important work in this field; to this end the first chapter is devoted exclusively to historical matters, a historical introduction giving the previous state of the art is appended to many of the later chapters, and in the final chapter on miscellanies the work of others on a number of topics which I have not yet had a chance to touch is discussed in some detail. The references and the index will also facilitate a comprehensive grasp of the whole field.

There are comparatively few previous books in this field; of these the book of Cohen and Schut, *Piezochemie Kondensierter Systeme* (Akademische Verlagsgesellschaft, Leipzig, 1919), is especially to be mentioned. This was written in 1914 and published in 1919. It aims to give a complete summary of work in the field of high-pressure physics and chemistry up to 1914, with some of the work of the period 1914–1919 treated in appendices. So much has been done since that time that no apology is necessary for a new book. In addition to this principal source of information in book form, the second part of Cohen's Cornell lectures, *Physico-Chemical Metamorphosis and Problems in Piezo-Chemistry* (M'Graw-Hill Book Co., New York, 1926), deals with certain aspects of his pressure work at Utrecht, and is a valuable source of information. Practically the only other work is that of Tammann, *Kristallisieren und Schmelzen* (Barth, Leipzig, 1903), republished with some changes under the title *Aggregatszustände* (Voss, Leipzig, 1922). This deals with the special topics indicated by the titles, and is concerned mostly with Tammann's own work.

The reader who is interested in the details of much of the early work should consult these books. Finally, there is my own recent article in the *Handbuch der Experimental Physik*, vol. 8^2, dealing with a limited aspect of the subject—namely, the effect of high pressure on various thermal properties of matter. The information contained in that article is, of necessity, similar to that in the corresponding sections of this book; the arrangement and general method of treatment are, however, different.

The titles of my own papers are collected in an appendix; in the body of the book reference is made to these by number, prefixed by a B. References to other work are numbered consecutively through each chapter, and are collected at the end of the chapter. At the end of the first chapter all these references to other work are given by title, but this was less necessary in the later chapters where the subject is more definitely indicated, and there the reference is to the periodical only. Many of these later references are duplicates of those given in the first chapter, which may therefore often be consulted for the titles.

It has not been possible in a book of this size to reproduce all the numerical data, but the attempt has been made in the various tables scattered through the text to give enough data to fix the broad features of the effects of pressure and temperature on the more important substances, particularly the elements. I believe that the data given here will be found sufficient for most theoretical use for which we are at present prepared in this field. For finer details and for many of the more complex substances the original papers must be consulted. Many of my own detailed results have been published in the *Proceedings of the American Academy of Arts and Sciences*, a somewhat inaccessible publication. It may be that some libraries which do not have the *Proceedings* may have the *Contributions* from the Jefferson Physical Laboratory, in which all my papers are collected.

PREFACE TO THE REPRINT OF 1949

The book has now been out of print for several years, during which there has been a demand for it deemed sufficient to justify this reprinting by the photographic process. A few modifications have been made, such as are possible within the mechanical limitations of the method. These consist mostly in the correction of minor misprints. The most serious modification has been the complete replacement of pages 177 through to the middle of page 183 with new material. The original discussion in those pages was concerned with the five alkali metals and was based to a great extent on calculations in which there was an error of sign, so that the picture there presented, particularly for the behaviour of potassium, was completely misleading. The material substituted for the erroneous material consists of a discussion of the volume relations of the five alkali metals, based on more recent measurements, up to 100,000 kg./cm.^{2}. This destroys the continuity of presentation, but seemed necessary in view of the mechanical limitations of the reproduction.

In addition to the reproduction of the original book, this reprinting contains a supplement devoted to recent work in the high-pressure field. In this supplement only a brief description will be attempted of some of the work done since the original publication in 1931. Limitations of space do not permit a completeness in covering this interval of time, short as it is, at all comparable to the completeness with which the original book covered the entire period of high-pressure investigation up to that time. Activity in the high-pressure field is rapidly accelerating, and the total number of titles between 1931 and 1948 is greater than for the entire previous history. Furthermore, completeness in the supplement is not as necessary as it might be otherwise, for I have published in *Reviews of Modern Physics* in January, 1946, an article entitled 'Recent Work in the Field of High Pressures' summarising the work since 1931. This article was almost entirely descriptive in character and did not attempt to reproduce numerical data. The bibliography given with that article was, however, fairly complete, reproducing the full titles of all the papers, so that the numerical data should be recoverable with the expenditure of some effort on the part of the reader.

The main emphasis of the supplement will be the same as that of the original book—namely, on my own work—and the principal object of the supplement will be to bring the picture of my own work as up to date as possible within the limitations of available space. To this end the appendix of the first printing, containing the titles of my own papers, is now revised by extension to include all the titles up to date, beginning with No. 74. The method of reference to these papers in the body of the text will be the same as before—namely, the number of the paper prefixed by a B.

A limited objective for the supplement is the more justifiable in view of the existence of the *Reviews* article. Furthermore, as in the case of the first printing, this supplement will contain an introductory section in which a very brief picture is presented of the total activity in the high-pressure field since 1931. There is obviously room here for a completely new book, covering the entire field of high-pressure physics and bringing it up to date; but this is a more ambitious undertaking than I am in a position at present to attempt.

P.W.B.

June, 1948.

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SUPPLEMENT

CHAPTER I

HISTORICAL INTRODUCTION

In this historical introduction only those experiments are to be especially considered which are the natural forerunners of experiments to high pressures. Many experiments dealing with pressure effects do not need the emphasis given by high pressures, as, for example, those dealing with the critical point liquid-vapour; such experiments will be considered only briefly if at all.

Perhaps the earliest experiment on our theme was the celebrated attempt of the Florentine Academy to find whether water is compressible. Water was sealed into a sphere of lead, which was then flattened between the jaws of a press until the water exuded through the lead walls. A measurement of the distortion of the lead showed no measurable loss of volume of the cavity containing the water. Apparently the tinsmith who soldered together the lead hemispheres was as confident of the integrity of his work as are present-day smiths, for the experiment was interpreted as meaning that the water had been forced through the pores of the homogeneous lead, and the conclusion was drawn that water must be incompressible, because it suffered no measurable loss of volume under a pressure so tremendous as to force it through the pores of solid lead. In view, however, of the very low strength of lead, it is improbable that the pressure in this experiment was more than a small fraction of 100 kg./cm.^{2}, so that the resulting change of volume would have been much less than 1 per cent., evidently too small to detect with such crude methods of measurement.

The next experiments take us to the years 1762 and 1764, when Canton[1] published experiments in the *Transactions of the Royal Society* to prove that water is compressible, often paradoxically misquoted because of a misprint in the index as experiments to prove that water is incompressible. Canton placed his liquids in a thermometer-like arrangement with a large bulb and fine capillary, anticipating the later piezometers, and with the great magnification obtained in this way was able to produce measurable changes of volume in water and other liquids with the small changes of pressure realisable under the receiver of an air pump. The phenomena of volume changes in liquids remained the principal object of high-pressure investigations for a long time, the era which was principally concerned with this theme culminating perhaps with the classical paper of Amagat in 1893.

The next name is that of Perkins,[2] an ingenious Yankee, who made his first experiments in America, and then later, after the example of his illustrious predecessor Rumford, emigrated to England, where he very much extended his original experiments. Perkins must have been a mechanical genius, for his experiments were cast in a mould heroic for those days. His first experiments were made to a pressure of 100 kg./cm.^{2}, using a cannon as the containing vessel. His pressure measurements were checked by sinking the apparatus in the sea to known depths, this being the first use of this method of producing high pressures. Later he reached pressures of 2000 kg./cm.^{2}, an enormous extension of range, and a pressure that was not again reached in accurate experiments until Amagat. His apparatus was so accurately made that no soft packing was necessary on the plunger with which pressure was produced. His pressures were measured with a sort of safety-valve arrangement, the precursor of the free piston gauge; a number of his other devices were later re-invented. He observed the decrease of compressibility of water with increasing pressure, but his absolute values of compressibility were four times too small. He also observed the raising of the melting-point of acetic acid with pressure, a phenomenon forgotten until the thermodynamic discussions of the Thomsons, and not even then connected with the name of Perkins

Following Perkins, one branch of pressure investigation was a long series of experiments concerned chiefly with the attempt to get consistent values for the compressibilities of liquids. There was nothing noteworthy about these experiments from the high-pressure point of view, the pressures often being of the low range obtainable in the receivers of air pumps, and the joints often being made with sealing-wax. The crucial point in all these experiments was to properly correct for the distortion of the containing vessel, which was a very appreciable fraction of the whole effect. All the early attempts to correct for the distortion of the containing vessel were indirect, based on calculations from elastic theory, using data obtained from deformations under stresses other than hydrostatic pressure. In those days when elastic theory was not well understood, there was much disagreement and serious errors were made even by men as skilful as Jamin. The principal names associated with this series of experiments are: Oersted,[3] 1823 and 1828; Colladon and Sturm,[4] 1838; Aimé,[5] 1843, who followed Perkins's scheme of using the ocean as a source of pressure, but who got very bad numerical results; Grassi,[6] 1851; Jamin, Amaury, and Descamps,[7] 1868–69; and Dupré and Page,[8] 1868.

The period of fifty years from 1819, the year of the first paper of Perkins, to 1869, the year of the first paper of Amagat, constitutes a self-contained period in high-pressure history, in which a good deal of the ground was mapped out, but few final or even good numerical results were obtained. Besides the papers mentioned as being concerned chiefly with the compressibility of liquids, the following also belong in this period. In 1833 Parrot and Lenz [9] in St. Petersburg observed several miscellaneous pressure effects to 100 kg./cm.^{2}; they showed that glass is compressible, checked Boyle's law for air, and measured pressure for the first time with a free piston gauge. Natterer [10] published three papers in 1850, 1851, and 1854, dealing with the attempted liquefaction of gases by high pressures. Being unable to obtain any apparatus capable of standing the desired pressures without leak, he was forced to become his own mechanic, and made apparatus capable of withstanding 3600 kg./cm.^{2}. He introduced several tricks of technique, among others that of making a tight joint with a hardened cone forced against a right-angled edge, which still is frequently used. With this apparatus he was unable to liquefy N_2, CO, H_2, air, and illuminating gas at ordinary temperatures by pressures up to 3600 kg./cm.^{2}, and he drew the conclusion that it was impossible to liquefy these gases by any pressure at this temperature. He attempted the liquefaction at $-80°$ C., but here his apparatus leaked because of the freezing of his oil. He made approximate measurements of the volume to these pressures, and observed the very great departures from Boyle's law. In 1857 and 1858 Jamin [11] observed with his interferometer the change of index of refraction of water at a few atmospheres, probably the first experiment on optical properties under pressure. Wartmann in 1859 [12] observed the change of electrical resistance of metals under pressure. These experiments were very crude, the metal was imbedded in gutta-percha, which was squeezed between the jaws of a press. The pressure, which could have been only very roughly hydrostatic, was estimated to be 400 kg./cm.^{2}. Joule in 1859 [12a] measured quantitatively the adiabatic temperature changes accompanying the sudden application of about 25 kg./cm.^{2} to water and sperm-oil, and obtained agreement with the theoretical values within about 5 per cent. The effect had been previously sought unsuccessfully by Regnault.

Andrews [13] in 1861 discovered the critical phenomena in gases, and immediately wide attention was attracted to this field. Although we have perhaps arbitrarily refused to consider these phenomena as part of our subject, nevertheless the work of Andrews had an important effect on high-pressure work proper. The pressures which he had to reach were several hundred kg., and were therefore much higher than the ordinary run of pressures at which the compressibilities of liquids had been measured, although low compared with the pressures reached by Perkins and Natterer, so that the technique which Andrews developed for reaching his pressures reacted on the whole high-pressure technique. Furthermore, the perspective opened by the discovery of critical phenomena embraced subjects proper to our range, such as the behaviour of gases at pressures much higher than the critical pressures, and the impetus given by the discoveries of Andrews lasted for a number of years.

The next important period is of nearly twenty-five years, terminated by the classical paper of Amagat in 1893 on the compressibility of gases and liquids over a pressure range of 3000 kg./cm.^{2} and a temperature range of 200°. This period is dominated by two Frenchmen; in the early part of the period Cailletet,[14] and, later, pre-eminently Amagat.[15] The direct inspiration of this work was the discovery of Andrews. Cailletet was mostly interested in the liquefaction of gases, although his measurements included also the compressibility of liquids. He considerably extended the pressure range of Andrews, up to something of the order of 1000 kg./cm.^{2}, and devised a convenient pump for reaching these pressures, which is still manufactured in nearly its original form and which still goes by his name. Cailletet also played a large part in devising accurate methods for measuring these pressures, including the use of compressed air manometers and an anticipatory form of the free piston gauge of Amagat, but his chief reliance was on long mercury columns in open steel tubes, with which he reached 300 or 400 kg./cm.^{2}.

The first paper of Amagat, in 1869, was on the departure of gases from Boyle's law; his papers continued with ever-increasing scope to the number of about thirty, until they reached their climax in the 1893 paper, the subject of which has been indicated above, and which is an epitome of nearly all his work. Amagat developed a special packing technique by which he was able consistently to reach pressures of 3000 kg./cm.^{2} or more. He devised special methods of measuring compressibility, including an arrangement utilising glass windows up to 1000 kg., and an arrangement with a series of electric contacts, adapted from Tait, to 3000 kg./cm.^{2}. He devised methods for measuring high pressures, improving the open air manometer, and for the maximum pressures devised his celebrated free piston gauge with large and small pistons. The difficult question of the proper method of correcting for the distortion of the containing vessel became finally understood from the theoretical side in this period, and Amagat took an experimental step which might have led to the practical resolution of this question as well, although he never carried the work through.

Amagat's experimental work came to a nearly abrupt stop in 1893, there being only one later paper dealing with the melting of ice when the pressure to which it has been exposed is released, and from this date on he contented himself with theoretical calculations and speculations on the large amount of experimental material that he had collected.

The period of Cailletet and Amagat was one of intense activity by other experimenters also, and there are a great many titles in this period. Regnault [16] published one of his latest papers in 1871 on a form of gas manometer to measure high pressures, seeing that the subject of high pressures was one of growing importance. Mascart [17] in 1874 had two papers on the index of refraction of compressed water, and in 1877 one on the index of compressed gases. Buchanan [18] in 1880 made the first experiments capable of giving the linear compressibility of a solid, without using any of the equations of elasticity, by observing with microscopes through a heavy glass tube the change of length of a rod of metal within the tube exposed to hydrostatic pressure. His numerical values were not good, probably due to irregular refraction effects in the glass. In 1880 Spring [19] published the first of a series of experiments dealing in general with cohesion effects and chemical reactions when dry powders of various solids were subjected to high pressure. Spring did not have the problem of leak of the transmitting liquid to trouble him, and so was able to reach pressures materially higher than previous observers, up to 6000 or 7000 kg. There has been considerable controversy about the results of Spring, many of which were highly spectacular, and it now seems certain that many of his results were not due to pressure alone, but involve in addition the rubbing motion of one particle on another with intense shearing stress. In 1880 Dewar [20] observed the lowering of the freezing point of ice by pressure up to 700 kg./cm.^{2}. In 1881 Tait [21] published a paper on the pressure errors of the thermometers of the *Challenger*. The temperature of the ocean at various depths was measured on this famous expedition with mercury-in-glass thermometers exposed directly to the action of the sea water. It was obvious enough that under the great pressure in the ocean errors were to be expected in such thermometer readings, and for a number of years after the return of the expedition Tait was occupied with reproducing in the laboratory the conditions met in the depths of the sea. His pressure range was about 600 kg./cm.^{2}. He measured the compressibility of pure water, sea water, and a number of solutions. He proposed that the pressure effect on the exterior of a thermometer should be used as a method of measuring pressure, and in a number of subsequent investigations the so-called Tait gauge was used, in which pressure was indicated by the change of internal volume of a cylinder exposed to external hydrostatic pressure.

In 1881 Roentgen and Schneider [22] determined the compressibility of dilute solutions and of solid NaCl, and followed this in 1886 with a paper in which a connection was sought between the compressibility and the surface tension of a number of liquids. Chwolson [23] in 1881 observed for apparently the first time the decrease of resistance of a metal when exposed to a truly hydrostatic pressure, the magnitude of which was only 60 kg./cm.^{2}. He attempted to avoid the errors arising from the temperature effects of compression by operating at the maximum density point of water. He also compared the change of resistance produced by hydrostatic pressure with the change to be expected from the change of dimensions, and showed that there is a specific pressure effect. Marshall and others [24] in 1882 observed the depression of the maximum density point of water with pressure. In 1883 Pagliani and Vicentini,[25] and Pagliani and Palazzo [26] determined the compressibility of a number of new liquids in a small range of pressure. Quincke [27] studied the compressibility and the change of index of refraction of a number of liquids, Chappuis and Rivière [28] measured the index of refraction of gases under pressure, and Tomlinson [29] published a most elaborate account of the effects of all kinds of mechanical stress on a wide variety of physical properties, including a few measurements of liquid compressibility and an unsuccessful attempt to detect an effect of hydrostatic pressure on magnetic permeability. In 1885 Creelman and Crockett [30] extended Joule's quantitative study of the changes of temperature accompanying an adiabatic application or release of pressure to several hundred kg./cm.^{2} and a miscellaneous collection of solids and liquids. There have been comparatively few repetitions of the experiments of Creelman and Crockett; it would appear that there may be useful possibilities here, particularly as a more direct method than any yet used for the determination of specific heats at high pressures. In 1888 Parsons [31] published the first accounts of investigations, which were later very much extended, of the behaviour of carbon at high pressures and temperatures, the ultimate interest being the artificial formation of diamond, a problem not yet solved. Hallock [32] in 1888, in the attempt to confirm or interpret the experiments of Spring, found that solids like wax or lead do not actually become fluid under pressure, as had been many times erroneously stated, but the appearance of flow arises from the resistance to yield being overcome by the enormous stresses.

Barus [33] in 1889 published the first account of work covered in great detail later in two long papers from the Geological Survey in Washington in 1892. He was interested in studying the question of rock formation and similar geological problems by reproducing in the laboratory, as far as possible, actual terrestrial conditions of pressure and temperature. He attained pressures of 2000 kg. and temperatures of 400° C., and drew a number of interesting conclusions. There is an individual quality about his work that makes interesting reading. Among other things he observed the enormous solvent action of water on glass at high pressures and temperatures, measured the electric conductivity of several solutions of electrolytes, studied in detail the hysteresis of several forms of pressure gauge, made several interesting additions to technique, observed the enormous increase of viscosity of a substance like marine glue under pressure, and made a number of observations of melting phenomena under pressure, the interpretation of which was unfortunately obscured by the effect of impurities.

Damien [34] in 1889 published his first paper on the melting of solids up to 2000 kg., and followed it with a second paper in 1891. De Metz [35] in 1890 investigated the compressibility of oils and colloids, and in 1892 the much more difficult question of the compressibility of mercury. The greater difficulty arises from the fact that the compressibility of mercury is so low compared with the compressibility of the container that an accurate evaluation of the correction for the distortion of the container becomes much more necessary. De Metz obtained values not far from the present accepted values. Roentgen and Zehnder [36] in 1891 measured the effect of pressure on the index of refraction of water, CS_2, and other liquids. In 1892 Roentgen [37] followed this with a paper dealing with a variety of new phenomena to a pressure of several hundred kg./cm.^{2}, including the conductivity of solutions of electrolytes, the velocity of inversion of sugar in an acid solution, the velocity of diffusion in a liquid, and a confirmation of the observation of Barus of the increased viscosity of glue. In 1891 Des Coudres [38] measured the effect of pressure up to two atmospheres on the thermo-elective quality of mercury and several dilute amalgams, the first observations of their kind. Galopin [39] in 1892 made one of the few repetitions of the experiments of Creelman and Crockett, observing the adiabatic changes of temperature in water up to 500 kg. In 1893 Voigt [40] attempted to find the effect of a hydrostatic pressure of 60 kg./cm.^{2} on the breaking strength of NaCl crystals. No effect was found on the differential stress required to produce rupture, which means that if a rod is stretched by hanging weights on it, it will rupture at the same weight, whether the rod together with the weights is immersed in an atmosphere under pressure or not. This is an important question, and the experiments should be repeated at a higher pressure, where probably some effect will be found.

Since the termination of Amagat's work in 1893 there have been a very large number of high-pressure investigations, mostly groups of a few papers by various investigators, who evidently have not made this work their chief activity, and which will be referred to in more detail later, but there have in addition been a few foci in which several individuals or institutions have devoted an important part of their effort to high-pressure work.

Without doubt the most important work done in the period immediately following that of Amagat was by Tammann and his pupils [41]; Tammann's first paper in this field was in 1893, dealing with internal pressures in solutions. His main thesis was that dilute solutions, under ordinary conditions, behave approximately like pure water under an external pressure equal to that part of the internal pressure in the solution due to the action of the dissolved substance. In support of this thesis Tammann published, in the few years following 1893, a number of papers dealing with such topics as the compressibility and expansion of solutions, specific heats, heats of neutralisation, and pressure effects on electrical conductivity of electrolytes. A number of interesting correlations were brought to light, and the thesis gives a qualitative account of a considerable range of phenomena. The idea must be applied with caution, however, in any new field; there are a number of phenomena known in dilute alcohol solutions which are the exact opposite of what would be expected. Tammann later became interested in phenomena of solidification, such as the velocity of solidification, and from this it was a natural step to determine the effect of pressure on melting temperature and on the transition temperature from one solid phase to another. In this field his work was by far the most extensive and systematic of anything that had yet been done. His pressure range was 3000 kg./cm.^{2}, the same as that of Amagat. Tammann did not make as many improvements in technique as might be expected of one occupied so extensively in this field; this is doubtless explained by the fact that his mechanical facilities were always limited, so that he had to content himself with more or less stock apparatus that could be purchased from instrument dealers. Tammann first extensively used the method of discontinuity of volume in locating a melting or transition point. He observed the universal direction of curvature of the melting curves, which is the same as that of the liquid-vapour curves. He followed the change of volume to high pressures along the melting curve, from this calculated the latent heat, and from this in turn drew certain conclusions about the general character of the melting curve, which will be the subject of much more detailed discussion later. He observed a number of new transitions between solids possible only under pressure, including the very interesting two varieties of ice, Ice II and III. Tammann's chief activity in this field terminated with the publication of his book *Kristallisieren und Schmelzen* in 1903, of which the second edition in 1922 is called *Aggregatszustände*. Here will be found a more complete reference list to his papers than that given here. He has, however, published sporadic papers dealing with this general topic down to the present day.

Next after Tammann in point of time is Lussana,[42] whose first paper was published in 1895, and who has published some twenty papers at irregular intervals ever since. This work has apparently not had the influence which would be the natural reward of the industry and ingenuity displayed. It is evident that much of the work has been done under heavy material handicaps, which have sometimes led to the adoption of methods not capable of the highest accuracy, and in fact sometimes effects have been found not verified even qualitatively by other observers. The pressure range of much of Lussana's later work is 3000 kg./cm.^{2}, the range of Amagat. Lussana began in 1895 with three papers: one on the resistance of solutions of electrolytes at various pressures and temperatures, one on the effect of pressure on the maximum density point of water, and one on the effect of pressure on the transformations of NH_4NO_3 and HgI_2. In 1897 there was a very extended paper on the resistance of electrolytes. In 1899 and 1903 there were papers on the resistance of metals under pressure, in which, in addition to the permanent effects, temporary effects were found immediately after the application of pressure which other observers have not been able to confirm. In 1903, 1904, and 1910 there were several papers entitled, "Thermal Properties of Solids and Liquids," dealing with the compressibility, thermal expansion, and melting of pure metals, alloys, and a