Physico-Chemical Determinations at High Pressures by Optical Methods

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IV. *Physico-Chemical Determinations at High Pressures by Optical Methods.*

(Research executed in the Davy Faraday Research Laboratory of the Royal Institution of Great Britain, London, W.)

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HISTORICAL.

IN the course of his well-known investigations concerning the compressibility of gases and liquids, AMAGAT made some series of measurements taking observations through

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two small glass windows fitted to his high-pressure bomb ("méthode des regards"),[*] and he also twice made an attempt to use a similar arrangement for the determination of melting and crystallization at high pressures. His first paper on these subjects deals with the melting and with the formation of two different kinds of crystals of carbon tetrachloride.[†] The highest pressure employed was 1,160 atmospheres. The second paper, in which a somewhat different arrangement of the glass windows was used, deals with the crystallization of ice at temperatures below zero under the influence of high pressures.[‡] In a summarizing paper AMAGAT[§] states that he occasionally was able to reach pressures of about 1,600 atmospheres before the glass windows were broken, but observations were not actually made at higher pressures than 1,000 atmospheres. In this paper a sketch of the apparatus is also given. AMAGAT states that he met with severe difficulties during these investigations, and he has not pursued the subject further.

Later melting-points and transition-points of some "liquo-crystalline" substances have been measured in Jena glass tubes up to 300 atmospheres by HULLETT,[||] and other optical observations at pressures above that of the atmosphere have been made by ROTHMUND (maximum 500 atmospheres),[¶] RÖNTGEN and ZEHNDER,[**] SIERSTEMA,[††] LIVEING and DEWAR,[‡‡] HUTTON and PETAVEL,[§§] and DUFFIELD,[||||] but in these investigations the pressures have, as a rule, not exceeded 100 atmospheres.

By a volumetric method melting-points were first determined at comparatively high pressures by BARUS in 1891.[¶¶] BARUS, who undertook these measurements in connection with an extensive series of measurements of compressibilities,[***] determined the melting-point of naphthalene up to pressures of 1,435 atmospheres. In 1898, MACK measured the melting-point of naphthalene at pressures between that of the atmosphere and 2,140 kg./cm.^{2}, by observing the volume change as indicated by the manometer when melting occurred.[†††] But our chief knowledge about equilibrium

[*] E. H. AMAGAT, 'Journ. d. Chem. Phys.,' 1893, 6 ser., XXIX., p. 68, 96, 505.

[†] E. H. AMAGAT, 'Compt. Rend.,' CV. (1887), p. 165.

[‡] E. H. AMAGAT, 'Compt. Rend.,' CXVII. (1893), p. 507.

[§] 'Notice sur les Travaux Scientifiques de M. E. H. AMAGAT,' Paris, 1896.

[||] G. A. HULLETT, 'Zeitschr. f. Phys. Chem.,' 28, p. 622 (1899).

[¶] V. ROTHMUND, 'Zeitschr. f. Phys. Chem.,' 20, p. 168 (1896).

[**] RÖNTGEN and ZEHNDER, 'WIEDEMANN'S Annal.,' 44 (1891), p. 280.

[††] L. H. SIERSTEMA, 'Communications from the Phys. Lab., University of Leyden,' No. 35, No. 39, No. 49, and Suppl. 1.

[‡‡] LIVEING and DEWAR, 'Phil. Mag.,' 26, p. 286 (1888); 'Roy. Soc. Proc.,' 46, p. 226 (1889).

[§§] HUTTON and PETAVEL, 'Phil. Mag.,' p. 569 (1903).

[||||] G. DUFFIELD, 'Phil. Trans.,' A, vol. 208, p. 111 (1908).

[¶¶] C. BARUS, 'Amer. Journ. of Sc.,' 3 ser., XLII., p. 125 (1891); 'Bull. of the United States Geological Survey,' 96 (1892).

[***] C. BARUS, 'Bull. of the United States Geological Survey,' Nos. 92 and 97, Washington, 1892.

[†††] E. MACK, 'Compt. Rend.,' 127, p. 361 (1898).

between solids and liquids and solids and solids is due to the work of TAMMANN carried out at Dorpat and later at Göttingen.*

TAMMANN has used two different volumetric methods: working partly at constant temperature and altering the pressure, and partly at constant pressure altering the temperature, but the former method was chiefly employed. Only in the case of Bismuth, Tin, and Lead, TAMMANN has used a thermometric method. The actual determination of pressure extends in TAMMANN'S work to between 3,000 and 4,000 kg./cm.^{2}, but in a few instances melting-point temperatures have been reached which correspond to extrapolated pressures of between 5,000 and 10,000 atmospheres.

Only quite recently BRIDGMAN has published a series of measurements on the melting-point of mercury at pressures from 1 to 12,000 kg./cm.^{2}.† The change of the state of the mercury was observed by three different methods, one electric and two volumetric. The pressures were measured by the change of the electrical resistance of a mercury thread and of manganin wire; the influence of pressure upon the resistance having first been determined by standardizing with absolute manometers of the Amagat type, constructed by BRIDGMAN, and rendering possible the exact measurement of pressures up to 6,800 and 12,000 kg./cm.^{2}.‡ At pressures above 12,000 kg./cm.^{2} the determination of the pressure in BRIDGMAN'S work is entirely based upon the change of the resistance of manganin wire, but BRIDGMAN has been able to measure accurately pressures as high as 20,000 kg./cm.^{2} by this method, and states that he occasionally has reached pressures as high as 40,000 kg./cm.^{2}.

Of a recent date are also the determination of the melting-points of Pb, Sn, Bi, and Cd by the thermometric method at pressures from 1 to 2,000 atmospheres, undertaken at the geophysical laboratory of the Carnegie Institution of Washington, D.C.,§ and COHEN'S investigation of the transition of $ZnSO_4 + 7H_2O$ at pressures up to 1,500 kg./cm.^{2} by means of electrical measurements.‖

One of the most interesting results of TAMMANN'S high-pressure investigations is the discovery of the occurrence of crystallized modifications which are stable only at high pressure, as, for instance, in the case of phenol, water, methylene iodide, and silver iodide. Of great interest also is the tracing of the boundary lines between the different crystalline modifications and between these and the liquid phase in the diagram of state, viz., the fixing of the triple points. These inquiries it has been

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* G. TAMMANN, 'Ann. d. Physik,' 68, pp. 553, 629 (1899). 'Kristallisieren u. Schmelzen,' Hamburg, 1903. 'Zeitschr. f. Phys. Chem.,' 69, p. 569 (1909); 72, p. 609 (1910); 75, pp. 75–733 (1910). 'Zeitschr. f. Anorg. Chem.,' 40, p. 54 (1904); 63, p. 285 (1909).

† P. W. BRIDGMAN, 'Proc. Amer. Acad. Arts and Sciences,' 47 (12), p. 377, December (1911).

‡ P. W. BRIDGMAN, 'Proc. Amer. Acad. Arts and Sciences,' 44 (8), p. 201; 44 (9), p. 221; 47 (11), p. 321.

§ J. JOHNSTON and L. H. ADAMS, 'Amer. Journ. of Science,' 4 ser., XXXI., p. 501.

‖ E. COHEN, 'Zeit. f. Phys. Chem.,' 75, p. 1 (1911).

possible to carry out by the volumetric methods of TAMMANN in those cases where the volume difference between the different phases is considerable. This is mostly the case with regard to the crystallization and melting of the solid form, and the volumetric method is therefore nearly always applicable to the determination of the melting-point curves. In the case of the transition of crystalline forms, one into another, many instances are known where the transition occurs with only slight change of volume, and in such cases a volumetric method, of course, is not applicable. The same remarks apply to the thermometric method of the determination of transition-points, though this method has not until now been at all employed at pressures differing from the atmospheric. In cases like that above referred to, the simplest method of studying the transition phenomena at ordinary pressure is the optical, and this method has further the advantage over the volumetric and the thermometric methods that only a quite small quantity of the substance is needed, which in many cases, of course, is of essential importance. Further, the change of the optical characters of a substance at the transition-point between two crystalline forms is generally much more striking than the volume change or the evolution of the latent heat, and this is probably the chief cause why optical observation has been used in most investigations at ordinary temperatures. The well-known polarization-microscope, with a device for heating, constructed by LEHMANN, has been the principal instrument employed.

The above considerations, together with the desirability of determinations of the optical properties of crystals and liquids, especially of those of liquids (refractive index) being undertaken at homogeneous pressures other than the atmospheric, led the present writer to undertake the working out of methods of optical determinations at high pressures and varying temperatures, that is, methods for the optical investigation both of the boundary lines in the diagram of state of a substance, and of the variation of the optical properties of the different phases within their existence fields.

PART I.—APPARATUS FOR OPTICAL DETERMINATIONS AT HIGH PRESSURE.

The apparatus consists of three chief units:—

(1) The plant for the production and measurement of high pressures;
(2) The "pressure-bomb" to hold the substances under investigation;
(3) The optical installation for observation and for optical measurements.

These may conveniently be described apart.

1. *The High-pressure Plant.*

The apparatus for producing the pressures consists of two screw-compressors—one for pressures up to 6,000 atmospheres, and one for pressures not exceeding 600 atmospheres—a small hand-compressing pump for filling the larger compressor with oil at pressures of about 800 atmospheres, a steel vessel, to which both compressors and the pressure-bomb holding the substance are connected by means of drawn-steel capillary tubes of 7 mm. outer diameter and 1 mm. bore, and a high-pressure valve, by which the smaller compressor, together with its manometers, can be shut off from the rest of the apparatus when working at pressures above 600 atmospheres. The whole of this apparatus is fixed to a heavy oak bench. The various parts are connected as shown by the diagram (fig. 1), thus forming a pressure-plant which may be used for

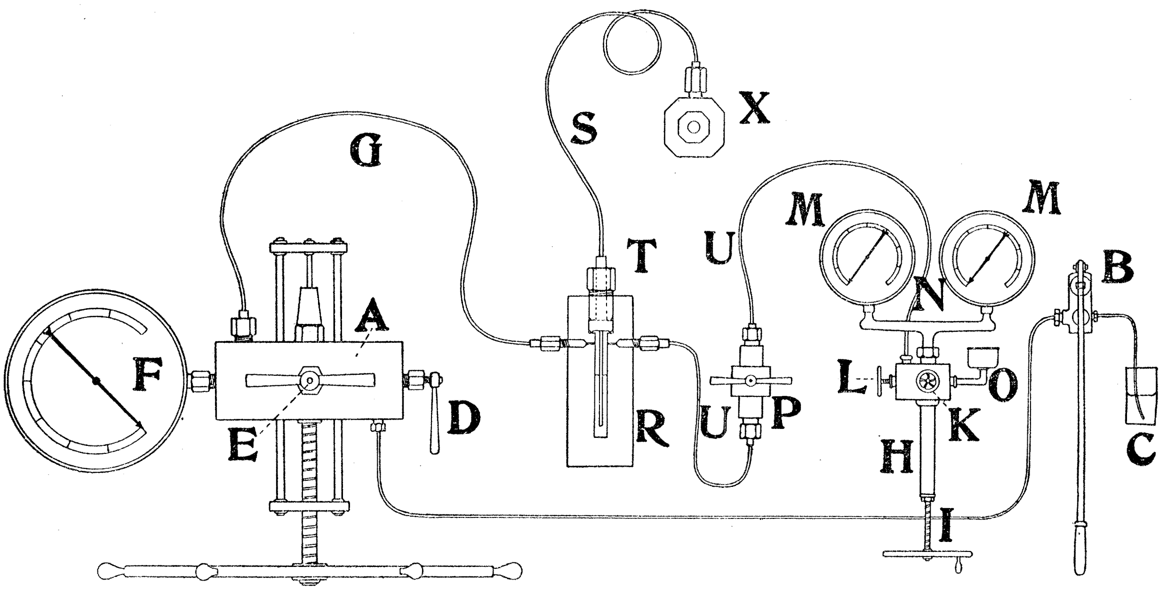

Fig. 1.

any kind of high-pressure work. The large compressor for high pressures (A, fig. 1) is of the Cailletet type, but made entirely of steel, and is of much larger size than the ordinary Cailletet apparatus. It is very similar to those used by Tammann in his high-pressure experiments.* As in the case of the Cailletet apparatus, a plunger is forced into a cylindrical compressing chamber in the central steel block A by a powerful screwing gear. Oil is pumped into this compressing chamber by means of the compressing pump B, which is connected to the oil reservoir C. D is a valve by which the compressing chamber is shut off from the pump B before the compressor is worked. By the valve E a fine capillary channel, which connects the compression chamber with the high-pressure manometer F and with the pressure-transmitting pipe G, can be shut off from these, thus leaving only the manometer connected with the pressure-transmitting pipe and the pressure-bomb, in which the investigation is

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* G. Tammann, 'Kristallisieren u. Schmelzen,' p. 195.

carried out. The manometer F is a "Stahlplatten-Hydraulik-Manometer," manufactured by Schäffer and Budenberg, of Magdeburg-Buckau, Germany, and is graduated to 4,500 kg./cm.^{2}, every division corresponding to 20 kg./cm.^{2}. The diameter of this manometer is 36 cm., and the scale is accordingly large, so that 2 kg./cm.^{2} may be easily read off on it. A second manometer of the same construction can be attached directly to the pressure-transmitting pipe, thus enabling a comparison of the manometers. This manometer is graduated to 5,000 kg./cm.^{2} and has been used as a standard.

The smaller compressor H is a screw compressor with a plunger of 15 mm. diameter, moved up and down in the compression chamber, in this case a thick walled bronze tube, directly by the screw I. K is a valve by which the oil reservoir O is shut off from the compressing chamber. L a valve which shuts off the compressing chamber from the pressure-conducting capillary tube and the manometers M, which then remain connected with the investigation bomb. The manometers M are of 26 cm. diameter, and graduated up to 600 kg./cm.^{2}, each division on the scale representing 1 kg./cm.^{2}. The two manometers are attached to a T-piece of bronze by which they communicate with each other and with the compressor. Each manometer is further provided with a safety-valve, protecting it against very sudden big changes in pressure by which they otherwise might be damaged. Also these manometers are of the "Stahlplatten-Hydraulic-Manometer" type, and manufactured by Schäffer and Budenberg. P is a valve capable of withstanding a pressure of more than 4,000 kg./cm.^{2}, by which the smaller compressor can be entirely shut off from the rest of the compressing machine.

The pressure-conducting pipes, G, from the large compressor, and U (U containing the valve P) from the small compressor, are connected to the upper part of the steel vessel R, through the top of which the long steel capillary tube S communicates with the lower part of the vessel, which thus forms a kind of strong steel bottle, on the same principle as wash-bottles. This steel flask or bomb contains mercury in its lower part, and as the pipe connected to the bomb containing the substance to be investigated dips into the mercury with its lower end, the mercury shuts off this part of the apparatus from the oil in the compressors and transmits the pressure without permitting the contents of the investigation bomb X to come into contact with the oil of the compressors. Oil can thus always be used in the compressors, any liquid being used in the pressure-bomb X. By the screw connection at T the investigation bomb is attached to, and detached from, the pressure plant, and this screw is the only one of the whole pressure plant which is opened between different series of experiments when a new substance is introduced into the investigation bomb X.* All the joints between different parts of the pressure apparatus are constructed on the principle of a hard, circular steel-edge, being forced by as crew

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* The compressing machine and manometers were manufactured by Messrs. Schäffer and Budenberg, of Magdeburg-Buckau, Germany.

into a softer steel surface, in the centre of which a capillary pressure-conducting channel enters. These steel edges have to be very carefully hardened, yet must be only slightly harder than the supporting surface. If they are too hard they easily break, and in any case a very much harder edge soon spoils the supporting steel surface. A joint which once has been got into good working order keeps perfectly tight for any length of time, and at any pressure it will stand without breaking. The oil used in compressors and pump was castor oil.

All four manometers have been standardized at the works of Schäffer and Budenberg in Magdeburg-Buckau by means of a hydraulic plant of a similar type to the Amagat absolute manometer. The manometers were standardized by the direct application of weights, the high-pressure ones up to 4,000 kg./cm.^{2} (the limit to which the testing plant can be used) and the smaller pair to 600 kg./cm.^{2}. The accuracy of the large manometers is about 5 kg./cm.^{2}, and that of the smaller ones about $\frac{1}{2}$ kg./cm.^{2}. The one large manometer is used as a standard whereby the three working manometers may be checked from time to time, to secure that their indications are constant. As all three working manometers communicate up to pressures of 600 kg./cm.^{2}, the two smaller ones give the exact value of the correction for the zero-point of the large one. If the indications of a single high-pressure manometer are not in some interval of pressure checked by another manometer grave errors may result with regard to the real position of the zero-point.

2. *The Pressure-Bomb in which the Optical Investigation is carried out and the Thermostat.*

The pressure-bomb fits into a U-shaped iron support, into which it can be firmly fixed by means of a screw. The U-piece is by a strong screw-bolt fixed to another inverted U-piece, which again is firmly screwed to an iron plate 3 feet long and 1 foot 2 inches wide. The connecting screw-bolt runs through the bottom of a water-jacket, and the joints are rendered tight by screw nuts and packings. There are also mica packings between the screw-bolt and the U-pieces in order to lessen the conduction of heat as much as possible. The water-jacket is of a square shape, flat, and only a few millimetres wider than the pressure-bomb. It holds about 2 litres. Opposite the two windows in the pressure-bomb are two holes in the sides of the water-jacket, and a short piece of brass tube with an outer, flat, ring-shaped edge can be screwed on to the window part of the pressure-bomb, pressing the side-plate of the water-jacket tightly against the pressure-bomb. These joints are rendered perfectly tight by inserting a sufficient number of rings of sheet lead 1 mm. thick on both sides of the water-jacket plate before the brass-tube caps are screwed on. In this way the pressure-bomb is kept fixed firmly inside the water-jacket, and a free view secured through the glass windows of the pressure-bomb. The details of construction of the pressure-bomb and the water-jacket are seen from fig. 2.

The water-jacket is heated by means of two small gas-burners, which are regulated by a mercury-regulator of ordinary type. In some series of measurements electrical heating by a platinum resistance coil has been used, and the regulator for the heating current was then electro-magnetic. The liquid in the bath was well stirred by a small turbine stirrer driven by an ordinary hot-air engine.

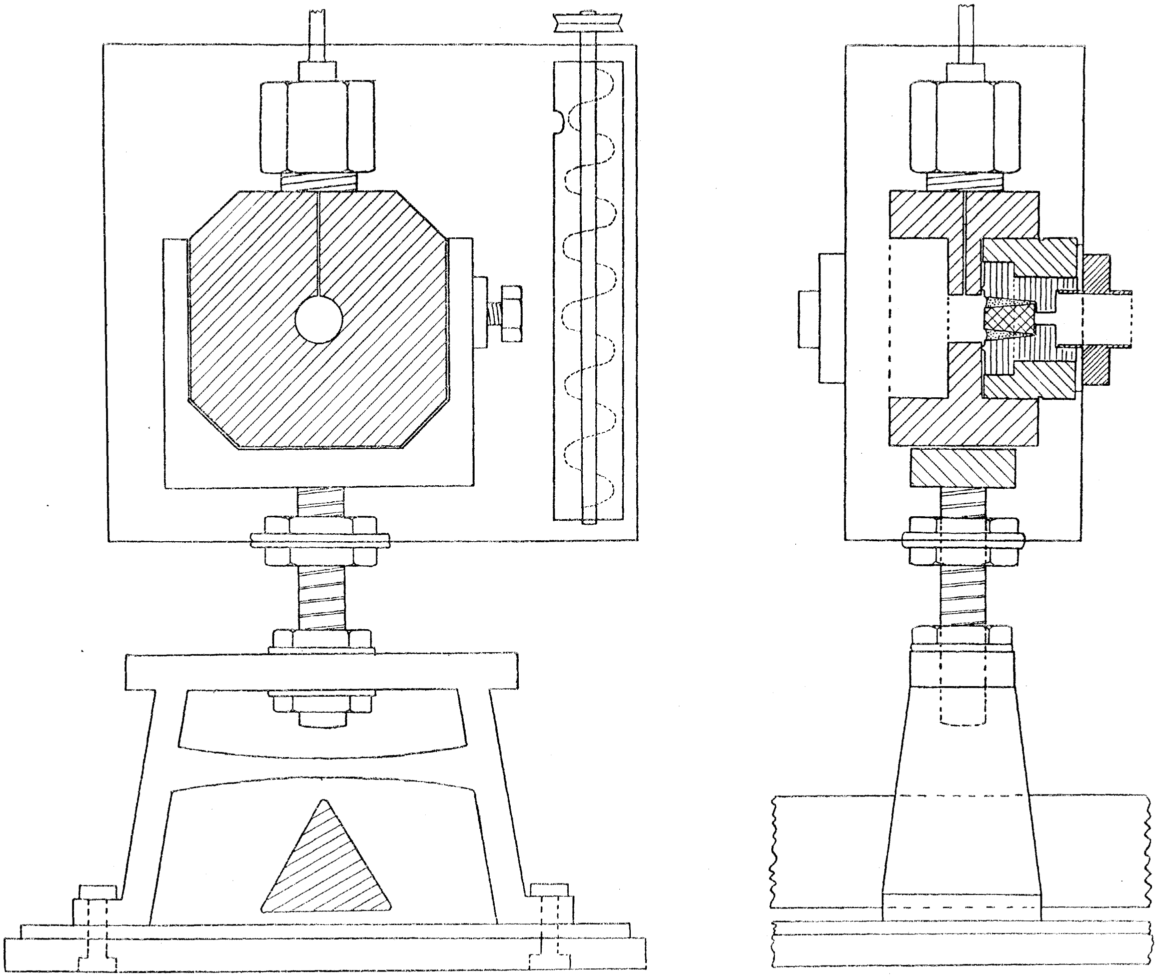

Fig. 2.

Temperatures were measured by thermometers, divided into tenths of a degree, which have been compared with similarly graduated thermometers standardized at the " Physikalisch-Technische Reichsanstalt " in Charlottenburg.

3. *The Optical Installation.*

(1) *The Optical Bench.*—The optical observations are made by means of an optical bench, each end of which is fitted with a screw-adjusting gear, the whole resting on

the iron plate to which the water-jacket and pressure-bomb are attached. With the aid of an autocollimation Gauss' eye-piece, the whole optical bench can, by means of the screw-adjusting gear, be brought exactly into such a position that its optical axis is at right angles to the surface of the window in the pressure-bomb, or any polished surface inside of this. The adjusting gear for the optical bench works practically in the same way as the crystal adjustment on a modern goniometer for measuring crystals, except that it, of course, can be adjusted at only a very small angle, and instead of the crystal or refractive index prism being adjusted on a goniometer, the object to be measured here remains in a fixed position, and the whole optical apparatus is adjusted with regard to this fixed position.

The optical part itself consists of an illuminating lens, polarizing Nicol-prism, condenser, objective, analysing Nicol-prism, and micrometer eye-piece. These optical parts are very much the same as those of the well-known Fuess Goniometer No. II. For crystal optical measurements the eye-piece can be replaced by a compensator eye-piece, and a stronger condenser-lens and objective-lens can be clamped on to the ends of the eye-piece and collimator-tubes, just as in the case of the Fuess Goniometer II., when used for optical axial-angle measurements. For such a purpose the eye-piece tube is also provided with a "Bertrand lens." The eye-piece system is focussed on infinite distance, but can be converted into a microscope of small enlarging power by means of an attachable lens. Thus, with this optical bench, the same measurements can be carried out as with the optical part of the Fuess Goniometer II. The description of the use of it for the determination of the refractive index and the dispersion of compressed liquids must be left for a paper dealing with this question.

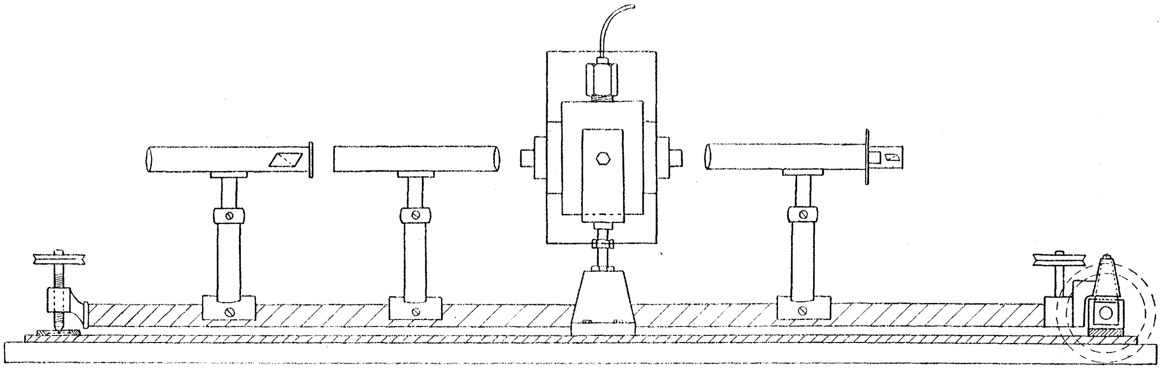

Fig. 3.

The optical bench and other optical parts were made by R. Fuess, of Steglitz, Berlin. The water-jacket with its fittings, and the gear for adjusting the optical bench, were made by the mechanician of the Davy Faraday Laboratory of the Royal Institution, Mr. Harry Payne, who also rendered valuable aid in getting the whole pressure plant with its numerous joints into good working condition.

(2) *The Glass Windows.*—AMAGAT states, in his first paper on the solidification of liquids by pressure, that he observed the liquid and the resulting crystals by means of a small glass window inserted into the wall of the pressure chamber in which the liquid was compressed. In form the window was a truncated cone, the smaller base being towards the observer. It was made of annealed glass, and was surrounded by a thin enveloping cone of ivory. With this arrangement of the windows AMAGAT was able to reach pressures of about 1,200 atmospheres. In the large series of measurements on the compressibility of liquids by the "méthode des regards," AMAGAT used cylindrical windows which were fixed simply by marine glue, this part of the apparatus always being kept cool, so that the marine glue did not get too soft. Experiments with windows fitted in this way were carried out up to 1,000 atmospheres. Later, also, AMAGAT used similar cylindrical windows, fitted with marine glue, for the measurement of the influence of pressure upon the freezing-point of water. In this paper AMAGAT states that he had met with very serious difficulties in getting the windows to withstand higher pressures than 1,000 atmospheres. Some of them stood 1,400 atmospheres, and in a single case he had even been able to carry the pressure up to 1,700 atmospheres before the glass was cracked, but generally about 1,200 atmospheres was the pressure-limit reached, and the work was then entirely given up by AMAGAT.

The first bomb intended for this research was constructed on the same principle as the bomb employed by AMAGAT in his earlier work. The method of gluing in the glass windows later used by AMAGAT would not permit work at higher temperatures in the case of the windows being close to each other, as is necessary in some cases of crystal-optical research, where the objective of the polarization instrument must be brought as close as possible to the crystal or section investigated. The "windows" were truncated cones 15 mm. thick, the diameter of the inner base being 10 mm. and that of the outer 7 mm. The enveloping conical mantle of ivory was about 1·5 mm. thick. The first cones tried were made out of an optical borosilicate-glass from Schott & Genossen, of Jena. In polarized light they very soon showed vivid polarization colours when pressure was increased, and at about 900 kg./cm.^{2} it became very difficult to see through them at all, but apparently they did not crack, and pressure was carried up to 2,000 kg./cm.^{2}—the limit for which the then used pressure apparatus had been tested—the apparatus being perfectly tight all the time. On relieving pressure, the compressed oil in the bomb, however, began to leak out at the windows, and when the apparatus was unscrewed it was found that the window cones now consisted of a very great number of thin plates, with surfaces as smooth as if polished. Some of these glass plates were very thin, others a millimetre or more thick, and it was possible to further cleave these by pressing a knife against the conic side of such a piece, the glass, after having been compressed in this way, thus behaving very much like mica. Tests were then made with different kinds of glass for cones and different material for the conical envelopes, soft ebonite and moderately hard vulcan-fibre being substituted for the comparatively hard ivory. Quartz-glass, a heavy soft "flint," and a hard "crown" behaved in very much the same way as the borosilicate, but usually a cracking was noticeable when the glass was split up into lamellæ, and this occurred in the case of flint glass, even at as low pressures as between 200 and 300 kg./cm.^{2}. During these tests some very remarkable optical phenomena were observed in the glasses in polarized light, but the description of these, as well as of the details of preliminary work, cannot be entered on here, it being sufficient to state that it was found that the "cleavage" developed in the glass windows was due to tension and not compression of the glass cones, these being more rigid than the enveloping cone which flows slightly, somewhat similarly to the way in which a rubber stopper flows and is stretched when it is forced into a bottle neck. The softer the material of the cone enveloping the glass the more marked this effect was, and the sooner cracks were developed, and always at right angles to the axis of the glass cone, that is, at right angles to the direction in which the hydraulic pressure in the interior of the bomb acts.

It was therefore thought that better results might be obtained by providing the glass windows with a steady support against which they would be pressed, so that no part of the glass could be stretched as described above. But as it at the same time was essential to have a conical joint between the glass and the steel wall of the bomb, in order to secure a tight fit even at high pressures, the following way of fitting the glass windows was finally adopted :—The glass cone was inserted the opposite way into the conical place in the steel bolt, the smaller basis of the cone thus being acted upon by the pressure transmitting fluid in the interior of the bomb, and the glass cone resting with its larger basis on a washer by which it is separated from its steel support. The steel and the washer supporting the glass cone are provided with a hole through the centre part, through which the observations are made, and the glass cone rests thus only with its outer part against the washer and steel. The remaining circular space between the conical glass and the conical bore in the steel is wedge-shaped, and thus the material in it is forced in towards the narrower part, and, if softer than the glass, makes the joint tight, and transmits at the same time an all-sided pressure to the glass cone. This conical wedge-shaped envelope has to be cut on the lathe exactly to the same angles as the conical surfaces of the glass and of the surrounding steel, the glass cone being finally ground in with very fine emery to fit exactly. This composite cone, consisting of the glass and its envelope of "fibre" or ebonite, is then ground into the conical space of the steel bomb, sufficient space being left for the washer supporting the base of the glass cone. The arrangement is shown in fig. 4, where *a* is the glass cone, *b* the conical wedge-shaped fibre envelope, *c* the washers, flat rings supporting the glass cone, *d* the steel-pressure bomb, *e* the steel bolt into which the glass window is fitted, and *f* a screw.

The chief object of these washers and conical packings may be described as being that of keeping the glass all the time surrounded by a half-plastic mass, which flows slightly, and thus transmits the pressure to the glass body in as even a manner as possible.

Originally the washers consisted of two flat rings about 0·5 mm. thick each, the one on which the glass rests directly being of ivory, the other one of fibre. The conical washer for temperatures up to about 70° C. has been of "galalith," a material used instead of ebonite for electric fittings, and for higher temperatures of fibre. With this arrangement of the windows a great many of the measurements up to about 1,600 kg./cm.^{2} have been carried out, and with some practical experience as to the way in which the glasses are fitted it is not difficult to get a pressure-bomb of this kind for optical investigations in working order. The glass used has chiefly been a borosilicate from Schott & Genossen, of Jena, which is used for the manufacture of "Durax-glass" high-pressure-and-temperature tubing. Suitable pieces of the glass were cut from glass rods, the pieces annealed very carefully, and the cones then ground from these pieces. When overstrained, a 20 mm. thick cone of this glass shows interference colours of the first order at about 200 atmospheres below the point at which it breaks. It is always necessary to watch the glass windows in polarized light when pressure is applied to them the first time after they have been fitted into the steel bomb, as the appearance of interference colours at once suggests that the fitting is not satisfactory, for glass cones which stand pressures of several thousand atmospheres break at a few hundred if precaution is not taken to watch their behaviour in polarized light, and to refit them if they show interference colours already at comparatively low pressures. Later it was found that the limit of 1,600 kg./cm.^{2}, mentioned above, was not really due to the resisting strength of the glass being reached at that pressure, but to the circumstance that the ivory washers began to flow readily at this pressure, and in consequence of the structure of the bone did not give way evenly, with the result that the support suddenly became less in some parts than in others, and the glass cracked. Later, washers made out of two layers of thin lead foil have been used, and also washers made out of rolled plates

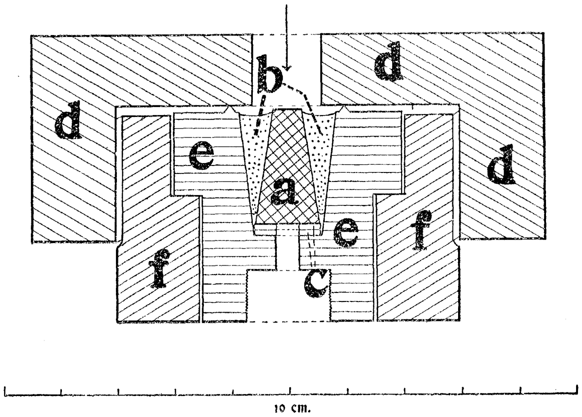

Fig. 4.

of silver chloride, these being protected from contact with the steel by lead paper. With both these arrangements pressures of up to 4,000 atmospheres have been reached without the glass being in any way injured. But in any case glass must be regarded as a very treacherous material when submitted to high pressure, and often a glass cone, which has withstood very high pressures, suddenly may crack at comparatively low pressures without having shown any signs of strain, and thus measurements are often suddenly interrupted. This circumstance adds, of course, to the difficulties experienced in this kind of research at high pressures, and to the time required to carry through such research.

The expenses for the construction of the above apparatus were defrayed by a grant made to the author from the "Herman Rosenberg Fund" of the University of Helsingfors.

The preliminary experiments with glass windows of varying construction were carried out during the winter of 1910 in the laboratory of physical chemistry at Göttingen. Prof. G. Tammann kindly lent me a set of his pressure apparatus for several months, and thus enabled me to make the tests which were necessary before the apparatus described above could be constructed. I am also greatly indebted to Prof. Tammann for many valuable suggestions, and for information on various points concerning the practice of high-pressure work.

The apparatus has been mounted and brought into working condition in the Davy Faraday Research Laboratory of the Royal Institution of Great Britain, and the actual research work which forms the subject of Part II. of this paper has been carried out entirely in the Davy Faraday Laboratory.

I have to acknowledge the liberality with which the Managers of the Royal Institution and the Director of the Laboratory, Prof. Sir James Dewar, have placed the technical resources of the Laboratory at my disposal. My thanks are also due to Sir James Dewar for the personal interest with which he has furthered the progress of the work.

PART II.—OPTICAL DETERMINATION OF DIAGRAMS OF STATE.

4. *General Methods.*

(1) *Method of Observing the Substance.*—In the case of the investigation of a body which remains liquid at all temperatures, and pressures at which the optical measurements are carried out, the substance may be allowed to fill up the entire interior space of the pressure bomb and the capillary tube through which the hydraulic pressure is transmitted. But, if the liquid has to be crystallized, the crystallization

may occur in any part of the apparatus between the manometer and the investigation bomb, and, especially if the entire contents of this is solidified, the part of the substance observed may remain under a very different pressure from that indicated by the manometers. Evident enough as such a cause of error may appear, it has been one of the principal practical difficulties to get over in all high-pressure work, and is one of the chief causes of errors in earlier work of this kind. TAMMANN refers in several instances to this circumstance as a cause of erroneous experimental results, and he has had to renew several of his earlier series of measurements. He has, in consequence, paid much attention to the problem of bringing the substance into the pressure bomb under such conditions that it is really submitted to homogeneous pressure during the entire investigation. In his most recent work TAMMANN has used a kind of bag or cylinder made out of parchment paper and coated with a varnish of collodium.* This cylindrical bag, when containing the substance and closed at both ends, is surrounded on all sides in the pressure bomb by some pressure-transmitting fluid, and as it is entirely soft the hydraulic pressure is evenly transmitted. The material for such a pressure-transmitting cover has of course to be chosen with regard to the nature both of the substance investigated and of the surrounding fluid, and in many instances it is not possible to find a material which is entirely insoluble, and which is not chemically acted upon by the substance to be investigated, especially when a large amount of substance is used, and the investigation is carried on at comparatively high pressures and temperatures.

In the case of an optical investigation it is, of course, essential to make observations upon a sufficiently thin layer of substance, so that it is possible to see the changes in the optical properties due to polymorphic transition. At first a small glass tube of about 2 mm. diameter was used as a vessel to hold the substance to be investigated. Both ends of the glass tube were bent over, approaching each other, and connected one to another by a small piece of rubber tube. The whole was filled with the substance, and the rubber tube part acted as pressure transmitter. Some melting-point determinations on dimethylether of oxalic acid were made in this way, but it was not easy to observe the optical characters of the crystallized body with this device, and subsequently the following arrangement has been used in most cases. The substance is melted between two circular glass plates, about $\frac{3}{4}$ mm. thick and of 10 mm. diameter, care being taken not to superheat the substance. When the substance has crystallized, a piece of black rubber tube, 5 mm. long and about 5 mm. wide, is slipped over the joint edges of the two glass plates, thus forming a surrounding cap, which at the same time gently presses the two glasses against each other, the whole forming a slightly elastic extremely narrow vessel. The rubber piece used is previously kept for some time in the molten substance to be investigated, and as the substance during the experiments comes into contact with the rubber only

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* G. TAMMANN, 'Zeitschr. f. Anorg. Chem.,' 63, p. 285 (1909), and 'Zeitschr. f. Phys. Chem.,' 75, p. 77 (1910).

at the extremely narrow fringe at the edge of the glasses, this device has proved itself to work very satisfactorily in most cases.

It has indeed been found that with the help of this little piece of apparatus the substances could be equally well observed at high pressures inside the pressure apparatus as under the ordinary polarization microscope between object-glass and cover-glass. Also, most crystal-optical determinations, such, for example, as those serving to identify the rock-forming minerals in thin sections of rocks, can be used during a research at high pressures with the above described apparatus.

(2) *Isothermal Melting and Crystallization.*—When an alteration of pressure at will is possible, the melting-point of a substance can, of course, be determined either at constant temperature by altering the pressure, or at constant pressure by altering the temperature. The determination at constant temperature, what one may conveniently call *isothermal crystallization* and *isothermal melting*, is by far the more convenient method of the two, and has throughout been employed in this research for the determination of melting-points. In the case of the determination of transition-points the method of work at constant pressure is of special use in some cases, and will be further referred to in cases where it has been applied. But, with regard to isothermal crystallization, there are some peculiarities which should be briefly discussed at this point. When a crystallized substance is melted in the ordinary way by being heated, it melts gradually at constant temperature, but at the same rate as the heat is supplied to it. It is not possible to heat instantly a melting mass of a substance through and through; the heat is taken up by the parts of the mass in contact with the heating device or vessel which is being heated, and spreads from those parts to the other parts of the mass. But in the case of isothermal melting matters are different in this respect, that any change of hydraulic pressure almost instantly takes place throughout the entire mass. As most crystals need a certain amount of time both to grow and to melt, the result is that, when working isothermally, we are able either slightly to compress the crystals in the "melt" of the substance to pressures above their melting-point pressure, or to lower the pressure beneath the pressure of the melting-point pressure. The extent to which this can be done depends almost entirely upon the velocity with which a crystal melts or crystallizes at its melting-point, and the rate at which this velocity is altered with increase or decrease of pressure, and these factors are very different for different substances. The two cases, pressures above and pressures below the actual melting-point pressures, correspond to a superheating of crystals in the presence of the liquid-phase or super-cooling of the liquid-phase in the presence of the crystal-phase at constant pressures. Only in the case of a totally melted substance is a super-cooling in most cases actually possible, and it has generally been thought that a superheating of a crystallized body to temperatures above its melting temperature could not be effected. According to some recent work, however, it seems probable that a superheating occurs in the case of some extremely slowly

melting substances.* A practical consequence of this difference between the ordinary "isobaric" melting at constant pressure and the "isothermic" melting, is that the melting-point can be instantly passed in either direction, and regions of a different degree of super-cooling and a correspondingly different degree of velocity of crystallization and of rate of spontaneous formation of crystal-nuclei can be experimentally reached and studied. In nearly all the cases investigated observations bearing upon the above have been made, and the more important will be quoted in connection with the description of the determination of the diagrams of state.

5. *The Diagram of State of Carbon Tetrabromide* CBr_4.

LEHMANN first observed that carbon tetrabromide, which crystallizes from the molten state in growth-structures belonging to the cubic system and appearing quite dark between crossed nicols, on further cooling down, changes into highly double-refracting crystals.† SCHWARZ found that this transition from one crystalline form to another takes place at 46°·1 C.‡

This transition-point, and the influence of admixtures of carbon tetrachloride on it, has since been very carefully studied by ROTHMUND by means of a thermometric method.§ ROTHMUND gives the transition-point of pure carbon tetrabromide as 46°·91 C. The melting-point is 92° C. The double-refracting modification of carbon tetrabromide crystallizes also from solutions in acetone. The crystals are monoclinic, but have crystal angles which differ very little from those of the cubic octahedron; they have been measured by ZIRNGIEBL.||

In order to determine the diagram of state of carbon tetrabromide a small quantity of it was brought into the pressure-bomb between two round object-glasses in the manner described on p. 130. The carbon tetrabromide had been purified by recrystallization from petrol-ether, and finally by sublimation in a charcoal vacuum from room temperature to that of liquid air.

(1) *Melting-point Determinations.*—When the pressure is increased at temperatures above 92° C.—the melting-point at ordinary pressure—crystalline growth-structures suddenly appear and grow rapidly. At constant temperature this does not always take place at exactly the same pressure, and these pressures at which the rapid growth, in the form of growth-structures, begins are not identical with the pressure corresponding to the melting-point, but slightly higher. At the melting-point pressure the crystals grow only slowly, and the rate of growth is about equal in all directions, so that compact crystals result, and no growth-structures; but if the

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* A. L. DAY and E. T. ALLEN, 'Publications of the Carnegie Institution,' Washington, No. 31, p. 57 (1905); G. TAMMANN, 'Zeit. f. Phys. Chem.,' 68, p. 257 (1910).

† O. LEHMANN, 'Molekularphysik.,' I., p. 178 (1888).

‡ W. SCHWARZ, 'Preisschrift Göttingen,' 1892, p. 47.

§ V. ROTHMUND, 'Zeitschr. f. Phys. Chem.,' 24, p. 705 (1897).

|| Quoted by GROTH, 'Chem. Kristallographie,' I., p. 230.

pressure is rapidly raised, the crystals begin at a certain pressure to grow more rapidly in a certain direction than in others, and so the cubic structures of growth are produced. In this way it is possible to determine at each temperature two crystallization pressures: one at which the crystals can just be observed to grow—this is the pressure closest to the true crystallization pressure we are able to observe—and a second higher pressure at which very rapid growth in a certain crystallographic direction takes place.

This behaviour is not peculiar to carbon tetrabromide, but is common to all substances hitherto investigated, and is probably a phenomenon of quite general character. It depends upon the following circumstances :—

GERNEZ* and MOORE† have shown that the velocity of crystallization, when measured in thin-walled glass tubes, increases with decreasing temperature, that is, when the degree of super-cooling increases. Later, TAMMANN and his pupils have found‡ that this increase of the velocity of crystallization occurs only up to a certain temperature, when a maximum of velocity is reached, which in many cases remains constant for a certain interval of temperature, and then very rapidly diminishes and assumes quite small values. The general case may be diagrammatically represented by fig. 5: *a* represents the melting-point temperature, at which the velocity of crystallization is very small. With descending temperature the velocity at first increases slowly, but at temperatures *b* a much more rapid increase takes place, and continues until the maximum velocity *c* is reached. At temperatures *d* the velocity again very rapidly drops to small values, and diminishes then at low temperatures *e* quite slowly. The part *a* to *c* of this curve is that which is of interest in this particular case, because it gives the explanation of the crystallization phenomena observed when pressure is increased. The comparatively short interval of temperature, where the rapid increase of the velocity of crystallization takes place, evidently corresponds to the pressures at which such an amount of super-cooling is reached that rapid crystallization ensues and the growth-structures are produced. This view is

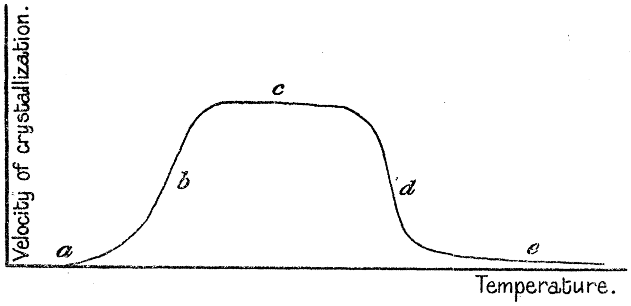

Fig. 5.

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* G. GERNEZ, 'Compt. Rend.,' 95, p. 1278 (1892).

† B. MOORE, 'Zeitschr. f. Phys. Chem.,' 12, p. 545 (1893).

‡ G. TAMMANN, 'Zeitschr. f. Phys. Chem.,' 27 (1897), p. 152; 29 (1899), p. 58.

supported by the observation by TAMMANN that at temperatures near *a* the growth in some cases occurs in the form of comparatively large crystals, which point in different directions inside the tube, and crystal faces are richly developed, but that at temperatures *b* growth occurs in a certain direction only, so that long crystal threads are produced in the tube.* In the case of the unstable modification III. of benzophenane melting at 26° C., TAMMANN found that the crystal grows inside the tube pushing forward a crystal corner, terminated by even crystal faces.*

As TAMMANN occasionally points out, every crystal face probably possesses its own velocity of crystallization at a given degree of super-cooling, and it is also probable that the velocity of the different crystal faces changes at a different rate with the degree of super-cooling. The result of this is that at a certain temperature, or pressure corresponding to this temperature, the velocity of crystallization in one crystal direction so much exceeds the velocity in other directions that, in consequence, only these crystal faces are developed and crystal-growth structures produced. It may suffice in this place to point out that these considerations give the clue to the general explanation of the production of growth-structures and of spherulites, and are of interest with regard to the origin of crystal-growths and spherulites in the igneous rocks; a fuller discussion of these problems, however, being outside the scope of the present communication. But the possibility of determining two distinct crystallization pressures, one at which the growths of the crystal only just takes place (at *a*, fig. 5), and one at which the formation of growth-structures begins (at *b*, fig. 5), is also of practical importance when the melting-point is determined at constant temperature, and the problem has therefore been discussed here already before the data of measurements are given. These two pressures will in the following tables be indicated as P_1 = the melting-point pressure, and as P_2 = the higher pressure at which growth-structures are developed.

As seen from the figures in Table I. the melting-point of CBr_4 is raised very rapidly by pressure, the pressure required to raise the melting-point 1° C. being only 16 kg./cm.^{2}. This ratio remains constant, within the limits of accuracy of the measurements, up to about 10° C. above the melting-point at 1 atmosphere. Unfortunately it is not possible to determine the melting-points at higher temperatures and pressures as a slight decomposition then begins, and as the decomposition products tend to lower the melting-point, higher melting-point pressures are recorded the longer the substance has been kept at high temperatures. This becomes still more marked at 120° C. and at 130° C., at which temperatures the melting-point pressures in different series of measurements differ very widely from each other. The melting-point pressure for preparations on which even only a single rapidly carried out observation at 120° C. was made, was, after cooling down, at 95°·4 C. about 200 kg./cm.^{2} higher than it originally had been. Under such circumstances it is, of course, not possible to determine if the raising of the melting-

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* G. TAMMANN, 'Zeitschr. f. Phys. Chem.,' 23, p. 68 (1899).

point by pressure continues at high pressures to be linear as it is at low pressures. This slight decomposition of CBr_4 at temperatures above that of the melting-point at ordinary pressures is not surprising, since it is known that CBr_4 decomposes on distillation, and that the carbon tetraiodide decomposes even when only just melting.

Table I.

Temperatures (corrected).	Pressures, P_1 (corrected).	Pressures, P_2 (corrected).
° C.		
94·84	45 kg./cm.².	65 kg./cm.².
97·84	98 ,,	—
100·29	134 ,,	160 kg./cm.².
104·92	274 ,,	295 ,,
104·87	280 ,,	295 ,,
(110·94	420 ,,	440 ,,)
(115·48	630 ,,	—)

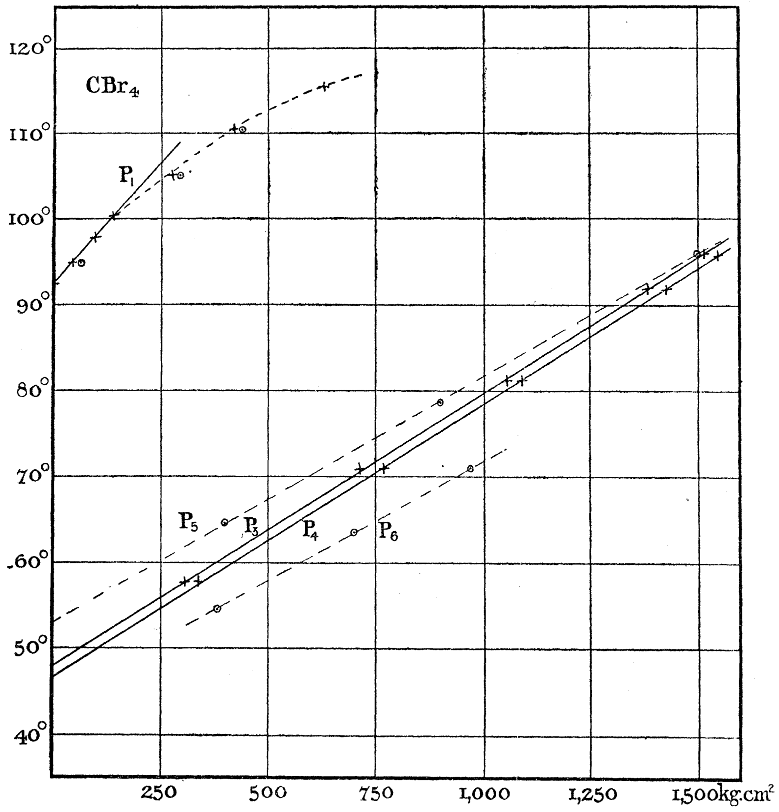

Fig. 6.

It is, therefore, not probable that the increased pressure plays any part in producing this decomposition, although this, of course, cannot be proved.

These melting-points are plotted in the diagram, fig. 6, and connected by the upper curve P_1 of that diagram. The curve P_2 is not shown in the diagram as it runs very close and parallel to P_1.

The difference between the pressures P_1 and P_2 is about 20 kg./cm.^{2}, and the amount of super-cooling necessary to reach the part C of the crystallization-velocity curve as shown in fig. 5, where the velocity of crystallization attains large values and growth-structures also appear, is thus only about one degree in the case of CBr_4—one degree on the melting-point curve corresponding to 20 kg./cm.^{2}. From the fact that the difference between the values P_1 and P_2 does not change at higher pressure, it may be concluded that pressure does not influence the degree of super-cooling which is necessary in order that growth-structures may be produced. The curves showing the velocity of crystallization in its dependence on the degree of super-cooling (diagram, fig. 5) will, therefore, be similar in shape at all pressures, although the absolute value of the velocity at corresponding degrees of super-cooling may vary with the pressure.

(2) *Transition-point Determinations.*—When the molten carbon tetrabromide is cooled between glass plates it first crystallizes in isotropic crystals, and on further cooling a crystallization of the anisotropic crystal modification suddenly starts. The anisotropic crystallization begins usually from one or from a few points at the border line of the isotropic crystal mass, and the anisotropic crystals grow at the expense of the isotropic just as if they were growing in the liquid phase. The growth is rapid, and long, blade-like crystals are formed which cover the space earlier occupied by several of the isotropic crystals, and no connection whatever seems to exist between the border lines of the isotropic crystals and the growing anisotropic crystals. On the other hand, when the transition of the anisotropic modification to the isotropic occurs, on raising the temperature of the preparation, the isotropic crystals are not seen to grow at all, but it looks rather as if the anisotropic crystals were simply melting. Dark isotropic spots of quite irregular shape appear both at the border lines and in the interior of the crystals, and continue to be formed and to grow larger until the whole has changed into an isotropic mass.

Pressure raises this transition-point rapidly, as seen from Table II., and the same general difference which exists between the transition from isotropic to anisotropic, and from anisotropic to isotropic at ordinary pressure, exists also when transition takes place at high pressures. But, in addition, it is found that the transition from isotropic (*i.e.*, regular) form takes place extremely slowly at the true transition-point pressure. When the transition-point curve is passed at constant temperature by lowering the pressure slowly, the anisotropic phase at first appears in the form of small, bright, coloured spots on the dark field. These are a kind of crystal globulæ, crystal germs, which then grow to bigger crystals. This, as is well known, is the general case when crystals begin to form in a liquid, and the related phenomena have been described at length by VOGELSANG, who especially investigated the growth of sulphur crystals, but it has not been known that the crystallization of one crystal phase out of one other crystalline phase may take place in exactly the same way. These anisotropic crystal germs appear at any point inside the isotropic crystal grains or at their border. They are very few at the melting-point pressure, and are scarcely seen to grow at all, but if the pressure is lowered they begin to be more numerous, and grow more and more rapidly. The lower pressure given in Table II. at any given temperature is the pressure at which the anisotropic crystal germs are seen only just to begin to grow with noticeable speed. The higher pressure given again is that at which the transition from anisotropic to isotropic form is seen to take place when pressure is increased. In this case it is not possible to see when transition really begins, and only a quite small increase of pressure is necessary in order to produce a very rapid transition into the isotropic modification. The change is thus more like melting, and the opposite change, from isotropic to anisotropic crystal form, takes place in a similar way to crystallization.

TABLE II.

Temperatures (corrected).	Pressures, P_3 (corrected).	Pressures, P_4 (corrected).
° C.		
57·54	310 kg./cm.^{2}	340 kg./cm.^{2}
70·89	715 ,,	770 ,,
81·20	1,055 ,,	1,090 ,,
91·96	1,385 ,,	1,430 ,,
95·72	1,515 ,,	1,550 ,,

The difference between the pressure values P_3 and P_4 range between 30 and 55 kg., the average being 40 kg./cm.^{2}, but this value is apparently not dependent upon the pressure at which the transition takes place.

Determinations were further made at constant pressure, both at rising temperature, Table III., and at falling temperature, Table IV., Series A and B.

TABLE III.

Observations at rising temperatures, about	Constant pressures, P_5.
° C.	
64·5	400 kg./cm.^{2}
78·6	900 ,,
96·0	1,500 ,,

TABLE IV.

Observations at falling temperatures, about	Constant pressures, P_6.
SERIES A.	
° C.	
71	970 kg./cm.^{2}
63·5	700 ,,
54·5	385 ,,
SERIES B.	
73·2	1,000 kg./cm.^{2}
67·8	760 ,,
61·3	510 ,,
55·0	299 ,,
51·9	200 ,,

The pressures P_3, P_4, P_5, and P_6, given in the Tables II., III., and IV., Series A, are plotted in the diagram, fig. 6, and form the lower group of curves in this. The curve P_3 intersects with the temperature axis of the diagram at 47°·8 C. and the curve P_4 at 46°·6 C.

The significance of these transition-point curves P_3, P_4, P_5, and P_6, may be explained in the following manner:—

P_3 represents the temperatures and pressures at which the growth of the anisotropic modification just attains a noticeable velocity when both modifications coexist. P_4 again the pressures and temperatures at which the isotropic modification is formed with noticeable speed under these same conditions. In the small strip between these two curves the two modifications of carbon tetrabromide will thus coexist without changing one into the other. The true equilibrium curve must lie between these two curves of "false equilibrium," probably nearer to the curve P_4 than to P_3, as the velocity of transition seems to increase more rapidly in directions at right angles to this curve than to the curve P_3.

If we work by a volumetric method we may, according to these curves, expect to find that the transformation takes place at a lower temperature when working at descending temperature than when working at rising temperature, and the horizontal distance (40 kg./cm.^{2}) between the curves would represent the pressure values obtainable by the method at constant temperature which has been employed by TAMMANN in his transition-point determinations.

The curves P_5 and P_6 again represent the temperatures and pressures at which each modification is at first spontaneously formed from the other. The much greater distance at which these run from the true equilibrium curve shows to what a much larger extent the equilibrium can be exceeded when no crystal germs of the modification, stable at that temperature and pressure, are present.

The curve P_5 runs nearer and nearer to P_3 as the temperature of the transition-point rises, which means that the unstable region grows gradually smaller at high temperatures, and probably would disappear at about 1,700 kg./cm.^{2}

As seen from both series of measurements (Table III.), which were made at a different rate of cooling, the transition-point is exceeded to a higher degree at high temperatures than at low. The unstable region in the case of the transition from the isotropic to the anisotropic modification would thus become larger with increasing temperature, which is just opposite to what takes place in the case of the inverse transition, as we have seen, and is not what one should expect. The extent to which the equilibrium curve may be crossed on cooling at constant pressure seems also to depend to a certain amount on the rate at which the cooling takes place, but this circumstance does not furnish an explanation for the general trend of the curve P_6, as this remains similar in direction in the different series of measurements. The conclusion to be drawn, in the present state of knowledge, would thus be that pressure influences this transition from the isotropic state to the anisotropic in such a way as to facilitate a retardation of the transition.

The distance between the curves P_3 and P_4 remains quite constant, and this shows that the conditions of transition of the one form of the substance to the other form are not influenced by pressure as far as regards the degree to which the equilibrium-curve is crossed, just as the conditions of crystallization are not changed by pressure, as far as regards the degree of super-cooling, as pointed out on p. 136. This may be considered a proof that the curve for the velocity of crystallization and the curve for the velocity of transition of polymorphic crystal forms of a substance are similar in shape, a similarity which might be expected. So far a curve of velocity of transformation has only once been actually measured, that is in the case of the transformation of a "monotropic," unstable modification to the stable one (Benzophenone III. to I.).*

This group of four curves, limiting the areas in the diagram of state where a false equilibrium exists between the two crystalline forms of carbon tetrabromide or where spontaneous formation does not occur, are quite analogous to those found by TAMMANN in his latest researches on phenol,† silver iodide,‡ and ice.§ In these cases the equilibrium curve is found to split up at low temperatures into four different curves, corresponding to the above. The distance between the curves is at low temperatures very large, and the transformation at last entirely ceases to take place when the temperature is sufficiently lowered. The transition in the case of carbon

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* G. TAMMANN, 'Zeitschr. f. Phys. Chem.,' 29, pp. 58, 67 (1899).

† G. TAMMANN, 'Zeitschr. f. Phys. Chem.,' 75, pp. 75 (1911).

‡ G. TAMMANN, 'Zeitschr. f. Phys. Chem.,' 75, p. 733 (1911).

§ G. TAMMANN, 'Zeitschr. f. Phys. Chem.,' 72, p. 602 (1910).

tetrabromide is, on the other hand, one which takes place more readily than in most cases of enantiotropic transformation which are known, and the possibility of studying the same phenomena of "false equilibrium" in a substance like this indicates the sensitiveness of the method.

As seen from the Tables I. and II., 16 kg./cm.^{2} suffice to raise the melting-point of CBr_4 1°, whereas the transition-point is only raised 0·5 degree by this pressure. The melting-point curve and the transformation-point curve will, therefore, not intersect at high pressure to form a triple-point. The consequence of this direction of the melting-point curve and the transition-point curve is *that the anisotropic monoclinic modification of carbon tetrabromide cannot be caused to melt*, even at any pressure. The theoretical triple-point deduced from these curves would lie at low temperature and high negative pressures (0° and -1500 kg./cm.^{2}). A case like this has not been experimentally met with earlier, but the possibility of the occurrence of such a case has been theoretically foreseen by BACKHUIS ROOZEBOOM in his treatise on the applications of the phase-rule.*

6. *The Diagram of State of αβ-bibrompropionic Acid*, $CH_2Br.CHBr.COOH$.

Among "monotrope"-polymorphic substances bibrompropionic acid is probably unique in this respect, that it melts twice when slowly heated. The unstable modification of lower melting-point is nearly always obtained when the fused substance is allowed to cool, and on heating again it melts at 51° C., but at a few degrees higher the stable modification crystallizes out of the "melt" and then on further heating melts at 64° C. This behaviour was described in detail by TOLLENS,† who first prepared this substance, and it has later been studied by LEHMANN.‡ The crystals of both these modifications have been measured by ZEPHAROWICH,§ who found that both crystallize in the monoclinic system.

This behaviour of αβ-bibrompropionic acid, together with the comparatively great stability of the "unstable" modification, made it probable that it, in this case, would be possible to determine the melting-point curve of two different modifications of a polymorphic substance, which would be of interest, as hitherto only melting-point curves of stable modifications have been measured.‖ Before giving the results of

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* H. W. BACKHUIS ROOZEBOOM, 'Die Heterogenen Gleichgewichte I.,' p. 185, fig. 41 (Braunschweig, 1901).

† TOLLENS, 'LIEBIG'S Ann.,' 167, pp. 222, 337.

‡ O. LEHMANN, 'Molekularphysik,' I., p. 690.

§ ZEPHAROWICH, 'Jahresber.,' 1878, p. 693.

‖ TAMMANN'S statements about melting-point curves of alleged unstable modifications of *p*-xylol, carbon tetrachloride, acetic acid, diethylamin, trimethylcarbinol, and ethylendibromide ('WIED. Ann.,' 66, p. 473, and 68, pp. 553, 629) have been withdrawn by him in his later publication of the measurements in "Kristallisieren u. Schmelzen."

these determinations the crystallization at ordinary temperature must be briefly described.

When the acid is fused between two glass plates and allowed to cool super-cooling invariably takes place. When crystallization sets in a few round crystal germs of the modification melting at 51° C. are formed, and these then grow at moderate speed in all directions, forming hexagons remarkably regular in shape. These are, however, not homogeneous crystals, but are built up of crystal fibres radiating from a central crystal germ. If a small particle of the stable modification is brought into contact with these crystals, a transition begins to occur and the stable modification grows at the expense of the unstable, very much in the same way as this grows in the "melt." The growth of the stable modification melting at 64° C. is fan-like, the crystal threads being very similar to those of the modification melting at 51° C. Both modifications show approximately the same interference colours, and this adds to the similarity of their appearance when crystallized between two glass plates. At ordinary temperatures the velocity of crystallization of the unstable modification is greater than the velocity of transformation to the stable form.

Considerable difficulty was met with in trying to get a sufficiently pure preparation for the melting-point determinations. The substance is very soluble in most solvents, and the degree of purity is not much improved by repeated crystallization. It was at length found that a pure product may be obtained by treating the acid with a large quantity of petrolether at ordinary temperature, and evaporating part of the petrolether by an air current. Crystals of the unstable modification about 1 mm. in diameter are formed, but these clear, transparent crystals change, while still in the evaporating solution, into the stable form whereby they become porcelain-like, white and non-transparent.

Unfortunately a great many measurements on unstable melting-points were made on a specimen that was not quite pure, and these had then to be repeated on a pure one. But as some interesting observations were made during these measurements with the less pure material they are given here in Table VII., beside the measurements carried out with the pure substance, Table VI.

(1) *Determination of the Melting-point Curve of the Stable Modification.*—Under pressure the molten acid behaves very much in the same way as at ordinary pressure in this respect, that it almost invariably crystallizes to the unstable modification. It is therefore not possible to work at constant pressure, and a curve connecting the points where this modification is spontaneously formed has therefore not been determined. In order to determine the melting-point curve of the stable modification it is necessary to melt the acid between glass plates, and when it has crystallized to the unstable form, to inoculate with a crystal of the stable form, whereby the transition takes place, and then to bring the preparation into the pressure apparatus. Care must be taken during the whole series of measurements not to melt the stable form totally, as we then nearly always pass over to the unstable curve, when the

"melt" is crystallized either by decreasing temperature or by increasing pressure. The crystals both grow very slowly and melt very slowly. The growth of the crystals is not much hastened even by increasing the pressure by as much as 200 atmospheres, but a great many new crystal germs then appear and grow in all directions to remarkably evenly-developed small crystals. In spite of the slowness with which these crystals grow, the force developed in crystallizing is so great that they, even at pressures above 1,000 atmospheres, tend to push the glass plates apart in spite of the strong outer pressure acting on these. As a result the glass plates are bent, and if the crystals are allowed to grow too large the glass plates are broken by the pressure. For these reasons the curve connecting the points where formation of crystal growth-structures eventually would occur has not yet been determined.

In consequence of the slowness with which melting takes place at the equilibrium curve crystal—liquid, it is possible to slightly superheat the crystals by decreasing the pressure at constant temperature as described on p. 131. We are able to determine a pressure at which the melting of the crystals begins to take place with sufficient rapidity to be observed, and on further gradually decreasing the pressure the crystals are seen to melt slightly faster, but when a certain pressure, below the pressure at which melting is first seen to take place, is reached the melting suddenly becomes very rapid. This pressure is, at about 5° C. above the melting-point at ordinary temperatures, 40 atmospheres lower than the pressure at which melting is seen to take place quite slowly, and at temperatures about 15° C. above the melting-point it is 30 atmospheres lower. The extent to which the crystals may be superheated therefore diminishes towards higher temperatures on the melting-point curve, apparently because the rapidity of melting increases with the temperature of the melting-point. The pressure at which melting can be just observed is not so easy to determine accurately as the pressure at which crystallization can be just observed, and only the latter therefore has been determined. The points of the actual equilibrium curve are to be found between these two pressures, which,

TABLE V.

Temperatures, t (corrected).	Pressures, P_1 (corrected).	Pressures, P_2 (corrected).
° C.		
(64	1 kg./cm.^{2})	—
66·04	160 ,,	—
68·86	260 ,,	220 kg./cm.^{2}
73·24	470 ,,	440 ,,
79·21	790 ,,	760 ,,
84·73	1060 ,,	—

however, lie only a couple of atmospheres apart. The pressures at which the velocity of crystallization attains noticeable values are given in Table V. as P_1, and the pressures at which rapid melting takes place are given there as P_2.

(2) *Determinations of the Melting-point of the Unstable Modification.*—The melting and crystallization of the unstable modification at different pressures occurs in very much the same manner as in the case of the stable modification. The only difference is that the velocity of crystallization is greater. Working isothermically, it has been possible to determine the pressures at which growth-structures are suddenly formed. These pressures lie about 350 kg./cm.^{2} above the melting-point pressures, which corresponds to approximately 6°·5 C. All that has been said with regard to the superheating of the stable modification applies also to this case, but the slowness with which the melting takes place is here still more marked. The point where a rapid melting suddenly begins is not reached before at about 150 kg./cm.^{2} lower pressure than the melting-point pressure. This corresponds to a superheating of about 2°·5 C.

In consequence of the extreme slowness with which the melting and the crystallization takes place in the vicinity of the equilibrium-curve crystal—liquid we would, when working isothermically and increasing or decreasing pressure at a moderate speed, only be able to observe a somewhat sudden volume change at the pressures at which rapid melting and rapid crystalline-growth takes place. We would thus obtain pressure values as much as 500 kg./cm.^{2} apart, corresponding to 9° C., and if we assume—as is generally done—that the true equilibrium pressure lies halfway between the obtained limiting pressures, we would be about 100 kg./cm.^{2}, corresponding to 1°·8 C. in error. This is, of course, an extreme case, but it serves well to indicate the uncertainty of the volumetric methods, both with regard to the determination of melting-point curves and the determination of transition-point curves between different crystalline modifications in such cases where transition takes place very slowly.

Table VI.

Temperatures (corrected).	Pressures, P_3 (corrected).
° C.	
(51	1 kg./cm.^{2})
52·60	215 ,,
55·52	300 ,,
60·56	535 ,,
65·39	775 ,,
70·64	1,045 ,,
75·40	1,325 ,,

The pressures at which crystallization begins to take place at noticeable speed, determined on a very carefully purified sample, are given as P_3 in Table VI., and plotted in the diagram, fig. 7, forming the curve P_3. The values above 500 kg./cm.^{2} lie all on a straight line, which also passes through the melting-point at 1 kg./cm.^{2}, 51° C. At only a few degrees above the melting-point it is very difficult to judge exactly at what pressure the crystals really grow on account of the extreme slowness with which this takes place, and the pressure values obtained are much too large at temperatures just above 51° C.; but the difference between the obtained values and the values on the curve grows less with rising temperature and disappears at about 58° C. That these high values, up to values 200 kg./cm.^{2} too high, are obtained at temperatures near the melting-point at 1 atmosphere depends upon the circumstance that the absolute value of the velocity of crystallization is so very small that the crystallization becomes noticeable first at pressures much higher and further apart from the true melting-point curve than at higher temperatures. With rising temperature the absolute value of the velocity of crystallization gradually increases, and the values obtained for the pressure at which the growth of the crystals becomes noticeable asymptotically approach the equilibrium curves until they, from about 500 kg./cm.^{2}, are found to lie practically on a straight line.

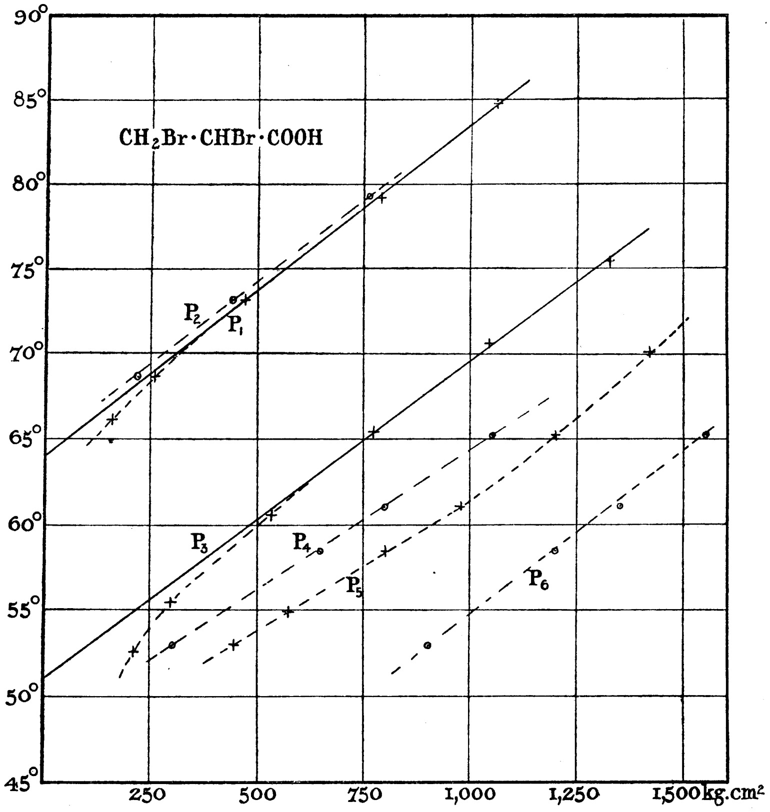

Fig. 7.

The pressure values at which crystallization begins to take place in the case of a not sufficiently purified sample of the acid are given as P_5 in Table VII. In this case the pressures at which rapid growth and the formation of growth-structures takes place were also determined, and are given as P_6 in the same table. Several points on the curve, where suddenly rapid melting sets in, were also determined, and are given as pressures, P_4. An interesting feature of this melting-point curve, P_5, is that it at higher pressure bends slightly towards the temperature axis, which the curve of the pure substance does not do. This behaviour of the curve will be discussed at a later stage with regard to its bearing upon the problem of the influence of impurities upon the form of the melting-point curve.

TABLE VII.

Temperatures (corrected).	Pressures, P_4.	Pressures, P_5 (corrected).	Pressures, P_6.
° C.			
(51	—	1 kg./cm.^{2}	—)
53	(about 300 kg./cm.^{2})	450 ,,	900 kg./cm.^{2}
55	—	575 ,,	1,000 ,,
58·6	650 kg./cm.^{2}	800 ,,	1,200 ,,
61·1	800 ,,	980 ,,	1,350 ,,
65·24	1,050 ,,	1,200 ,,	1,550 ,,
70·14	—	1,420 ,,	—

As seen from the diagram, fig. 7, and from the Tables V. and VI., the melting-point of the stable modification is raised one degree by a pressure of 51·28 kg./cm.^{2}, and the melting-point of the unstable modification one degree by a pressure of 53·48 kg./cm.^{2}. The melting-point curves will thus run further apart as the pressure is increased, and *the, at ordinary pressure, unstable modification will at all pressures melt at a lower temperature than the modification melting at* 64° *C. and remain unstable.*

7. *Discussion of Results.*

The fact that the melting-point curves of $\alpha\beta$-bibrompropionic acid do not intersect at high pressures, taken together with the somewhat similar relation between the melting-point curve and the transition-point curve of carbon tetrabromide, as given in the diagram, fig. 6, are of interest with regard to the theoretical explanations given as the cause of the occurrence of two different classes of polymorphic substances, the "enantiotropic" and the "monotropic." These terms were first used by LEHMANN, who called those polymorphic substances which pass reversibly into each other at a given transition-point "enantiotropic," and those which have one stable and one or several unstable modifications "monotropic." Later an explanation for this different behaviour of the two classes was given almost simultaneously by OSTWALD* and by

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* W. OSTWALD, 'Zeitschr. f. Phys. Chem.,' 22, p. 312 (1897).

SCHAUM,[*] who both considered the difference due to a different relative position of the transition-point with regard to the melting-point. In the case of enantiotropy the transition-point is situated below the melting-point, and the modification which is stable at temperatures below the transition-point cannot be melted; but if we suppose the transition-point of a modification to lie above its melting-point such a transition-point could not be observed, and we would have a case of monotropy. As pressure changes the melting-point and also the transition-point, it has been generally expected that it might be possible to change an "enantiotropic" body into a "monotropic" by pressure, and *vice versâ*. The pressures at which this ought to be possible were, in the case of sulphur, calculated by ROOZEBOOM.[†] TAMMANN then found that sulphur really behaves in this way,[‡] and determined the triple-point temperature and pressure, above which the monoclinic sulphur changes from an enantiotropic condition to a monotropic, as 153°·5 C. and 1,470 kg./cm.^{2}. This experimental result in the case of sulphur has generally been thought to be a verification of the theoretic explanation given by OSTWALD and SCHAUM,[§] and it has been expected that the change of an unstable, monotropic modification to a stable modification also would take place at high pressures.

ROOZEBOOM, in his systematical treatise of the application of the phase-rule, has pointed out that the explanation given by OSTWALD and SCHAUM is a possible one, but not necessarily the true one.[||] The experimental data given in this paper show that carbontetrabromide at all pressures remains an "enantiotropic" body, of which the modification, stable below the transition-point, cannot be caused to melt, and that $\alpha\beta$-bibrompropionic acid remains at all pressures a "monotropic" body, the unstable modification remaining unstable at all pressures. It remains, therefore, an open question whether the explanation given by OSTWALD and SCHAUM for the non-existence of a definite transition-point, in the case of monotropic bodies, is the true one or not. And the deduction from this theory, that a monotropic body might be changed into an enantiotropic by pressure, which, if it were true, would at the same time prove the correctness of the theory, is opposed by the behaviour of the melting-point curves of $\alpha\beta$-bibrompropionic acid.

The determination of the melting-point curves of the two modifications of $\alpha\beta$-bibrompropionic acid is also of interest in another respect. Generally it must be expected

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[*] R. SCHAUM, 'Habilitationschrift,' Marburg, 1897, p. 27.

[†] BACKHUIS ROOZEBOOM, 'Rec. Tr. Chim. Pays-Bas,' 6, p. 314 (1887), and 'Zeitschr. f. Phys. Chem.,' 2, p. 475 (1888).

[‡] G. TAMMANN, 'WIED. Ann.,' 68, p. 675 (1899); 'Ann. d. Phys.,' 3, p. 178 (1900); and "Kristallisieren u. Schmelzen," pp. 269–275.

[§] Some other cases where TAMMANN claims to have found a triple-point at higher pressures (dimethylether of oxalic acid, ortho-kresol) will be dealt with in a further communication, and in the case of acetic acid the curves given by TAMMANN do not intersect at the triple-point in the way required by theory. These substances, therefore, cannot be quoted as evidence in this case.

[||] BACKHUIS ROOZEBOOM, 'Die Heterogenen Gleichgewichte,' I., p. 160.

that a relation of some kind exists between the physical constants of polymorphic modifications if these are formed from the same molecules of the liquid phase, and, as will be shown, the measurements given above also indicate the existence of such a relationship. Conclusions may, to a certain extent, be drawn, even as to the nature of this relationship, but as this case is only a single one—the only one which until now has been investigated—the relationship observed might, of course, depend upon a singular coincidence, although this is not probable, and the discussion to follow is therefore given with all reserve.

The two melting-point curves are perfectly straight lines within the limits as set by the accuracy of the measurements. The upper one has been followed over a pressure range of 1,060 kg./cm.^{2}, the lower one over one of 1,330 kg./cm.^{2}. If we continued these melting-point curves towards negative pressures in the diagram we should find that they would intersect at a pressure value of about $-17,000$ kg./cm.^{2}, and at a temperature between $-270°$ C. and $-280°$ C., that is, *at the absolute zero.* The conclusion to be drawn therefrom is that *the difference between the absolute melting-points of the two modifications at any pressure is similar to the difference of the absolute melting-points at ordinary pressure,* the melting-point values thus converging towards unit value at the absolute zero.

If we further inquire into the cause of this relation, we find that the direction of the melting-point curve is determined by the product of the absolute melting-point into the quotient given by the volume change at the melting-point divided by the latent heat of crystallization in the Clapeyron-formula for the change of the melting-point by pressure. If the ratio between the absolute melting-points of two crystalline forms remains constant at all temperatures and the melting-point values converge toward unit value at the absolute zero, as in this case, it is therefore necessary that the ratio between these quotients in the Clapeyron-formula should also remain constant at all temperatures, and that the absolute values of the quotients should themselves also converge towards unit value at the absolute zero. Nothing at present is known about the absolute values of the factors entering into this quotient in the Clapeyron-formula, and of the absolute change of these factors with changing temperature, but the fact that a volume factor, as well as a heat factor, in the case of both modifications is affected by pressure in a similar way is of considerable interest.

The changes of the latent heats of crystallization must depend on the changes of the specific heats of the liquid and of the crystals, and to these changes the changes of the latent heat of transition between the two modifications probably also corresponds. The volume changes again must depend upon the compressibility of the liquid and of the crystals. The intersection of the melting-point curves at the absolute zero thus points to the probability that the values of all these properties for both modifications converge toward unit value at the absolute zero.

It may suffice here to point out briefly that in the case of the energy factors this is what is required by the heat theorem of Nernst, and that the other factors again are those which, according to the formula of LINDEMANN, determine the "molecular frequency" of the atoms. It seems therefore probable that the relation between the "molecular frequency" of the two crystalline forms determines the entire relationship between the physical constants of one form as compared with those of the other.

As a general result of the intersection of the melting-point curves at the absolute zero, we thus find that the physical properties of the two modifications—which apparently behave like two distinct crystalline substances—would, when the absolute temperature is lowered, change gradually, and in a similar way, and become identical at the triple-point, the absolute zero, which thus also would represent a "critical-point" between these two modifications of the $\alpha\beta$-bibrompropionic acid.