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J. W. POWELL, DIRECTOR

THE

COMPRESSIBILITY OF LIQUIDS

BY

CARL BARUS



WASHINGTON
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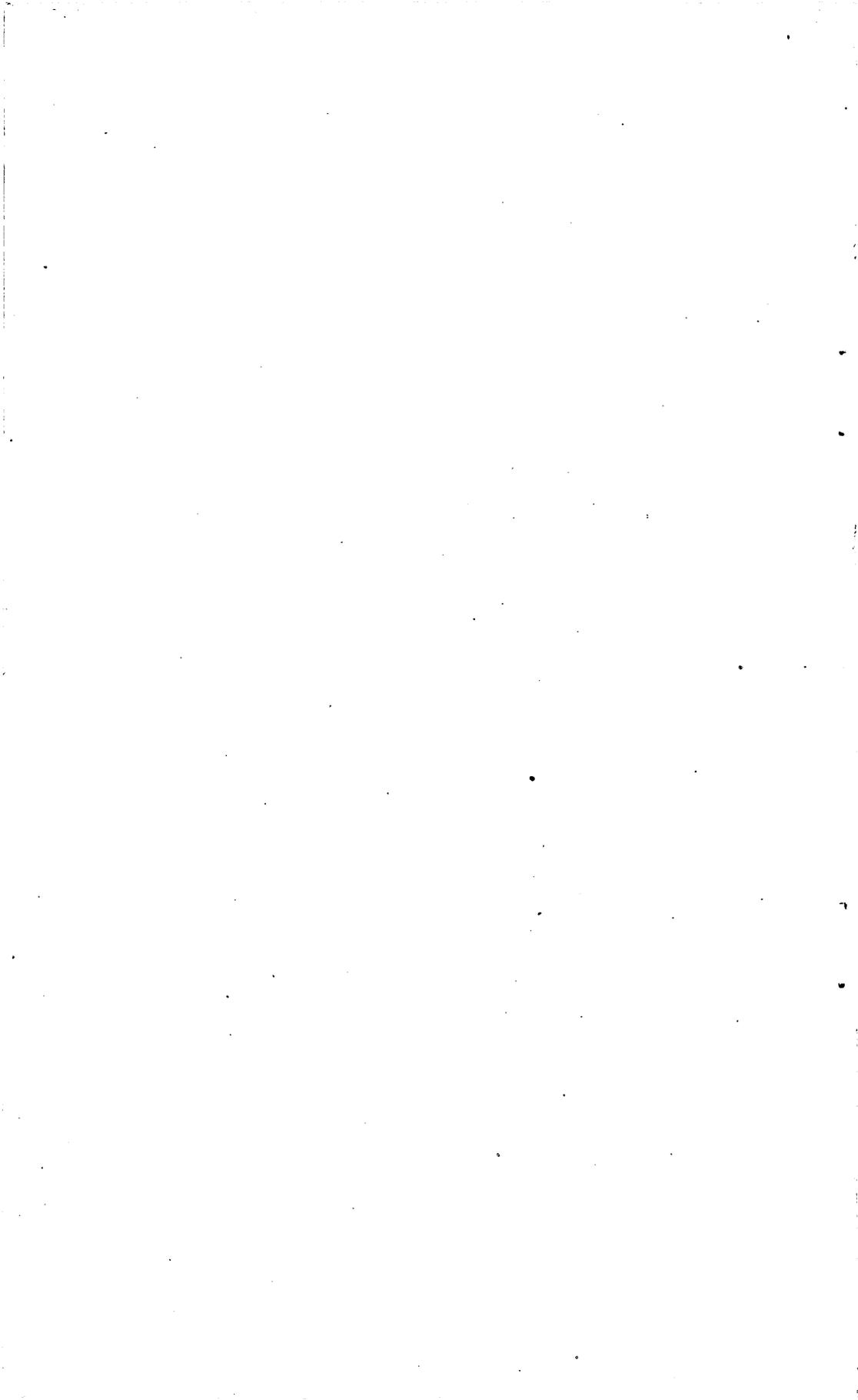


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LETTER OF TRANSMITTAL.

DEPARTMENT OF THE INTERIOR,
U. S. GEOLOGICAL SURVEY,
DIVISION OF CHEMISTRY AND PHYSICS,
Washington, D. C., July 31, 1891.

SIR: I have the honor to transmit herewith the manuscript of a report by Dr. Carl B̄arus on "The Compressibility of Liquids," and to request that it be published as a bulletin of the U. S. Geological Survey.

Very respectfully,

F. W. CLARKE,
Chief Chemist.

Hon. J. W. POWELL,
Director U. S. Geological Survey.



P R E F A C E .

The present volume is the outgoing installment of certain researches on the thermodynamics of liquids now in progress at this laboratory. The results are exhibited in four sections. In the first of these I endeavor to circumscribe the relation between the volume changes of a fluid, in their dependence on pressure and on temperature, fusion effects being excluded. In the second I describe the volume lag (hysteresis), identify it as a limit case of the phenomenon of viscosity, and discuss its fundamental bearing on the molecular structure of matter. In the third section (chapter II of this book) I submit an electric method by which the phenomenally small compressibility of metals can be studied with a facility unattainable in mere volume measurement. In the fourth part (chapter III), finally, the compressibility of water above 100° is shown, particularly in relation to the solvent action of water on glass, and to the contraction of liquid bulk due to such action. In preparing the work for publication it was expedient to add the data on lag phenomena to my second bulletin on the viscosity of solids, soon to appear. The other matter is contained in the present volume.

Chapter IV has been added as an illustration of the easy application of the results deduced in chapter III to industrial problems.

I am aware that the subject of compressibility has to a considerable extent engaged the attention of Maj. J. W. Powell. The present work, however, was suggested, and in its general scope and character sharply outlined, by Mr. Clarence King, as will appear from a perusal of the geological inferences to which the present results are tributary. The experimental methods and discussions are mine; and purely physical inferences are, as a rule, given on my own responsibility.

The casual reader may ask, What has the behavior of complex organic matter and of liquid metal to do with geology? To such a one I may reply: It is now generally conceded by the clearest thinkers that the crust of the earth is underlain by a liquid stratum, and that most surface phenomena of upheaval and subsidence are in some way (regarding which the clear thinkers by no means agree) referable to this liquid. Now, until quite recently the topography of the thermodynamic surface of fluids has been altogether unknown. Mathematicians like J. Willard Gibbs have done much toward mapping out its possible contours. But the experimental facts were vague and useless. To endeavor to obtain these from rock magmas, which can be operated on

only under formidable difficulties, would at the present stage of research be manifestly absurd. Hence other substances of more definite character and more convenient fusing points are appropriately selected for examination; and the observer is throughout his work stimulated by the belief that an available analogy in the thermodynamic behavior of liquid matter in general, whether fusing at temperatures high or low, is not beyond the province of probability. The reader who is willing to peruse the following chapters with me may find evidence here and there that the suggestion of an analogy is not unreasonable.

Since the following work was done I have succeeded in constructing a screw compressor by aid of which 2,000 atmospheres may be applied with facility. I have also constructed a gauge by which these pressures may be accurately measured. The general adjustment is such that all necessary electric insulation of different parts of the apparatus is provided for, and most of the measurements may, therefore, be made electrically. With this apparatus I hope to subject the data which the following pages have laboriously shaped to a direct and more satisfactory test.

CARL BARUS.

WASHINGTON, *January, 1889.*

THE COMPRESSIBILITY OF LIQUIDS.

BY CARL BARUS.

CHAPTER I.

FLUID VOLUME: ITS DEPENDENCE ON PRESSURE AND TEMPERATURE.

INTRODUCTION.

1. The present chapter purposes to investigate the probable contours of the isothermals and the isometrics of liquid matter, in so far as this can be done with the means now at my disposal.

2. *Literature of compressibility.*—The literature of the subject has recently been critically digested by Tate¹. Excellent excerpts are often to be found in the *Fortschritte der Physik*, so that I may content myself with brief mention. The work of Canton (1762–1764), Perkin (1820–1826), Oersted (1822), Colladon and Sturm (1827), Regnault (1847), Grassi (1851), Amaury and Descamps (1869), is discussed in most text books. Since that date the contributions have been manifold and are fast increasing. I shall, therefore, principally confine myself to papers in which volume changes produced by the simultaneous action of both pressure and temperature are considered.

Setting aside the literature² of critical points, which is too voluminous for discussion here, the work of Cailletet³ is first to be noticed as introducing a long range of pressures (700 atmospheres). Amagat's⁴ early work contains a larger temperature interval (0° to 100°), but applies for pressures below 9 atmospheres. The results are discussed in reference to Dupré's⁵ equation. Passing Buchanan's⁶ and Van der Waals's⁷ results for the compressibility of water and of solutions, I came to an exceedingly important step in the subject made by Lévy,⁸ though he had been considerably anticipated by Dupré.⁹

Lévy seeks to prove that the internal pressure of a body kept at constant volume is proportional to its temperature, which follows thermodynamically if the internal work done by heating is a volume function only or if specific heat in case of constant volume is a temperature func-

¹ Tate: *Properties of Matter*.

² See Landolt and Börnstein's *Physikalisch-chemische Tabellen*, Berlin, J. Springer, 1883, p. 62.

³ Cailletet: *C. R.*, vol. 75, 1872, p. 77.

⁴ Amagat: *C. R.*, vol. 85, 1877, p. 27, 139; *Ann. ch. et phys.*, vol. 11, 1877, p. 520.

⁵ Dupré: *C. R.*, vol. 59, 1864, p. 490; *ibid.*, vol. 67, 1868, p. 302.

⁶ Buchanan: *Nature*, vol. 17, 1878, p. 439.

⁷ Van der Waals: *Beiblätter*, vol. 1, 1877, p. 511.

⁸ Lévy: *C. R.*, vol. 87, 1878, pp. 449, 488, 676, 554, 649, 826.

⁹ Dupré: *Théorie mécanique de la chaleur*, 1869, p. 51.

tion only. The position of Lévy is sharply antagonized by H. F. Weber,¹ Boltzmann,² Clausius,³ and Massieu.⁴ See below.

Amagat's⁵ important work on the compression of gases may be mentioned because of its important bearing on methods of pressure measurement. In two critical researches Mees⁶ perfects Regnault's piezometer and redetermines the compressibility of water. Tait⁷ and his pupils, Buchanan,⁸ Marshall, Smith, Omond,⁹ and others, carry the inquiry of compressibility and maximum density of water much further, and the data are theoretically discussed by Tait. Pressures as high as 600 atmospheres are applied. Solutions of salt and alcohol are also tested. Pagliani,¹⁰ Palazzo, and Vicentini,¹¹ using Regnault's piezometer, publish results for water and a number of other substances, mostly organic. They also examine mixtures. Temperature is varied between 0° and 100°, and the results are considerably discussed and utilized to show that Dupré's formula is only approximate. De Heen,¹² who has spent much time in studying volume changes of liquids, deduces a formula of his own, chiefly in reference to the thermal changes of compressibility. The theoretical results are tested by many experiments.

The research which Amagat¹³ published at about this time is remarkable for the enormous pressure applied hydrostatically (3,000 atmospheres). Ether and water are operated on. In later work¹⁴ these researches are extended to other liquid substances, with the ulterior object of finding a lower critical temperature. The behavior of water is fully considered. Grimaldi¹⁵ critically discusses the earlier work on the maximum density of water. He¹⁶ also examines the volume changes produced in a number of organic substances by temperature (0° to 100°), and pressure (0 to 25 atmospheres), and finds both Dupré's and De Heen's formulae insufficient.

In further discussion he¹⁷ also shows the insufficiency of Konowalow's¹⁸ formula. At this stage of progress the points of view gained in the

¹ H. F. Weber: C. R., vol. 87, 1878, p. 517.

² Boltzmann: C. R., vol. 87, 1878, pp. 593, 773.

³ Clausius: C. R., vol. 87, 1878, p. 718.

⁴ Massieu: C. R., vol. 87, 1878, p. 731.

⁵ Amagat: C. R., vol. 89, 1879, p. 437; *ibid.*, vol. 90, 1880, pp. 863, 995; *ibid.*, vol. 91, 1880, p. 428, and elsewhere.

⁶ Mees: *Beiblätter*, vol. 4, 1880, p. 512; vol. 8, 1884, p. 435.

⁷ Tait: *Challenger Reports*, vol. 2, 1882, appendix, pp. 1 to 40; *Nature*, vol. 23, 1881, p. 595; *Proc. Roy. Soc. Ed.*, vol. 12, 1883-'84, p. 757; *ibid.*, vol. 13, 1884-'85, p. 2; *ibid.*, vol. 11, 1882-'83, p. 813; *ibid.*, vol. 12, 1883, pp. 45, 223, 226.

⁸ Buchanan: *Proc. Roy. Soc. Ed.*, vol. 10, 1880, p. 697.

⁹ Marshall, Smith, and Omond: *Proc. Roy. Soc. Ed.*, vol. 11, 1882, pp. 626, 809.

¹⁰ Pagliani and Palazzo: *Beiblätter*, vol. 8, 1884, p. 795; *ibid.*, vol. 9, 1885, p. 149.

¹¹ Pagliani and Vicentini: *Beiblätter*, vol. 8, 1884, p. 794; *Journ. de phys.* (2), vol. 30, 1883, p. 461.

¹² De Heen: *Bull. Soc. Roy. Belg.* (3), vol. 9, 1885, p. 550.

¹³ Amagat: C. R., vol. 103, 1886, p. 429.

¹⁴ Amagat: C. R., vol. 104, 1887, p. 1159; *ibid.*, vol. 105, 1887, pp. 165, 1120; *Journal d. phys.* (2), vol. 8, 1889, p. 197.

¹⁵ Grimaldi: *Beiblätter*, vol. 10, 1886, p. 338.

¹⁶ *Ibid.*, vol. 11, 1887, pp. 136, 137, 138.

¹⁷ Grimaldi: *Zeitschr. f. phys. Chem.*, vol. 2, 1888, p. 374.

¹⁸ Konowalow: *Zeitschr. f. phys. Chem.*, 2, 1888, p. 1.

extensive researches of Ramsay and Young¹ throw new light on the subject. They prove experimentally that, if pressure, p , and temperature, θ , vary linearly ($p = b\theta - a$), the substance operated on does not change in volume. The substances tested are ether, methyl and ethyl-alcohol, acetic acid, and carbon dioxide. Exceptional results for the case of acetic acid and nitrogen tetroxide are referred to dissociation. Utilizing James Thomson's² diagram they point out that the locus of the isothermal minima and maxima intersects the locus of maximum vapor tensions at the critical point. They show this to be the case for ether. Fitzgerald,³ reasoning from Ramsay and Young's results, proves that for such liquids as obey the linear law specific heat must be a temperature function only, and internal energy and entropy must be expressible as the sum of two terms, one of which is a temperature function only and the other a volume function only. Thus Fitzgerald and Ramsay and Young arrive at the same position from which Dupré and Lévy originally started. My own work was brought to a conclusion before I had read the above researches; it was therefore specially gratifying to me to find my results according with those of Ramsay and Young. The data which I give apply emphatically for liquids, that is, for substances very far below the critical temperature. My pressures are, therefore, over six times as great as those of the English chemists. In case of thymol and of para-toluidine I even observed 25° and 15° below the respective melting points (under-cooling). Furthermore, my method of discussion is different. Fitzgerald,⁴ has further applied Clausius's⁵ equation to a discussion of Ramsay and Young's results. Sarrau⁶ similarly endeavored to adapt Amagat's data. Dickson⁷ has digested Andrews's data. Tait,⁸ who is still actively at work on high pressures, has recently made publication on the effect of dissolved substances on internal pressure.

3. Literature of heat expansion.—A few words relative to thermal expansion of liquids, which enters incidentally into the present paper, may be added. Many formulæ have recently been devised or tested by Avenarius,⁹ De Heen,¹⁰ Mendeleeff,¹¹ Thorpe and Rücker,¹² Jouk,¹³ and others,¹⁴ not to mention older observers. None of the forms seem to be

¹Ramsay and Young: *Phil. Mag.* (5), vol. 23, 1887, p. 435; *ibid.*, vol. 24, 1887, p. 196; *Proc. Roy. Soc. Lond.*, vol. 42, 1887, p. 3.

²James Thomson: *Phil. Mag.*, vol. 43, 1872, p. 227; *Nature*, vol. 9, 1873, p. 392.

³Fitzgerald: *Proc. Roy. Soc.*, vol. 42, 1887, p. 50.

⁴*Ibid.*, p. 216.

⁵Clausius: *Wied. Ann.*, vol. 9, 1880, p. 337.

⁶Sarrau: *C. R.*, vol. 94, 1882, pp. 639, 718, 845; *ibid.*, vol. 101, 1885, p. 941.

⁷Dickson: *Phil. Mag.*, vol. 10, 1880, p. 40.

⁸Tait: *Challenger Reports, Phys. and Chem.*, vol. 2, part 4, 1888; *Proc. Roy. Soc. Edinb.*, vol. 15, 1888, p. 426.

⁹Avenarius: *Mécl. phys. Ac. St.-Petersb.*, vol. 10, 1877, p. 697; *Beiblätter*, vol. 2, 1878, p. 211; *ibid.*, vol. 8, 1884, p. 806.

¹⁰De Heen: *Bull. Ac. Roy. Belg.* (3), vol. 4, 1882, p. 526; *Journ. Chem. Soc.*, vol. 45, 1884, p. 408.

¹¹Mendeleeff: *Chem. Ber.*, vol. 17, 1884, p. 129; *Beiblätter*, vol. 8, 1884, p. 806.

¹²Thorpe and Rücker: *Journal Chem. Soc.*, vol. 45, 1884, p. 135.

¹³Jouk: *Beiblätter*, vol. 8, 1884, p. 808.

¹⁴Rosenberg: *Journ. d'Almeida*, vol. 7, 1878, p. 350.

satisfactory when long ranges of temperature are introduced. This is shown in a critical research by Bartoli and Stracciati¹ relative to Mendeleeff's and Thorpe and Rücker's formulæ and by the discussion between Mendeleeff and Avenarius.

4. *Remarks on the literature.*—Surveying the forementioned researches as a whole, it appears that at their present stage more work has been spent on the compressibility of water than the exceptional behavior of this substance justifies. In other words, the volume-pressure-temperature changes of the great majority of liquids probably conform closely to a general thermodynamic law discovered by Dupré and Lévy, and by Ramsay, Young, and Fitzgerald, severally. It is therefore first desirable to find experimentally the full importance of this law, and then to interpret exceptional cases with reference to it. Again, it appears that researches in which long-pressure ranges are applied simultaneously with long-temperature ranges are urgently called for, and that it is from such work that further elucidation of this important subject may be obtained.

Among pressure experiments the late researches of Amagat stand out by their originality and importance. One can not but admire the experimental prowess which has enabled him to penetrate legitimately into a region of pressures incomparably high without lowering his standard of accuracy.

Special mention must be made of the celebrated papers of J. Willard Gibbs,² by whom the scope of graphic method in exhibiting the thermodynamics of fluids has been surprisingly enlarged. The terms *isometric*, *isopiestic*, *isothermal*, *isentropic*, etc., are used in the present paper in the sense defined by Gibbs (*loc. cit.*, p. 311).

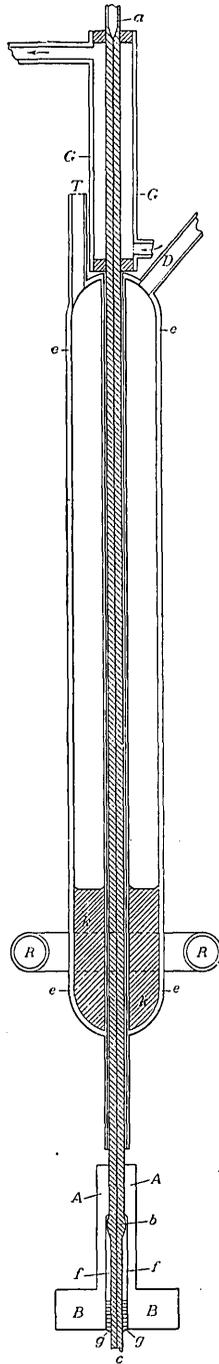
APPARATUS.

5. *Force pump and appurtenances.*—In making the experiments detailed in the following pages I used a large Cailletet compression pump, in the form constructed both by Ducretet, of Paris, and by the Société Gènevoise. Its efficiency is 1,000 atmospheres. It is made to be fed with water, but I found that by using thin mineral sperm oil it was possible to facilitate operations, because there is less danger of rusting the fine polished steel parts of the machine. The pump consists of two parts: the pump proper and the strong cylindrical wrought-iron trough in which the compression tubes are screwed. This trough is cannon-shaped, its axis vertical, and the open end uppermost. Pump and trough are connected by strong phosphor-bronze tubing, and similar tubes lead to the large Bourdon manometer, by which the pressures are measured.

6. *Pressure tube and appurtenances.*—The substance to be tested is inclosed in capillary tubes of glass of very fine bore (0.03^{cm} or less) and

¹ Bartoli and Stracciati: Beiblätter, vol. 9, 1885, p. 510.

² J. W. Gibbs: Trans. Conn. Acad., II (2), 1873, pp. 309, 332.



Capillary tube, with appurtenances, for measuring the compressibility of liquids.
(Scale, one-third.)

about 0.6^{cm} thick, such as are often used for thermometers. In my earlier experiments I had cylindrical bulbs blown near the middle of these tubes, and to give them greater strength a cylinder of solder was cast in brass around the bulb. This arrangement is very much more delicate than a plain capillary; but the tubes broke under pressures exceeding 200 atmospheres. For this reason, and because of the difficulty of adjusting a suitable vapor bath, the bulb tube was rejected in favor of a straight capillary tube. The length used was about 50^{cm} or 60^{cm}. To insert them into the trough the solid glass of the capillary tube *abc*, Pl. I, was swelled or bulged at *b*, about 5^{cm} from one end, and then pushed through an axially perforated steel flange *ABBA*, in which it fitted snugly. The bulged end and the flange faced the inside of the trough, so as to be acted against by the pressure. To seal the tube in the steel flange fusible metal *ff* was cast around it at the bulge, and the joint was then further tightened by a thick coating of marine glue, *gg*. A strong hollow nut of iron, surrounding both the lower end of the tube and the flange, fastened it to the trough, by forcing it against a leather washer. When completely adjusted the capillary tube projected about 40^{cm} or 50^{cm} clear, above the trough. Pressure was communicated through the oil of the pump to the mercury in the trough, which was in immediate connection with the open lower end of the capillary tube.

7. *Method of charging the tube.*—A thread of the solid substance to be acted on was introduced into the capillary between threads of mercury. This is a difficult operation, requiring much care. My first method was to pump out the air with a Sprengel pump; then to let the substance run down into it from a reservoir at the top of the tube by appropriate fusion. This method was far from perfect, and I found it almost impossible to insert the two mercury threads at the right place. After a variety of other trials of this kind I finally abandoned the vacuum method in favor of the following: Wide glass tubes (reservoirs) were fused both to the upper and the lower end of the capillary. The wide tube at the lower end was bent nearly at right angles to the axis of the capillary. I then poured mercury into the bent end, a continuous thread of which could be made to run quite through the capillary by properly inclining it. The substance was introduced into the upper reservoir and fused, care being taken to boil out the air, so that eventually the thread of mercury came directly in contact with the fused substance. The capillary is now less inclined. Mercury thread slowly ran back toward the lower end, followed by a thread of the substance, kept fused by applying a burner on the outside of the tube. This operation was repeated a number of times, so as to cleanse the tube with the substance and expel the little bubbles of air which might adhere to the walls of the capillary canal. Finally, when the mercury thread, capped by the thread of substance, was of suitable length, a globule of mercury was also put into the upper reservoir, covered by the fused substance

in such a way as to exclude air. By a quick motion the tube was then placed in nearly a vertical position, whereupon the lower thread of mercury ran down farther, followed by the thread of substance and an upper thread of mercury. The tube was now again brought back to the former position, with the thread of substance between the two threads of mercury, nearly in place. At this point the upper reservoir was cleansed with bibulous paper and, to seal it, filled with fused paraffine, in such a way that no air was left at the upper end of the upper mercury thread. Gently inclining the tube again, paraffine ran into the capillary, following the other threads. When the paraffine thread was sufficiently long the tube was left to itself till the threads solidified. During the whole operation the capillary tube must be kept heated. Considerable skill is required to obtain a properly charged tube, and the method must be varied, of course, when volatile liquids are to be introduced. It is not advisable to seal the upper end of the glass by fusing it, because the strains introduced during cooling greatly diminish the strength of the tube. The paraffine thread must be kept solid by a cold-water jacket, *GG*. Under these conditions its viscosity is too great to admit of its being forced out of the capillary tube by any pressure (1,000 atmospheres) compatible with the strength of the tube. Faultless adhesion of the paraffine to the glass is essential. In case of hygroscopic substances, therefore, this method fails, and the tube must be sealed in other ways.

Passing from the top to the bottom of the charged capillary one therefore encounters the following succession of threads: Paraffin (5^{cm}), mercury (5^{cm}), substance (20^{cm}, depending on its compressibility however; in case of ether a thread 1^{cm} long is sometimes essential), mercury (25^{cm}), in communication with the mercury of the trough. Measurements are therefore made by observing the distance apart of the lower meniscus of the upper thread of mercury, and the upper meniscus of the lower thread, with Grunow's cathetometer. When the adjustment is perfect the motion at the upper thread is nearly zero. Any sliding here is fatal, and the tube must be readjusted when this occurs.

8. *Method of heating.*—To heat the sample to any required temperature I surrounded the capillary tube, *abc*, with one of my closed boiling tubes,¹ *eee*, Pl. I, of clear glass.

By connecting the latter with a condenser at *D*, the ebullition may be prolonged for any length of time. The whole thread of the substance is thus virtually exposed in a vapor bath. Methyl alcohol (65°), water (100°), aniline (185°), and diphenylamine (310°) are available for boiling points. The position of these liquids is shown at *kk*, and they are heated by Dr. Wolcott Gibbs's ring burner, *R, R*. A thermometer is inserted at *T*. At high temperatures it is of course necessary to

¹ Cf. Bulletin, U. S. Geol. Survey, No. 54, 1889, pp. 86 to 90.

jacket the boiling tube appropriately with asbestos wicking, leaving only two small windows exposed through which the substance may be seen with the telescope. When the tube is fully heated it is clear, and condensation takes place only in the condenser. By adjusting suitable white and black screens with reference to the line of sight the image of the meniscus may be sharpened. Intermediate temperatures are reached by boiling the substances under low pressures. For this purpose it is merely necessary to attach the open end of the condenser to Prof. R. H. Richards's¹ pneumatic exhausting pump. The temperature is read on the thermometer at *T*.

It is scarcely necessary to state that the manipulations are difficult throughout, and that with the best of care breakage of tubes is a frequently recurring annoyance. Special attention must be given to obtain capillary tubes well annealed; otherwise internal strains add themselves to external strains and the strength of the tube is insufficient. Vapor baths must not be removed until the tube is thoroughly cold. With the best of care a tube will not outlast many series of experiments, for as pressure continues the glass undergoes a change very analogous to permanent set, so that eventually a tube may be broken at less than one-half the original test pressure.

9. *Pressure measurement.*—As is easily seen the method of experiment must necessarily be such that temperature is kept constant while pressure is varied at pleasure. To measure pressures I used a Bourdon gauge² graduated in steps of 10 atmospheres each, up to 1,000. So graduated, the gauge registers smaller differences of pressure than can be measured in terms of the volume changes of the liquid in the capillary tubes. Hence the gauge is suitable.

To test the gauge³ I compared it with a similar gauge graduated as far as 300 atmospheres and found the lack of accordance no larger than the error of reading. Again I compared the gauge indications with the changes of electrical resistance of mercury under identical conditions of pressure, with results equally satisfactory, as will be explained in the next chapter.

10. Curious results were obtained on comparing the gauge with a closed manometer, the essential part of which was a capillary tube containing air. The results calculated with reference to Boyle's law, *i. e.*, for isothermal expansion, were found to be wholly discrepant. The difficulty was interpreted by computing with reference to Poisson's law, *i. e.*, for adiabatic expansion. Some results are given in Table 1:

¹ Richards: *Trans. Am. Inst. Mining Eng.*, vi, 1879, p. 1.

² I think Prof. Tait, who has constructed other gauges based on Hooke's law, underestimates the ingenuity of Bourdon's gauge; and I believe that, either by increasing the number of coils or by suitably adjusting a mirror index, the gauge can be made serviceable without a multiplying gear. Read off directly, the only limit to the scientific efficiency of the gauge is the viscosity of the Bourdon tube.

³ I have since compared the gauge directly with Amagat's "*Manomètre à pistons libres*" and found my surmises substantiated.

p , v , k denotes pressure, volume, and the specific heat ratio, respectively. The error at $p = 100$ is due to the time lost in making the measurement, since it is here that volume changes are large and require special adjustments of telescope.

TABLE 1.—*Compressibility of air. Test of gauge.*

p	v	$\log v^k p$	v	$\log v^k p$
100	1,030	6.25	1,040	6.25
200	550	6.16	552	6.17
300	400	6.15	393	6.14
400	329	6.15	324	6.16
500	-----	-----	285	6.16

It appears that in case of quick manipulation this method is available for the measurement of k , particularly with reference to its variation with pressure. It appears also that when work is done on gases much time must be allowed in capillary tube experiments before the changes of volume obtained can be pronounced isothermal.

Since the gauge is based on Hooke's law, errors of the zero point are eliminated by working between indicated pressures and taking differences of reading. So far as relative pressure data are concerned it is then merely necessary that the attached dial and mechanism be virtually a scale of equal parts.

Finally, I compared the Bourdon gauge with a form of Tait gauge of my own, in which the volume expansion of a suitable steel tube is measured externally. Leaving further description to be given elsewhere, I will here insert a mere example of the results obtained. N. G. denotes the reading of the new gauge, an arbitrary scale being attached.

TABLE 2.—*Comparison of gauges.*

Bourdon.	N. G.	Bourdon.	N. G.
0	0	600	1045
100	160	700	1210
200	335	800	1370
300	520	900	1530
400	690	1000	1700
500	870		

Constructing the data graphically and remembering that all deviations are to be apportioned between the gauges, it appears that the error must everywhere be less than 10 atmospheres in most unfavorable cases.

No stress was placed on the absolute correctness of the standard atmosphere employed. The results sought follow equally well for an approximate standard, correctly multiplied.

11.—*Volume changes of the glass tubes.*—Prof. Tait¹ has given the following expression for the volume increment of a cylinder, subjected to internal hydrostatic pressure:

$$\frac{\Pi a_0^2}{a_1^2 - a_0^2} \left(\frac{1}{k} + \frac{a_1^2}{a_0^2 n} \right)$$

where Π is the pressure, $\frac{1}{k}$ and n the compressibility and the rigidity of the glass, and where a_0 and a_1 are the inner and the outer radius of the tube, respectively.

The internal and external radii of my tubes were 0.015^{cm} and 0.3^{cm}, respectively. It is easily seen that in case of so small a ratio the term of the above expression involving the compressibility of glass may be neglected with no greater error than a few tenths per cent. Hence, if proper value² of n be introduced and pressure be measured by atmospheres, the above expression reduces, approximately, to $4\Pi 10^{-6}$.

Unfortunately this correction is by no means negligible³ and may in unfavorable cases amount to as much as 5 per cent of the corresponding volume decrement of the liquid to be tested. The case is worse; most of the experiments are to be made at temperatures between 60° and 300°, for which interval the rigidity of glass can not be said to be known. To determine it myself was out of the question. Hence, instead of introducing arbitrary considerations, I resolved to neglect the correction altogether in favor of direct test experiments with mercury and with water.

12. *Mercury tests.*—The compressibility of mercury is too small to be amenable to the present method of measurement. Hence, since its compressibility is known, it is well adapted for testing the errors of the apparatus.

In Table 3 I have given the temperature, θ , and the length of the mercury thread, L , observed; also the volume decrement v/V per unit of volume, for each pressure p , as well as the corresponding mean compressibility β . Many methods were tried; best results were obtained for a thread of mercury inclosed between end threads of melted paraffin. At the low temperature, 30°, the lower thread was alcohol. The first column, v/V , was obtained by increasing p from 20 to 400 atmospheres, the second by decreasing p from 400 to 20 atmospheres, though the data given are means of a number of such measurements. Great care must be taken to keep the mercury thread free from adhering bubbles of air or volatile liquid (alcohol, for instance). At high temperatures these globules expand and may utterly vitiate the results, as I found in more than one instance.

¹ Tait: Challenger Reports, 1882, Appendix, p. 29.

² Everett: Units and Physical Constants, Macmillan, 1879, p. 53.

³ Since the sectional expansion alone enters, the correction is smaller than the above estimate.

TABLE 3.—*Compressibility of mercury.*

θ, L	p	$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$	$\beta \times 10^6$
30° 16.7 ^{cm}	20	0.0	0.0
	100	0.0	0.3	2
	200	0.3	0.3	2
	300	0.9	0.6	3
	400	1.8	1.2	4
65° 16.8 ^{cm}	20	0.0	0.0
	100	1.2	0.0	8
	200	2.1	2.0	14
	300	2.4	1.7	8
	400	3.0	2.9	8
100° 16.9 ^{cm}	20	0.0	0.0
	100	0.9	0.6	10
	200	1.2	1.8	9
	300	2.4	1.8	8
	400	2.7	3.0	8
185° 17.1 ^{cm}	20	0.0	0.0
	100	1.0	1.2	14
	200	2.3	2.2	13
	300	2.6	2.6	9
	400	4.5	3.9	11

ANOTHER THREAD, BETWEEN PARAFFIN.

185° 19.3 ^{cm}	10	0.0	0.0
	100	0.8	0.8	10
	200	2.9	3.0	17
	300	3.7	3.9	14
	400	4.9	4.5	13
310° 19.7 ^{cm}	20	0.0	0.0
	100	1.0	1.4	15
	200	2.6	2.6	14
	300	3.9	4.1	15
	400	5.3	5.2	14

Some of these results are shown in Pl. II, pressure being the abscissæ and volume decrements, $10^3 \times v/V$ the ordinates. This figure should be compared with the subsequent figures for organic substances.

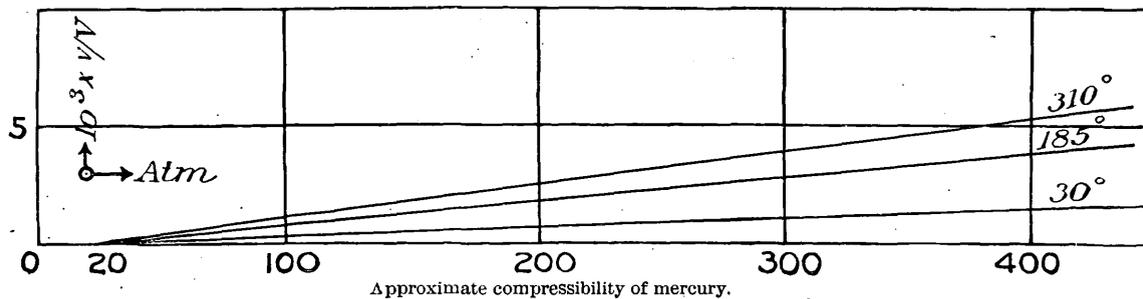
Table 3 is reassuring. From the known low-temperature compressibility of mercury¹ it appears that the error of β , made by neglecting Tait's correction, is about 10^{-6} , and that it is not greater than the unavoidable errors of measurement. Again, since the compressibility of the organic substances to be examined is in almost all cases much greater than 60×10^{-6} , the said error of β is not much above 2 or 3 per cent.

By comparing table 3 with tables 4 to 18 (*β*) it will be seen that the results at high temperatures are even more favorable.

Similar results were obtained for water, which may therefore be omitted here.

13. Isothermals and adiabatics.—To obtain the isothermals of the compressed liquids it would be necessary to wait a long time after each

¹ Everett: Loc. cit., pp. 52, 53. Amagat: C. R., vol. 108, 1889, p. 228; Journ. de phys. (2), vol. 8, 1889, p. 197. Tait: Loc. cit.



compression. But by so doing, at high temperatures, the tube would be seriously weakened in virtue of the diminished viscosity¹ of the material, if not even distorted. It appears, moreover, that the distinction between isothermal and adiabatic compression is beyond the scope of the present method of volume measurement. Finally, since the substance is in the form of an *extremely fine* (capillary) *filament*, the conditions are exceptionally favorable to isothermal expansion, for the excess of heat of the thread is at once imparted to the thick walls of the capillary tube. For this reason the discrepancy is not of such serious moment as would otherwise be the case. Hence I made my observations by varying pressure from 20 atmospheres to the maximum and then from the maximum back to 20 atmospheres, with only such allowance of time as was necessary for observation at the successive stages of pressure.

Near the critical temperature only is the distinction between isothermal and adiabatic decidedly larger than the errors of volume measurement.

The chief reliance was placed on the constancy of the fiducial zero. The volume increments must be identical, no matter whether they are observed during the pressure-increasing or during the pressure-decreasing march of the measurements.

14. *Thermal expansion.*—My measurements of thermal expansion are incidental; but they are necessary for the coordination of results. Without a bulb-tube such measurements are not very accurate, and the inaccuracy is much increased by the breaking off of the ends of the mercury thread whenever the substance operated on solidifies. In passing from one constant temperature to another an exchange of boiling tubes is to be made, and it is almost impossible to keep the substance in the capillary tube fused during the whole of the time for readjustments. On solidification the substances contract as much as 10 per cent. The mercury thread is therefore forced into the vacuities in the axis of the solid thread. After fusing again, it will be found that the lower column of mercury has broken into distinct little pieces, sometimes in great number, alternating with little threads of the substance. All of these must be measured, an operation which is not only excessively tedious, but makes the expansion measurement very inaccurate. For the same reason no correction need be added for the expansion of the glass. The error thus introduced is usually small, and not greater than 2 or 3 per cent in unfavorable cases of low temperature. See Tables 5 et seq. At high temperatures such a correction would be arbitrary, for the reason given in § 11. In these cases, however, it is probably altogether negligible, particularly so near the critical temperature.

¹ It is interesting to note that continued pressure weakens glass *gradually*, but without any apparent change of volume. The conditions of rupture may not be reached till after the lapse of much time. The tubes used must be of well annealed glass. Any temper strain is sure to cause rupture at relatively low pressures.

EXPERIMENTAL RESULTS.

15. *Explanation.*—My first results were obtained with capillary tubes, the middle part of which had to be blown out into a bulb. Around this a jacket of solder was cast and the whole contained in a brass tube. I found, however, that breakage took place from pressures of only 200 atmospheres, that corrections for glass expansion could not be estimated, and that the adjustment of the bath for constant temperature was unsatisfactory. I will therefore omit the data obtained, as they only corroborate the following results. Having thus found that compressibility would be measureable in cylindrical tubes, my next experiments were made in somewhat wider and thicker tubes than those discussed in §6. They have an advantage inasmuch as a filamentary thermocouple can be drawn through the tube without vitiating the volume measurement; but they broke under 300 atmospheres and were not conveniently thin for the thermal bath. These results are also rejected here, but will be cited in § 42, where the direct observations of contraction on cooling under pressure are exhibited. Finally I made use of the thermometer capillaries already described, § 6. In the earlier work (naphthalene, monochlor acetic acid), I did not introduce the upper thread of mercury, sealing the tube with a solid cold thread of the substance of the sample. This introduces arbitrary errors at the point where solid and fused substances meet; for on increasing pressures some of the liquid will be converted into solid, thus decreasing the length of the column. The reverse takes place on removing pressures. Nor is it possible to measure the length of thread of substance accurately, since the point of meeting of solid and liquid rises as the heating continues or when the stationary distribution of temperature is interfered with. Hence the facility of charging the tube is not compatible with accuracy of measurement, and I give these results only because many subsequent trials made to repeat them failed through accidents.

The bulk of the following experiments were made as detailed in § 6.

Throughout the following tables L is the length of the thread of substance, at the temperature θ ; v/V , the corresponding volume-decrement due to the acting pressure p . Finally, β is the mean compressibility between p_0 , the initial pressure, and the pressure given. Values marked observed and calculated and other information in the tables will be discussed below, §34 et seq.

16. *Ether.*—My results for ether are given in Table 4. Manipulations were made exceedingly difficult because of some sulphur present in the liquid. This at once attacks the mercury and destroys the cohesion of the thread. Above 100° , the thermal expansion increases enormously, so that I found it necessary to operate with two threads, the long one for low temperature and the short one for 310° . The tubes were filled by the U-tube method, § 7.

For the reasons given the initial pressure could not be kept constant,

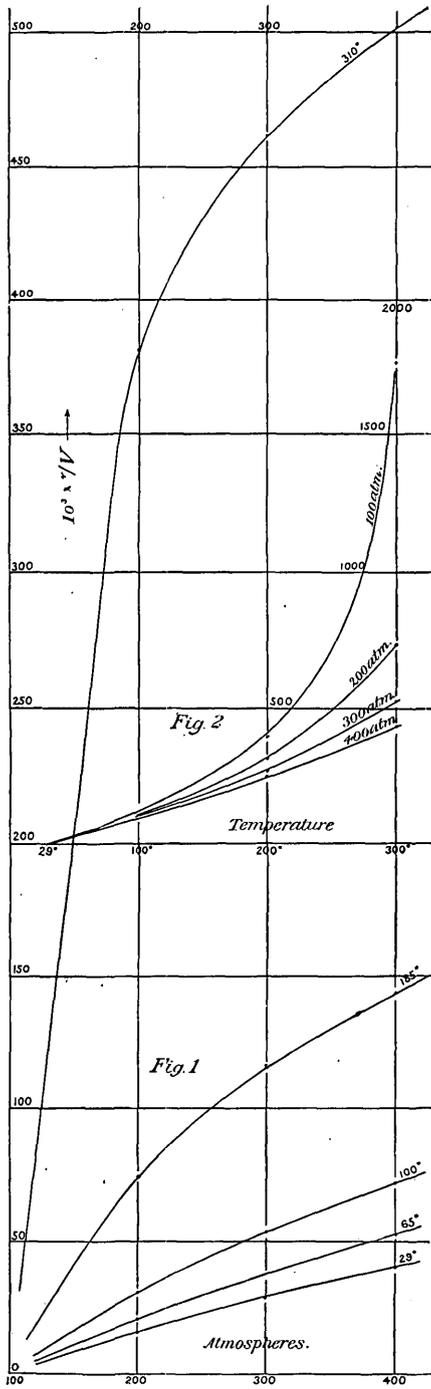


FIG. 1. Relative isothermals of ether. $p_0=100$ atmospheres, $\theta_0=29^\circ$
 FIG. 2. Relative isopiestic curves of ether. $p_0=100$ atmospheres, $\theta_0=29^\circ$.

the tubes not being long enough. Hence Table 5 has been computed, in which all data are reduced to the uniform initial pressure, $p_0 = 100$ atmospheres.

Table 6 finally shows the corresponding expansion data. It may be noticed that, supposing the given conditions to continue, ether would cease to expand at 1,100 atmospheres. These results are graphically repeated in Pl. III, Fig. 1, of which the curves are isothermal volume decrements referred to unit of volume, at the temperature given on the curve, and at the initial pressure $p_0 = 100$ atmospheres. In Pl. III, Fig. 2, I have similarly given the isopiestic volume increments referred to unit of volume at 29° and at the pressure given on the curve.

The two rows of results for $10^3 \times v/V$, given in tables 4, 7, et seq., were obtained during the pressure-increasing and the pressure-decreasing series of the experiments. This has already been explained in §13.

TABLE 4.—Compressibility of ether. Direct measurements. B. P., 34° ; critical temperature, 195° .

L, θ	p	$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$	$\beta \times 10^6$	Mean $\beta \times 10^6$ 0 to 400 atmospheres.
14.6cm 29°	20	0.0	0.0
	100	14.1	13.4	172
	200	29.1	29.1	162
	300	42.8	41.8	151
	400	54.1	53.8	142
15.5cm 64°	20	0.0	0.0
	100	20.1	19.7	248
	200	39.7	41.0	224
	300	57.1	56.8	203
	400	71.6	71.9	189
16.8cm 100°	10	0.0	0.0
	100	36.0	35.4	396
	200	65.8	64.9	344
	300	87.8	87.5	302
	400	106.5	105.5	272
21.8cm 177°	50	0	0
	100	80	80	1,600
	150	122	1,220
	200	148	148	990
	250	169	815
	300	186	186	745
	350	200	667
	400	211	212	605

SHORT FIBER, $L_{27} = 5.34$ cm.

14.6cm 310°	100	0	0
	150	287	287	5,740
	200	382	382	3,820
	250	431	431	2,870
	300	463	463	2,320
	350	485	484	1,930
	400	502	502	1,660

TABLE 5.—Compressibility of ether, referred to 100 atmospheres.

θ, L	p	Observed.	$\beta \times 10^5$	Com- puted.	Diff. $\times 10^3$	$\vartheta \times 10^6$	$\vartheta_0 \times 10^6$
		$\frac{v}{V} \times 10^3$		$\frac{v}{V} \times 10^3$			
29° 14·37 ^{cm}	100	0·0	-----	0·0	-----	-----	-----
	200	15·6	156	15·4	+0·2	165	194
	300	28·9	145	28·9	·0	-----	-----
	400	40·8	136	40·9	-·1	-----	-----
65° 15·18 ^{cm}	100	0·0	-----	0·0	-----	-----	-----
	200	20·7	207	20·5	+·2	226	282
	300	37·7	189	37·8	-·1	-----	-----
	400	52·8	176	52·8	±·0	-----	-----
100° 16·25 ^{cm}	100	0·0	-----	0·0	-----	-----	-----
	200	30·5	305	29·9	+·6	343	497
	300	53·6	268	53·4	+·2	-----	-----
	400	72·2	241	72·8	-·6	-----	-----
185° 20·08 ^{cm}	100	0·0	-----	0·0	-----	-----	-----
	200	74·1	741	71·5	+2·6	1,005	10,060
	300	115·5	577	114·7	+·8	-----	-----
	400	143·5	478	145·6	-2·1	-----	-----
310° *14·59 ^{cm}	100	0	-----	0	-----	-----	-----
	200	382	3,820	383	-1	34,250	-----
	300	462	2,310	460	+2	-----	-----
	400	502	2,510	503	-1	-----	-----

* Second sample.

TABLE 6.—Thermal expansion of ether $\frac{v}{V} \times 10^3$, referred to 29°.

Atm. =		100.	200.	300.	400.
$\theta =$	29°	0	0	0	0
	65°	57	51	48	43
	100°	131	114	103	93
	185°	397	315	274	246
	310°	1,770	733	528	435

COMPUTED VALUES $\frac{v}{V} = \ln(1 - \beta(\theta - b))^{-\tau, \beta}$. See § 41.

$\theta =$	29°	- 9	- 5	- 6	- 4
	65°	59	50	45	40
	100°	136	112	100	89
	185°	389	305	266	232
	310°	1,750	869	690	562

17. *Alcohol*.—The alcohol used was not free from water, though commercially absolute. Table 7 contains the observations made for compressibility. The initial pressure had again to be changed at high temperatures. Hence I have computed Table 8, in which the initial pressure is uniformly 150 atmospheres. The corresponding values of thermal expansion are given in Table 9. Of the charts, Pl. iv, Figs. 1 and 2, the former are isothermal decrements, each referred to unit of volume at the initial pressure, 150 atmospheres, and at the temperature marked on the curve. Similarly the isopiestic, Fig. 2, are referred to unit of volume at 28° and at the pressure on the curve. The results

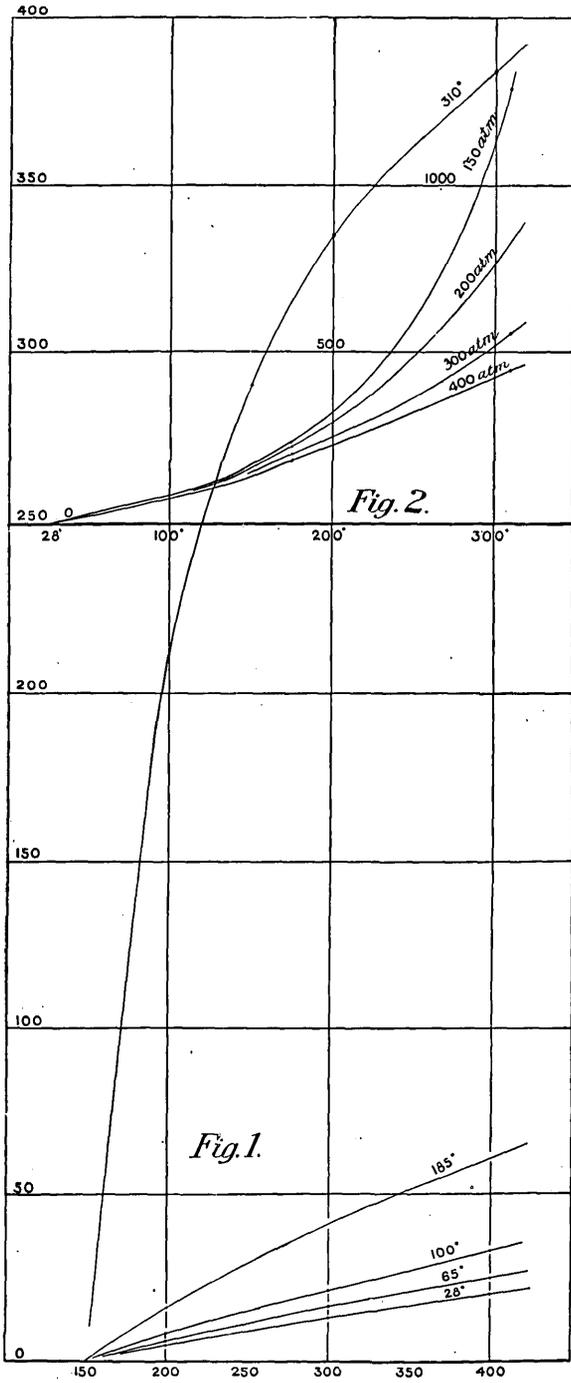


FIG. 1. Relative isothermals of alcohol. $p_0=150$ atmospheres, $\theta_0=28^\circ$.
 FIG. 2. Relative isopiestic curves of alcohol. $p_0=150$ atmospheres, $\theta_0=28^\circ$.

are more satisfactory than other, because a single thread only was used. In constructing Tables 5 and 8 I had to sacrifice some observations. But it seemed better to do this than to reach the lower initial pressure by more or less arbitrary hypotheses. The two sets of data (§ 16) are given side by side.

TABLE 7.—*Compressibility of alcohol. Boiling point, 78°; critical temperature, 236°.*

t, θ	p	$\frac{v}{V} \times 10^3$	$\frac{v}{\bar{V}} \times 10^3$	$\beta \times 10^6$
9.58 ^{cm} 27°	20	0.0	0.0	-----
	100	9.7	8.9	116
	200	18.6	17.8	101
	300	27.1	26.0	95
	400	34.1	33.6	90
9.93 ^{cm} 63°	20	0.0	0.0	-----
	100	9.4	9.6	118
	200	20.2	20.6	113
	300	31.5	30.8	111
	400	40.0	39.5	104
10.49 ^{cm} 100°	20	0.0	0.0	-----
	200	15.1	14.3	184
	300	28.4	29.1	160
	300	42.0	41.6	150
	400	52.9	53.1	140
12.25 ^{cm} 180°	20	0.0	0.0	-----
	100	35.9	35.3	445
	200	67.1	66.6	372
	300	91.1	90.3	324
	400	110.0	110.0	290
21.75 ^{cm} 310°	150	0	0	-----
	200	212	208	4,200
	250	289	291	2,900
	300	334	333	2,220
	350	363	364	1,820
	400	380	385	1,530

TABLE 8.—*Compressibility of alcohol, referred to 150 atmospheres.*

θ, t	p	Observed.	$\beta \times 10^5$	Com- puted.	Diff. $\times 10^3$	ϑ	ϑ_0
		$\frac{v}{V} \times 10^3$		$\frac{v}{\bar{V}} \times 10^3$			
28° 9.45 ^{cm}	150	0.0	-----	0.0	0	-----	-----
	200	4.3	86	4.3	0	89	101
	300	12.7	85	12.6	+1	-----	-----
	400	20.2	81	20.2	0	-----	-----
65° 9.78 ^{cm}	150	0.0	-----	0.0	0	-----	-----
	200	5.5	110	5.6	-1	115	136
	300	16.4	109	16.0	+4	-----	-----
	400	25.1	100	25.5	-4	-----	-----
100° 10.27 ^{cm}	150	0.0	-----	0.0	0	-----	-----
	200	8.4	166	7.6	+8	158	201
	300	21.6	144	21.5	+1	-----	-----
	400	33.1	132	34.0	-9	-----	-----
185° 11.62 ^{cm}	150	0.0	-----	0.0	0	-----	-----
	200	16.0	320	15.4	+6	331	598
	300	41.1	274	40.9	+2	-----	-----
	400	61.2	245	61.8	-6	-----	-----
310° 21.75 ^{cm}	150	0	-----	0	0	-----	-----
	200	211	4,200	219	-8	13,860	-----
	300	335	2,220	330	+5	-----	-----
	400	384	1,530	385	-1	-----	-----

TABLE 9.—*Thermal expansion of alcohol, $\frac{v}{V} \times 10^3$, referred to 28°.*

Atm. =		150	200	300	400
$\theta =$	28°	0	0	0	0
	65°	35	35	31	30
	100°	87	82	78	73
	185°	229	217	195	178
	310°	1,290	826	555	447

18. *Palmitic acid*.—The data are given in Tables 10 and 11, on a plan uniform with the above. Owing to accidents, two threads were observed; the first between 65° and 185°, and the second between 65° and 310°. At 65° solidification set in at 400 atmospheres. The necessary result is distortion of the curvature of the loci. Much difficulty was encountered because of breaks in the mercury thread. Hence the circumflexure in the isopiestic is probably an error of observation (Cf. Pl. v).

TABLE 10.—*Compressibility of palmitic acid, C₁₆H₃₂O₂. Melting point, 62°; boiling point, 350°.*

L, θ	p	Observed.		$\beta \times 10^6$	Computed.	Diff. $\times 10^3$	$\vartheta \times 10^6$	$\vartheta_0 \times 10^6$
		$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$		$\frac{v}{V} \times 10^3$			
65° 16.72 ^{cm}	20	0.0	0.0	*0.0	0.0	91	93
	100	7.2	7.2	90	7.1	-0.1
	200	15.0	15.3	85	15.3	-0.1
	300	22.8	23.1	82	23.0	-0.1
	†400	31.1	31.1	82	30.1	+0.2
100° 17.16 ^{cm}	20	0.0	0.0	0.0	0.0	102	104
	100	8.1	8.1	101	7.8	+0.3
	200	16.9	16.3	93	16.9	-0.3
	300	25.5	25.5	91	25.4	+0.1
	400	33.3	33.3	88	33.2	+0.1
185° 18.50 ^{cm}	20	0.0	0.0	0.0	0.0	160	165
	100	12.1	12.1	151	12.1	0.0
	200	26.3	26.3	146	25.5	-0.2
	300	37.2	37.8	134	37.5	0.0
	400	48.2	47.7	127	48.5	-0.4

* Including the lower series for 65°.

† Solidifying.

SECOND SAMPLE.

65° 14.63 ^{cm}	20	0.0	0.0
	100	6.5	6.9	84
	200	15.1	15.1	84
	300	22.9	22.3	81
	400	29.5	29.5	78
310° 17.54 ^{cm}	20	0.0	0.0	0.0	0.0	330	351
	100	23.4	24.6	300	23.7	+0.3
	200	47.4	48.3	265	47.5	+0.4
	300	66.3	67.9	240	67.2	-0.1
	400	82.6	84.3	220	83.8	-0.3

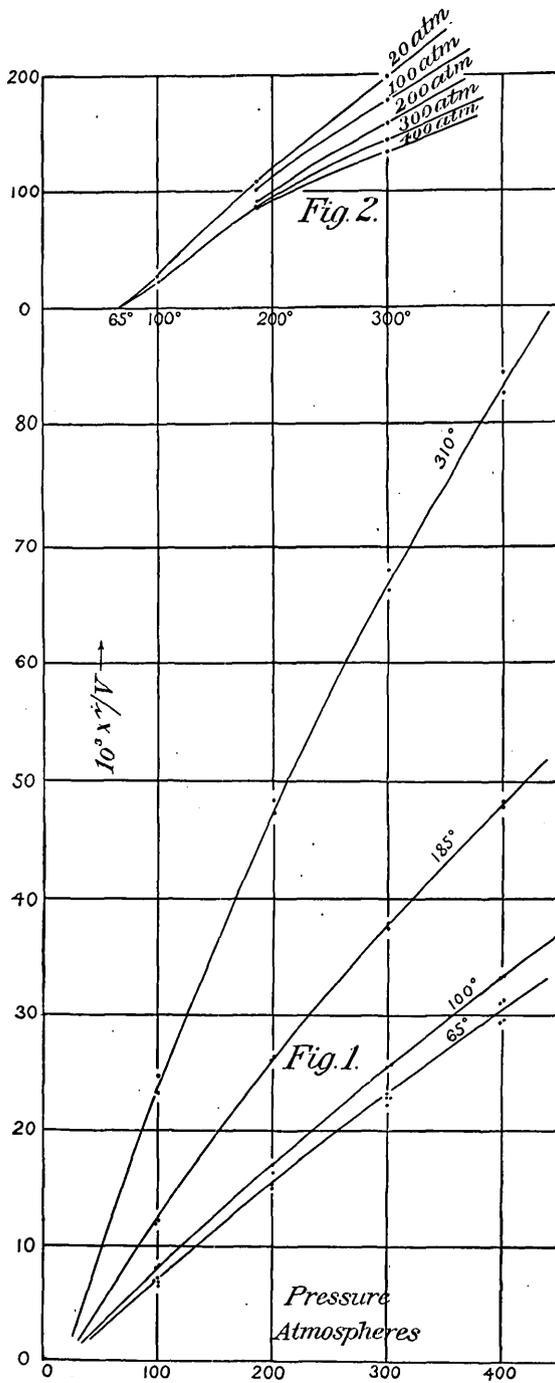


FIG. 1. Relative isothermals of palmitic acid. $p_0=20$ atmospheres, $\theta_0=65^\circ$
 FIG. 2. Relative isopiestic of palmitic acid. $p_0=20$ atmospheres, $\theta_0=65^\circ$.

TABLE 11.—*Thermal expansion of palmitic acid, $\frac{v}{V} \times 10^3$ referred to 65°.*

Atm. =		20	100	200	300	400
$\theta =$	65°	0	0	0	0	0
	100°	26	25	24	23	24
	185°	107	101	93	91	87
	310°	199	179	159	145	133

19. *Para-toluidine.*—The following data, Tables 12 and 13, and the diagrams, Pl. VI, were obtained for toluidine. A feature of these results is the circumflexure of the isopiestic increments in the undercooled part of their course. This is probably not an error, since it recurs again under similar conditions, in case of thymol, § 25. It may be noted that if contraction due to cooling under pressure continued at the same rate as shown in Table 13, there would be no volume change at 1,400 atmospheres. I found that to solidify the undercooled liquid as much as 500 atmospheres were necessary.

TABLE 12.—*Compressibility of para-toluidine, C₇H₇NH₂. Boiling point, 198°; melting point, 43°.*

θ, L	p	Observed.		$\beta \times 10^6$	Computed. $\frac{v}{V} \times 10^3$	Diff. $\times 10^3$	$\delta \times 10^6$	$\delta_0 \times 10^6$
		$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$					
*28° 14.14 ^{cm}	20	0.0	0.0	0.0	±0.0
	100	4.3	4.6	56	4.6	-0.1	59	60
	200	10.0	10.0	56	10.2	-0.2
	300	15.8	15.6	56	15.5	+0.2
	400	20.6	20.9	55	20.5	+0.2
65° 14.73 ^{cm}	20	0.0	0.0	0.0	±0.0
	100	5.5	5.5	69	5.3	+0.2	68	69
	200	11.6	11.9	65	11.7	±0.0
	300	17.4	17.4	62	17.7	-0.3
	400	23.5	23.5	62	23.4	+0.1
100° 15.02 ^{cm}	20	0.0	0.0	0.0	0.0
	100	6.3	6.3	79	6.8	-0.5	87	88
	200	14.5	14.5	81	14.7	-0.2
	300	22.2	22.3	79	21.1	+0.1
	400	29.0	29.3	77	28.8	+0.4
185° 16.36 ^{cm}	20	0.0	0.0	0.0	0.0
	100	11.0	10.9	137	10.6	+0.4	138	142
	200	22.8	22.8	127	22.5	+0.3
	300	33.4	33.4	119	33.1	+0.3
	400	42.4	42.2	112	43.1	-0.8
310° 19.05 ^{cm}	20	0.0	0.0	0.0	392	422
	100	29.0	29.4	365	27.6	+2.0
	200	56.1	52.0	300	54.5	+2.0
	300	76.2	75.7	271	76.3	-0.0
	400	92.7	92.5	243	94.5	-0.2

* Liquid, undercooled. Solidifies under 500 atmospheres.

TABLE 13.—*Thermal expansion of para-toluidine, $\frac{v}{V} \times 10^3$, referred to 23°.*

Atm. =		20	100	200	300	400
$\theta =$	28	0	0	0	0	0
	65	42	41	40	39	38
	100	63	60	57	56	53
	185	158	149	142	136	131
	310	348	313	287	265	247.

20. *Diphenylamine.*—In the value for diphenylamine, given in Tables 14 and 15, the initial pressure is unfortunately zero. This introduces a discrepancy between the present and the other results, in which the initial pressure is significant. The observations are not as uniform as the above. Cf. Pl. VII. It may be noted that at 2,000 atmospheres, supposing the given conditions of Pl. VII, Fig. 2, to last, no contraction would occur on cooling.

TABLE 14.—*Compressibility of diphenylamine. Melting point, 54°; boiling point, 310°.*

L, θ	p	Observed.		$\beta \times 10^5$	Computed. $\frac{v}{V} \times 10^3$	Diff. $\times 10^3$	$\vartheta \times 10^6$	$\vartheta_0 \times 10^6$
		$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$					
16.2 ^{cm} 65°	0	0.0	0.0	0.0	-0.0
	100	6.5	6.0	63	6.3	-0.0	65	65
	200	11.9	11.9	60	12.2	-0.2
	300	17.9	17.3	59	17.9	-0.3
	400	23.2	22.5	57	23.5	-0.7
	500	29.2	28.4	57	28.4	+0.9
16.4 ^{cm} 100°	0	0.0	0.0	0.0	0.0
	100	6.1	6.3	62	6.7	-0.5	69	69
	200	12.8	13.1	64	13.1	-0.2
	300	19.3	19.3	64	19.0	+0.3
	400	24.6	25.1	63	24.7	+0.1
	500	29.9	30.5	60	30.1	+0.1
17.7 ^{cm} 185°	0	0.0	0.0	0.0	+0.0	110	110
	100	11.2	10.7	110	10.4	+0.6
	200	20.6	20.3	102	20.0	+0.5
	300	29.2	28.9	97	28.9	-0.1
	400	37.1	36.1	91	37.0	-0.4
	500	44.1	44.3	89	44.7	-0.5
19.7 ^{cm} (20.3) ^{cm} 310°	0	0.0	0.0	0.0	0.0
	100	18.5	17.8	202	19.4	-1.2	213	213
	200	36.1	36.1	190	36.0	+0.1
	300	51.5	50.7	176	50.3	+0.7
	400	62.4	63.5	161	63.1	-0.1
	500	74.1	75.1	152	74.6	0.0

TABLE 15.—*Thermal expansion of diphenylamine, $10^3 \times \frac{v}{V}$, referred to 66°.*

Atm. =		0	100	200	300	400	500
$\theta =$	65°	0.0	0.0	0.0	0.0	0.0	0.0
	100°	12.4	12.4	11.3	10.1	10.1	11.0
	185°	93.0	88.0	83.1	80.0	78.0	76.0
	310°	235.0	221.0	205.0	193.0	186.0	178.0

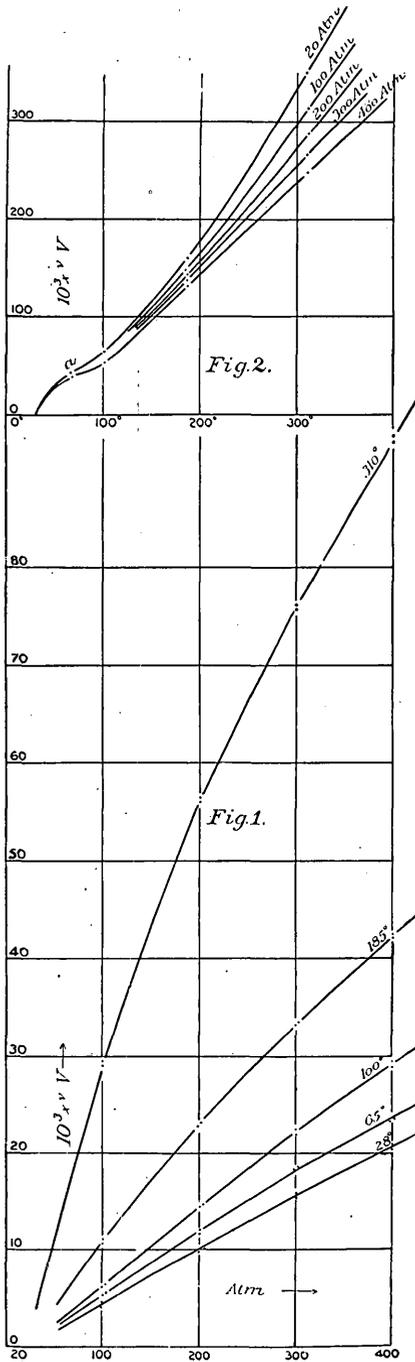


FIG. 1. Relative isothermals of toluidine. $p_0=20$ atmospheres, $\theta_0=28^\circ$.
 FIG. 2. Relative isopiestic curves of toluidine. $p_0=20$ atmospheres, $\theta_0=28^\circ$.

21. *Caprinic acid.*—Tables 16 and 17, and Plate VIII, contain the results for caprinic acid. The thermal expansion is irregular, probably due to motion of the thread in the tube, so that virtually two different threads were observed. The substance has a low melting point, 30°. Undercooled to 25° I found that it solidified at 300 atmospheres pressure.

TABLE 16.—*Compressibility of caprinic acid, C₁₀H₂₀O₂. Melting point, 30°; boiling point, 269°.*

θ, L	p	Observed.		$\beta \times 10^5$	Com- puted. $\frac{v}{V} \times 10^3$	Diff. $\times 10^3$	$\vartheta \times 10^6$	$\vartheta_0 \times 10^6$
		$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$					
30° (Under- cooled.) 15.91 ^{cm}	20	0.0	0.0	0.0	0.0
	100	4.9	5.7	66	5.9	-0.6	76	76
	200	13.4	12.9	73	12.9	+0.3
	300	19.5	19.8	71	19.5	+0.2
	400	25.5	25.8	68	25.7	0.0
65° 14.39 ^{cm}	20	0.0	0.0	0.0	0.0
	100	7.3	7.0	90	7.3	-0.1	95	97
	200	16.1	15.9	89	16.0	0.0
	300	23.6	23.9	84	23.8	0.0
	400	31.4	31.1	82	31.3	0.0
100° 16.85 ^{cm}	20	0.0	0.0	0.0	0.0	119	121
	100	8.5	9.1	110	9.0	-0.2
	200	19.1	20.1	109	19.5	+0.1
	300	29.1	28.9	104	29.1	-0.1
	400	36.8	36.8	97	37.8	+0.2
185° 18.30 ^{cm}	20	0.0	0.0	0.0	0.0	200	207
	100	15.3	15.1	190	14.9	+0.3
	200	31.2	31.1	173	31.2	0.0
	300	45.4	45.5	163	45.2	+0.3
	400	57.4	57.1	151	57.7	-0.4

TABLE 17.—*Thermal expansion of caprinic acid, $\frac{v}{V} \times 10^3$, referred to 30°.*

Atm. =		20	130	200	300	400
$\theta =$	30°	0	0	0	0	0
	65°	30	28	28	26	25
	100°	59	55	52	49	47
	185°	151	139	129	120	113

22. *Benzoic acid.*—In view of the high melting point only a single series of measurements was made. Table 18 contains the results.

TABLE 18.—*Compressibility of benzoic acid, C₇H₆O₂. Melting point, 121°; boiling point, 249°.*

L, θ	p	Observed.		$\beta \times 10^6$	Com- puted.	Diff. $\times 10^3$	$\vartheta \times 10^6$	$\vartheta_0 \times 10^6$
		$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$					
185° 11.88 ^{cm}	20	0.0	0.0	0.0	0.0
	100	11.4	11.4	142	10.5	+0.9	138	141
	200	22.3	22.1	124	22.3	-0.1
	300	32.8	33.1	118	33.2	-0.2
	400	42.1	42.5	112	42.9	-0.6

23. *Paraffin*.—I made many measurements with paraffin, of which the following digest, Tables 19 and 20, probably contains the best results. At 64° solidification set in at 400 atmospheres. This is well seen in Pl. IX. Supposing the conditions to hold indefinitely, there would be no contraction on cooling under a pressure of 1,200 atmospheres.

TABLE 19.—*Compressibility of paraffin. Melting point, 50° .*

L, θ	p	Observed.		$\beta \times 10^6$	Computed.		$\delta \times 10^6$	$\delta_0 \times 10^6$
		$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$		$\frac{v}{V} \times 10^3$	Diff. $\times 10^3$		
64° 15.86^{cm}	20	0.0	0.0	—	0.0	—0.0	—	—
	100	6.8	6.5	83	6.8	—0.1	88	89
	200	14.9	14.9	83	14.8	+0.1	—	—
	300	23.6	23.8	84	—	—	—	—
	400	(*)	(56.6)	(149)	—	—	—	—
100° 16.28^{cm}	20	0.0	0.0	—	0.0	—0.0	—	—
	100	8.5	8.5	106	8.5	0.0	111	114
	200	18.5	18.7	103	18.5	+0.1	—	—
	300	27.6	27.7	99	27.4	+0.2	—	—
	400	35.6	35.8	94	35.8	—0.1	—	—
185° 17.57^{cm}	20	0.0	0.0	—	0.0	0.0	—	—
	100	13.8	13.8	172	13.3	+0.5	178	184
	200	27.0	28.2	156	28.1	0.0	—	—
	300	41.2	41.4	147	41.1	+0.2	—	—
	400	52.3	52.0	137	52.7	—0.5	—	—
310° 19.70^{cm}	20	0.0	0.0	—	0.0	0.0	—	—
	100	26.8	26.2	331	26.0	+0.5	366	392
	200	51.9	52.1	289	51.7	+0.3	—	—
	300	72.4	71.8	257	72.7	—0.6	—	—
	400	89.9	89.6	236	90.3	—0.6	—	—

* Solidifying.

TABLE 20.—*Thermal expansion of paraffin, $\frac{v}{V} \times 10^3$, referred to 64° .*

$\Delta t_m =$	20	100	200	300	400
$\theta = 64$	0.0	0.0	0.0	0.0	0.0
100	26.4	24.1	23.1	22.6	22.1
185	108.0	109.0	92.9	87.8	83.8
310	241.0	210.0	196.5	181.0	167.0

24. Further results for paraffin are given in Table 21 and the chart, Pl. x. In this case the capillary tube was closed above by fusion, and the paraffin introduced in vacuo. Solidification takes place at 65° under 500 atmospheres. The divers columns v/V were obtained in separate experiments on different days.

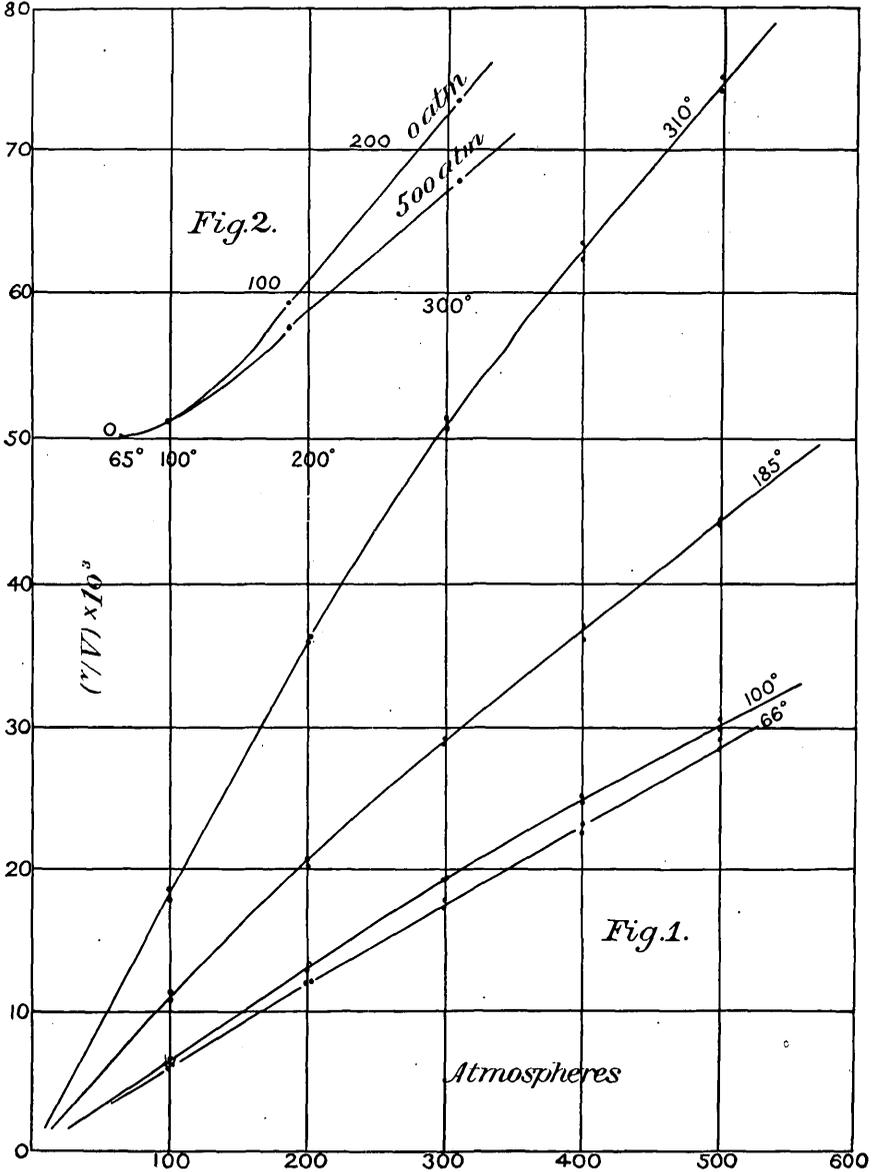


FIG. 1. Relative isothermals of diphenylamine. $p_0=0, \theta_0=66^\circ$.
 FIG. 2. Relative isopiestic of diphenylamine. $p_0=0, \theta_0=66^\circ$.

TABLE 21.—Compressibility of paraffin. Melting point, 55°.

θ, L	p	$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$	$\beta \times 10^6$	Computed.	$\delta_0 \times 10^6$
							$\frac{v}{V} \times 10^3$	
185° 18.9 ^{cm}	0	0.0	0.0	0.0	0.0	0.0
	100	17.6	17.8	17.1	18.1	176	17.2	186
	200	31.8	32.2	32.2	32.4	161	31.9
	300	45.0	45.3	45.8	45.7	151	45.2
	400	56.1	55.9	56.4	56.9	141	56.8
	500	67.1	(*)	134	67.4
100° 17.6 ^{cm}	0	0.0	0.0	0.0	0.0	0.0
	100	11.4	11.4	11.4	11.4	114	11.2	118
	200	22.0	21.8	21.7	21.5	109	21.4
	300	31.6	31.0	30.6	30.6	102	30.7
	400	39.2	39.2	39.4	38.9	98	39.3
	500	46.9	46.9	94	47.2
65° 17.0 ^{cm}	0	0.0	0.0	0.0	0.0	0.0
	100	10.3	9.9	10.0	9.8	100	9.5	100
	200	18.6	18.1	18.4	18.4	92	18.4
	300	26.3	26.2	87	26.6
	400	†34.6	34.3	86
	500	80.0	(160)

* Tube breaks.

† Solidifying, solid at 500 atmospheres.

25. *Thymol*.—Tables 22 and 23 and the accompanying Pl. XI, give full account of the behavior of thymol. Like toluidine, §19, thymol admits of considerable undercooling, and the isopiestic increments show circumflexure in this region. (See Fig. 2, at *a*.) Supposing all conditions to hold, no volume change would ensue on cooling under 1,200 atmospheres pressure.

TABLE 22.—Compressibility of thymol, C₁₀H₁₄O. Melting point, 53°; boiling point, 233°.

θ, L	p	Observed.		$\beta \times 10^6$	Computed.	Diff. $\times 10^3$	$\delta \times 10^6$	$\delta_0 \times 10^6$
		$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$		$\frac{v}{V} \times 10^3$			
* 28° 14.67 ^{cm}	20	0.0	0.0	0.0
	100	5.5	5.3	67	5.1	+0.3	65	66
	200	10.9	11.0	61	11.1	-0.1
	300	17.0	17.0	61	16.7	+0.3
	400	21.8	21.7	57	22.1	-0.4
64° 15.29 ^{cm}	20	0.0	0.0	0.0
	100	5.6	5.4	69	5.7	-0.2	74	75
	200	12.4	12.3	69	12.6	-0.2
	300	19.6	19.9	70	19.0	+0.7
	400	25.5	24.5	66	25.1	-0.1
100° 15.78 ^{cm}	20	0.0	0.0	0.0
	100	7.6	7.5	94	7.4	+0.1	96	97
	200	16.2	16.2	90	16.0	+0.2
	300	24.4	24.2	86	23.9	+0.4
	400	30.7	30.9	80	31.4	-0.6

* Liquid undercooled.

TABLE 22.—*Compressibility of thymol, C₁₀H₁₄O—Continued.*

θ, L	p	Observed.		$\beta \times 10^6$	Computed. $\frac{v}{V} \times 10^3$	Diff. $\times 10^3$	$\phi \times 10^6$	$\phi_0 \times 10^6$
		$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$					
185° 17·05 ^{cm}	20	0·0	0·0	-----	0·0	-----	-----	-----
	100	12·3	12·2	153	12·2	0·0	161	166
	200	26·1	25·9	144	25·8	+0·2	-----	-----
	300	38·0	37·8	135	37·8	+0·1	-----	-----
	400	48·3	48·5	127	48·8	-0·4	-----	-----
310° 19·5 ^{cm}	20	0·0	0·0	-----	0·0	-----	-----	-----
	100	33·0	32·0	407	31	+0·2	448	487
	200	61·1	60·5	338	61	+0·1	-----	-----
	400	83·6	83·6	299	84	-0·1	-----	-----
	300	102·0	101·0	267	103	-0·2	-----	-----

ANOTHER SAMPLE.

310° 16·47 ^{cm}	20	0·0	-----	-----	-----	-----	-----	-----
	100	34·0	-----	425	-----	-----	-----	-----
	200	62·4	-----	347	-----	-----	-----	-----
	300	82·5	-----	295	-----	-----	-----	-----
	400	102·0	-----	269	-----	-----	-----	-----

TABLE 23.—*Thermal expansion of thymol, $\frac{v}{V} \times 10^3$, referred to 28°.*

Atm. =		20	100	200	300	400
$\theta =$	28°	-----	-----	-----	-----	-----
	65°	42	43	41	39	39
	100°	76	73	71	68	65
	185°	162	154	145	138	130
	310°	329	293	263	239	220

26. In §§ 26 to 29 results are given for a variety of substances. In view of the high melting points, only two series for each were feasible. At 310° azobenzol decomposes. The results were rejected. The use of this colored substance pointed out an irremediable error, due to the adhesion of a film of substance to the glass, between the mercury and the walls of the tube. In case of compression, the advancing thread of mercury therefore moves on a cushion, as it were.

TABLE 24.—*Compressibility of monobrom camphor, C₁₀H₁₅BrO. Melting point, 76°; boiling point, 274°.*

θ, L	p	Observed.		$\beta \times 10^6$	Computed. $\frac{v}{V} \times 10^3$	Diff. $\times 10^3$	$\phi \times 10^6$	$\phi_0 \times 10^6$
		$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$					
100° 14·03 ^{cm}	20	0·0	0·0	-----	0·0	0·0	-----	-----
	100	6·6	6·6	82	6·6	0·0	83	85
	200	14·1	14·1	78	14·3	-0·2	-----	-----
	300	21·5	21·5	77	21·4	+0·1	-----	-----
185° 14·80 ^{cm}	20	0·0	0·0	-----	0·0	0·0	-----	-----
	100	9·8	9·9	123	9·5	+0·4	123	126
	200	20·0	19·9	111	20·2	-0·2	-----	-----
	300	29·7	29·9	106	30·1	-0·3	-----	-----

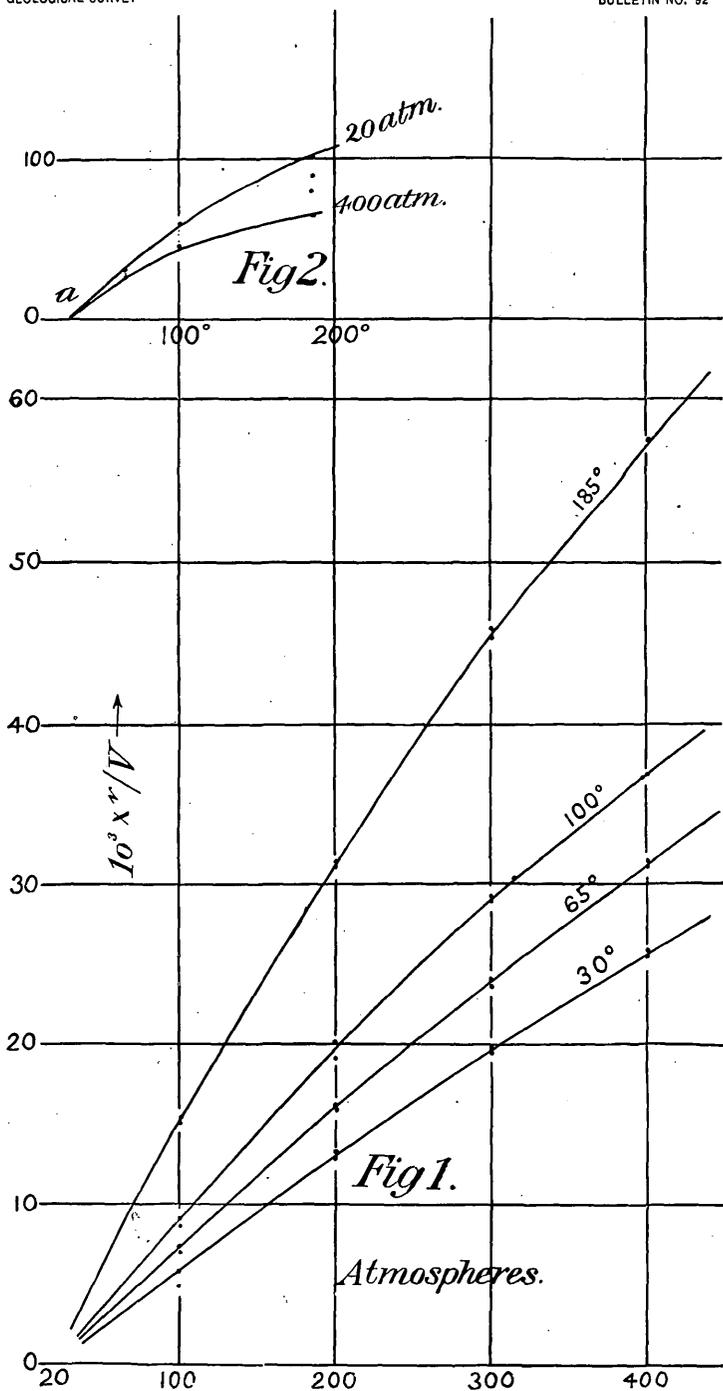


FIG. 1. Relative isothermals of capric acid. $p_0=20$ atmospheres, $\theta_0=30^\circ$.
 FIG. 2. Relative isopiestics of capric acid. $p_0=20$ atmospheres, $\theta_0=30^\circ$.

TABLE 25.—*Thermal expansion of monobrom camphor, $\frac{v}{V} \times 10^3$, referred to 100°.*

Atm. =		20	100	200	300
$\theta =$	$\begin{cases} 100^\circ \\ 185^\circ \end{cases}$	0.55	0.51	0.49	0.46

TABLE 26.—*Compressibility of α -naphthol, $C_{10}H_8O$. Melting point, 94°; boiling point, 279°.*

θ, L	p	Observed.		$\beta \times 10^6$	Computed.	Diff. $\times 10^3$	$\delta \times 10^6$	$\delta_0 \times 10^6$
		$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$		$\frac{v}{V} \times 10^3$			
100° 15.10 ^{cm}	20	0.0	0.0	-----	0.0	0.0	-----	-----
	100	5.6	6.0	72	4.9	+0.9	62	62
	200	10.3	10.7	58	10.6	-0.1	-----	-----
	300	15.9	16.1	57	16.1	-0.1	-----	-----
	400	20.5	20.5	54	21.3	-0.8	-----	-----
185° 15.97 ^{cm}	20	0.0	0.0	-----	0.0	0.0	-----	-----
	100	6.7	6.8	85	6.6	+0.2	85	87
	200	14.3	14.4	80	14.4	0.0	-----	-----
	300	21.3	21.6	77	21.6	-0.1	-----	-----
	400	28.6	28.4	75	28.4	+0.1	-----	-----

TABLE 27.—*Thermal expansion of α -naphthol, $\frac{v}{V} \times 10^3$, referred to 100°.*

Atm. =		20	100	200	300	400
$\theta =$	$\begin{cases} 100^\circ \\ 185^\circ \end{cases}$	0	0	0	0	0
		58	57	54	51	49

TABLE 28.—*Compressibility of azobenzol, $C_{12}H_{10}N_2$. Boiling point, 293°; melting point, 66°.*

θ, L	p	Observed.		$\frac{v}{V} \times \frac{1}{p}$	Computed.	Diff. $\times 10^3$	$\delta \times 10^6$	$\delta_0 \times 10^6$
		$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$		$\frac{v}{V} \times 10^3$			
100° 16.29 ^{cm}	20	0.0	0.0	-----	0.0	0.0	-----	-----
	100	6.5	6.3	80	6.2	+0.2	79	80
	200	13.2	13.3	74	13.3	0.0	-----	-----
	300	20.3	20.4	72	20.1	+0.3	-----	-----
	400	26.4	26.2	69	26.6	-0.3	-----	-----
185° 17.49 ^{cm}	20	0.0	0.0	-----	0.0	0.0	-----	-----
	100	10.1	9.8	125	10.0	0.0	131	134
	200	21.2	21.3	118	21.3	0.0	-----	-----
	300	31.6	31.6	113	31.4	-0.2	-----	-----
	400	41.1	40.9	108	40.9	-0.1	-----	-----

TABLE 29.—Expansion of azobenzol, $\frac{v}{V} \times 10^3$, referred to 100° .

Atm.=		20	100	200	300	400
$\theta =$	$\left\{ \begin{array}{l} 100^\circ \\ 185^\circ \end{array} \right.$	$\begin{array}{l} 0 \\ 74 \end{array}$	$\begin{array}{l} 0 \\ 71 \end{array}$	$\begin{array}{l} 0 \\ 66 \end{array}$	$\begin{array}{l} 0 \\ 6\frac{1}{2} \end{array}$	$\begin{array}{l} 0 \\ 61 \end{array}$

29. TABLE 30.—Compressibility of vanilline, $C_8H_8O_3$. Melting point, 80° ; boiling point, 235° .

θ, L	p	Observed.		$\beta \times 10^6$	Computed.	Diff. $\times 10^3$	$\delta \times 10^5$	$\delta_0 \times 10^6$
		$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$					
100° $15 \cdot 04^{cm}$	20	0.0	0.0	0.0	0.0
	100	4.1	3.9	50	4.6	-0.6	58	58
	200	9.5	9.6	53	9.9	-0.3
	300	16.1	15.6	57	15.0	+0.9
185° $16 \cdot 10^{cm}$	20	0.0	0.0	0.0	0.0
	100	7.1	7.2	90	7.1	+0.1	92	93
	200	15.5	15.9	87	15.4	+0.3
	300	22.7	22.7	81	23.1	-0.4

TABLE 31.—Expansion of vanilline, $\frac{v}{V} \times 10^3$, referred to 100° .

Atm.=		20	100	200	300
$\theta =$	$\left\{ \begin{array}{l} 100^\circ \\ 185^\circ \end{array} \right.$	$\begin{array}{l} 0 \\ 71 \end{array}$	$\begin{array}{l} 0 \\ 67 \end{array}$	$\begin{array}{l} 0 \\ 65 \end{array}$	$\begin{array}{l} 0 \\ 64 \end{array}$

30. *Naphthalene*.—The results of the following two tables were obtained without an upper mercury thread, and are therefore affected by the error discussed in § 15. They contain many points of special interest, however, and, in view of the long threads ($L=20^{cm}$), I think the discrepancy in question slight. It will be seen that at 100° naphthalin solidifies at 600 atmospheres. Monochlor-acetic acid did not solidify outright. The compressibility observed for the solid column I believe to be due to the presence of an excess of water of crystallization in the hygroscopic acid. Compressibility here is a *solution phenomenon*, and the excessively large value of β is thus explicable. The same phenomenon will be observed below, Chapter III, in case of silicated water.

A few other substances (phenanthrene, sodic acetate) were tried, but without obtaining publishable results.

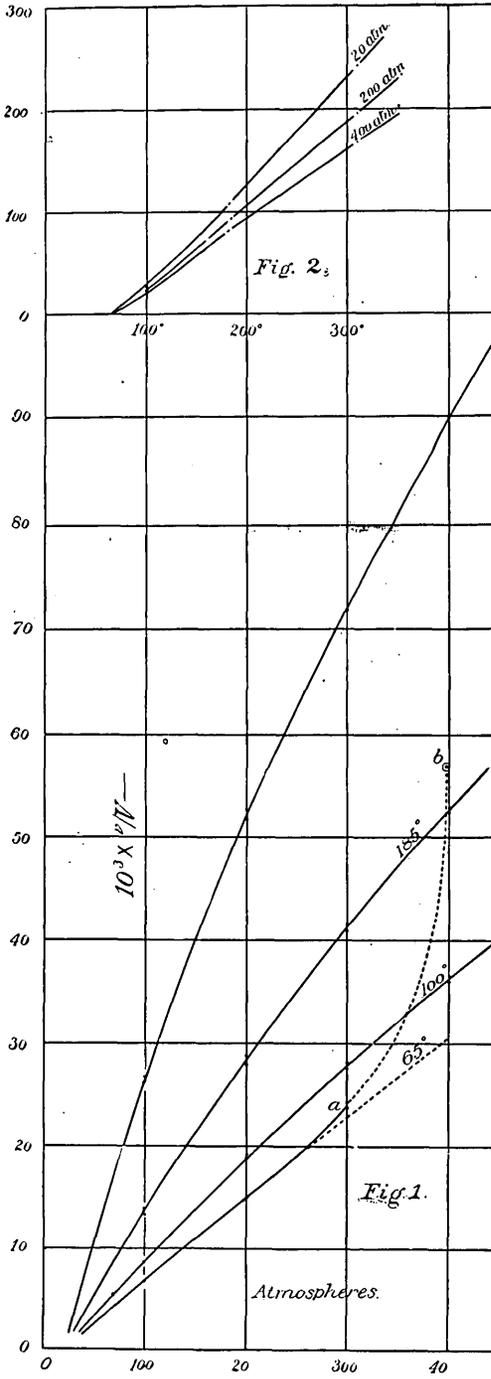


FIG. 1. Relative isothermals of paraffin. $p_0=20$ atmospheres, $\theta_0=65^\circ$.
 FIG. 2. Relative isopiestic of paraffin. $p_0=20$ atmospheres, $\theta_0=65^\circ$.

TABLE 32.—Compressibility of naphthalene. Melting point, 80°; boiling point, 215°.

L, θ	p	Observed.		$\beta \times 10^6$	Computed.			
		$\frac{v}{V} \times 10^3$	$\frac{v}{\bar{V}} \times 10^3$		$\frac{v}{V} \times 10^3$	$\vartheta \times 10^6$	$\vartheta_0 \times 10^6$	
21.2 ^{cm} 185°	50	0.0	0.0	0.0	133	14i
	150	13.2	12.5	129	12.5
	250	24.3	24.3	122	23.8
	350	33.7	33.7	112	34.0
	450	43.2	42.4	106	43.4
20.8 ^{cm} 153°	50	0.0	0.0	115	12i
	150	11.1	111	10.9
	250	21.4	107	20.8
	350	30.1	101	29.9
	450	37.8	94	38.4
21.7 ^{cm} 100°	50	0.0	0.0	0.0	93	97
	150	8.5	8.3	84	8.9
	250	17.3	16.8	85	17.2
	350	25.1	24.6	83	24.9
	450	32.3	32.3	81	31.9
	550	39.1	78	38.8
21.7 ^{cm} 100°	50	0.0
	300	20.7	83
	400	29.5	84
	500	36.9	82
	*600	52.5	96

* Solid.

31. TABLE 33.—Compressibility of monochlor-acetic acid. Melting point, 62°; boiling point, 188°.

θ, L	p	Observed.		$\beta \times 10^6$	Computed.		
		$\frac{v}{V} \times 10^3$	$\frac{v}{\bar{V}} \times 10^3$		$\frac{v}{V} \times 10^3$	$\vartheta_0 \times 10^6$	
185° 22.2 ^{cm}	50	0.0	0.0	142
	150	14.9	149	13.3
	250	25.2	126	25.2
	350	36.0	120	36.0
	450	44.6	112	45.7
65° 20.3 ^{cm}	50	0.0	0.0	0.0	72
	150	7.4	7.4	74	6.9
	250	13.8	13.8	69	13.6
	350	20.3	20.0	68	19.8
	450	25.7	25.2	64	25.7
	550	30.7	61	31.2
*50° 17.8 ^{cm}	50	0.0
	150	10.0	100
	250	17.0	85
	350	21.4	71
	450	24.2	61

* Column solid.

METHOD OF DISCUSSION.

32. Plan pursued.—I shall endeavor to discuss the above data in the following way: Having given certain relations between volume and pressure obtaining at any given temperature, let a close-fitting function be investigated, such that for the same pressures the calculated values of volume decrement must eventually be *greater* than the observed values will be. Let another function be investigated, such that for the same pressures the calculated values of volume decrement must eventually be less than the observed values can be. The actual data must therefore lie within the band or pathway included between the two functions in question. In other words, the couple of functions maps out an isothermal zone, as it were.

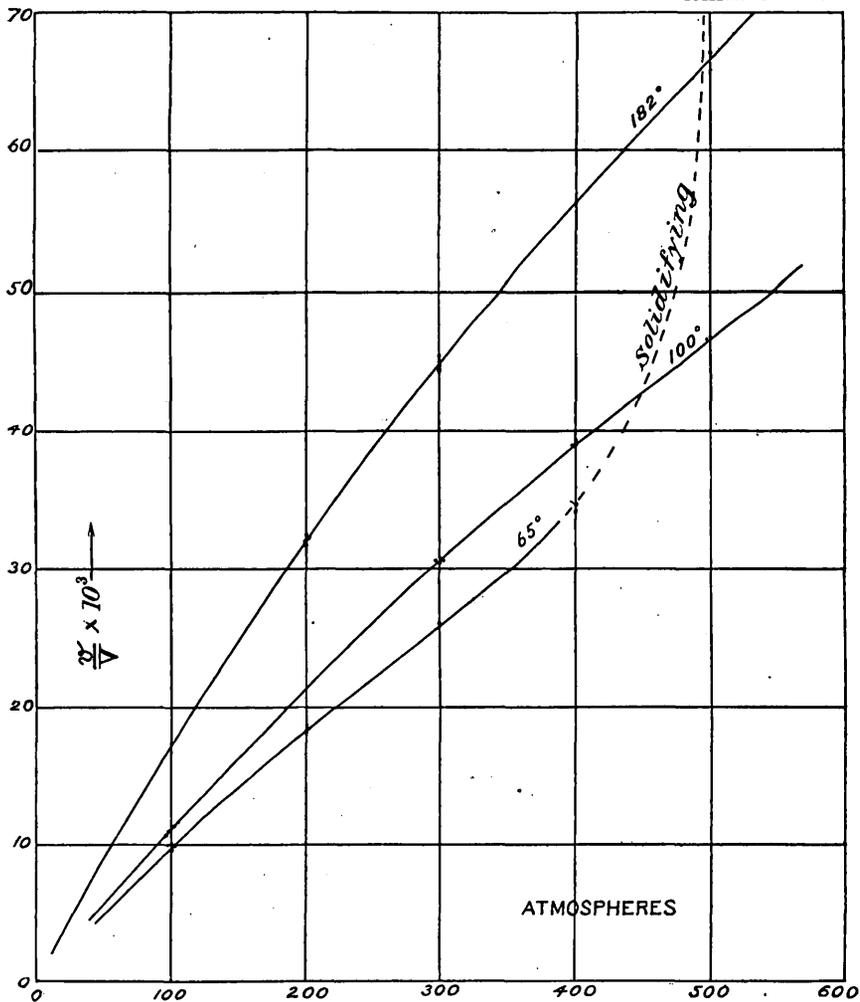
Now, suppose it is possible (the proof will be given by trial) to so adjust the two functions that throughout the interval of observation they both fall within the limits of error, then it is probable that any property which is simultaneously predicted by both functions may confidently be assumed as the property of the unknown isothermal. So long, therefore, as the two functions do not diverge seriously, there is here given a judicious method of extrapolation, by which relations beyond the limits of experiment may be apprehended.

33. Quadratic constants.—Now, in order to arrive at the probable nature of such functions, it is expedient to pass parabolas through the observations. The ordinary vertical parabola is clearly inapplicable. It predicts a maximum, and is therefore incompatible with the nature of the locus to be found. Nevertheless, the zero compressibility may thus be deduced with some certainty, and, moreover, from the relation of the two constants, additional inferences may be gleaned.

In Table 34 I have entered the two constants in question, respectively denoted by m and n , supposing that

$$y_{\theta} = 10^3 v/V = mp - np^2,$$

where y_{θ} is the volume decrement at the pressure p , under conditions of constant temperature θ . The table further contains boiling and melting points (B. P. and M. P., respectively), as well as the total thermal expansion E , from $\theta = 0^{\circ}$ to the value of θ cited, when $p = 0$.



Relative isothermals of paraffin. $p_0=0, \theta_0=65$.

TABLE 34.—*Quadratic constants which reproduce the isothermal decrements.*

Substance.	θ	$10^3 \times m.$	$10^6 \times n.$	$10^3 \times E.$	Substance.	θ	$10^3 \times m.$	$10^6 \times n.$	$10^3 \times E.$				
Palmitic acid: B. P., 350° M. P., 62°	310°	315	267	199	Monobrom cam- phor: B. P., 274° M. P., 76°	185°	129	80	55				
	185°	161	93	107									
	100°	100	36	26		100°	85	28	0				
	65°	83	25	0									
Para-toluidine: B. P., 198° M. P., 43°	310°	387	404	348	α Naphthol: B. P., 280° M. P., 94°	185°	85	29	58				
	185°	141	81	158									
	100°	81	6	63	100°	70	50	0					
	65°	69	25	42									
28°	56	3	0										
Diphenylamine: B. P., 310° M. P., 54°	310°	197	92	235	Azobenzol: B. P., 293° M. P., 68°	185°	127	52	74				
	185°	113	54	93									
	100°	64	3	12	100°	80	29	0					
	65°	62	12	0									
Caprylic acid: B. P., 270° M. P., 30°	185°	196	125	151	Vanilline: B. P., 285° M. P., 80°	185°	92	39	71				
	100°	116	46	59									
	65°	92	27	30		100°	47	32	0				
	30°	71	5	0									
Benzoic acid: B. P., 249° M. P., 121°	185°	143	93	Alcohol: B. P., 78°	310°	3,280	6,970	1,290				
										185°	341	418	229
				100°									
					65°	111	28	35					
					28°	87	20	0					
Paraffine: M. P., 55°	310°	349	320	210	Ether: B. P., 34°	310°	3,583	6,367	1,770				
	185°	177	110	100									
	100°	110	43	24						185°	776	992	397
	65°	83	9	0									
65°					224	170	57						
					29°	167	107	0					
Thymol: B. P., 233° M. P., 53°	310°	435	484	329									
	185°	159	85	162									
	100°	97	40	76									
	65°	69	2	42									
	28°	67	26	0									

COMPRESSIBILITY INCREASING INVERSELY AS THE PRESSURE BINOMIAL.

34. *Transition to exponential constants.*—There are two points of view from which the data of Table 34 are important:

(1) Compressibility m increases at a rapidly accelerated rate with temperature, caet. par. (2) Compressibility m and the datum for curvature n are intimately related. This points out that a fundamental relation for y_0 and p will probably exist independently of the material operated upon. § 13. The quantity E serves for orientations only, since it is not a coefficient.

It is necessary to look at these points more in detail. In case of alcohol and ether at 310°, quadratic constants are impossible: for the maximum would either lie within the field of observation, or the observations would have to be grossly slighted. This is to some extent true for ether at 185°. The alcohol and ether data in Table 34 are therefore inserted merely for comparison.

Rejecting these exceptional cases, it appears, if the dependence of n on m be considered separately for each substance as well as collectively

for all, that the quantities vary nearly linearly with each other. Suppose $2n = b(m - a)$.

To return to the above equation,

$$y = mp - np^2 \quad \dots \dots \dots (1)$$

$$\text{or } dy/dp = m \left(1 - \frac{2n}{m} p \right) \quad \dots \dots \dots (2)$$

replace m by \mathcal{S} and $2n/m$ by α , for the sake of distinction. Then inasmuch as (1) applies more accurately in proportion as p is small, equation 2 may be put

$$dy/dp = \mathcal{S} \sqrt{1 + \alpha p} \quad \dots \dots \dots (3)$$

whence

$$y = \ln(1 + \alpha p)^{\mathcal{S}/\alpha} \quad \dots \dots \dots (4)$$

This equation has an advantage over the equation (1): it does not predict a maximum. It is, therefore, compatible with the character of the isothermals in the above tables. Furthermore, in view of its simplicity, and of the fact that generally $y = \infty$ when $p = \infty$, it may be taken as the lower limit of the isothermal ribband described in § 32. For it is clear that when $p = \infty$, v/V can not be greater than unity.

In passing I may insert a few remarks on the relation of constants. Since $\mathcal{S} = m$ and $2n/m = \alpha$, it follows that $\alpha = b(m - a)/m$ and $\mathcal{S}/\alpha = m^2/b(m - a)$. Hence approximate values for the constants in (4) may be derived from Table 34. From an inspection of this table I was moreover led to infer that at the melting point, compressibility is constant and independent of pressure. In other words, since $1/\mathcal{S} = 1/a - \alpha/ab$, $\mathcal{S} = a$ would be the criterion of fusion. Subsequent results did not substantiate this surmise, § 38. Another similar notion that the resistance to compression is equal to the incipient resistance to extension even in liquids, and that therefore $1/\mathcal{S}$ must have a constant value at the boiling point independent of substance, is not warranted by the experiments made. Such a relation was suggested by the experiments of Kahlbaum¹ corroborated by O. Schumann,² according to which the boiling point corresponding to a given pressure is higher than the temperature of the same vapor tension. Ramsay and Young,³ who tested these experiments, do not corroborate them. They effectually substantiate Regnault's law according to which vapor tensions, whether obtained by the static or the dynamic method, are identical.

35. Properties of the exponential equation.—It will facilitate discussion if certain salient properties of equation (4) are grouped together here. I may state that, *a priori*, the occurrence of $y = 10^3 v/V = \infty$ for $p = \infty$, is not a fatal objection to its application; for the use of the

¹ Kahlbaum: Chem. Ber., vol. 18, 1885, p. 3146.

³ Ramsay and Young: Chem. Ber., vol. 18, 1885,

² O. Schumann: Chem. Ber., vol. 18, 1885, p. 2085.

p. 2855; vol. 19, 1886, p. 69.

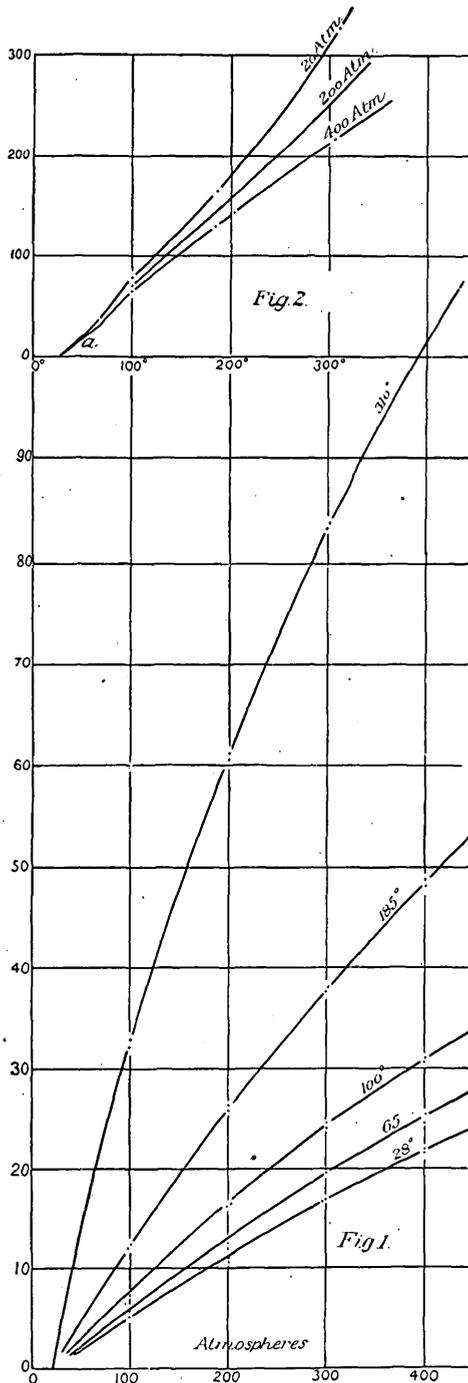


FIG. 1. Relative isothermals of thymol. $p_0=20$ atmospheres, $\theta_0=28^\circ$.
 FIG. 2. Relative isopiestic of thymol. $p_0=20$ atmospheres, $\theta_0=28^\circ$.

equation ceases at the point of solidification by pressure; therefore, at some finite value of p , as far as which the equation $y = \ln(1 + \alpha p)^{\delta/a}$ may faithfully represent the volume changes (decrements) observed. For this reason I originally accepted this equation with the assurance of its possessing a value beyond that of defining an arbitrary limit of the isothermal band.

Suppose for a given substance

$$y' = \ln \left(1 + \alpha_0 (p_0 + p) \right)^{\delta_0/a_0} \dots \dots \dots (5)$$

and, simultaneously,

$$y_0 = \ln \left(1 + \alpha_0 p_0 \right)^{\delta_0/a_0} \dots \dots \dots (6)$$

where p_0 and p are any two consecutive intervals of pressure. Then

$$y = y' - y_0 = \ln \left(\frac{1 + \alpha_0 (p_0 + p)}{1 + \alpha_0 p_0} \right)^{\delta_0/a_0} = \ln \left(1 + \frac{\alpha_0}{1 + \alpha_0 p_0} p \right)^{\delta_0/a_0} \dots (7)$$

Hence if

$$\alpha = \frac{\alpha_0}{1 + \alpha_0 p_0} \quad \text{and} \quad \mathcal{S} = \frac{\mathcal{S}_0}{1 + \alpha_0 p_0} \dots \dots \dots (8)$$

equation (7) may be put

$$y = \ln(1 + \alpha p)^{\delta/a} \dots \dots \dots (4)$$

Thus from the observations y , made along any arc of the whole curve, between p_0 and p , it is at once possible to obtain the constants of the whole curve referred to the origin at 0 atmosphere, by equations (8) or the equivalent equations:

$$\alpha_0 = \frac{\alpha}{1 - \alpha p_0} \quad \text{and} \quad \mathcal{S}_0 = \frac{\mathcal{S}}{1 - \alpha p_0} \dots \dots \dots (9)$$

so that the reductions are simple. Equations (9) suggest an important consequence: when $\alpha p_0 > 1$, both α_0 and \mathcal{S}_0 become imaginary. Now it is a matter for curious remark that this takes place in case of ether and alcohol near or above the critical temperature. Hence I inferred that the compressibility of liquids $d \frac{v}{V} / dp = -\mathcal{S} / (1 + \alpha p)$ changes form and passes into the compressibility of gases

$$\frac{d \frac{v}{V}}{dp} = -\frac{1}{p}$$

through an imaginary expression.

In such a consideration the condition for critical temperature would be $p = 1/\alpha$.

When p is small, equation (4) becomes

$$y = \mathcal{S}p - \frac{1}{2} \alpha \mathcal{S}p^2 + \dots,$$

which is shown to be capable of further simplification in the next section.

The expression for compressibility

$$d\left(\frac{v}{V}\right)/dp = \mathcal{S}/(1 + \alpha p)$$

has a counterpart which is applicable for thermal expansion, viz,

$$d\left(\frac{v}{V}\right)/d\theta = \tau/(1 - \beta\theta),$$

as will be shown in § 41.

Finally, the change of p , when regarded as the function of the radius ρ of any unit sphere within the compressed liquid, is of interest. Let p be expressed by $f(\rho)$, where ρ in the uncompressed liquid is unity. Then

$$1 - \rho^3 = \ln(1 + \alpha f(\rho))^{\theta/\alpha}$$

$$f(\rho) = \frac{1}{\alpha} \left(e^{\alpha(1-\rho^3)/\theta} - 1 \right)$$

This equation shows the nature of the inadequacy of (4); for if ρ decrease indefinitely, $f(\rho)$ eventually becomes $\frac{1}{\alpha} \left(e^{\alpha/\theta} - 1 \right)$. In the next paragraph α/\mathcal{S} is found to be nearly 9. Hence the limit in question is $8290/\alpha$. In the cases where equation (4) applies this value is somewhere between 10^6 and 10^7 atmospheres. Hence the interval within which equation (4) may apply satisfactorily is reasonably large.

36. Exponential constants computed.—After the suggestion contained in § 34 approximate values for the exponential constants in the equation $v/V = \ln(1 + \alpha p)^{\theta/\alpha}$ are easily derived.¹ The constants thus obtained are very crude, and the calculated results show a wide margin of error. Hence, starting with these, I computed the accurate values by a method of gradual approximation, finally selecting such values of \mathcal{S} and α as reduced the errors to a reasonably small limit. This computation is exceedingly tedious and unsatisfactory at best, because pairs of values of \mathcal{S} and α , differing very widely from each other, are often found to satisfy the equation about equally well. Nevertheless, it was necessary to avoid any scheme of selection other than the criterion of errors specified, the object being to obtain a set of constants independent of any ulterior purposes or considerations.

The results are given in Table 35, in which the first column contains the boiling point (B. P.), melting point (M. P.), of the divers substances

¹ Reference to y is conveniently dropped here. The constants refer to $\frac{v}{V}$.

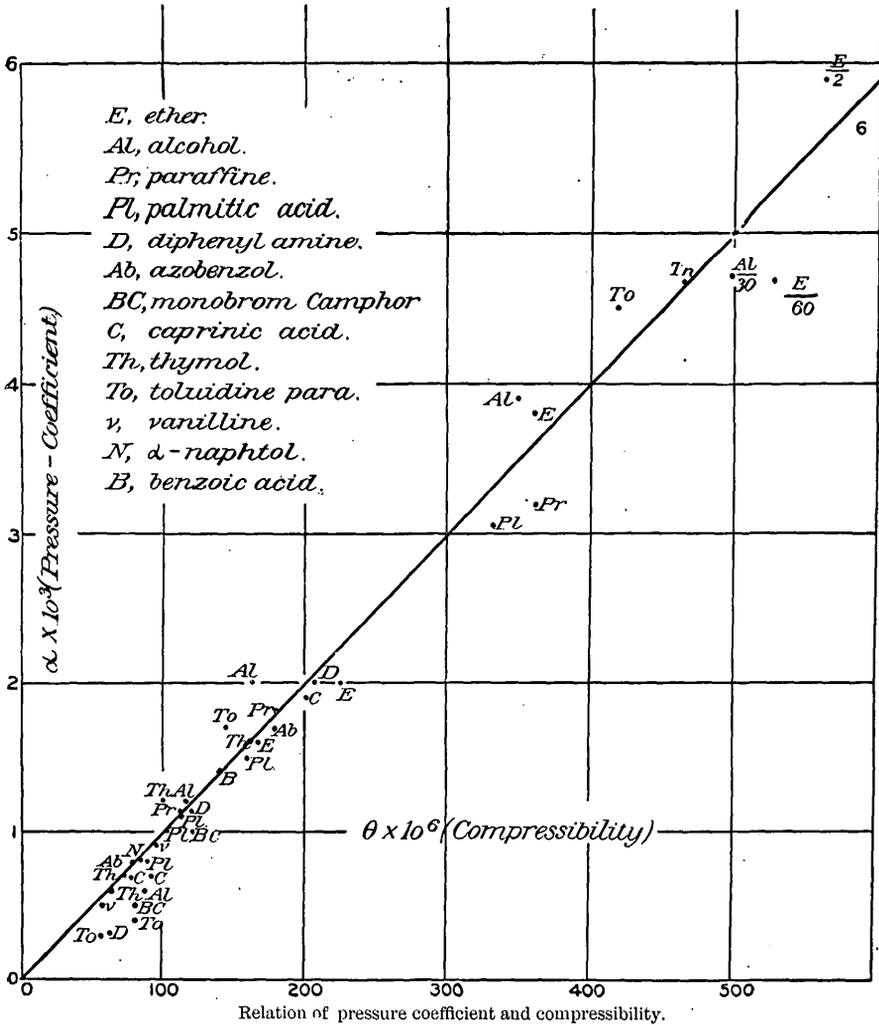


TABLE 35.—Exponential constants, etc.—Continued.

Substance.	θ	$\vartheta \times 10^5$	$\alpha \times 10^3$	$1/\vartheta$	$\vartheta_0 \times 10^5$	$\alpha_0 \times 10^3$	$1/\vartheta_0$	$2.3 \frac{\vartheta_0}{\alpha_0} \times 10^3$
Vanilline: B. P., 285°..... M. P., 80°..... $P_0=20$	} 185° 100°	96	0.90	10,420	98	0.92	10,200	235
		59	0.50	16,950	60	0.51	16,700	271
Azobenzol: B. P., 293°..... M. P., 68°..... $P_0=20$	} 185° -100°	130	1.20	7,690	133	1.23	7,520	250
		80	0.80	12,500	81	0.81	12,350	229
Alcohol: B. P., 78°..... M. P., 65°..... $P_0=150$	} 310° 185° 100° 65° 30°	15,000	140.00	67	(*)	(*)	(*)	247
		351	3.90	2,850	836	9.29	1,200	207
		164	2.00	6,100	234	2.86	4,270	189
		116	1.20	8,620	142	1.46	7,040	223
		88	0.60	11,360	97	0.66	10,310	336
Ether: B. P., 35°..... $P_0=100$	} 310° 185° 100° 65° 30°	31,800	280.0	314	(*)	(*)	(*)	261
		1,130	12.0	885	(*)	(*)	(*)	217
		361	3.8	2,770	583	6.13	1,720	218
		225	2.0	4,440	281	2.50	3,560	259
		167	1.6	5,990	199	1.91	5,020	240

* Equation fails, indicating transition into gaseous state.

$$\text{Mean } 2.3 \frac{\vartheta_0}{\alpha_0} = .2575 \pm .0083 \quad \frac{\vartheta_0}{\alpha_0} = .1119 = \frac{1}{9} \text{ (say).}$$

37. *Mean exponential constants derived.*—The tabulated constants for ether and alcohol above 185° substantiates the remarks made in § 35 relative to the limit of application if the equation $v/V = \ln(1 + \alpha p)^{\vartheta/\alpha}$. The critical temperatures of these substances¹ are 195° and 234°, respectively. Hence ether shows an imaginary ϑ_0 as low as 185°, and both substances do so at 310°.

The point of special interest relative to this table follows from a consideration of the last column $2.3\vartheta_0/\alpha_0$. In Fig. 21, where these results are given graphically (ϑ as abscissa, α as ordinate), their signification fully appears. To obtain a figure of reasonable dimensions for ether and alcohol, I have divided large pairs of ϑ and α , each by the same convenient number, as is indicated in the figure. This does not change their ratio. Looking at these results as a whole, and taking the enormous range of variation fully into consideration, it appears beyond question that ϑ and α are not only closely related, but that this relation is probably linear. The computation of Table 35 was an entirely independent procedure, and I could easily have obtained data more nearly in keeping with the mean ratio ϑ/α had I entered upon the work with any bias.

Hence I am justified in considering the equation given at the end of Table 35,

$$v/V = \ln(1 + 9\vartheta p)^{1/9}$$

as applicable to the whole series of organic substances examined. With

¹ Ramsey: Proc. Roy. Soc., London, vol. 31, 1880, p. 194; Hannay, *ibid.*, vol. 30, 1880, p. 484; and others. Cf. Landolt and Boernstein's tables, l. c.

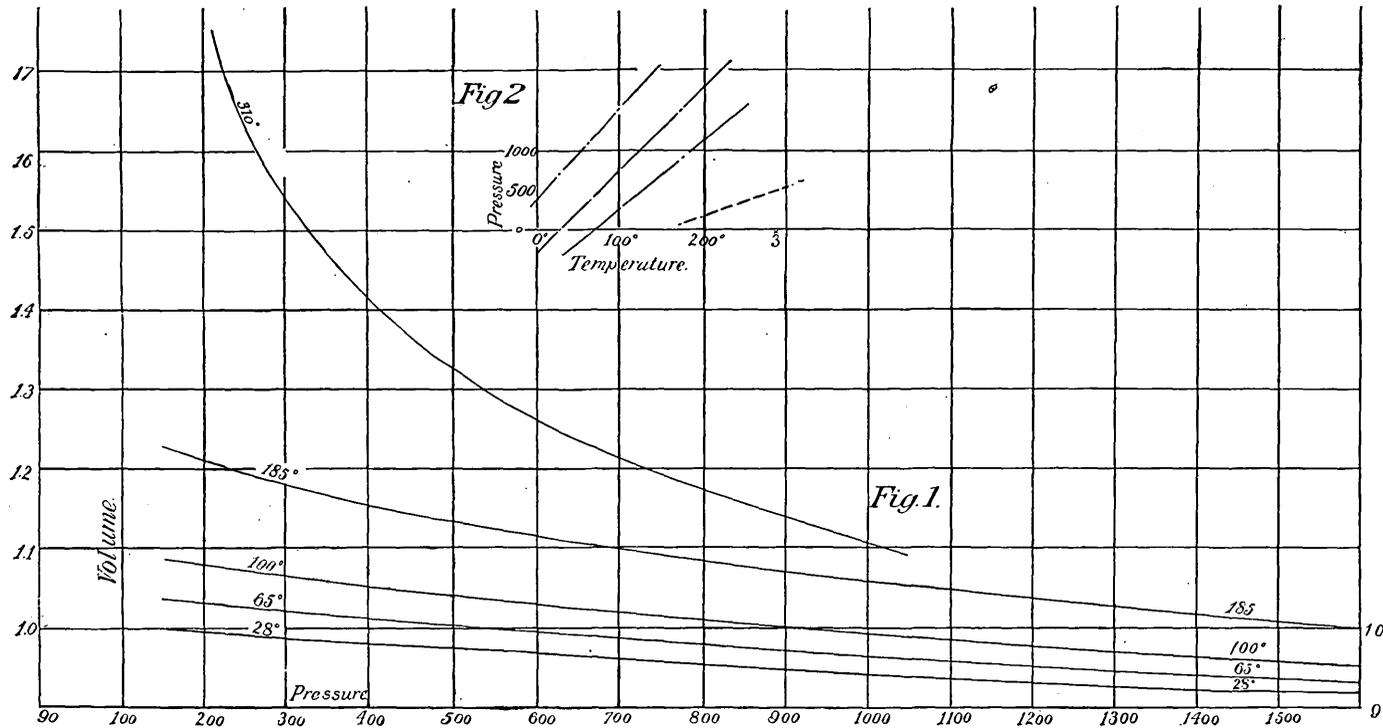


FIG. 1. Isothermals of alcohol.

FIG. 2. Isometrics of alcohol.

this as a point of departure, I made a recalculation of \mathcal{S} and have inserted the results in Table 36. Naphthalin and monochlor acetic acid are added.

TABLE 36.—Mean exponential constants $v/V = \ln(1 + 9\mathcal{S}p)$ †.

Substance.	θ	$\mathcal{S} \times 10^6$	$\mathcal{S}_0 \times 10^6$	$1/\mathcal{S}_0$	Substance.	θ	$\mathcal{S} \times 10^6$	$\mathcal{S}_0 \times 10^6$	$1/\mathcal{S}_0$
Ether: $p_0 = 100$ atm. B. P. = 34°	29°	165	194	6,061	Paraffin, other samples: $p_0 = 0$	65°	†100	10,000
	65°	226	282	4,425		109°	118	8,470
	100°	343	497	2,915		185°	186	5,380
	185°	1,005	10,060	995					
	310°	34,250	(*)	292					
Alcohol: $p_0 = 150$ atm. B. P. = 78°	28°	89	101	11,240	Thymol: $p_0 = 20$ M. P. = 5.3° B. P. = 233°	28°	65	66	15,150
	65°	115	136	8,700		64°	74	75	13,330
	100°	158	201	6,330		100°	96	97	10,310
	185°	331	598	3,020		185°	161	166	6,020
	310°	13,830	(*)	722		310°	448	487	2,050
Palmitic acid: $p_0 = 20$ M. P. = 62° B. P. = 350°	65°	91	93	10,750	Monobrom cam- phor: $p_0 = 20$ M. P. = 76° B. P. = 274°	100°	83	85	11,760
	100°	102	104	9,610		185°	123	126	7,940
	185°	160	165	6,060					
	310°	330	351	285					
Paratoluidine: $p_0 = 20^\ddagger$ M. P. = 43° B. P. = 198°	28°	59	60	16,670	α -Naphthol: $p_0 = 20$ M. P. = 94° B. P. = 280°	100°	62	62	16,130
	65°	68	69	14,490		185°	85	87	11,490
	100°	87	88	11,360					
	185°	138	142	7,040					
	310°	392	422	2,370					
Diphenylamine: $p_0 = 0$ M. P. = 54° B. P. = 310°	65°	65	65	15,380	Azobenzol: $p_0 = 20$ M. P. = 68° B. P. = 293°	100°	79	80	12,500
	100°	69	69	14,490		185°	131	134	7,460
	185°	110	110	9,090					
	310°	213	213	4,690					
Caprylic acid: $p_0 = 20$ M. P. = 30° B. P. = 270°	30°	76	76	13,160	Vanillin: $p_0 = 20$ M. P. = 83° B. P. = 285°	100°	58	58	17,210
	65°	95	97	10,310		185°	92	93	10,750
	100°	119	121	8,260					
	185°	200	207	4,830					
Benzoic acid: $p_0 = 20$ M. P. = 121° B. P. = 249°	185°	138	141	7,090	‡ Naphthalin: $p_0 = 50$ M. P. = 82° B. P. = 215°	100°	93	97	10,310
						153°	115	121	8,260
						185°	133	141	7,090
Paraffin: $p_0 = 20$ M. P. = 55°	64°	88	†89	11,240	† Monochlor acetic acid: $p_0 = 0$ M. P. = 62° B. P. = 188°	65°	72	13,800
	100°	111	114	8,770		185°	142	7,040
	185°	178	184	5,430					
	310°	366	392	2,550					

* Results of an older method. In ether and alcohol the reciprocals of \mathcal{S} are taken instead of $1/\mathcal{S}_0$.

† Discrepancy in these results due to solidification.

‡ Imaginary.

Availing myself of these constants, I computed the values of v/V given in Tables 4 to 33. By consulting the differences between observed and calculated, it will be seen that the errors are as a rule within the range of accuracy specified in the critical paragraphs 9 to 15.

38. *Subsidiary results.*—Certain subsidiary results of Table 36 are to be mentioned. If $1/\mathcal{S}$, the resistance to compression, be constructed as a function of temperature, θ , it will be seen that, except in the extreme cases of alcohol and ether, $1/\mathcal{S}$ decreases nearly proportional to θ . This rate of decrease is nearly the same for all substances examined.

In Table 37 I have given the approximate values of \mathcal{S} at melting

points, M. P., and at boiling points, B. P. No perspicuous relation is discernible, thus substantiating the inferences already drawn in § 34. It appears that compressibility is a quantity depending on other causes than the stability of molecular groups.

TABLE 37.—*Compressibility at melting and at boiling points.*

Substance.	M. P.	$\phi_0 \times 10^6$	B. P.	$\phi_0 \times 10^6$
Palmitic acid	62°	90	350°	(290)
Toluidine	43	62	198	160
Diphenylamine	54	60	310	213
Capric acid	30	76	270
Paraffin	55	83
Thymol	53	70	233	240
Brom. camphor	76	76	274
α -Naphthol	94	60	260
Vanilline	80	55	285
Azobenzol	68	65	293
Naphthalene	80	90	215	(170)
Chlor acetic acid	62	72	188	145
Alcohol (ϕ_{150})	78	130
Ether (ϕ_{100})	34	170

39. *Isothermals computed.*—With these results in hand I am able to reach the chief issue of the present paper, viz., the construction of the actual isothermals for the substances in hand. The computation being somewhat laborious, it will scarcely be fruitful to consider those substances in which the heat expansion could not be accurately measured. § 14. The data to be discussed are notably alcohol, ether, paraffin, thymol, para-toluidine, and diphenylamine.

To recapitulate: The volume decrement,

$$v/V = \ln(1 + 9Sp)^{1/9} \quad \dots \quad (10)$$

refers in all cases to unit of volume at the temperature θ of the isothermal and under the initial pressure P_0 . The compressed volume is therefore.

$$1 - \ln(1 + 9Sp)^{1/9}$$

and if in consequence of the *observed* thermal expansion at P_0 , the volume at θ be V_θ the actual isothermal is obviously

$$v_{\theta p} = v_\theta(1 - \ln(1 + 9Sp)^{1/9}) \quad \dots \quad (11)$$

referred to the initial temperature θ_0 . It is to be observed that v_θ is directly measured, and that, therefore, the only hypothesis occurring in equation (11) is equation (10).

In Tables 38 to 43, I have given $v_{\theta p}$ computed conformably with equations (11) for pressure as high as 1,500 atmospheres and for the temperatures of observation. A chart accompanies each table, in which pressures, p , are given as abscissæ volumes $v_{\theta p}$ as ordinates. From these charts, Plates XIII to XVIII, the conditions subject to which temperature and pressure must vary in order that $v_{\theta p}$ may remain constant are at once given by drawing horizontals. Hence, to each of the Tables 38 to 43 I have a supplement, in which values of θ and p for

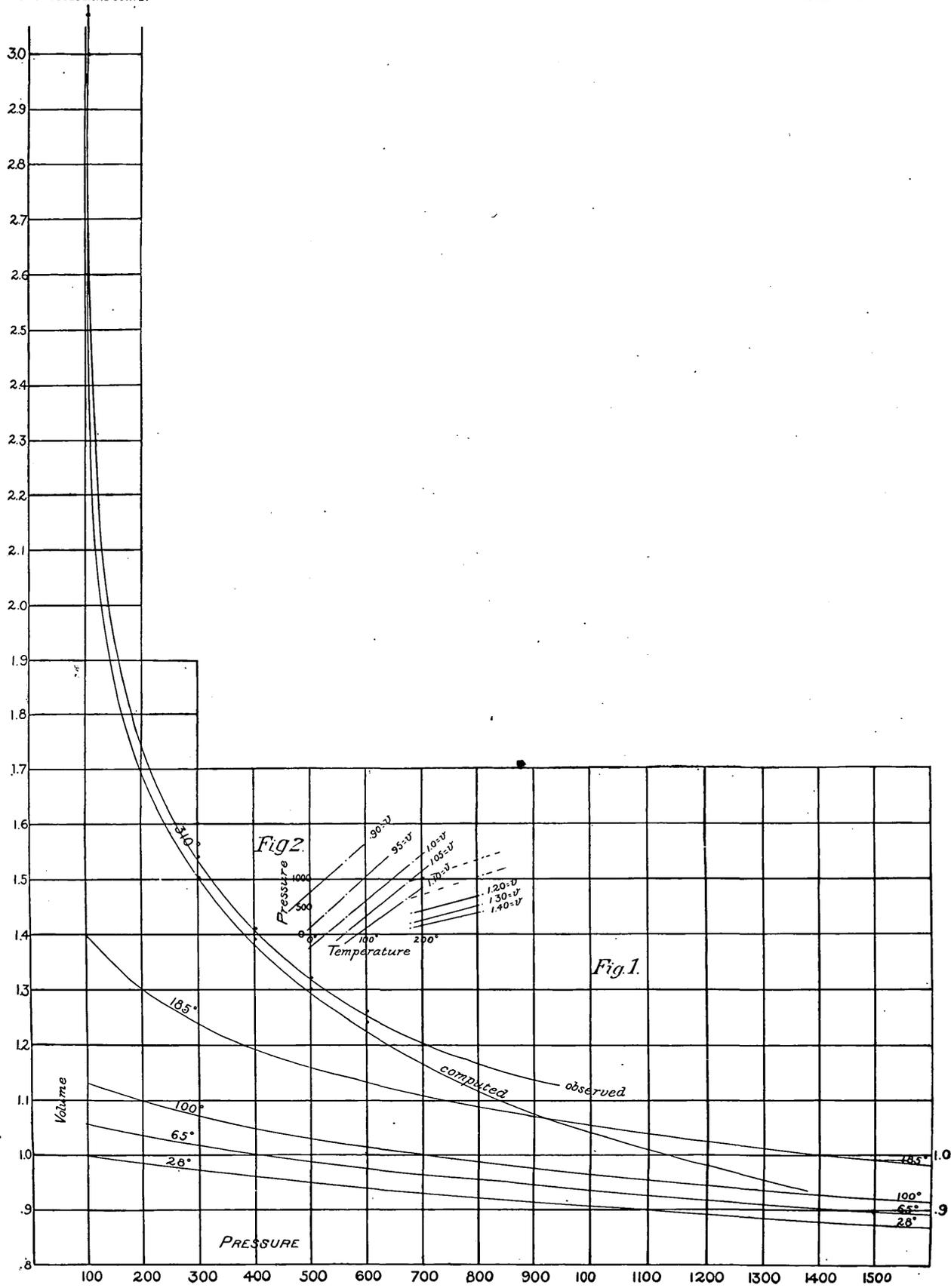


FIG. 1. Isothermals of ether.
 FIG. 2. Isopiestic of ether.

$v_{\theta p} = \text{const.}$ are inscribed. These supplementary tables indicate the nature of the isometrics. $V_{\mu\theta}$ will be computed in the next section.

TABLE 38.—*Isothermals of ether, referred to unit of volume at 28° and 100 atmospheres.*

p	$V_{\mu\theta}$	$V_{\theta\theta}$								
	*310°		185°		100°		65°		28°	
0	(†)	2.77	(†)	1.397	1.131	1.131	1.057	1.057	1.000	1.000
100	1.70	1.298	1.096	1.097	1.035	1.035	0.984	0.984
200	1.50	1.236	1.070	1.071	1.017	1.017	0.971	0.971
300	1.38	1.193	1.050	1.049	1.002	1.001	0.959	0.959
400	1.29	1.159	1.033	1.030	0.988	0.987	0.949	0.948
500	1.22	1.132	1.020	1.014	0.977	0.974	0.939	0.938
600	1.16	1.109	1.008	1.000	0.967	0.963	0.931	0.929
700	1.12	1.088	0.999	0.986	0.958	0.953	0.923	0.921
800	1.08	1.069	0.991	0.975	0.951	0.944	0.917	0.913
900	1.04	1.053	0.983	0.964	0.944	0.935	0.910	0.906
1,000	1.01	1.039	0.976	0.955	0.937	0.927	0.905	0.899
1,100	0.93	1.001	0.962	0.929	0.922	0.904	0.890	0.881
1,400	0.88	0.983	0.955	0.914	0.893	0.882	0.870	0.870

* Special measurement made later. † Equation fails.

Critical conditions of constant volume.

θ	$\Delta p.$	Volume.
28	0	1.00
65	310
100	600
185	1,300

Rate = 0.12° per atmosphere.

TABLE 39.—*Isothermals of alcohol, referred to unit of volume at 28° and 150 atmospheres.*

p	$V_{\mu\theta}$	$V_{\theta\theta}$								
	310°		185°		100°		65°		28°	
0	(†)	2.29	1.229	1.229	1.087	1.087	1.035	1.035	1.000	1.000
150	1.63	1.193	1.193	1.070	1.071	1.024	1.024	0.991	0.991
250	1.47	1.165	1.165	1.056	1.057	1.013	1.014	0.983	0.983
350	1.37	1.143	1.142	1.043	1.044	1.004	1.004	0.975	0.976
450	1.29	1.125	1.122	1.032	1.033	0.995	0.996	0.968	0.969
550	1.24	1.111	1.105	1.022	1.022	0.987	0.988	0.962	0.963
650	1.19	1.098	1.089	1.013	1.013	0.980	0.980	0.956	0.956
750	1.16	1.088	1.075	1.005	1.004	0.974	0.973	0.951	0.951
850	1.12	1.079	1.063	0.998	0.995	0.963	0.966	0.945	0.945
950	1.09	1.071	1.051	0.991	0.988	0.962	0.960	0.940	0.940
1,050	1.06	1.064	1.041	0.985	0.980	0.956	0.954	0.935	0.935
1,150	1.00	1.047	1.013	0.969	0.961	0.942	0.938	0.923	0.921
1,450	0.96	1.038	0.997	0.960	0.949	0.934	0.928	0.916	0.912

Critical conditions of constant volume.

θ	$\Delta p.$	Volume.
28	0	1.0
65	360
100	740
185	1,470

Rate = 0.12° per atmosphere.

TABLE 40.—*Isothermals of paraffin, referred to unit volume at 65° and 20 atmospheres.*

p	$V_{\mu\theta}$	$V_{\partial\theta}$	$V_{\mu\theta}$	$V_{\partial\theta}$	$V_{\mu\theta}$	$V_{\partial\theta}$	$V_{\mu\theta}$	$V_{\partial\theta}$
	310°		185°		100°		65°	
	20	1.241	1.241	1.108	1.168	1.026	1.026	1.000
120	1.201	1.232	1.090	1.090	1.015	1.015	0.991	0.991
220	1.171	1.171	1.074	1.074	1.005	1.005	0.983	0.983
320	1.147	1.146	1.060	1.060	0.996	0.996	0.975	0.975
420	1.129	1.125	1.045	1.047	0.988	0.988	0.969	0.968
520	1.113	1.107	1.037	1.036	0.980	0.980	0.962	0.962
620	1.101	1.091	1.027	1.025	0.973	0.973	0.955	0.956
720	1.091	1.076	1.018	1.016	0.967	0.966	0.951	0.950
820	1.081	1.063	1.011	1.007	0.960	0.959	0.946	0.945
920	1.074	1.051	1.003	0.999	0.955	0.953	0.941	0.939
1,020	1.067	1.040	0.997	0.991	0.949	0.947	0.936	0.935
1,320	1.051	1.012	0.982	0.970	0.935	0.931	0.924	0.921
1,520	1.043	0.995	0.973	0.958	0.928	0.922	0.916	0.912

Critical conditions of constant volume.

θ	$\Delta p.$	Volume.
65	0	1.00
100	250	-----
185	880	-----
310	1,430	-----

Rate = 0.13° per atmosphere.

TABLE 41.—*Isothermals of diphenylamine, referred to unit volume at 65° and 0 atmospheres.*

p	$V_{\mu\theta}$	$V_{\partial\theta}$	$V_{\mu\theta}$	$V_{\partial\theta}$	$V_{\mu\theta}$	$V_{\partial\theta}$	$V_{\mu\theta}$	$V_{\partial\theta}$
	310°		185°		100°		65°	
	0	1.235	1.235	1.093	1.093	1.012	1.012	1.000
100	1.211	1.211	1.081	1.082	1.005	1.006	0.994	0.994
200	1.191	1.191	1.071	1.071	0.999	0.999	0.987	0.988
300	1.173	1.173	1.061	1.061	0.993	0.993	0.981	0.982
400	1.159	1.157	1.052	1.053	0.987	0.988	0.976	0.977
500	1.146	1.143	1.044	1.044	0.982	0.982	0.971	0.971
600	1.134	1.130	1.034	1.036	0.977	0.976	0.966	0.967
700	1.124	1.119	1.030	1.029	0.970	0.972	0.962	0.962
800	1.116	1.108	1.023	1.022	0.967	0.967	0.957	0.957
900	1.107	1.098	1.017	1.016	0.963	0.962	0.954	0.953
1,000	1.100	1.089	1.012	1.010	0.959	0.958	0.950	0.949
1,300	1.082	1.061	0.997	0.993	0.948	0.945	0.938	0.937
1,500	1.073	1.050	0.989	0.983	0.941	0.938	0.932	0.930

Critical conditions of constant volume.

θ	$\Delta p.$	Volume.
65	0	1.00
100	190	-----
185	1,200	-----

Rate = 0.09° per atmosphere.

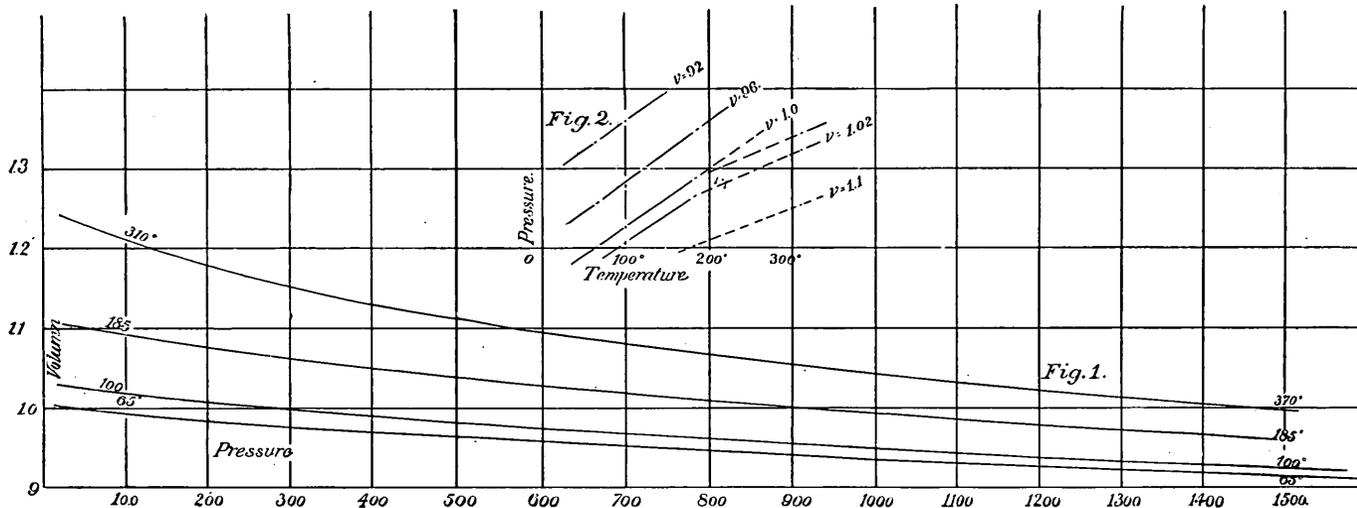


FIG. 1. Isotherms of paraffin.

FIG. 2. Isometrics of paraffin.

TABLE 42.—*Isothermals of paratoluidine, referred to unit volume at 28° and 20 atmospheres.*

p	V _{μθ}	V _{∂θ}								
	310°		185°		100°		65°		28°	
20	1.348	1.348	1.158	1.158	1.063	1.063	1.042	1.042	1.000	1.000
120	1.301	1.303	1.143	1.143	1.054	1.054	1.035	1.035	0.996	0.994
220	1.267	1.268	1.129	1.130	1.046	1.046	1.029	1.028	0.989	0.989
320	1.241	1.240	1.117	1.117	1.039	1.038	1.022	1.022	0.983	0.983
420	1.220	1.216	1.106	1.106	1.031	1.030	1.016	1.016	0.978	0.978
520	1.204	1.196	1.096	1.096	1.025	1.023	1.011	1.011	0.973	0.973
620	1.190	1.178	1.087	1.087	1.019	1.017	1.006	1.006	0.968	0.969
720	1.179	1.162	1.079	1.078	1.013	1.011	1.001	1.001	0.964	0.965
820	1.169	1.147	1.071	1.069	1.007	1.005	0.996	0.996	0.960	0.960
920	1.160	1.134	1.065	1.062	1.002	1.000	0.992	0.992	0.954	0.956
1,020	1.154	1.122	1.058	1.055	0.997	0.994	0.987	0.987	0.952	0.952
1,320	1.136	1.090	1.042	1.035	0.984	0.979	0.976	0.974	0.942	0.941
1,520	1.127	1.072	1.032	1.023	0.977	0.970	0.969	0.967	0.936	0.934

Critical conditions of constant volume.

θ	Δp.	Volume.
28	(-650)
65	25	1.04
100	270
185	1,200
310	(1,850)

Rate=0.10° per atmosphere.

TABLE 43.—*Isothermals of thymol, referred to unit volume at 28° and 20 atmospheres.*

p	V _{μθ}	V _{∂θ}								
	*310°		185°		100°		65°		28°	
20	1.329	1.329	1.162	1.162	1.076	1.076	1.042	1.042	1.000	1.000
120	1.277	1.279	1.145	1.145	1.066	1.066	1.035	1.035	0.994	0.994
220	1.240	1.242	1.129	1.129	1.057	1.057	1.028	1.028	0.987	0.988
320	1.212	1.212	1.116	1.116	1.048	1.049	1.021	1.021	0.981	0.982
420	1.192	1.188	1.104	1.103	1.040	1.041	1.015	1.015	0.976	0.977
520	1.175	1.167	1.093	1.092	1.033	1.033	1.010	1.009	0.971	0.972
620	1.162	1.148	1.084	1.081	1.026	1.026	1.004	1.003	0.965	0.967
720	1.151	1.131	1.075	1.072	1.020	1.020	0.999	0.998	0.961	0.962
820	1.142	1.116	1.067	1.064	1.014	1.013	0.994	0.993	0.956	0.957
920	1.134	1.103	1.060	1.055	1.008	1.007	0.989	0.988	0.952	0.953
1,020	1.127	1.091	1.053	1.047	1.003	1.002	0.983	0.983	0.948	0.949
1,320	1.111	1.059	1.037	1.026	0.989	0.986	0.973	0.970	0.937	0.937
1,520	1.103	1.040	1.027	1.014	0.981	0.977	0.966	0.961	0.931	0.930

* Special experiment, made later.

Critical conditions of constant volume.

θ	Δp.	Volume.
28	(-620)
65	40	1.04
100	410
185	1,090
310	1,500

Rate=0.10° per atmosphere.

40. *Isometrics.*—From the importance of the subject it is necessary to peruse the Tables 38 to 43 somewhat more in detail than was done in earlier work. In case of alcohol (Table 39) the curves for 28° to 185° , Pl. XIII, are a family of like properties; the curve for 310° , however, intersects these in the region of high pressures (1,500 atmospheres). Here, therefore, is additional corroboration of the remarks made in § 35, that above the critical temperature equation (10) is not applicable. The case may be more serious. It is also supposable that the 310° is only an accentuated expression of the shortcomings of equation (4) in general. I call to mind that this equation has only been used as the upper numerical limit of the isothermal band, for volume decrements; hence a lower limit for volumes. See next section.

The chief result of the present table is given by the supplemental tables: for $V_{\theta p} = V_{28,150} = 1$, θ and p as far as 185° are linear functions of each other. This is well shown in Pl. XIII, Fig. 2, and Pl. XIX below. The rate of change is one-tenth degree C. per atmosphere.

Results of the same kind hold for ether, Table 38, Pl. XIV, although the high temperature discrepancy conformably with the lower critical temperature is somewhat more pronounced. The rate of variation of θ and p for $V_{\theta p} = V_{28,100} = 1$ is here 0.12° C. per atmosphere. This also is clearly shown in Pl. XIII.

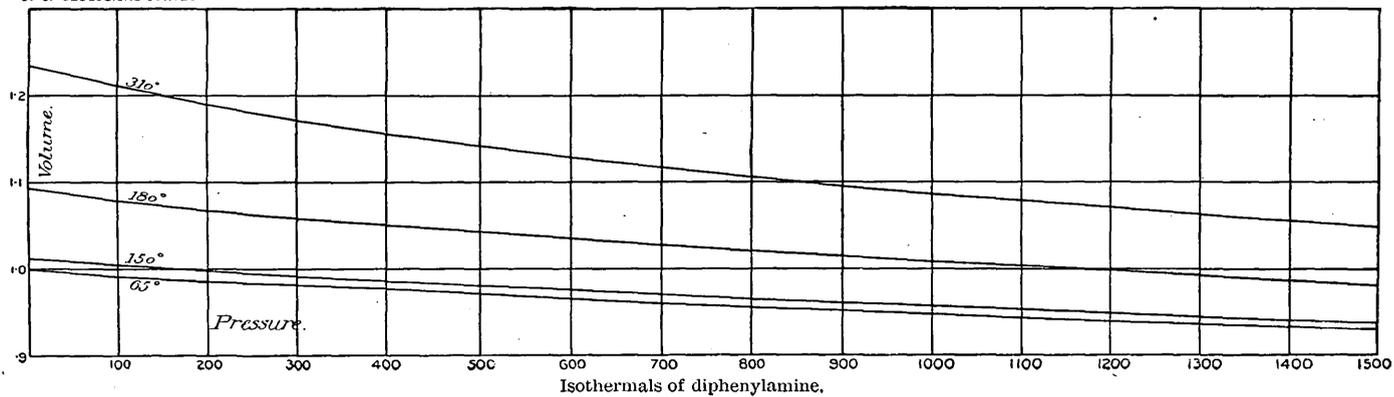
In case of paraffin, Table 40, which is the first substance solid at ordinary temperatures $V_{\theta p} = V_{65,120} = 1$ also shows a somewhat larger variation of θ and p , the rate being 0.13° C. per atmosphere. A notable peculiarity of these curves is the occurrence of a discrepancy at 310° similar to that of ether and alcohol, but much less pronounced.

For thymol Table 43, Pl. XVIII and XIX, the results obtained resemble those for paraffin, but the agreement is not so good. The rate is 0.11° C. per atmosphere, when $V_{\theta p} = V_{65,120} = 1.04$. Toluidine Table 42, Pl. XVII, shows the rate 0.10 per atmosphere, when $V_{\theta p} = V_{65,120} = 1.04$. For diphenylamine finally, Table 41, and Pls. XVI and XIX, the rate is 0.09° C. per atmosphere. In most of the solid substances the expansion difficulties, § 14, render the results inaccurate particularly in cases where two or more distinct threads were observed.

But taking the results as a whole (0° to 185°), it follows with considerable certainty, I think, that *if temperature and pressure vary linearly with each other at the mean rate of about 0.11 C. per atmosphere, there will be no change of volume.* Changes of state of aggregation are excluded from the considerations.

More rigorously this is expressed thus: If with the observed thermal expansion, compressibility be supposed to increase inversely as the first power of the pressure binomial ($1/\alpha + p$), then temperature and pressure must vary linearly to maintain constancy of volume.

In Pl. XIX the chief isometrics have been grouped together for comparison. The linear march between 0° and 185° is well shown by ether, alcohol, and paraffin. For toluidine and thymol the irregularities are



Isothermals of diphenylamine.

in an opposite sense, and for thymol the distribution of points is actually zigzag as far as 310°. Hence a march of errors can not be said to be discernible. The break in the undercooled region *a*, like the break between 185° and 310°, is marked. The latter will be specially discussed in the final paragraph of this chapter in connection with direct data.

The thermodynamic signification of the above results has already been suggested, § 2. It follows, therefore, so far as the present work (§ 40) goes, that the thermodynamic surface $V_{\theta p}$ will probably possess oblique symmetry as shown in Pl. xx. This curve is generated by moving the initial section *vp*, parallel to itself, but in the oblique direction, so that ten units of pressure may be passed for each unit of temperature. In this motion the left-hand branch of the curve which issues from the plane θ , *v* would rapidly run up to infinity, so that the surface is everywhere bounded on the left by an oblique infinite plane. This points out a recurrence of the insufficiency of equation (4) already adverted to in § 35. From an inspection of this surface it is, therefore, not possible to deduce the corresponding expression for thermal expansion.

The cause of this difficulty is probably to be referred to the fact that the ratio of θ and *p* is not independent of $V_{\theta p}$. Hence, in moving the initial section parallel to itself, the curve must be conceived to expand in its own plane in such a way that the oblique horizontal lines described by the consecutive points of the initial curve are not all parallel. In Pl. xx, therefore, 1, 5=3, 7; 2, 6=4, 8; b, e=d, g; etc. But 1, 3, 2, 4, b, d, etc., are not parallel.

DIGRESSION ON THERMAL EXPANSION.

41. *Exponential equation proposed.*—Before proceeding to the computations of the next paragraph, it is convenient to insert a digression here relative to thermal expansion. I made many computations, but the results are much more inaccurate and the equations less satisfactory than was the case with compression. Expansion occurs at a rapidly accelerated rate with temperature, *t*, in case of low pressures.

Hence the equation

$$\frac{d\left(\frac{v}{V}\right)}{dt} = \frac{\tau}{1-\beta t} \dots \dots \dots (11)$$

whence

$$\frac{v}{V} = \ln \left(1 - \beta t \right)^{-\tau/\beta} \dots \dots \dots (12)$$

suggests itself. The first difficulty is the choice of an initial temperature, so that the two equations will be put

$$d\left(\frac{v}{V}\right)/dt = \tau / \left(1 - \beta(t-b) \right) \text{ and } v/V = \ln \left(1 - \beta(t-b) \right)^{-\tau/\beta}$$

An application of this equation to the data for ether is given in Table 44, and the difference between observed and calculated inserted above in Table 5. Δp is the pressure increment, the initial pressure being 100 atmospheres. The table is one of double entry, so that \mathcal{S} has also been inserted.

TABLE 44.—*Expansion and compression constants of ether.*

t	$\Delta p=0.$		$\Delta p=100.$		$\Delta p=200.$		$\Delta p=300.$	
	$\tau \times 10^3.$	$\mathcal{S} \times 10^6.$	$\tau \times 10^6.$	$\mathcal{S} \times 10^6.$	$\tau \times 10^6.$	$\mathcal{S} \times 10^6.$	$\tau \times 10^6.$	$\mathcal{S} \times 10^6.$
29°	1,824	165	1,530	165	1,380	165	1,240	165
65°	1,824	226	1,530	226	1,380	226	1,240	226
100°	1,824	343	1,530	343	1,380	343	1,240	343
185°	1,824	1,005	1,530	1,005	1,380	1,005	1,240	1,005
310°	1,824	34,250	1,530	34,250	1,380	34,250	1,240	34,250

$$y_p = \ln \left(1 + 9\mathcal{S}p \right)^{1/9}$$

$$y_t = \ln \left(1 - 2\tau(t-b) \right)^{-1/2} \quad (\text{nearly}).$$

$$b = 34^\circ$$

It is seen that the change of τ with pressure is less curvilinear and not nearly so rapid as the change of either \mathcal{S} or $1/\mathcal{S}$ with temperature. The curve $\left(\frac{v}{V} \right)$ itself, though fitting the extreme results very well, does so less nearly for the moderate expansions under 400 atmospheres, as the expansion under these conditions becomes more rapidly linear than the curve predicates.

Making the final step in these considerations, I supposed that the discrepancies in question might be remedied by a more general form.

$$v/V = \ln \frac{(1 + \alpha p)^{\mathcal{S}/\alpha}}{(1 - \beta(t-b))^{\tau/\beta}}$$

whence

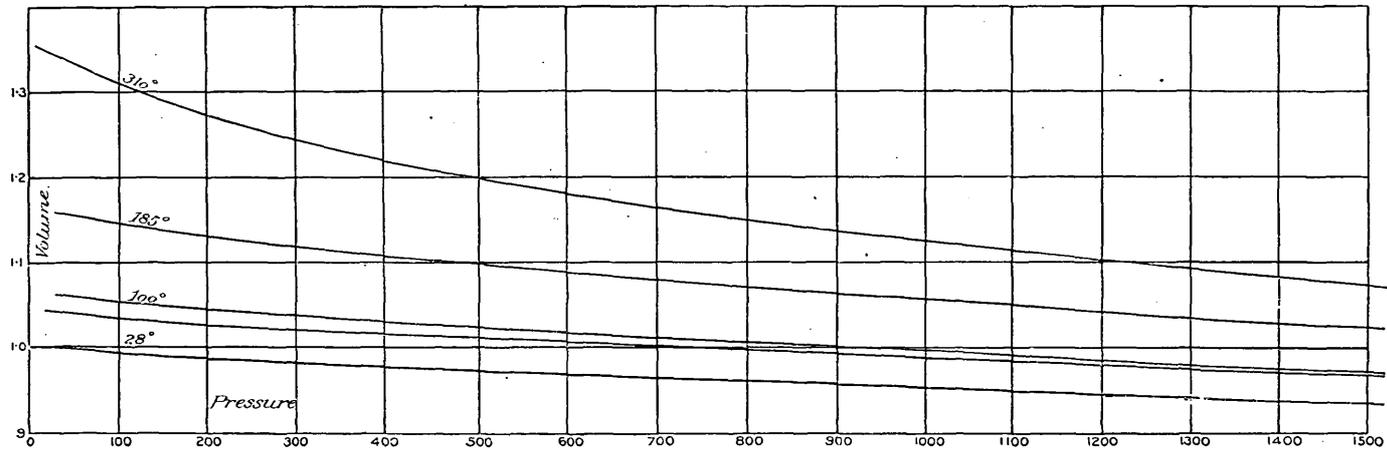
$$d \frac{v}{V} dp = \mathcal{S} / (1 + \alpha p) + (t-b) \frac{\tau}{\beta} \frac{d\beta}{dp} / (1 - \beta(t-b))$$

and

$$d \frac{v}{V} dt = \tau / (1 - \beta t) + p \frac{\mathcal{S}}{\alpha} \frac{d\alpha}{dt} / (1 + \alpha p)$$

But these relations are too complicated to be fruitfully discussed here.

42. *Observed contractions due to cooling under pressure.*—To corroborate the above results as a whole, I will also insert a series of direct



Isothermals of toluidine.

measurements on the contraction of substances, cooling under pressure. Experiments of this kind are difficult. The strain resulting from the continued application of high pressure produces much breakage, either of the parts of the apparatus or of the capillary tubes. It is clear that in method pursued the fiducial volume must be constantly redetermined. I therefore made the experiments at high pressures, alternate with low-pressure experiments, keeping the same interval of pressure and the same thermal environment throughout the series. In Table 45 the results were obtained with a relatively wide capillary, so that the filamentary platinum / platinum-iridium thermo-couple could be drawn *through* the tube, with its junction in the substance. This insures accuracy of thermal measurement; but tubes of this kind can not withstand high pressures. Hence, in subsequent experiments, Tables 46 to 50, the filamentary couple was wrapped around the outside of the capillary in the thermal bath. Temperatures here merely subserve the purpose of coordinating the high and low pressure results. In all the experiments leaks were carefully guarded against and unsatisfactory attempts rejected.

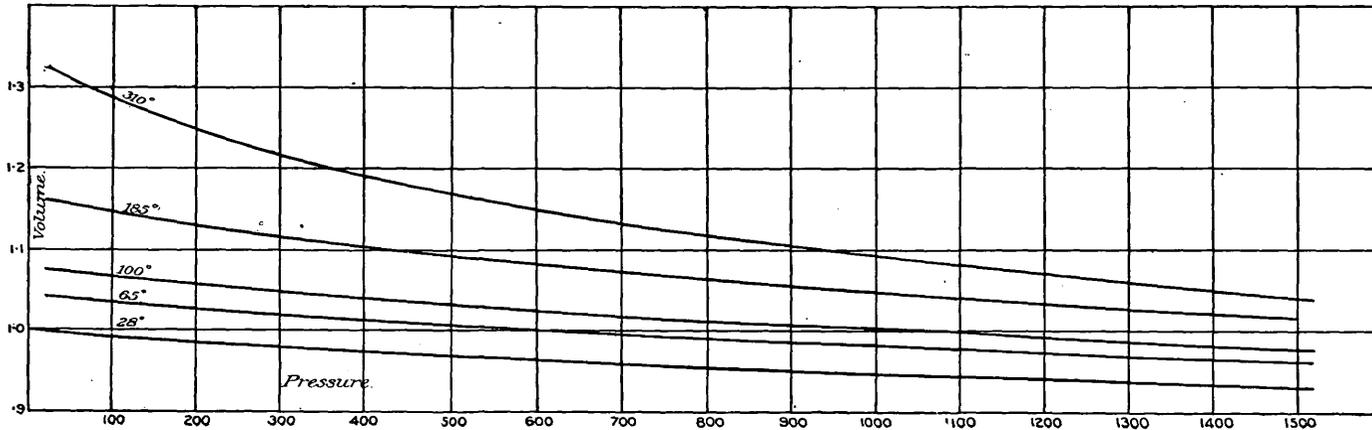
In the tables P is the acting pressure, L the observed length of column, and v_p/V the volume contraction per unit of volume due to P . Temperature θ is given in arbitrary thermoelectric degrees, and $\frac{v}{V}$ are the successive volume decrements due to cooling. A chart accompanies each table. Cooling took place between 185° and 100° , care being taken that at the higher temperature the parts of the tube had been equally heated throughout before the ebullition of the vapor bath was stopped.

TABLE 45.—*Contraction due to cooling under pressure. Paraffin (first sample).*

	θ	$\frac{v}{V} \times 10^3$		θ	$\frac{v}{V} \times 10^3$
$P = 150 \text{ atm.}$ $L = 22.0^{\text{cm.}}$ $\frac{v_p}{V} \times 10^3 = 23.0$	0	0.0	$P = 150 \text{ atm.}$ $L = 22.0^{\text{cm.}}$ $\frac{v_p}{V} \times 10^3 = 23.0$	0	0.0
	2	0.9		2	1.4
	5	2.7		6	3.2
	10	4.1		11	5.5
	16	7.7		18	8.6
	23	10.5		24	10.5
	31	13.2		34	14.1
	48	19.5		50	20.5
	58	24.5		58	24.1
	64	27.3		66	26.8
	72	30.5		74	30.0
	78	32.7		82	33.2
	88	35.9			
94	39.1				
102	42.3				
$P = 0 \text{ atm.}$ $L = 22.6^{\text{cm.}}$	0	0.0			
	7	0.5			
	19	5.3			
	35	12.4			
	54	20.0			
	67	26.5			
	83	33.6			
	99	40.0			
	113	46.0			

TABLE 46.—*Contraction due to cooling under pressure. Paraffin (second sample).*

	θ	$\frac{v}{V} \times 10^3$		θ	$\frac{v}{V} \times 10^3$		θ	$\frac{v}{V} \times 10^3$
$P = 400 \text{ atm.}$ $L = 19.0^{\text{cm.}}$ $\frac{v_p}{V} \times 10^3 = 57.0$	0	57 + 0.0	$P = 0 \text{ atm.}$ $L = 20.2^{\text{cm.}}$	0	0.0	$P = 400 \text{ atm.}$ $L = 19.0^{\text{cm.}}$ $\frac{v_p}{V} \times 10^3 = 57.0$	0	57 + 0.0
	30	1.1		34	2.4		19	1.0
	65	3.7		104	10.0		64	3.2
	115	7.9		154	14.8		154	10.5
	174	12.1		244	23.7		214	14.7
	255	18.9		329	32.2		314	24.2
	325	24.2		424	42.1		404	30.5
	405	30.0		484	48.5		474	36.3
	510	37.9		564	56.4		554	42.6
	585	45.8		614	61.9		604	47.4
	660	52.1		674	68.3		659	52.1
	715	57.9		724	73.7		694	55.8
	$I = 0 \text{ atm.}$ $L = 20.2^{\text{cm.}}$	0		0.0	$P = 400 \text{ atm.}$ $L = 19.0^{\text{cm.}}$ $\frac{v_p}{V} \times 10^3 = 57.0$		0	57 + 0.0
15		1.0	24	3.2				
65		6.0	64	5.3				
140		14.3	149	11.6				
240		23.3	239	19.0				
320		30.7	314	23.7				
410		39.6	414	31.6				
470		46.5	484	40.0				
550		54.9	564	45.3				
605		60.4	664	54.7				
660	66.8	709	60.0					
720	72.8							
770	78.7							
$P = 400 \text{ atm.}$ $L = 19.0^{\text{cm.}}$ $\frac{v_p}{V} \times 10^3 = 57.0$	0	57 + 0.0	$P = 0 \text{ atm.}$ $L = 20.2^{\text{cm.}}$	0	0.0			
	30	3.7		34	2.0			
	85	7.4		84	6.9			
	175	13.2		134	12.4			
	260	21.1		234	22.3			
	345	26.8		309	30.2			
	425	34.2		394	38.6			
	495	39.5		474	46.5			
	565	44.7		544	53.9			
	660	54.2		609	60.9			
720	59.5	669	67.3					
		714	72.3					



Isothermals of thymol.

TABLE 47.—Contraction due to cooling under pressure. Paraffin (third sample).

	θ	$\frac{v}{V} \times 10^3$		θ	$\frac{v}{V} \times 10^3$		θ	$\frac{v}{V} \times 10^3$	
$P=400$ atm. $L=21.3$ cm. v_p $\frac{v_p}{V} \times 10^3=52.9$	0	0.0	$P=500$ atm. $L=21.1$ cm. v_p $\frac{v_p}{V} \times 10^3=62.7$	0	0.0	$P=600$ atm. $L=20.8$ cm. v_p $\frac{v_p}{V} \times 10^3=72.4$	0	0.0	
	13	0.1		20	1.9		18	*0.0	
	43	2.4		52	3.8		58	4.3	
	98	7.0		109	9.0		140	9.1	
	178	13.2		192	14.7		200	14.0	
	266	21.1		277	20.9		270	20.2	
	348	27.7		327	25.1		335	25.5	
	433	33.8		392	30.0		405	30.3	
	504	40.0		458	34.6		450	34.2	
	603	48.3		507	38.4		515	38.0	
			558	42.6	570	42.8			
$P=20$ atm. $L=22.5$ cm. v_p $\frac{v_p}{V} \times 10^3=0$	0	0.0	$P=20$ atm. $L=22.5$ cm. v_p $\frac{v_p}{V} \times 10^3=0$	0	0.0	$P=20$ atm. $L=22.5$ cm. v_p $\frac{v_p}{V} \times 10^3=0$	0	0.0	
	14	0.5		15	1.0		15	2.2	
	48	5.3		51	6.0		55	5.8	
	103	10.7		165	17.8		145	15.6	
	178	18.2		240	25.3		235	25.3	
	306	31.1		313	33.3		320	33.3	
	378	37.8		375	39.0				
	456	46.2		440	45.0				
	526	53.8		500	51.1		$P=600$ atm. $L=20.8$ cm. v_p $\frac{v_p}{V} \times 10^3=72.4$	0	0.0
	623	63.6		555	57.8			13	2.0
$P=400$ atm. $L=21.3$ cm. v_p $\frac{v_p}{V} \times 10^3=52.9$	0	0.0	$P=500$ atm. $L=21.1$ cm. v_p $\frac{v_p}{V} \times 10^3=62.7$	0	0.0	$P=600$ atm. $L=20.8$ cm. v_p $\frac{v_p}{V} \times 10^3=72.4$	(**)	-----	
	18	1.0		32	3.8				
	68	5.6		85	8.0				
	128	10.3		148	11.8				
	202	16.4		217	17.5				
	314	24.4		290	22.7				
	410	32.4		351	27.5				
	513	41.3		415	32.7				
	567	45.1		480	37.9				
	622	50.0		545	42.6				
662	54.4								

* Tube slips (?).

** Tube breaks.

Rates of contraction.

P	$\Delta\theta$	$\Delta \frac{v}{V} \times 10^3$
20	500	51.1
400	500	41.1
500	500	38.7
600	500	37.7

TABLE 48.—*Contraction due to cooling under pressure. Paraffin (fourth sample, closed capillary tube).*

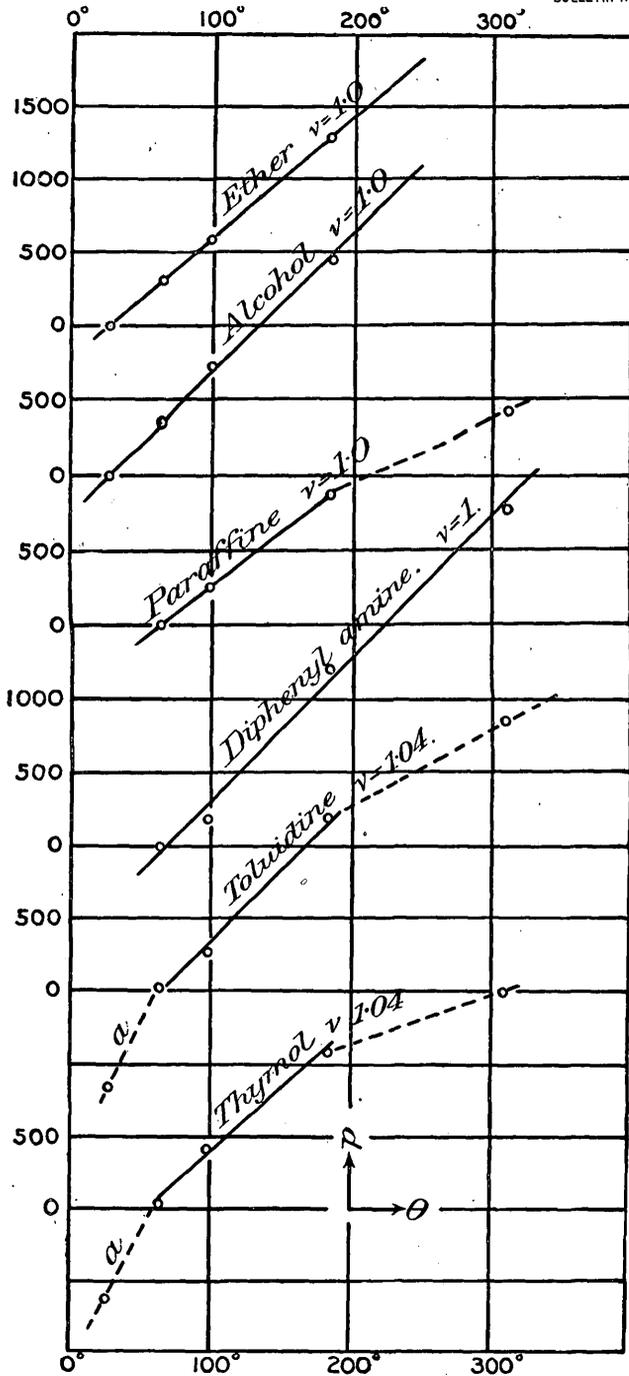
	θ	$\frac{v}{V} \times 10^3$		θ	$\frac{v}{V} \times 10^3$		θ	$\frac{v}{V} \times 10^3$
$P=200$ atm. $L=18.3^m$. $v_p \times 10^3=28.7$	0	0.0	$P=200$ atm. $L=17.8^m$. $v_p \times 10^3=28.7$	0	0.0	$P=20$ atm. $L=18.8^m$.	0	0.0
	15	1.6		15	2.7		26	2.7
	120	10.4		56	6.1		85	9.6
	165	16.4		130	13.7		148	16.0
	242	23.5		188	18.1		210	22.9
	297	28.4		250	23.5		280	30.3
	370	33.9		370	34.4		330	35.1
	412	38.3		430	39.9		382	41.0
	466	43.2		491	45.4		440	46.3
	514	47.5					490	51.6
				540	56.9			
$P=20$ atm. $L=18.8^m$.	0	0.0	$P=400$ atm. $L=17.8^m$. $v_p \times 10^3=53.2$	0	0.0	$P=400$ atm. $L=17.8^m$. $v_p \times 10^3=53.2$	0	0.0
	16	2.7		20	0.6		26	1.2
	70	8.5		80	5.6		73	6.2
	112	13.3		129	10.1		125	8.9
	185	21.8		190	14.0		192	14.0
	227	26.1		250	19.6		260	19.6
	294	33.0		315	24.1		315	23.5
	360	33.9		372	28.5		380	29.1
	442	48.4		430	33.0		435	34.1
	488	53.2		482	38.0		480	36.9
525	56.9	520	40.8	520	40.2			
				500	43.1			

TABLE 49.—*Contraction due to cooling under pressure. Naphthalene.*

	θ	$\frac{v}{V} \times 10^3$		θ	$\frac{v}{V} \times 10^3$		θ	$\frac{v}{V} \times 10^3$
$P=400$ atm. $L=20.4^m$. $v_p \times 10^3=37$	0	0.0	$P=20$ atm. $L=21.1^m$.	0	0.0	$P=400$ atm. $L=20.3^m$. $v_p \times 10^3=37$	0	0.0
	35	3.4		38	2.4		29	2.0
	85	6.9		88	6.1		69	4.4
	170	13.3		178	13.2		181	13.3
	250	18.7		270	20.9		254	18.7
	345	26.6		354	28.0		334	24.6
	435	33.0		428	34.6		411	31.0
	505	39.9		503	41.7		490	38.9
	575	46.8		568	48.8		566	45.3
	624	50.2		638	55.9		616	48.3
677	55.1	678	60.2	689	55.6			
$P=20$ atm. $L=21.1^m$.	0	0.0	$P=400$ atm. $L=20.3^m$. $v_p \times 10^3=37$	0	0.0			
	24	0.5		35	2.0			
	57	4.2		105	6.4			
	142	11.3		185	12.3			
	209	17.1		270	17.2			
	302	24.2		355	24.1			
	382	31.3		485	36.4			
	481	39.8		545	42.4			
	530	45.0		615	46.8			
	594	51.2		675	54.2			
648	56.9	730	61.5					
$P=400$ atm. $L=20.4^m$. $v_p \times 10^3=37$	0	0.0	$P=20$ atm. $L=21.1^m$.	0	0.0			
	40	4.4		35	1.9			
	112	9.4		93	6.2			
	175	13.8		167	13.3			
	262	19.7		245	19.5			
	348	26.1		415	35.1			
	420	33.0		493	41.2			
	507	39.4		577	48.8			
	585	45.8		615	53.5			
	638	50.7		683	60.7			
695	57.6							

Relative rates (initial).

P .	$\Delta\theta$.	$\Delta \frac{v}{V} \times 10^3$
20	500	41.0
400	500	36.6



Isometrics of ether, alcohol, paraffin, diphenylamine, toluidine, and thymol compared.

TABLE 50.—Contraction due to cooling under pressure monochlor acetic acid.

$P=200$ atm. $L=20.7^{\text{cm}}$.	θ	$\frac{v}{V} \times 10^3$	$P=400$ atm. $L=20.3^{\text{cm}}$.	θ	$\frac{v}{V} \times 10^3$	$P=600$ atm. $L=19.9^{\text{cm}}$.	θ	$\frac{v}{V} \times 10^3$
	0	0.0		0	0.0		0	0.0
	10	1.9		29	3.4		10	1.5
	50	7.2		166	17.8		40	7.1
	100	13.5		266	20.6		100	12.6
	168	21.3		336	37.4		165	20.1
	238	29.5		402	44.3		233	26.6
	316	38.6		466	52.3		300	34.2
	366	44.9		516	58.6		357	40.7
	427	52.2		556	63.9		428	43.7
480	58.5	603	69.0	485	53.8			
528	64.8	641	74.9	530	60.4			
$P=20$ atm. $L=21.2^{\text{cm}}$.	θ	$\frac{v}{V} \times 10^3$	$P=20$ atm. $L=21.2^{\text{cm}}$.	θ	$\frac{v}{V} \times 10^3$	$P=20$ atm. $L=21.1^{\text{cm}}$.	θ	$\frac{v}{V} \times 10^3$
	0	0.0		0	0.0		0	0.0
	18	1.9		13	1.4		29	4.8
	53	7.5		48	7.1		85	12.7
	108	15.1		104	14.2		155	22.2
	192	25.0		168	23.2		225	30.7
	256	33.1		218	32.5		285	39.6
	318	41.1		316	41.1		353	49.1
	377	49.1		368	48.2		415	57.1
	503	66.5		431	56.1		487	64.6
528	69.9	483	63.2	535	70.3			
598	78.4	538	70.8	600	79.8			
$P=200$ atm. $L=20.7^{\text{cm}}$.	θ	$\frac{v}{V} \times 10^3$	$P=400$ atm. $L=20.3^{\text{cm}}$.	θ	$\frac{v}{V} \times 10^3$	$P=600$ atm. $L=---$.	θ	$\frac{v}{V} \times 10^3$
	0	0.0		0	0.0		0	0.0
	27	2.9		35	3.5		20	2.0
	72	8.2		75	7.4		70	8.1
	134	15.5		145	15.3		195	21.1
	208	24.6		217	23.2		265	29.6
	277	32.4		295	32.1		335	37.2
	342	40.6		370	40.4		405	45.2
	400	46.9		403	44.3		453	50.3
	462	54.6		460	51.3		500	55.3
548	66.2	520	58.1	545	60.9			

$P.$	$\Delta\theta$	$\Delta \frac{v}{V} \times 10^3$
20	500	64.8
200	500	59.8
400	500	58.5
600	500	54.5

These data very fully corroborate each other and the statements of the above §§ 23, 30, 31, 35 and 41. Contraction under pressure when referred to unit of volume at the initial (high) temperature, decreases at a rapid rate with pressure. In case of paraffin, were the observed conditions to hold indefinitely, contraction would altogether cease at a pressure less than 2,000 atmospheres. This follows in a less pronounced degree for naphthalene and chloracetic acid. The lines of cooling for the same low pressure are parallel.

COMPRESSIBILITY INCREASING INVERSELY AS THE SECOND POWER OF THE PRESSURE BINOMINAL.

43. *Properties of the hyperbolic equation.*—The expression $v/V = \ln(1 + \alpha p)^{\beta/\alpha}$, as utilized in § 39, furnishes a family of curves which must in their ultimate contours necessarily fall below the corresponding isothermals of the substance under discussion. It is the object of the

present section to investigate a similar family, the ultimate contours of which must be above the actual isothermals. This may be done by assuming

$$\frac{d}{dp} \frac{v}{V} = \frac{\mu}{(1 + \nu p)^2} \dots \dots \dots (1)$$

whence by integration

$$v/V = \frac{\mu p}{1 + \nu p} \dots \dots \dots (2)$$

In this case when $p = \infty$, $(v/V)_{p=\infty} = \mu/\nu$, or, as will be seen in the following tables, $(v/V)_{p=\infty} = 2/9$. In the actual case, v/V , though it can not be greater than 1, will in all probability eventually exceed $2/9$.

The method of discussion to be adopted is similar to that in the foregoing section.

Suppose in the first place that

$$y_0 = \mu_0 p_0 / (1 + \nu p_0)$$

and

$$y' = \mu_0 (p_0 + p) / (1 + \nu (p_0 + p)).$$

Then

$$y = y' - y_0 = \mu_0 p / (1 + \nu p_0) \left(1 + \frac{\nu_0}{1 + \nu_0 p_0} p \right),$$

or if

$$\mu = \mu_0 / \sqrt{1 + \nu_0 p_0^2} \quad \text{and} \quad \nu = \nu_0 (1 + \nu_0 p_0) \dots \dots \dots (3)$$

there results

$$y = \mu p / (1 + \nu p),$$

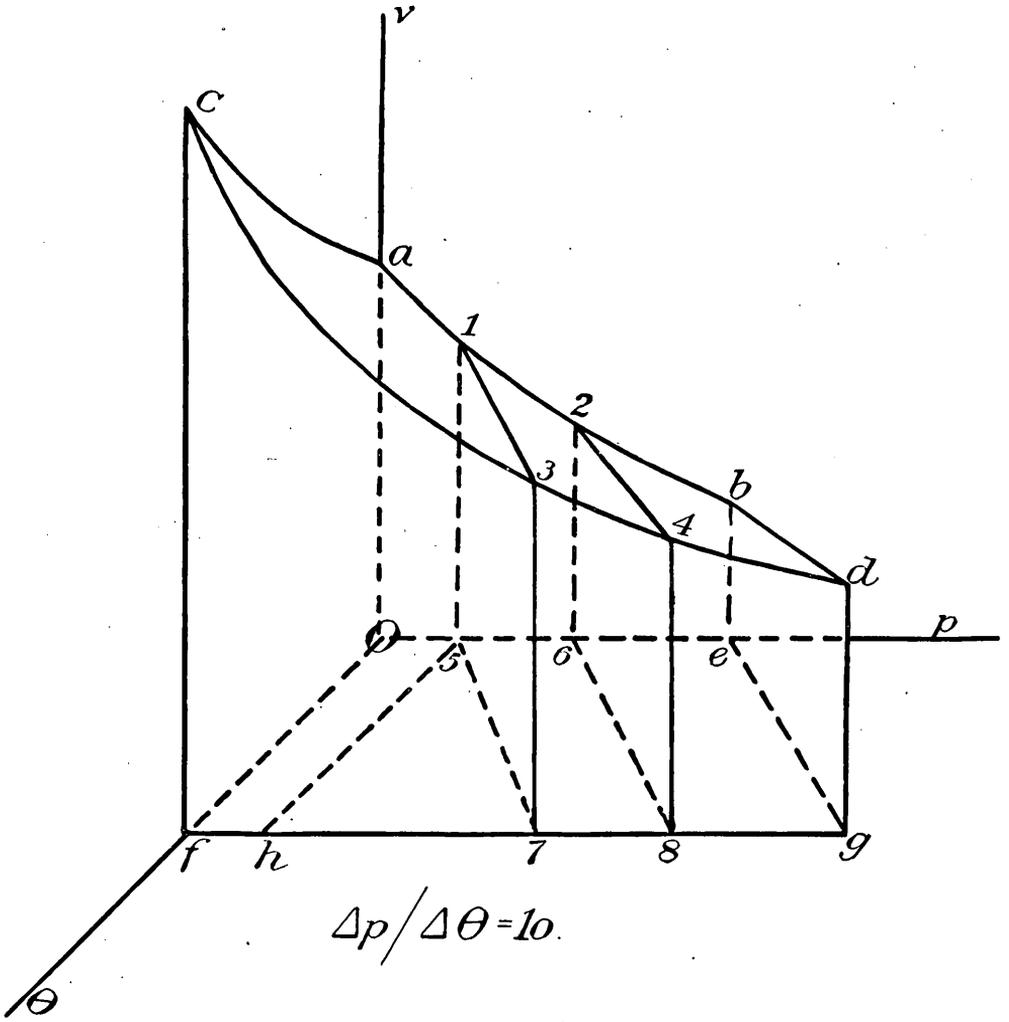
which is identical with the form (1). Hence if p_0 and p are consecutive pressure intervals between 0 and $p + p_0$, then the constants obtained from observation within the interval p may be reduced to those applying for the whole interval by equations (3), or the equivalent expressions

$$\mu_0 = \mu / \sqrt{1 - \nu p_0^2} \quad \nu_0 = \nu / \sqrt{1 - \nu p_0} \dots \dots \dots (4)$$

44. Presumptive character of the isometrics.—According to Mendeleef, Thorpe, and Rücker (l. c.) the volume of liquids in case of thermal expansion may be represented by

$$V_\theta = 1 / (1 - k\theta) \dots \dots \dots (5)$$

where pressure is constant. Here V_θ is the actual volume, θ the temperature and k the specific constant. Introducing equation (1)



Thermodynamic surface.

and denoting by V the volume for the pressure p and temperature θ , I obtain

$$V = \frac{1 + (\nu - \mu)p}{(1 - k\theta)(1 + \nu p)},$$

which for pressures and temperatures not too great may be put

$$V = \frac{1 + (\nu - \mu)p}{1 - k\theta + \nu p}.$$

If therefore $V = V_c = \text{constant}$,

$$\theta = -\frac{1 - V_c}{kV_c} + p \frac{\nu(1 - V_c) - \mu}{kV_c} \dots \dots \dots (6)$$

so that in case of constant volume temperature varies linearly with pressure, small intervals of variation presupposed. The rigorous deduction of (1) and (5) is

$$\theta = -\frac{1 - V_c}{kV_c} - \frac{\mu}{kV_c} \frac{p}{1 + \nu p} \dots \dots \dots (7)$$

which is linear in proportion as νp is small compared with 1. In § 40 it has been shown that the relation of θ to p is probably linear throughout a much greater interval. Hence it follows that equation (1) is insufficient for large pressures.

Regarding equation (5) it follows that if θ_0 and θ be two consecutive intervals of temperature, the former measured from zero, and if

$$V_{\theta_0} = 1/(1 - k_0 \theta_0), \quad V'_\theta = 1/(1 - k_0(\theta_0 + \theta)),$$

and

$$k = k_0/\sqrt{1 - k_0\theta_0},$$

then

$$V_\theta = 1 + (V'_\theta - V_{\theta_0}) = \frac{1 + k^2\theta_0\theta}{1 - k\theta}$$

Equation (8) with the exception of the corrective member $k^2\theta_0\theta/(1 - k\theta)$ has the same form as (5). Hence the observations may be referred to any convenient temperature as a point of departure.

45. *Hyperbolic constants computed.*—Applying equation (1) § 43 to the observations in §§ 16, 17, 19, 20, 23, 25, which are the most complete in hand, I obtained the constants given in Table 51. It is clear that ν must be some function of μ ; but the observations are too crude to indicate the precise nature of this function. If ν be plotted as dependent on μ , the points are seen to group themselves about a straight line passing through the origin. Again if the ratios ν/μ be found, the consecutive results show no discernible march or grouping. Hence I have assumed the ratio as constant, and have added its mean value in the table.

The ether and the alcohol points for 310° are not amenable to this method of treatment, and the discrepancy is somewhat apparent in the ether point for 185°. In case of alcohol the relation of constants is irregular, showing unusually large errors of observation.

TABLE 51.—*Hyperbolic constants which reproduce the isothermal decrements. Direct computation.*

$$v/V = \mu p (1 + \nu p).$$

Temp.	$\mu \times 10^6$	$\nu \times 10^6$	Temp.	$\mu \times 10^6$	$\nu \times 10^6$	Temp.	$\mu \times 10^6$	$\nu \times 10^6$
Ether.			Toluidine.			Paraffin.		
29°	169.0	830	28°	56.5	53	65°	85.1	191
65°	228.2	1.028	65°	70.0	413	100°	111.5	475
100°	352.9	1.573	100°	81.4	110	185°	181.5	845
185°	1,027.6	3,870	185°	145.6	801	310°	368.1	1,510
*310°	10,842.0	18,400	310°	401.1	1,730			
Alcohol.			Diphenylamine.			Thymol.		
28°	87.0	243	65°	61.3	162	28°	67.8	465
65°	111.5	276	100°	69.3	285	65°	69.5	157
100°	181.7	1,630	185°	114.4	613	100°	99.3	553
185°	348.2	1,755	310°	214.6	889	185°	162.5	715
*310°	7,553.0	15,770				310°	465.2	2,000

* Exceptional values due to partial adiabatic expansion.

$$\text{Mean ratio } \frac{\nu}{\mu} = 4.5.$$

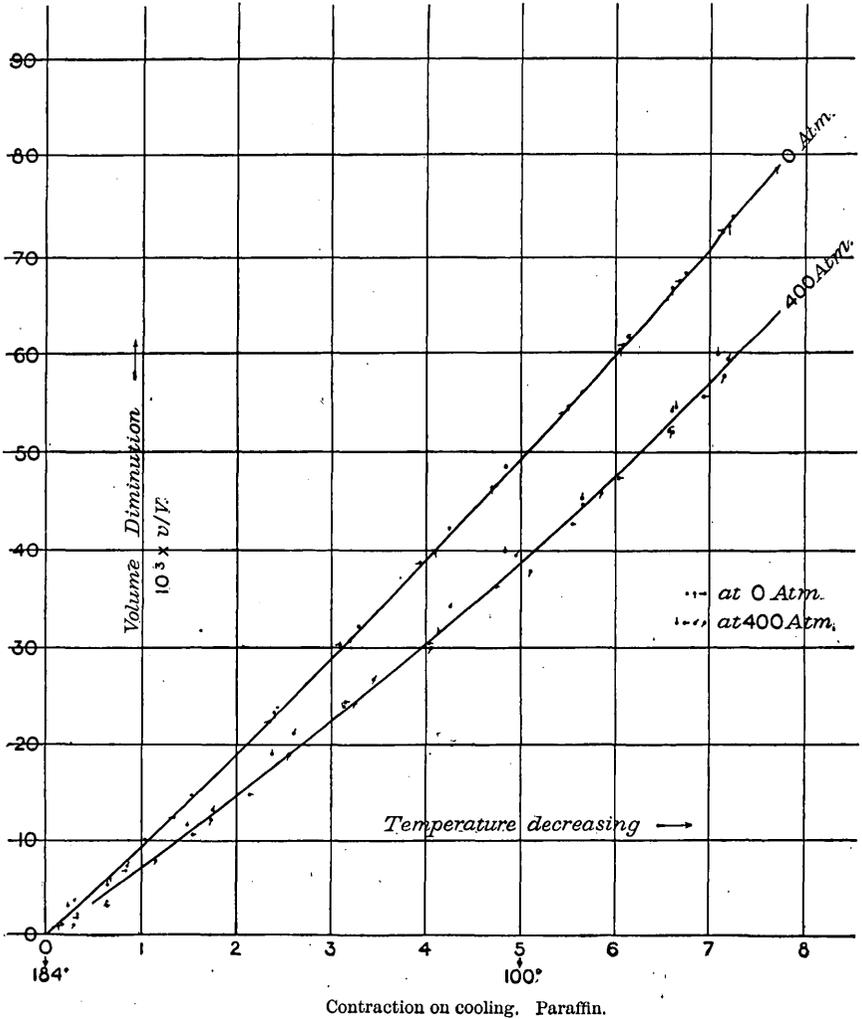
46. *Mean hyperbolic constants derived.*—The next table, 52, contains the values of μ obtained by accepting the equation $\nu = 4.5 \mu$, derived at the end of the last table. The exceptional alcohol and ether points have been rejected. In general it will be seen that the diagram of μ and ν is not so smooth as was Plate XII, in § 37, for α and ϱ . This shows, I think, that the equation of the last section is more in keeping with the character of the observations made, than is the equation of this section.

TABLE 52.—*Mean hyperbolic constants.*

$$v/V = \frac{\mu p}{(1 + 4.5 \mu p)}$$

Substance.	θ	$\mu \times 10^6$	Substance.	θ	$\mu \times 10^6$	Substance.	θ	$\mu \times 10^6$
Ether.....	29°	167	Toluidine-para	28°	59	Paraffin.....	65°	88
	65°	229		65°	69		100°	112
	100°	351		100°	85		185°	181
	*185°	1,221		185°	141		310°	382
	310°			310°	412			
Alcohol.....	28°	89	Diphenylamine	65°	64	Thymol.....	28°	66
	65°	115		100°	69		65°	73
	100°	163		185°	112		100°	97
	185°	340		310°	216		185°	162
	310°						310°	481

* Equation begins to fail.



47.—*The isothermal band.*—Making use of the constants in Table 52, I calculated the actual isothermals in the way suggested in § 39. The expansions are directly observed, and the only hypothesis introduced is equation 1, § 43. The results so obtained are inserted in Tables 38 to 43, where $V_{\mu\theta}$ are the actual volumes obtained by the hyperbolic equation § 43, and $V_{\theta\theta}$ refer to the exponential equation, § 35. These two quantities, constituting the upper and lower limit of the isothermal band, are to be discussed together somewhat in detail.

In case of ether the divergence or width of the band at 1,000 atmospheres is about 0.4% at 28°, 1% at 65°, and 1% at 100°. At 185° the divergence would be 8%, but the hyperbola here begins to fail. Better accordance could here be obtained as far as 185° by introducing $\nu = 0.0003 + \frac{5.3}{14}\mu$, as found from Table 51; but in consequence of the labor already spent I desisted from this additional trial. My purposes are sufficiently answered by the above computation. Constructing the relations (isometrics) for p and θ when $V_e = 1$, it will be seen that whereas in the case of the exponential formula the straight line is predicted even as far as 185° and 1,300 atmospheres, this is not the case for the hyperbolic form. Divergence from the linear curve begins very appreciable at 100° and 600 atmospheres.

In case of alcohol the conformity of results is better throughout. At 1,000 atmospheres the curves for 28° do not diverge; at 65° the divergence is 0.2%; at 100°, 0.3%; at 185°, 2%. Putting $V_e = 1$, it appears that whereas the exponential relation holds linearly as far as 185° and 1,500 atmospheres, the hyperbolic equation holds only as far as 100° and 700 atmospheres.

Divergence in case of paraffin at 1,000 atmospheres is 0.1% at 65°; 0.2% at 100°; 0.7% at 185°; 6% at 310°. As far as 185° and 900 atmospheres both isometrics are linear. At 310° both fail, but on opposite sides of the isometric. The agreement of the exponential is preferable throughout.

The observations for diphenylamine are less satisfactory, partly because of the choice of 0 atmospheres as initial pressure, partly because of some error in the expansion data. At 1,000 atmospheres the divergence of curves is 0.1% at 65°; 0.1% at 100°; 0.2% at 185°; 1% at 310°. The interesting feature of these results is the fact that the isometrics seem to retain their linear character as far as 310°.

In case of thymol the divergence at 1,000 atmospheres is 0.1% at 28°; 0.2% at 65°; 0.1% at 100°; 0.6% at 185°; 3% at 310°. Irregularities in expansion have also distorted these results.

Finally, in case of para-toluidine the divergence at 1,000 atmospheres at 28° is nil; at 65°, nil; at 100°, 0.3%; at 185°, 0.3%; at 310°, 3%.

48. *Conclusion.*—Summarizing these results, it appears that the exponential $v/V = \ln(1 + \alpha p)^{\theta/a}$ is more in keeping with the general character of the isothermals discussed than is the hyperbolic form $v/V = \mu p / (1 + \nu p)$. Both equations fail at 310°. It is difficult to assign

a reason for this. It is not probably due to occluded air since the substances were boiled and introduced into a hot capillary tube. Moreover, in case of mercury (Table 3) an air-bubble discrepancy if present would necessarily have shown itself at 310° . The error, due to the fact that my curves must be in some small part adiabatic, would induce too slow a variation of volume and hence emphasize the high temperature break of the isometrics. There may be dissociation of many of the above organic substances at this high temperature. Azo-benzol, for instance, actually decomposes and turns black at 310° . But just what the effect of dissociation will be, in modifying the computed isothermal, is not easily conjectured, for the greater compressibility resulting is compensated by larger initial volumes. The high temperature break might result from inconstancy of temperature in the boiling tube. I did not explore the distribution of temperature, for the behavior was such that I had no reason to suspect inconstancy.

To interpret these discrepancies I resolved to make direct measurements for ether, a case in which the high temperature break is most pronounced. Finding a tube which was strong enough to resist 1,000 atmospheres at 310° , I obtained the following example, Table 53, of many similar results. The volumes are all referred to unit of volume at 100 atmospheres and 22° . To reduce them to 100 atmospheres and 29° (which hold for the above designated isothermals, Table 38), the volumes at 300° must be decreased about 1.5%. By doing this I obtain the "observed" isothermal inserted in Pl. XIV, Fig. 1. Since the length of thread L is now only 1.85cm, the low temperature isothermal can not be accurately given. The tube broke, in my final endeavors to repeat the experiments, in such a way to exclude adiabatic conditions.

TABLE 53.—*Isothermals of ether. Direct measurement. $\theta = 300^{\circ}$; $L = 6.00\text{cm}$.*

p	Volume.	Volume.	p	Volume.	Volume.	p	Volume.	Volume.
<i>atm.</i>			<i>atm.</i>			<i>atm.</i>		
100....	3.30	3.12	400....	1.43	1.41	700....	1.24	1.23
200....	1.83	1.76	500....	1.34	1.32	800....	1.19	1.19
300....	1.56	1.52	600....	1.28	1.26	900....	1.16	1.16

$\theta = 22^{\circ}$; $L = 1.85\text{cm}$.

100....	1.00	1.00	300....	.97	.97			
200....	.99	.99	400....	.96	.96			

It follows from this table that the 300° point of the ether isometric may be looked for in the region of 2,000 atmospheres. Hence the observed results substantiate the computed isometric for ether given in Plate XIV, which predicts the corresponding point at about 2,200 atmospheres. Nevertheless it can not be too carefully noted that if the isometrics for volumes 1.2, 1.3, 1.4 . . . be constructed (185° and 310° being now available) the break between 185° and 310° remains in full force, quite in conformity with the other data (alcohol, paraffin,

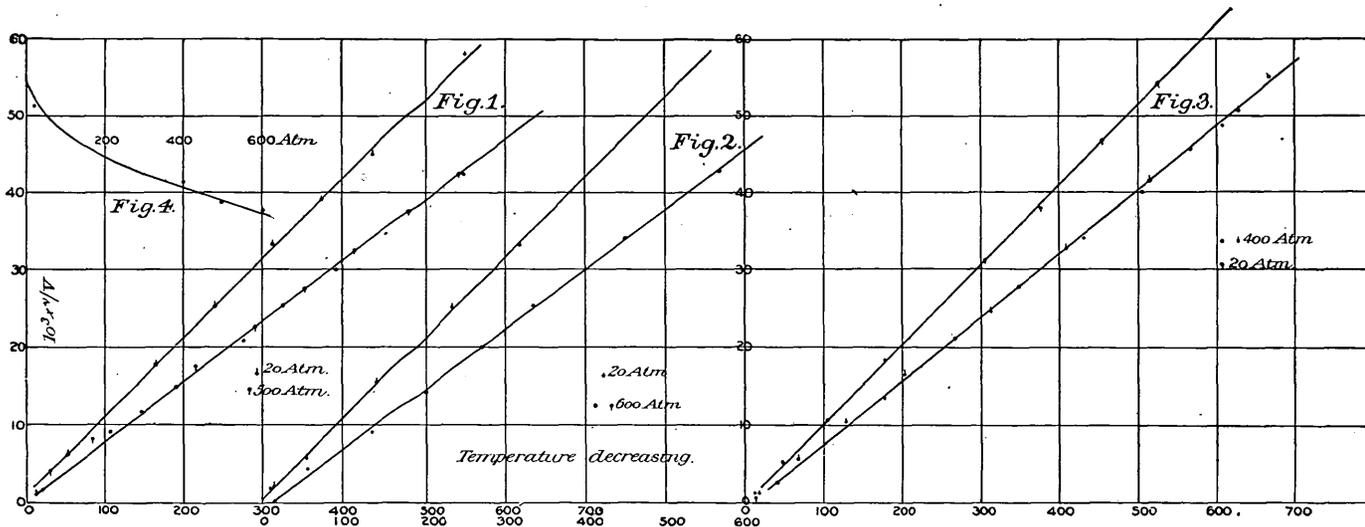


FIG. 1. Contraction on cooling under pressure. Paraffin. 20 and 400 atmospheres.

FIG. 2. Contraction on cooling under pressure. 20 and 500 atmospheres.

FIG. 3. Contraction on cooling under pressure. 20 and 600 atmospheres.

FIG. 4. Relative rates of contraction. Paraffin.

etc.). The full explanation of the occurrences here met with is of exceedingly great importance in its geological bearing and will therefore be made the subject of my subsequent work. Curved isometrics lead to certain interesting conditions of maximum volume.

The chief observational discrepancy encountered in these results is the expansion error in case of substances which solidify between observations at different temperatures. Hence the effect of different volumes on the slope of the isometrics can not be satisfactorily discussed. Since compression measurements retain their value independent of the thermal expansions and since the method pursued is such that all necessary measurement for thermal expansion can be made at atmospheric pressure, the difficulties may easily be rectified. By using a thermometer tube the purely thermal data can be supplied with any desired degree of accuracy. This I conceive to be the advantage of the mode of investigation set forth in the present paper.

Among the important results of the above tables is the fact that compressibility moves on the even tenor of its way quite independent of normal boiling points and melting points, provided of course the conditions are not such that boiling and melting can actually occur. For this reason compressibility is particularly adapted for exploring the nature of the environment of the molecule in its relations to temperature, i. e. for exhibiting the character of the thermal changes of the molecular fields of force.

49. The above work, though confined to relatively low ranges of pressure, was believed to have a more general value for reasons such as these: Instead of tracing the isothermals of a single substance throughout enormous ranges of pressure, similarly comparable results may possibly be obtained by examining different substances, conceived to exist in as widely different thermal states as possible. For in such a case, inasmuch as the actual or total pressure is the sum of the pressures applied externally and the internal pressure, the total pressure in question virtually varies enormously. This calls to mind the remarks made in §§ 35 and 43 relative to observations confined to limited parts of an isothermal.

Finally, the work of the present paper may be looked at from quite a different point of view. Suppose, for instance, I regard the linear isometric proposed by Ramsey and Young (*loc. cit.*) as an established fact. Then the chief result of the present work, viz, that the exponential equation (2) if applied to the observed changes of volume predicts a linear isometric throughout an enormous range of pressure, affords favorable evidence of the probable truth of the exponential equation in question. In other words, it is probable that along any isothermal compressibility increases inversely as pressure augmented by a constant. The interpretation of this constant can not now be given,

CHAPTER II.

THE EFFECT OF PRESSURE ON THE ELECTRICAL CONDUCTIVITY OF MERCURY.

INTRODUCTORY.

50. *Purposes of the work.*—In the endeavor to obtain data for the relation between melting point and pressure, a question which in its higher phases is of extreme geological importance, the difficulties of the general problem make it advisable to begin with material which can easily be operated on. Mercury suggests itself at once. Its melting point is very low, at temperatures where most resinous cements, marine glue for instance, are practically rigid. This greatly facilitates the construction of high-pressure apparatus, and the experiments therefore become of a less formidable character. The molecular structure of the metal is relatively simple, which is another advantage. Apart from practical considerations the behavior of any substance of definite character has its own intrinsic importance and must contribute essentially to a general diagram of the fusion phenomena in question.

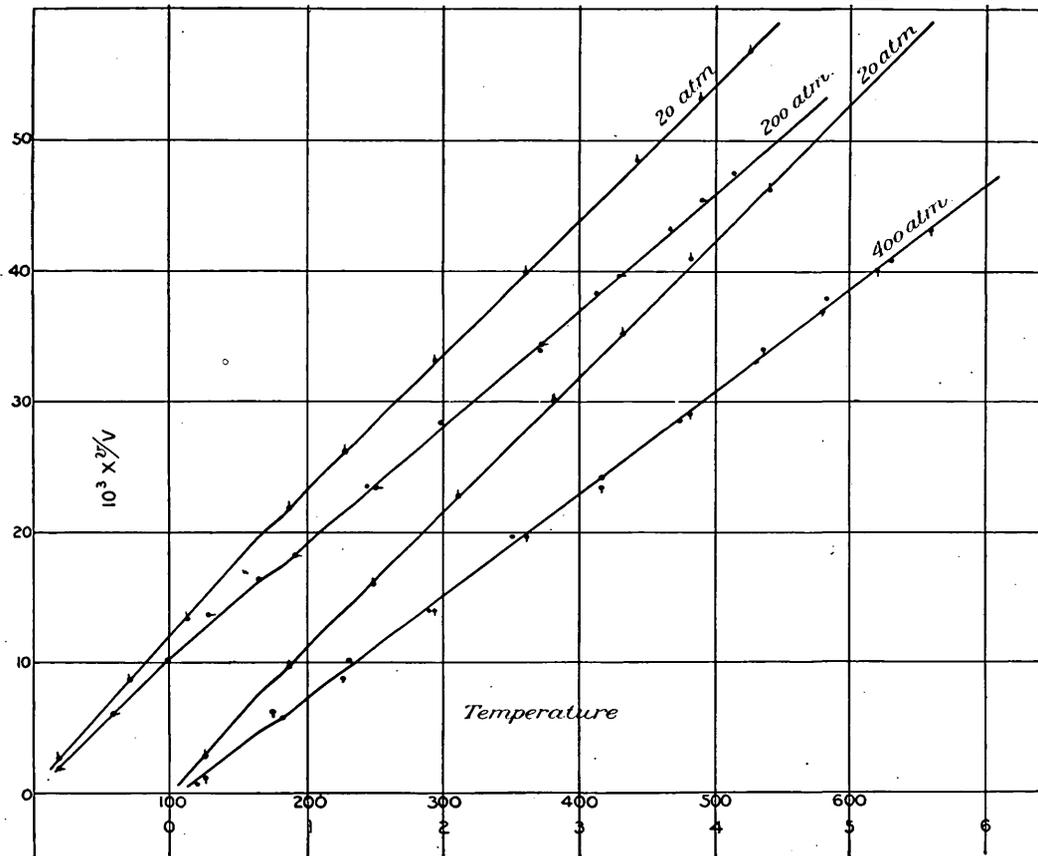
Again, mercury in common with many other metals (K, Na, Sn, etc.) shows a marked increase of electrical resistance on passing from the solid to the liquid condition. Indeed, the resistance of the liquid may be from two to five times that of the solid metal, as the researches of Matteucci, Matthiessen, Siemens, L. de la Rive, Cailletet and Bouty,¹ C. L. Weber,² Grunmach,³ and others show. The change of resistance in question may therefore be expediently selected as a *criterion of fusion*, a principle which may be used, cautiously of course, in the cases of metals and even of some solid electrolytes. The conductivity of glass, for instance, increases at a phenomenally rapid rate while the solid passes through the viscous stages into fluidity (Buff, Beetz, Gray, Foussereau, Perry, and others⁴). From all this it follows that the somewhat cumbersome problem of *melting point and pressure* may in many instances be translated into *electrical resistance and pressure*, a form in

¹ Cailletet and Bouty: C. R., vol. 100, 1885, p. 1188.

² C. L. Weber: Wied. Ann., vol. 25, 1888, p. 245; *ibid.*, vol. 37, 1889, p. 587; *ibid.*, vol. 38, 1889, p. 227.

³ Grunmach: Wied. Ann., vol. 35, 1888, p. 764; *ibid.*, vol. 36, 1889, p. 587; *ibid.*, vol. 37, 1889, p. 508.

⁴ The literature is given in my paper on stressed glass (*Am. Jour. Sci.*, vol. 37, 1889, pp. 339, 340).



Contraction on cooling under pressure. Paraffin.

which it is much better adapted for experimental attack. This indicates the general trend of my present work.

The present chapter shows this method to be feasible. I measure the effect of pressure on the conductivity of mercury at ordinary temperatures, the results of which work afford a sufficient preliminary test.

51. *Literature.*—The effect of pressure on the conductivity of liquid metals is not well known. Chwolson¹ operated on solid metals, obtaining results of .01% (copper and brass) to .1% (lead), per 100 atmospheres. These data are too small to be of practical use of the kind above in view, except in the case of lead perhaps. They are too easily distorted by the thermal effect of compression. Compared with my results for liquid mercury they suggest that distinctions between the solid and the liquid states may perhaps be feasible in a scale of compressibility. R. Lenz,² operating on mercury, found a diminution of resistance of 2% per 100 atmospheres, proportional to the pressure of 1 to 60 atmospheres, a very favorably large result quite in keeping with my purposes. E. Pfeiffer,³ using Cailletet's pump, communicates a method for the measurement of electrolytic resistance under pressure, and data for an aqueous solution of CO₂. J. W. Clarke⁴ electrolyzed dilute sulphuric acid in a closed space. L. Graetz⁵, taking a somewhat different line of departure, endeavors to arrive at the effect of pressure on the resistance of solid salts.

Foussereau⁶ discovered some remarkable effects of long continued high pressure (175 atmospheres) on the conductivity of metallic chlorides (Fe, Al) in very dilute solution. The effect of pressure on the resistance of carbon, which lies beyond the present work, has been studied by Mendenhall⁷ and others.

This practically closes the list of more or less closely allied researches. The results of R. Lenz seem, therefore, to be the only special data in hand. Again, a study of the combined effect of temperature near the melting point of a metal and the superincumbent pressure has never been made.

SIMPLE METHODS AND RESULTS.

52. *Cailletet's tubes described.*—My first experiments were made with Cailletet's oxygen tubes, into the small end of which a platinum terminal was either fused or cemented with marine glue. The tubes themselves proved to be badly annealed and unexpectedly fragile when subjected to high pressure. I therefore took Prof. Rood's precaution of annealing them at 450°, until traces of polarization disappeared. For this purpose it was convenient to cover the glass with

¹Chwolson: Carl's Repertorium, vol. 14, 1878, p. 26, 27. Beiblätter, vol. 5, 1881, p. 449.

²R. Lenz: Beiblätter, vol. 6, 1882, p. 802. Original (Stuttgart, 1882) not accessible.

³Pfeiffer: Wied. Ann., vol. 23, 1884, p. 625.

⁴Clarke: Phil. Mag. (5), vol. 20, 1885, p. 435.

⁵Graetz: Wied. Ann., vol. 29, 1886, p. 314.

⁶Foussereau: C. R., vol. 104, 1887, p. 1161.

⁷Mendenhall: Am. Jour. Sci., 3d ser., vol. 24, 1882, p. 43.

asbestos, surround this with a piece of iron gaspipe also covered with asbestos, and then expose it in a combustion furnace, Fletcher's being preferable. In spite of all precautionary preparation, I found the tubes in hand (external diameter $2\rho_2 = 1.8\text{cm}$, internal diameter $2\rho_1 = 0.17\text{cm}$) to be incapable of withstanding more than 200 atmospheres internal pressure. In future experiments it will therefore be necessary to take advantage of smaller diameters.

Instead of platinum, amalgamated zinc terminals were used in case of the zinc sulphate solutions.

53. Electrical apparatus.—The tubes were made part of a Wheatstone bridge of which the corresponding branch was a suitable rheostat X . If $a/b = x/R$, and if I know the deflections of the galvanometer for any increment δx , I can at once compute the quantity δR produced by a given pressure. For in the case of like deflections, $\delta x/x = \delta R/R$. By this simple and convenient method I obtained the data of Table 54, by alternately increasing and decreasing the pressure by increments of 25 atmospheres each. In Table 54, δp is the increment of pressure in atmospheres, practically in megadynes per square centimeter, since the Bourdon gauge (§ 9, 10) used is neither absolute nor very sensitive. $\delta R/R$ is the corresponding increment of resistance for each δp . By adding to $\delta R/R$ the correction $\delta r/r$ due to the expansion of the glass tube (the method of computing $\delta r/r$ will presently be shown, § 55) I obtain the final column $\delta R_0/R_0$, or the resistance effect of the hydrostatic pressure p . I may state that my galvanometer, in case of mercury, was sensitive enough to show deflections of 21cm readable to 0.01cm per 100 atmospheres.

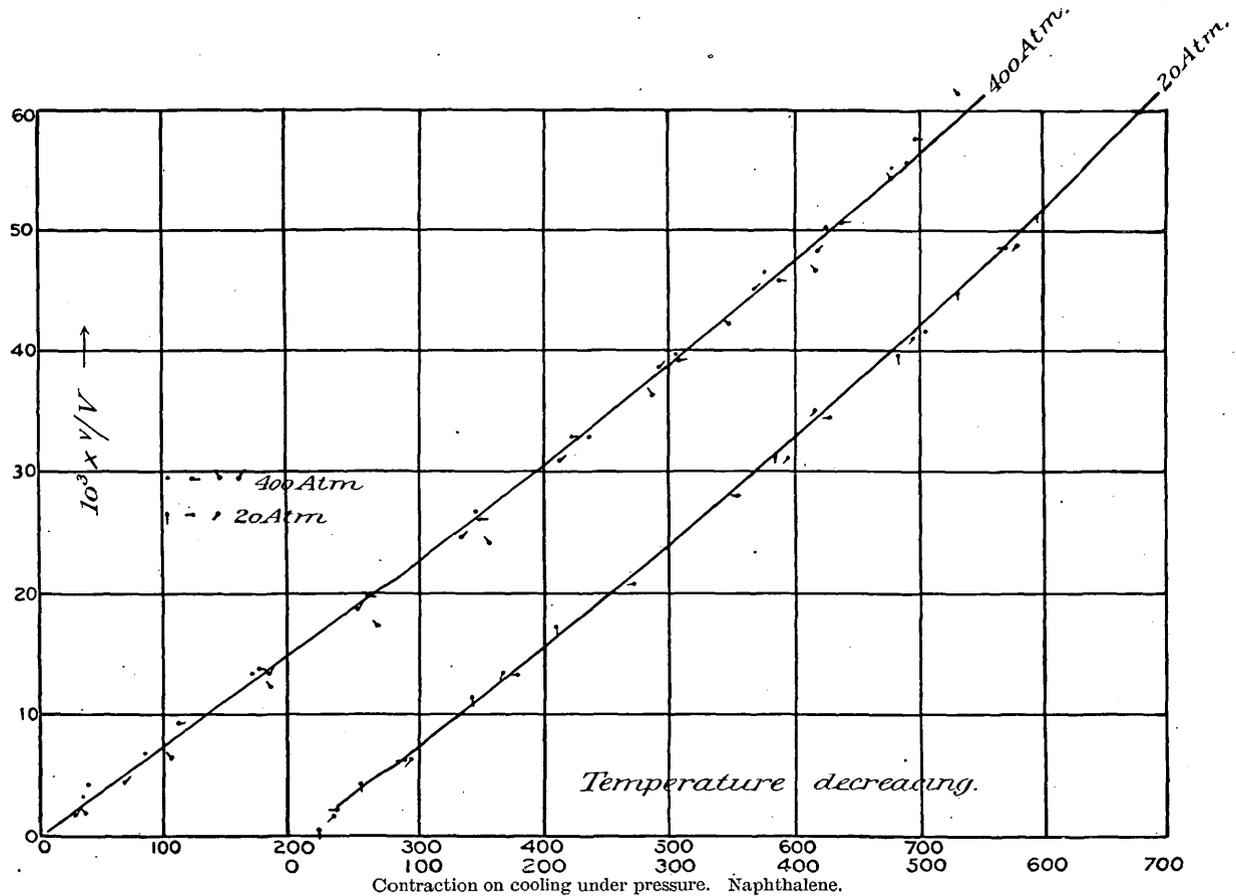
54. Preliminary data.—The initial pressure in the following table is 25 atmospheres, insuring fixed positions of parts, and absence of small air bubbles. Commercial mercury was used.

TABLE 54.—Effect of compression on the resistance of mercury, and of zinc sulphate solution.

[Cailletet tubes: Internal diameter, 0.08cm ; external diameter, 0.90cm .]

Commercial mercury.				Concentrated solution, sulphate zinc.			
δp .	$10^3 \times \delta R/R$.	$10^3 \times \delta r/r$.	$10^3 \times \delta R_0/R_0$.	δp .	$10^3 \times \delta R/R$.	$10^3 \times \delta r/r$.	$10^3 \times \delta R_0/R_0$.
<i>Atm.</i>				<i>Atm.</i>			
25....	—1.1	—0.1	—1.0	(1) 40	—2.7	—0.2	—2.5
50....	—2.2	—0.2	—2.0	70	—4.0	—0.3	—3.7
75....	—3.2	—0.3	—2.9				
100....	—4.3	—0.4	—3.9	(2) 50	—2.5	—0.2	—2.3
125....	—5.5	—0.5	—5.0				

It can not be said that the effect of gaseous polarization in case of zinc sulphate is thus eliminated. I was not surprised, therefore, to find these results less regular than in case of mercury. In the mean of two series of measurements with pressure increasing and pressure decreasing, respectively, the thermal effect of compression may be considered



eliminated, provided the observer waits long enough between series and observations. During these intervals of waiting the assistant easily keeps the pressure constant by moving the screw injector of the Cailletet pump.

55. *Correction for volume changes of tube.*—Allowance may be made for the volume changes of the tube as follows: If r be the resistance, σ the specific resistance of a column of length l , section q and volume v , then

$$r = \sigma l / q = \sigma l^2 / v; \delta r / r = 2 \delta l / l - \delta v / v \quad \dots (1)$$

In case of internal pressure and a long cylindrical tube¹

$$\delta v / v = p \frac{\rho_1^2}{\rho_2^2 - \rho_1^2} \left(\frac{1}{k} + \frac{\rho_2^2}{\rho_1^2} \frac{1}{n} \right) \dots (2)$$

where p is the hydrostatic pressure applied, ρ_1 and ρ_2 the radii internal and external of the tube, $1/k$ the compressibility, n the rigidity of the glass. Again, nearly enough,

$$\delta l / l = \frac{\rho_1^2}{\rho_2^2 - \rho_1^2} p \mu \dots (3)$$

where μ is Young's modulus. Hence

$$\delta r / r = p \frac{\rho_1^2}{\rho_2^2 - \rho_1^2} \left\{ \frac{2}{\mu} - \frac{1}{k} - \frac{\rho_2^2}{\rho_1^2} \frac{1}{n} \right\} \dots (4)$$

in which equation, in case of capillary tubes, the last term is alone of interest. Everett's (*loc. cit.*) values for flint glass, this being the substance of my tubes, are

$$k = 4.1 \times 10^{11}; \quad n = 2.4 \times 10^{11} \quad \mu = 6.0 \times 10^{11} \text{ atm.} = 10^6.$$

Introducing these into equation (4), the values $\delta r / r$ given in Table 54 follow.

In addition to the gauge inaccuracies, the resistance of the mercury column of the Cailletet tube is too small for fine measurements. The galvanometer deflection is more or less fluctuating. Hence I have rounded off the data in Table 54. The resistance of the zinc sulphate column in such a tube is about 20,000 ohms. Having no sufficiently sensitive telephone or dynamometer, I made galvanometer measurements, though these are less well adapted for electrolytic work. Other technical difficulties are to be passed over here.

56. *Preliminary result stated.*—The interesting result of table 54 is this: Both in the case of mercury (metal) and of zinc sulphate solution (electrolyte), the electrical effect of compression without change of temperature is a decrement of specific resistance, proportional to pressure. Relatively speaking the order of this decrement in the two

¹Tait, *loc. cit.*

cases is not very different, being less than one-half per cent per 100 atmospheres. The greater coefficient found for zinc sulphate may be too large, because of the condensation of the polarization gases during compression.

PIEZOMETER METHODS AND RESULTS.

57. *Tabular piezometer described.*—After these encouraging results I resolved to repeat the mercury experiment with greater accuracy. I availed myself for this purpose of a change of method, by which much greater pressure could be applied to filamentary capillary tubes, simultaneously within and without. The apparatus used is practically a tubular piezometer of steel, the dimensions of which are necessarily slender. Filamentary tubes and metallic vessels insure greater constancy of temperature. In a thick glass tube the temperature of the mercury thread can not be certainly known.

The piezometer is shown in Pl. XXVI. Here *ddd* . . . is the steel tube screwed below into a flange *FF*, by which it is attached to the Cailletet pump. Cf. § 5. The mercury to be compressed is contained in a glass tube *acfk*, the lower part *cf* of which is drawn out into a very fine capillary. The lower end communicates with another glass tube *f*, carrying a platinum capillary tube bent hook-shaped, *k*. Above, the platinum wire *ac* (one electrode) has been inserted into the wide part *a* of the tube and extends down as far as *c*, where it is in contact with the mercury. The top is closed with a thread of marine glue, which secures the platinum wire in place. To introduce the mercury into the capillary tube *ack*, it is withdrawn from the apparatus and filled in a suitable way by aid of a mercury air pump. A layer of marine glue *gg* holds the tube in place. The perforated screw *b*, through which the platinum wire *a* passes without contact, closes the tube. Leakage is prevented by putting in *b*, when hot, and dipping it in liquid marine glue before inserting. After these adjustments are made the steel tube *ddd* . . . is inverted and mercury *hhh* . . . poured in from below. A prolongation *ee*, ending below in a hook, is screwed to *ddd* . . .; so that when the tube is in position again it remains filled with mercury. The air pump may also be carefully used to make this filling. To facilitate the adjustment various other appliances are necessary. I omit them here, as they easily suggest themselves to the physicist. Electric current enters on the outside of the iron trough, § 5, and passes via *h* into *k* and the mercury *i*; thence through the capillary mercury thread *cf* and the platinum wire *ca* back to the battery.

Let me add that the end *a* of the tube *ack* is much stronger and of finer bore than has been shown in the figure. It will be noticed that *fk* is a reservoir, permitting contractions of the inclosed mercury during compression. When different low temperatures are necessary for observations, the whole length of steel tube *ddd* . . . is to be jacketed with an appropriate thermal bath.

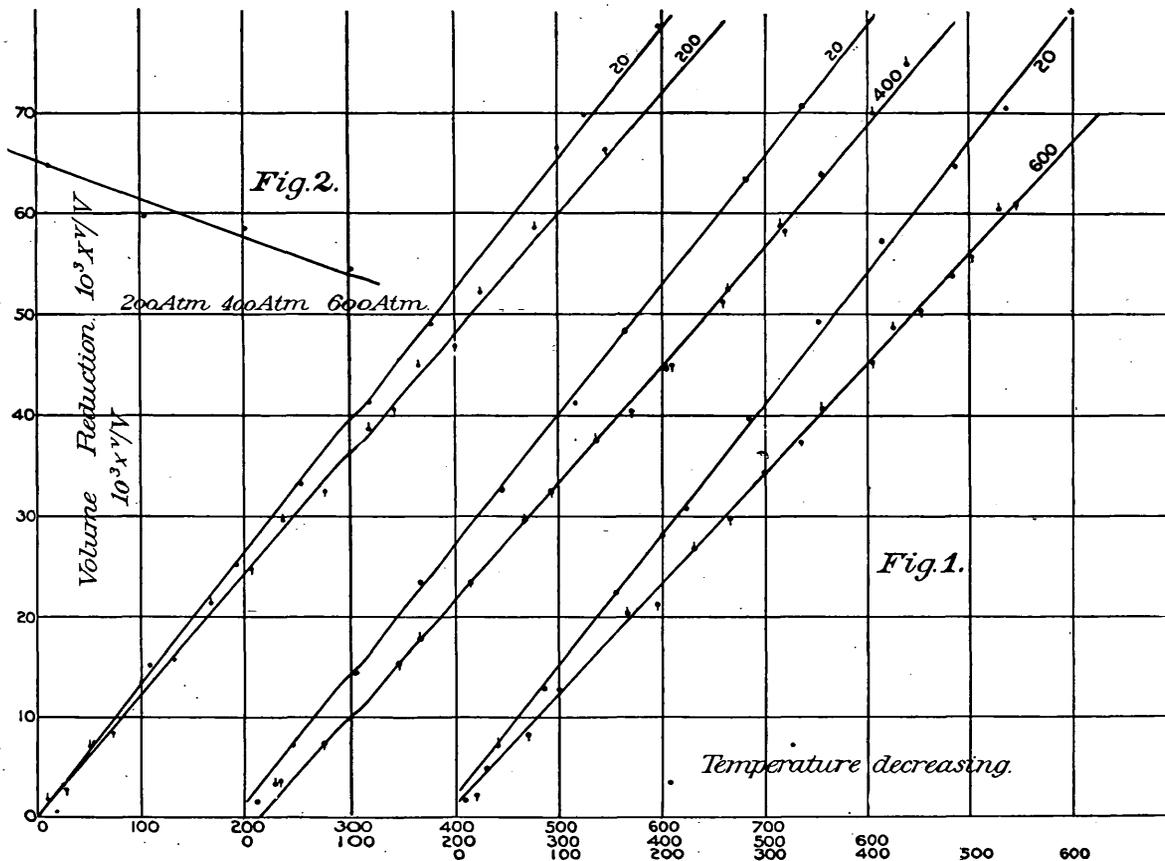


FIG. 1. Contraction on cooling under pressure. Monochloroacetic acid.

FIG. 2. Relative rates of contraction. Monochloroacetic acid.

58. *Results.*—Most of the data of Table 55 were obtained at about 20°. In case of the work detailed in the last column, however, I surrounded the tube with a cold-water jacket, in this way guarding against thermal errors. p denotes the hydrostatic pressure, $\delta R_0/R_0$ the corresponding corrected decrement of resistance. Correction is easy in this case, being simply p/n , where n is the rigidity of the glass. The table also gives R , the resistance in ohms of the divers mercury threads whose approximate length is l and mean radius ρ_1 . The mean external diameter of the filamentary tubes is ρ_2 . Experiments (1) and (4) were made with the same glass tube differently adjusted. Experiments (5), (6), (7), (8) with two other tubes. The last three experiments are the most complete of the series, pressure having been increased from zero to the maximum (300 to 500 atmospheres), and then again decreased from the maximum to zero. The mean of these pairs of data appears in the table. Again, (6) is obtained with a small Bourdon gauge (0 to 300 atmospheres, cf. § 9), (7) and (8) with a large Bourdon gauge (0 to 1,000 atmospheres). Hence the agreement of data (6), (7), (8), is an excellent check on the gauges used, as well as a warrant for the validity of the results. This appears clearly in Pl. XXVII, thus substantiating certain remarks made in Chapter I, § 9.

TABLE 55.—Effect of isothermal compression on the electric resistance of mercury. Piezometer method.

δp	$10^3 \times \delta R_0/R$	δp	$10^3 \times \delta R_0/R$						
<i>Atm.</i>	*(1)	(2)	(3)	(4)	<i>Atm.</i>	(5)	(6)	(7)	†(8)
15.....	—0.63	—0.49	—0.37	—0.58	25.....	—0.92	—0.79	—0.76
40.....	—1.50	—1.29	—1.22	—1.37	50.....	—1.69	—1.56	1.44
65.....	Break.	—2.03	—1.95	—2.13	75.....	—2.47	—2.31	—2.19
90.....	—2.75	—2.69	—2.89	100.....	—3.24	—3.10	3.02
115.....	—3.47	—3.41	—3.61	125.....	—4.01	—3.75	—3.82
140.....	Break.	—4.11	—4.38	150.....	—4.71	—4.57	4.42
165.....	—4.84	Break.	175.....	Break.	—5.31	—5.35
190.....	—5.45	201.....	—6.07	5.91
215.....	—6.21	225.....	—6.87	—6.77
240.....	—7.09	250.....	—7.50	7.43
265.....	—7.67	275.....	—8.28	—8.22
290.....	—8.20	300.....	8.96
315.....	Break.	325.....	—9.73
					350.....	10.41
					375.....	—10.81
$R=$	18 ω	18 ω	18 ω	18 ω	$R=$	10 ω	7.5 ω	7.5 ω	
$l=$	15 cm	15 cm	15 cm	15 cm	$l=$	15 cm	15 cm	15 cm	
$\rho_1=$.005 cm	.005 cm	.005 cm	.005 cm	$\rho_1=$.007 cm	.008 cm	.008 cm	
$\rho_2=$.03 cm	.03 cm	.03 cm	.03 cm	$\rho_2=$.035 cm	.035 cm	.035 cm	

* Average temperature, series (1) to series (7) is 18°.

† Average temperature, series (8), is 6°. At $\delta p=350$ atmospheres no change of resistance was observable during 6 minutes of waiting.

In Pl. XXVII, all these data are constructed graphically. The divers series of observations are numbered as in Table 55, and together they make up a diagonal line running quite across the chart. It is seen that the distribution of points differs quite as much for one and the same tube ((3), (2), (4), (1)), as it does for different tubes ((1) to (4), (5), (6) to (8)). As a rule the deviations are errors largely avoidable. I will omit a discussion, and merely refer to the good agreement of the final series (6) to (8) already mentioned.

DEDUCTIONS.

58. *Purely thermal variation of resistance.*—Accepting Grassi's¹ value for the compressibility of mercury, 3×10^{-6} per atmosphere, which is a fair mean of the data of Colladon and Sturm, and of Oersted, the chart easily enables me to pass from $\delta R/R$ as a function² of p , to $\delta R/R$ as a function of $\delta v/v$, where v is the symbol of volume. Again from the known electrical temperature coefficient³ of mercury (0.0008 at ordinary temperatures), and the known coefficient of expansion (0.00018), it is easy to construct $\delta R'/R'$ as a function of $\delta v/v$, when the cause of the simultaneous variation is change of temperature. Hence the chart contains two lines, showing the values of $\delta R/R$ corresponding to the same volume decrement $\delta v/v$, when the causes of variation are temperature alone, and pressure alone, respectively. Curiously enough, $-\delta R/R > \delta R'/R'$, an important result, which I shall presently interpret. The chart also contains the corresponding data for solution of zinc sulphate. $\delta R/R$ is in the region of negative δR ; $\delta R'/R'$, however, in the region of positive δR . Numerically $\delta R'/R'$ is very large in comparison with $\delta R/R$, besides having the opposite sign.

The line extending through the chart is very nearly straight. Compatibly with the accuracy of measurement it may, therefore, be inferred that the ratio of the quantity $\delta R/R$ to $\delta v/v$, or to pressure, is constant throughout an interval of about 500 atmospheres. Hence the conclusions, § 56, drawn from Table 54, are materially substantiated by Table 55. The chart expresses approximate relations which may be put succinctly as follows:

By subjecting commercial mercury to pressures between 10 and 400 atmospheres isothermally, $-\delta R/R = 30 \times 10^{-6} \delta p$, where $\delta R/R$ is the decrement of specific electrical resistance R , corresponding to the pressure increment δp . If v be the symbol of volume, then $\delta v/v = 3 \times 10^{-6} \delta p$. Hence $\delta R/R = 10 \delta v/v$.

If θ be the symbol of temperature, the results which apply isopiesticly at ordinary temperatures and pressures are $\delta R'/R' = 800 \times 10^{-6} \delta \theta$; $\delta v/v = 180 \times 10^{-6} \delta \theta$. Hence $\delta R'/R' = 4.4 \delta v/v$, where R' refers to electrical resistance considered in its thermal relations.

59. Again, by subjecting a concentrated solution of zinc sulphate to pressures between 10 and 150 atmospheres, isothermally, $-\delta R/R = 50 \times 10^{-6} \delta p$. The other relations corresponding to the above must be estimated:

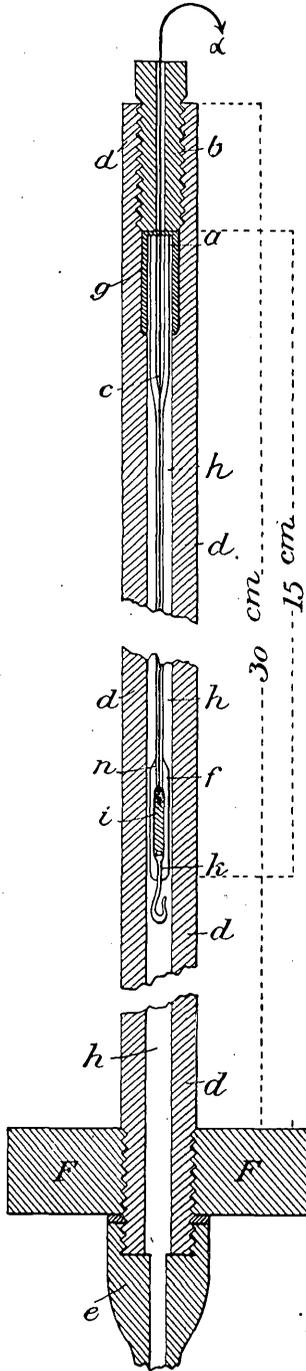
$$-\delta v/v = 50 \times 10^{-6} \delta p; \quad -\delta R'/R' = 0.4 \delta \theta; \quad \text{and} \quad \delta v/v = 200 \delta \theta.$$

The chief magnitudes are here of different order and even of sign from

¹ The newer values of Tait and of Amagat (loc. cit.) would not essentially modify the statements of the text.

² The subscripts zero, which were used above to accentuate the corrected values of R etc., are henceforth conveniently dropped.

³ I made a special measurement of this coefficient for the mercury used.



Apparatus for compressing mercury.

those applying to mercury. Therefore, this estimate is sufficient for the following inferences:

The chart shows at once that to bring the compression loci into coincidence with the thermal loci, the former must be rotated around the origin in a direction contrary to the hands of a watch. The angle of rotation is much greater for zinc sulphate solution than it is for mercury. Hence, as before, both in the case of the metal and of the electrolyte, the effect of isothermal compression is a decrement of resistance proportional to pressure, and by deduction, *the immediate electrical effect of rise of temperature, $\delta R'/R' - \delta R/R$, is a decrement of specific resistance, both in the case of the metal (Hg), and of the electrolyte ($ZnSO_4 + Aq$).*

This points out an inherent similarity between the metallic and the electrolytic conduction.

60. Comparison with J. J. Thomson's equation.—In J. J. Thomson's¹ expression for specific resistance $R = \sigma = (2\pi\beta/K)(q/mx)$, suppose, to fix the ideas, that β , K , and q are constant, whereas, m , the number of molecules splitting up per unit of volume, per unit of time, and x , the distance passed over by the partial molecule moving at a mean velocity c , during the interval of freedom t , are regarded as variable. Clearly x can not be independent of m . Taking active molecules alone into consideration, supposing them to be symmetrically distributed and to move parallel to each other, $x = \sqrt[3]{1/mt}$. Hence

$$R = (2\pi\beta q/K)x^3/c.$$

This is in accord with the above data. Reduction of volume $\delta v/v$, isothermally by pressure diminishes x only. Reduction of volume isopiesticly, by cooling, diminishes both x and c . Hence the greater diminution of R in the former instance (pressure). Finally, by partial differentiation under the given conditions $dR/dm = -(4\pi\beta q/3K)^3 \sqrt{t/m^5}$. From this it may be conjectured (conjectured because t and m are not independent of each other) that the effect of R on an additional number of molecules splitting up, decreases rapidly with the total number m splitting up; i. e., that the numeric of the immediate electrical effect of temperature, $\delta R'/R' - \delta R/R$, is smaller for the metal than for the electrolyte. This also is in accord with the above data.

61. Zero of resistance.—In connection with these results it is well to note in passing, that, supposing the laws to hold indefinitely, the zero of resistance would be reached only after compressing mercury with a force of 33,000 atmospheres; but that it would be reached considerably before the zero of volume.

62. Electrical pressure measurement.—It follows, furthermore, from the above measurements, that the variation of the resistance of mercury is sufficiently marked, and bears a sufficiently simple relation to the superincumbent pressure, to suggest the use of this principle for pressure measurement.

¹ J. J. Thomson: Application of dynamics, etc., London, Macmillan, 1888, p. 299.

63. *Measurement of melting point and pressure.*—Curiously enough the results of Lenz (*loc. cit.*) for mercury are much larger than mine. Working between 0 and 60 atmospheres, and upon pure mercury filled into a piezometer tube by Weinhold's vacuum apparatus, Lenz found a resistance decrement of $\cdot 02\%$ per atmosphere at zero degree centigrade. This is considerably larger than my result, $\cdot 003\%$ per atmosphere, at 18° . It is impossible to detect the cause of the difference. Lenz's work was done in a way which from the description accessible to me is faultlessly precise, and my own experiments were so frequently repeated that I can not believe them in error. Possibly slight changes of composition may effect a large difference of compressibility, and my mercury was not quite pure. It is useless to speculate on the causes of difference here. They are now of secondary interest. This part of the work can easily be perfected in any measure. The point of importance at present follows more emphatically from Lenz's large datum than from my smaller result. It is clear that in the usual course of my work I may anticipate electrical variations of resistance due to pressure to the extent of several per cent; but a resistance decrement, $\delta R/R$, of this value, whenever methods of differential comparison are available, is virtually a very large quantity, capable of being followed with great accuracy. It is interesting to note, moreover, that the numerical value of $\delta R/R$ in question is over ten times as large as the corresponding volume decrement, $\delta v/v$, and that the elastic or dimensional discrepancy is even in most unfavorable cases not above 10% of the total decrement.

Hence I may confidently infer that the method sketched in the present chapter is sufficiently sensitive to throw much light on experimental questions relative to the continuity of the solid and liquid states. Prof. J. Willard Gibbs (*loc. cit.*), by constructing entropy energy and volume in the direction of three rectangular axes, has devised exceedingly beautiful geometric methods for the general study of continuous changes of physical state. Prof. Poynting¹ has discussed the subject with especial reference to the transition solid-liquid. Among others Amagat (*loc. cit.*) is searching for the lower critical temperature. Apart from these suggestive contributions, our knowledge of what actually takes place in liquid matter is meager in the extreme. Hence any general method capable of elucidating the unknown topography of the thermodynamic surface of liquids deserves most painstaking scrutiny. The advantage of the above resistance method over the ordinary optic and other similar methods lies in the fact that in the above case the *character* of the fusion is described step by step. This is a much broader criterion than a merely arbitrary fusion test.²

64. *Conclusion.*—In conclusion I may advert to the fact that a study of fusion phenomena in the manner indicated is destined to throw much

¹ Poynting: *Phil. Mag.* (5), vol. 12, 1881, p. 32.

² Another available method for describing the degree of fusion is given by the volume changes at the melting point. Both of these I hope at an early date to apply.

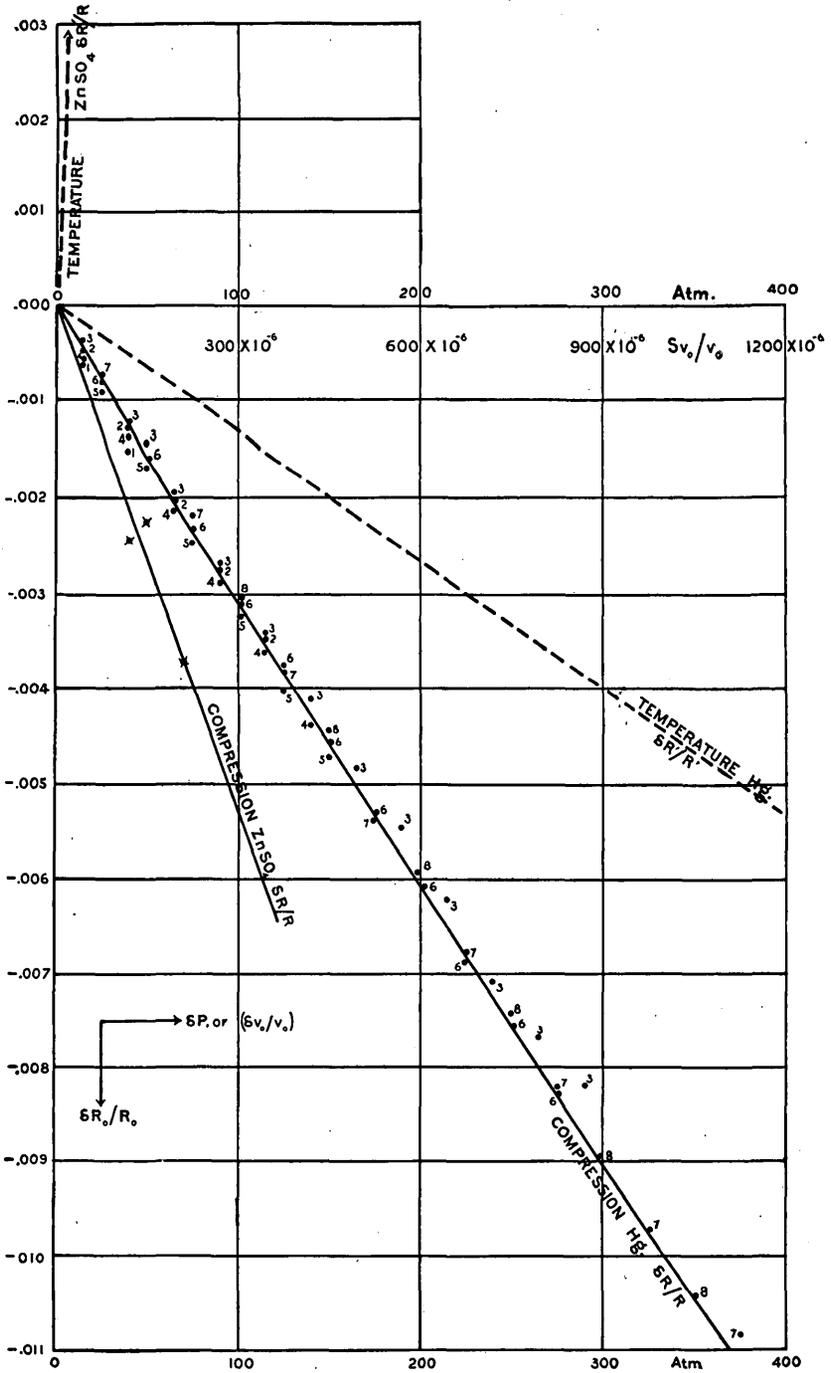


Chart showing the relations between corresponding values of the increments of specific resistance, hydrostatic pressure, and volume compression in case of mercury and a concentrated solution of zinc sulphate.

light on obscure points in physical chemistry. The molecular mechanism through which energy is potentialized during fusion can not on the basis of any atomistic theory even be rationally conjectured. Retarded solidification, supersaturation, and allied phenomena point to occurrences at the melting point the signification of which is much underestimated. Recent minute researches into the nature of solution should not blind us to the fact that questions which apparently lie much nearer home, viz, the underlying molecular causes of change of physical state of aggregation, are as yet unsatisfactorily fathomed.

CHAPTER III.

THE COMPRESSIBILITY OF WATER ABOVE 100° AND ITS SOLVENT ACTION ON GLASS.

INTRODUCTION.

65. *Behavior of water.*—When temperature rises the compressibility of water continually decreases until about 60° is reached. After this, temperature increasing further, the compressibility of water increases. It was my original purpose to supplement these results by determining the compressibility of water between 100° and 310°, but I did not get higher than 185°. At this temperature, and obviously much below it, water attacks ordinary glass so rapidly as to make the measurements in glass tubes worthless.

66. *Literature—Compressibility of water.*—The peculiar behavior in question has attracted many physicists. Grassi¹ was the first to find that the compressibility (β) of water decreases with temperature, being 50/10⁶ at 0° and 44/10⁶ at 53°. He also observed the compressibility of solutions to be less than that of water. Amaury and Descamps² substantiate the latter result, but they only observe at a single temperature, 15°, at which $\beta = 46/10^6$. In Cailletet's³ experiments, extended as far as 700 atmospheres, only a single temperature is given ($\beta = 45/10^6$), and the same is true of Buchanan's⁴ results. After this the subject was vigorously attacked by Tait⁵ and his pupils, at first particularly with reference to the depression of the temperature of maximum density of water⁶ produced by pressure. In further experiments Tait⁷ studies the thermal relations of the compressibility of water. Further results are due to Pagliani and Palazzo,⁸ working with mixtures of water and alcohol, but more directly to Pagliani and Vicentini.⁹ The last ob-

¹ Grassi: *Ann. de ch. et de phys.* (3), vol. 31, 1851, p. 437. Cf. Wertheim: *Ann. ch. et phys.* (3), vol. 23, 1848, p. 434.

² Amaury and Descamps: *C. R.*, vol. 68, 1869, p. 1504.

³ Cailletet: *C. R.*, vol. 75, 1872, p. 77.

⁴ Buchanan: *Nature*, vol. 17, 1878, p. 439.

⁵ Tait: *Proc. Roy. Soc. Ed.*, vol. 11, 1881, p. 204. Marshall, Smith, and Omond: *Ibid.*, vol. 11, 1882, pp. 626, 809. Tait: *Ibid.*, p. 813; *ibid.*, vol. 12, 1882-'83, p. 226; *ibid.*, vol. 13, 1884-'85, p. 2.

⁶ The probability of such an occurrence had been inferred by Puschl and by Van der Waals. Cf. Grimaldi, *loc. cit.*

⁷ Tait: *Proc. Roy. Soc. Edinb.*, vol. 12, 1882-'83, p. 45; *ibid.*, p. 223; *ibid.*, 1883-'84, p. 757.

⁸ Pagliani and Palazzo: *Beiblätter*, vol. 8, 1884, p. 795.

⁹ Pagliani and Vicentini: *Beiblätter*, vol. 8, 1884, pp. 270, 794; *Journal d. Phys.* (2), vol. 30, 1883, p. 461.

servers corroborate Grassi's work, and find that water shows a minimum compressibility at 63°. Grimaldi¹ critically reviews the maximum-density experiments of Puschl, of Van der Waals,² of Marshall, Smith and Omond, and of Tait. Amagat,³ applying a new method of pressure measurement, "à pistons libres," operates with pressures as high as 3,000 atmospheres and at temperatures between 0° and 50°. He shows that the peculiarities of the behavior of water vanish at high pressures and increasing temperatures (interval, 0° to 50°), corroborating Grassi. Tait,⁴ in a final paper, summarizes much of his work, and begins a series of experiments showing that the effect of solution is analogous to an increase of internal pressure.

67. *Literature. Solvent action of water.*—From this brief summary it appears that results anticipating the contents of the present paper are not at hand. There is another class of experiments relating to the expansion of water compressed in glass tubes, to which I must advert. The experiments of Waterston⁵ are probably the most complete and carried as far as 300°, although for very high temperatures Daubrée's⁶ experiments relative to the action of water on hot glass are to be cited.

METHOD OF MEASUREMENT AND RESULTS.

68. *Apparatus.*—The apparatus used in the present work is the arrangement already described, § 5 to 14. Pressures are applied by aid of Cailletet's large pump. The thread of water is inclosed in a capillary tube between two threads of mercury, and the distance apart of the two inner menisci, measured by Grunow's cathetometer. The tube, suitably closed above, is exposed in a vapor bath (boiling tube). At 185° (aniline), the thread of water soon loses its transparency, becoming white and cloudy. This makes the observation difficult. Fortunately the siliceous water is translucent. By placing a very bright screen behind it, the demarkation between water and mercury remains sufficiently sharp for measurement. After the action has continued for some time, say an hour, the column is solid at high pressure (300 atmospheres), though it is probably only partially so at 20 atmospheres. The result is that threads of mercury break off during advance and retrogression of the column. Further measurement is therefore not feasible. Toward the close of the experiment, moreover, the mercury thread advances inclosed by walls of semisolid siliceous water. The thread is, therefore, of smaller diameter, and the measurement correspondingly inaccurate.

In obtaining these data I followed the customary plan of increasing pressure from zero to the maximum, then decreasing it from the maxi-

¹ Grimaldi: Beiblätter, vol. 10, 1886, p. 338.

² Cf. Van der Waals: Beiblätter, vol. 1, 1877, p. 511.

³ Amagat: C. R., vol. 103, 1886, p. 429; *ibid.*, vol. 104, 1887, p. 1159; *ibid.*, vol. 105, 1887, p. 1120.

⁴ Tait: Challenger Reports, vol. 2, part 4, 1888.

⁵ Waterston: Phil. Mag., (4) vol. 26, 1863, p. 116, Journ. de Phys. 2 (2) vol. 8, 1889, p. 197.

⁶ Daubrée: Études synthét. de géologie expér., Paris, Dunod edit. 1879, p. 154 et seq.

imum to zero, and taking the mean of the volume changes corresponding to a given pressure. When water does not attack glass, the fiducial mark (pressure zero) at the beginning of the series is regained at the end. When water attacks glass there is considerable shifting.

Boiled distilled water was used, and the glass is common lead glass.

69. *Low temperature data.*—In Table 56 I have given some results for low temperature compression of water. The data are not very sharp, owing to the fact that I did not succeed in sealing the thread of water with its end threads of mercury faultlessly. I think I detected motion of the whole system, which, however, is to some extent eliminated by the method of experiment. The results serve a purpose in introducing the subsequent high temperature experiments. At 400 atmospheres the tube broke. L and θ denote the length of the column of water and its temperature. v/V is the observed amount of volume reduction per unit of volume, due to the burden of p . Finally, $\beta = (v/V)(1/p)$ denotes the mean compressibility between $p=0$ and the pressure corresponding. In view of the irregularities, it did not seem worth while to compute compressibility by more rigorous methods, and the last column simply gives the mean value of β .

TABLE 56.—Compressibility of water at low temperatures.

L, θ	p	$\frac{v}{V} \times 10^3$	$\frac{v}{V} \times 10^3$	$\beta \times 10^5$	Mean $\beta \times 10^5$ 0 to 400 atm.
9.8cm 31°	atm. 0	0.0	0.0	46
	100	5.3	5.2	52	
	200	9.5	9.7	48	
	300	13.4	12.3	43	
	400	15.6	16.1	40	
9.9cm 64°	0	0.0	0.0	49
	100	4.3	4.2	42	
	200	10.4	9.1	49	
	300	16.2	12.6	48	
	400	22.3	19.2	57	
10.1cm 100°	0	0.0	0.0	56
	100	6.6	6.1	63	
	200	11.1	11.9	57	
	300	15.9	16.4	54	
	*400	20.0	19.2	49	

* Tube breaks.

These results contain a mere corroboration of the work of earlier observers. The initial compressibility decreases between 28° and 64°, after which it increases to 100°. Cf. § 12.

70. *High temperature data.*—In the next table (57) the first experiments proper of this paper are described. The symbols used are the same as those in § 4, an additional datum, the time, t , of the observations having been added. The first series of data were obtained at 28°, and are similar to those of Table 56. The next 7 series for 185° are new. Unfortunately I did not observe when ebullition commenced, so that the first dates are not available. After closing the experiment, I

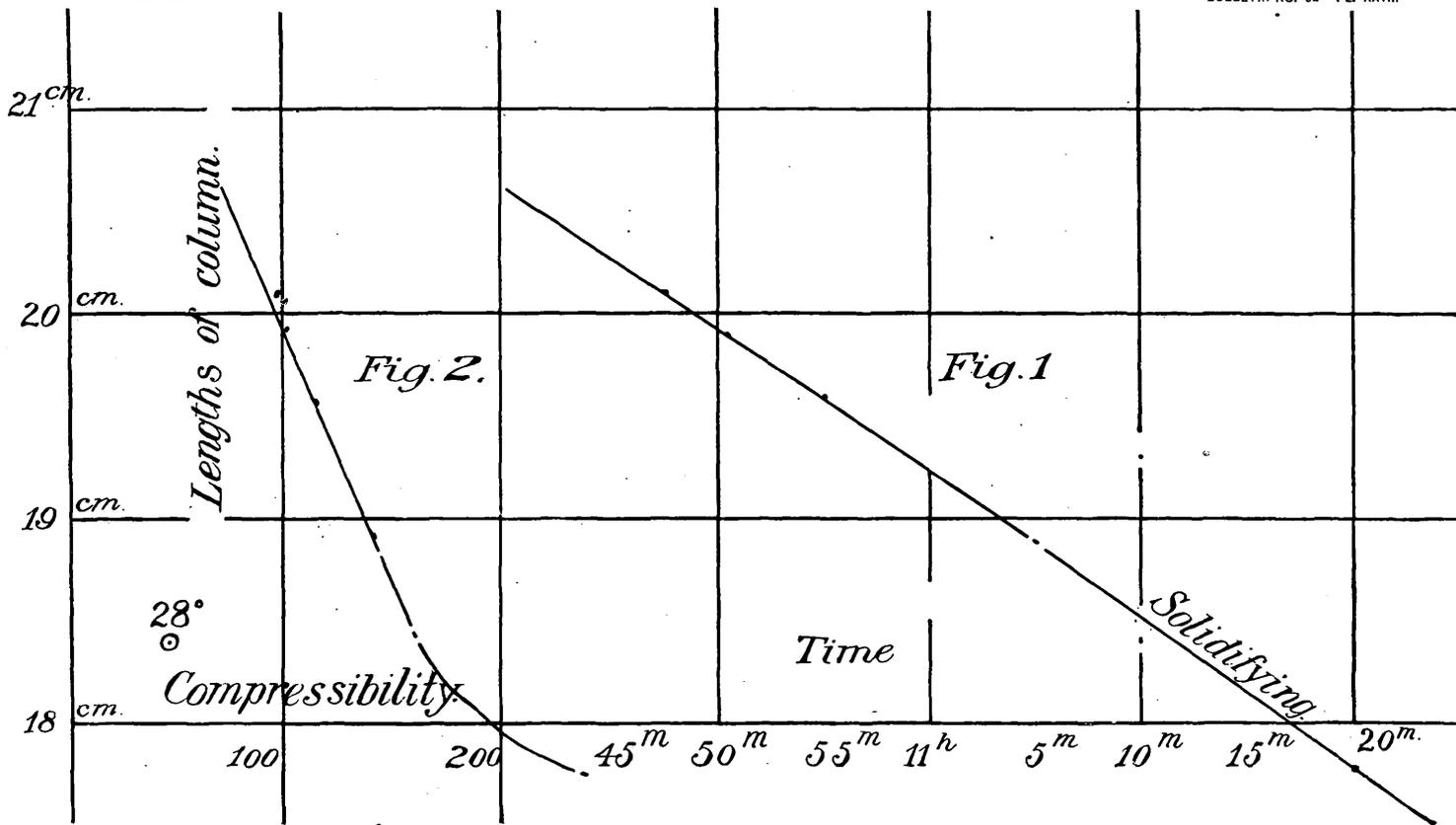


FIG. 1. Time and contraction of superheated silicated water.

FIG. 2. Contraction and compressibility of silicated superheated water.

noticed that a filament of the upper thread of mercury had run down into the core of the silicated water below it. This means that the action had eroded its way between the mercury and glass. In this respect the observations are uncertain.

TABLE 57.—*Compressibility of water at higher temperatures.*

<i>L, θ, t</i>	<i>p</i>	$\frac{v}{V} \times 10^3$	$\beta \times 10^6$	<i>L, θ, t</i>	<i>p</i>	$\frac{v}{V} \times 10^3$	$\beta \times 10^6$
28° 18.44 ^{cm}	<i>atm.</i>			185° 19.57 ^{cm}	<i>atm.</i>		
	20	0.0	-----		20	0.0	-----
	100	3.5	44		100	9.3	116
	200	9.4	52		200	23.6	114
	300	13.4	48		300	32.7	117
400	18.5	49	400	42.8	113		
185° 20.45 ^{cm}	20	0.0	-----	185° 11 ^h 05 ^m	20	0.0	-----
	100	6.7	84		100	11.7	146
	200	14.4	80		200	25.9	144
	300	21.1	75		300	39.7	142
	400	29.3	77		400	55.5	146
185° 20.10 ^{cm}	20	0.0	-----	185° 10 ^h 10 ^m	20	0.0	-----
	100	8.8	109		100	30.1	167
	200	17.1	95		200	44.6	159
	300	27.4	98		300	60.2	158
	400	34.7	91		400		
185° 19.94 ^{cm}	20	0.0	-----	185° 11 ^h 20 ^m	20	0.0	-----
	100	8.1	101		100	15.0	188
	200	18.3	102		200	31.7	170
	300	27.9	100		300	56.2	201
	400	38.3	101		*400	71.8	189

* Solid since threads break off here. Compressibility still increasing.

71. *Discussion of these results.*—To discuss these results I first plotted v/V as a function of p , thus obtaining a series of curves of somewhat irregular contour, the character of which is, however, obvious. This will be more accurately observed (Pl. XXVIII, Fig. 2) by plotting β as a function of the length L of the column, since the time data are imperfect. The result is striking. It shows a mean increment of β of about 50/10⁶ per centimeter of decrement of length of column. Toward the end of the experiment the values of β increase much faster; but here they are uncertain because of solidification. The total observed decrement of L is therefore (20.1-17.8)/20.1, or more than 11%. Since the column at the moment when ebullition started must have been much longer, it follows that the *combined volume* of pure water and solid glass shrinks more than 11%, in virtue of the solution of glass in water up to the point of solidification at 185°. By plotting length L as a function of time (Pl. XXVIII, Fig. 1) the data, though incomplete, show that the volume contraction took place at the rate of 11 per cent per 40 minutes; that is (say), 0.3% per minute. The column therefore soon contracts to a smaller length than the original column at 28°. This is an enormously rapid rate; for were it possible for such action to be indefinitely prolonged the column would be quite swallowed up in 5 hours. Hence it appears improbable that the action of water on glass will be unaccompanied by heat phenomena. (See below, § 74.)

72. *High-temperature measurement repeated.*—From the importance of these results I resolved to repeat them with greater precautions. Table 58 contains the results given on the plan of Tables 55 and 56. The first series holds for 24°; the remaining 9 series for 185°. Time is given in minutes, dated from the period when ebullition had fairly commenced. The experiment therefore lasted about one hour. A subsidiary table, 59, contains the essential results (time, temperature θ , volume decrement (v/V), compressibility β) of Table 58. The course of the experiment was very satisfactory.

TABLE 58.—*Compressibility of water.*

θ, L, t	p	$\frac{v}{V} \times 10^3$	$\beta \times 10^6$	θ, L, t	p	$\frac{v}{V} \times 10^3$	$\beta \times 10^6$
24° 13·96 ^{cm}	Atm.	0·0	185° 14·58 ^{cm} 40 ^m	Atm.	0·0
	20	3·6	45		20	11·7	146
	100	7·9	44		100	24·9	138
	200	12·2	44		200	38·9	139
*185° 15·42 ^{cm} 18 ^m	20	0·0	185° 14·34 ^{cm} 45 ^m	20	0·0
	100	6·2	77		100	12·9	161
	200	14·2	79		200	29·3	163
	300	21·0	75		300	46·1	165
185° 15·17 ^{cm} 25 ^m	20	0·0	185° 14·03 ^{cm} 50 ^m	20	0·0
	100	7·6	95		100	14·7	184
	200	17·7	98		200	32·8	182
	300	27·8	99		300	52·0	186
185° 15·01 ^{cm} 30 ^m	20	0·0	185° 13·75 ^{cm} 55 ^m	20	0·0
	100	8·7	109		100	18·3
	200	20·6	114		200	39·4
	300	31·9	114		300	60·5
185° 14·80 ^{cm} 35 ^m	20	0·0	185° 13·56 ^{cm} 60 ^m	Threads broken off; measurement uncertain; siliceous water, solid.
	100	9·8	123		
	200	22·9	127		
	300	35·0	125		

* Commenced boiling at 0^m, say.

TABLE 59.—*Contraction and compressibility of silicated water. Referred to water at 24° and 20 atmospheres.*

θ	$\frac{v}{V} \times 10^3$	$\beta \times 10^6$	Time.
24°	± 0	44
185°	+103	77	18 ^m
185°	+ 86	97	25 ^m
185°	+ 75	112	30 ^m
185°	+ 60	125	35 ^m
185°	+ 44	141	40 ^m
185°	+ 27	163	45 ^m
185°	+ 07	184	50 ^m
185°	— 15	221	55 ^m
185°	— 29	60 ^m

73. *Discussion of these results.*—The discussion of this table can be made on the lines followed in case of the other (§ 71). Note at the outset that after 55^m have elapsed since exposure to 185° the turbid

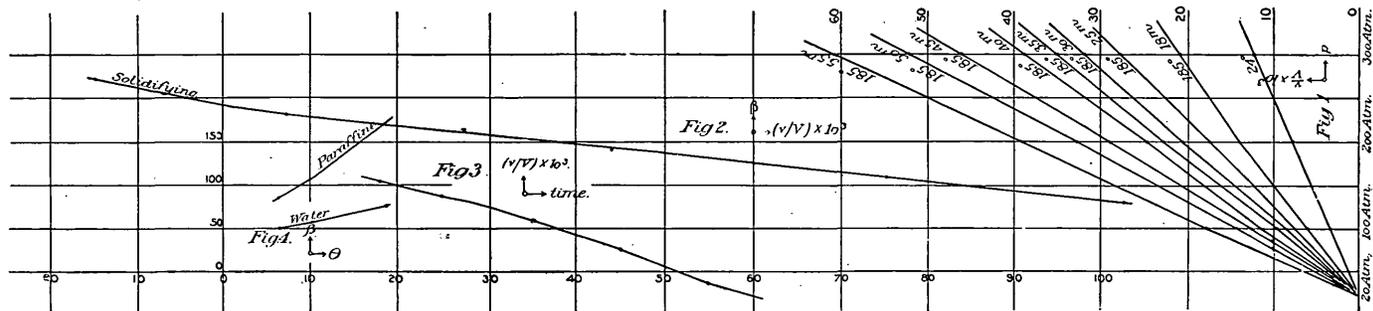


FIG. 1. Successive isothermals of superheated silicated water. 24° and 185°.

FIG. 2. Relation of compressibility and contraction of superheated silicated water.

FIG. 3. Time and contraction of superheated silicated water.

FIG. 4. Compressibility of paraffin and water compared.

column is not so long as the original cold clear column at 24° . The hot compressibility after 55^m has increased to five times the cold compressibility and more than three times the original hot compressibility. Some allowance must, however, be made for the finer advancing thread of mercury, as explained in § 68. If v/V be plotted as a function of p , a series of curves is obtained as shown in Pl. XXIX, Fig. 1. Considering the difficulties of measurement, they are satisfactorily regular. Temperature and time have been inscribed on each curve. As usual, compressibility decreases with pressure. In Table 59 (v/V) is really the ratio of increment of length to the original length at 24° , due to thermal expansion with concomitant chemical action. It is not the ratio of volumes of solution, because the radius of the tube widens in proportion as solution proceeds. Nevertheless, the datum suffices for the present purposes. Let β be represented in its dependence on (v/V). The plotted curve is a line of remarkable regularity, as shown in Pl. XXIX, Fig. 2. It follows from the chart that β increases $11/10^6$ for each per cent of volume decrease of water undergoing silicification. This is about $75/10^6$ per centimeter of decrement of length, thus agreeing substantially with the former results. Again v/V decreases 13% for the interval of observation of 42 minutes; that is, say, 18% during the whole hour of exposure, or 0.3% per minute, again agreeing with the above result § 71. See Pl. XXIX, Fig. 3.

The regularity of the present results enables me to draw a further inference. Suppose the line for β , v/V to be prolonged as far as $v/V=150/10^3$, which holds for time = 0. Since in this case the water is pure, the datum for β is the normal compressibility of water at 185° . Making the prolongation (see Pl. XXIX, Fig. 3), I find $\beta=30/10^6$ nearly. This is, of course, too small a result, and shows that the time at which chemical action began is not well indicated. But since β_{185} can not be greater than $70/10^6$, the compressibility of water above 100° continues to increase at an exceptionally slow rate, about one-fourth as slow as paraffin, for instance (Pl. XXIX, Fig. 4). This indicates exceptional stability of the water molecule.

74. Conclusion.—Now what is the underlying cause of this action? Clearly, I think, an instability of the glass molecules at 185° , much rather than any instability of the water molecule. This is in accordance with the evidence I obtained from the study of the electrolytic conduction of stressed glass,¹ and corresponds also to the viscosity of glass at the stated temperature. At 185° the cohesive affinities of the water are sufficient to disintegrate the glass molecule.

The increase of β with time must be due to solution of silicate. Indeed it would be difficult to devise an experiment in which the effect of continued solution can be so well discerned as is possible in the present incidental results. Curiously enough the effect of solution is here an increment of compressibility, whereas in most other cases (cf.

¹ Barus: Am. Journ. Sci., vol. 37, 1889, p. 350.

literature, § 66) it is a decrement of compressibility. I leave this without comment, believing, however, that the silicate is in unstable equilibrium with its water when pressure is small, and that the compressibilities measured are solution effects. The possible occurrence of lag here (though I did not search for it) is obscured by the contraction of the silicated column of water. At all events, we have here a case of solidification by pressure from solution, analogous to solidification by pressure from fusion.

Finally, I may advert to the far-reaching geological importance of these results. In so far as the solvent action of hot water is accompanied by a contraction of the original bulk of silicate and water, it is presumably accompanied by the evolution of heat. Hence, if water at a temperature above 200° and under a pressure sufficient to keep it liquid be so circumstanced that the heat produced can not easily escape, the arrangement in question is virtually a furnace; and since such conditions are necessarily met with in the upper layers of the earth's crust, it follows that the observed thermal gradient (i. e., the increase of temperature in depth below the earth's surface) will be steeper than a gradient which would result purely from the normal distribution of terrestrial heat. In other words, the observed rate of increase of temperature with depth is too large, since it contains the effects of a chemical phenomenon superimposed on the pure phenomenon of heat conduction.

CHAPTER IV.

THE SOLUTION OF VULCANIZED INDIA RUBBER.

75. In my work¹ on the solubility of glass in water, chapter III, I showed that in proportion as the state of dissociation, or the molecular instability of glass is increased with rise of temperature, the solvent action of water also increases at an enormously rapid rate; that inasmuch as the solution takes place between a solid and a liquid, sufficient pressure must be applied to keep the fluid in the liquid state whenever the vapor tension at the temperature in question exceeds the atmospheric pressure. Thus, at 100° C. the action of liquid water on glass is nearly negligible, whereas at 180° solution occurs at so rapid a rate that the capillary tubes may become filled with solid hydrated silicate in place of water in an hour. Here, however, at least 10 atmospheres must be applied to keep the water in the liquid state essential to speedy reaction.

76. *The present application.*—Having attempted to apply the same principle to the actual solution of vulcanized India rubber I obtained confirmatory results at once. To my knowledge this material has not heretofore been thoroughly dissolved in a volatile reagent, or in any reagent by which it is speedily and copiously taken into solution, and from which it may be speedily and easily obtained. It follows by analogy from § 75 that the rubber must be heated hot enough to be in a state of dissociation, i. e., that the coherence of the solid rubber-sulphur molecule must show an instability in relation to whatever solvent may be used. It follows, moreover, that to facilitate reaction the system of rubber and solvent is to be kept under a pressure sufficient to insure the liquid state of the solvent. It follows obviously that this temperature must not be so high, caet. par., as to change the useful character of the rubber deposited from solution. Hence I act on vulcanized India rubber at the lowest convenient temperature facilitating the solvent action, and at a pressure necessarily exceeding the vapor tension of the solvent at the given temperature. Whatever other favorable action pressure may exert, such, for instance, as forcing the fluid into the physical pores of the rubber by a principle akin to Henry's

¹ Am. Jour. Sci., vol 38, 1889, p. 408. The paper was published in full in the February number of the Am. Jour. Sci., 1891.

law, is clear gain. In my machine¹ it is rather more convenient to act under 100 or 200 atmospheres than at lower pressures. Hence I did not scruple to use pressures as large as this.

77. *Solution in carbon disulphide.*—I will state here that the samples of vulcanized rubber acted on were five in number and of the character detailed as follows. By elastic I mean stretchable or extensible, with resumption of the original form when the pull ceases:

(a) Very elastic sheet rubber, usually non-pigmented and translucent in thin films, brownish in color. Used for rubber bands, for bellows, for chemical rubber tubing, etc.

(b) Less elastic and harder rubber, pigmented gray, opaque. Largely used for rubber tubing, sheeting, etc.

(c) Non-elastic pigmented rubber, used for low-class rubber tubing and low-class merchandise in general.

(d) Ebonite.

(e) Same as a, rotted by age and exposure.

From experiments made at 100° and 160° C., it appears that elastic sheet rubber (a) is not fully soluble in liquid carbon disulphide in a reasonable time, if at all. It is quite soluble at 185° and soluble to a remarkable degree and at a remarkably rapid rate at 210°. Hence the pressure under which solution takes place is here necessarily greater than 15 atmospheres, and need never exceed 30 or 40 atmospheres. Inasmuch as carbon disulphide thus unites with rubber in any proportions clear brown solutions of any degree of viscosity may be obtained. On diluting such solutions with *cold* CS₂ the solvent is at first greedily absorbed, but the final complete dilute solution (without agitation) takes place very slowly. Hence it is well to complete the process for any desirable degree of solution at the high temperature. Finally, by exposing any of the solutions to air the carbon disulphide evaporates and the dissolved vulcanized India rubber is regained without sacrifice of its original non-viscid quality so far as I can judge from laboratory experiments. Similarly fissured sheet rubber (e) which has become useless for practical purposes by age, is quite as soluble in CS₂ at 200°, so far at least as the undecomposed parts are concerned. Again, elastic gray rubber (b) dissolves completely to a gray liquid in which the pigment is suspended. The concentrated solution hardens at once on exposure to air, to a rubber of nearly the original qualities (b). In treating rubbers of this class a difficulty is sometimes

¹See Proc. Am. Academy, vol. 25, 1890, p. 93, or Phil. Mag., October, 1890, p. 338. My method of work was simple: Glass tubes 10^{cm} or 15^{cm} long and 3^{cm} or 4^{cm} in diameter, closed at one end and drawn out to a capillary canal with two or three enlargements at the other, were filled with a charge of vulcanized rubber and solvent, and then introduced into the steel piezometer tube. I made use of the temperatures of boiling turpentine (160°), naphthaline (210°), aniline (185°), and diphenylamine (310°). To separate the charge from the oil of the piezometer which transmits pressure, I first employed a thread of mercury inserted into the capillary canal. Finding, however, § 91, that the metal acted on the charge I replaced it with much advantage by a thread of water. Charges were usually introduced in the ratio of one part, by volume, rubber to three or more of solvent, unless more concentrated solutions were desired. About 1^{cc} to 2^{cc} were obtained per heating. I made considerably over 150 experiments, most of them at 200° and 100 atmospheres to 200 atmospheres.

encountered in consequence of their action on the hot CS_2 . Gas is often evolved, and I was therefore at first inclined to attribute this effect to the pigments. For example, at 200° such a reaction as $\text{CS}_2 + 2\text{ZnO} = 2\text{ZnS} + \text{CO}_2$ might be surmised, but I shall disprove this in §§ 89, 93 by direct tests. Samples of gray non-elastic rubber (*c*) can be partially devulcanized and softened in CS_2 at 200° . They do not easily dissolve, however. Gas is often evolved. Little advantage is gained by treating with CS_2 at 300° , in which case much of the rubber is converted into a granular state, probably due to decomposition.

Commercial ebonite (*d*) at 200° is at first partially devulcanized, and eventually dissolves in excess of the solvent. The partially devulcanized ebonite is elastic on drying, but finally hardens further to a tough solid having a leathery quality. The solution leaves a glossy black stain with much sulphur apparent after evaporating. Gases are usually evolved. As a whole, my experiments show that excess of sulphur is first removed by the solvent, after which the vulcanized rubber itself passes into solution. Cf. § 89, where similar experiments are given.

78. Solution in liquids of the paraffin series.—Both the fresh (*a*) and the rotten (*e*) elastic sheet rubber dissolve easily in liquid mineral oils at 200° . The pressure necessary will of course vary with the boiling point of the oil used. It may be as high as 50 atmospheres in some of the very volatile gasolines. Commercial gasoline is a good solvent of the elastic rubbers (*a* and *e*). The most concentrated solutions, however, appear to be less thick than in § 77. On exposure to air gasoline evaporates; leaving a residue which gradually hardens. The gray rubbers (*b* and *c*) dissolve with less facility.

Petroleum¹ dissolves the rubbers *a* and *e* very easily. The solutions, however, only harden after much time, and probably only in thin films.

79. Solution in turpentine.—In case of *a*, complete solution is at once effected at 200° , forming a viscid sirup-like liquid. It seems to dry in thin films, after long exposure, thus possibly indicating a difference in the product obtained by dissolving rubber suddenly, out of contact with air, and by dissolving it more or less in contact with air by long-continued digestion. The latter mixtures are permanently sticky. Special experiments made at 160°C . showed that no reasonably speedy solution takes place in liquid turpentine, thus corroborating the inferences and experiments of §§ 75-77. Gray rubber is acted on with greater difficulty. The solution leaves a white glossy stain, which hardens. Pressure need not exceed 5 atmospheres.

80. Solution in chloroform and carbon tetrachloride.—Elastic sheet rubber (*a*) dissolves at once in the liquid chloroform at 200° . Pressure

¹ Looking up the literature of the subject, I found that John J. Montgomery, of Fruitland, California (cf. Letters Patent No. 308,189, November, 1884, United States Patent Office), describes a process for the solution of vulcanized rubber. His statements of the temperature and pressure necessary are substantially correct, and he makes use of a petroleum oil boiling at about 200°C . The oil is subsequently driven off by injections of steam. This is the nearest approach to a case of an available solution (a solution which does not remain permanently sticky) which I have found. It will be seen that the essential peculiarity of the above methods is the solution in volatile solvents.

must exceed 15 atmospheres and need never be larger than 25 or 30 atmospheres. Solutions of any degree of viscosity seem to be obtainable. They dry at once on exposure to air, leaving a hard residue. Rubber dissolved in this way turns darker in color, and the elasticity is in part sacrificed, so far as I can judge.¹ Gray rubber is attacked with decomposition of the solvent and evolution of gas. Although at 200° a simple reaction like $3\text{ZnO} + 2\text{CHCl}_3 = 3\text{ZnCl}_2 + \text{H}_2\text{O} + 2\text{CO}$ might be suspected, I believe the gas to be obtained in the way set forth in § 89.

81. *Solution in aniline.*—Solution in the liquid at 200° takes place at once in case of rubbers like *a*. Pressure need not exceed a few atmospheres. Thin films, apparently dry after long exposure.

82. *Solution in animal oils.*—Neither in the case of sperm oil or of lard oil at 200° was the sample (*a*) dissolved on removing from the press. Both, however, disintegrated on standing to a quasi-solution, often with slow evolution of gas.

83. *Treatment with glycerine.*—At 200° no solution occurs. Glycolic alcohols were not examined. Cf. § 86.

84. *Solution in benzol and higher aromatic hydrocarbons.*—The elastic sheet rubber (*a*) dissolves at once in the liquid at 200°. Pressure must exceed 7 atmospheres, but need never be higher than 30 atmospheres. The solution exposed to air hardens at once. Solution of gray rubber is more difficult.

Solution of elastic rubber (*a*) in toluol at 200° takes place with great ease. The liquid dries slowly. Pressures of less than 10 atmospheres suffice.

85. *Solution in ethylic and higher ethers.*—Elastic sheet rubber (*a*) dissolves at once in ethylic ether at 200°. Pressure must exceed 25 atmospheres, but need not be greater than 40 or 50 atmospheres. The solution hardens immediately on exposure to air. Gray rubber is attacked with difficulty.

86. *Treatment with alcohols.*—At 200° india rubber (*a*) is not dissolved in methyl or ethyl alcohol, and only slightly so in amyl alcohol. In the latter case the sample shows some change, toward a pasty consistency.

87. *Treatment with ketones.*—India rubber (*a*) treated with acetone at 200° is converted into a sticky paste, from which it hardens at once on exposure to air. Pressure must exceed 15 atmospheres, but need not be greater than 30 or 40 atmospheres.

88. *Treatment with water and mineral acids.*—In no case was there a trace of true solution at 200°. Pressure must exceed 7 atmospheres, but need not be greater than 15 atmospheres. Water probably enters the physical pores of the rubber (*a*); at least this substance becomes superficially rough and warty on drying at 200° in steam after being treated with water at 200°. It does not melt (§ 92). Strong hy-

¹ Such an effect would be produced, for instance, by the presence of sulphur in the chloroform.

drochloric acid has no obvious effect, while strong sulphuric acid (diluted with twice its bulk of water) seems only to char the rubber. Treating the gray rubber (*b*) with HCl, I found its solubility in CS₂, C₆H₆, and gasolene to have decreased. The quality of the rubber has therefore been injured, so far as its solubility is concerned.

89. Treatment for vulcanization.—Liquid ebonite.—Ammonium polysulphide acting on elastic gray rubber much above 200° converts it externally into a chocolate-like friable skin, covering a mushy gray core. This disintegrates in CS₂ to a brown solution and a gray granular precipitate. The solution hardened on exposure to air, to decomposed rubber.

Ammonium polysulphide at 185° or 200° does not change the appearance of the same rubber markedly; but the sample has lost its elasticity and shows a semiplastic leathery consistency. This I believe to be due to further vulcanization induced by the polysulphide. If now this sample be treated with liquid CS₂ at 200°, the solvent is decomposed with evolution of much gas and the rubber restored to its original elastic quality. It is interesting to note that gas is liberated throughout the mass of rubber, so that the sample when taken out of the tube has the form of an enormously inflated cellular sack, which issues from the glass tube explosively, but soon collapses on exposure to air. As a whole the present results agree with the behavior found for ebonite in § 77. In both cases it is possible to pass from the more vulcanized india rubbers to a less vulcanized product.

It will be shown below that the gas evolved is due to double decomposition of water and CS₂ (§ 93).

More interesting is the direct vulcanization of rubber solution to liquid ebonite by aid of a sulphur solution. In case of elastic rubber (*a*) this begins at 160°, but is more complete at 185° and 200°. In case of *pure* nonvulcanized rubber dissolved in CS₂ scarcely any change in flesh-color is observed at 160° and the sulphur crystallizes out in needles on exposure. At 185° and 200°, however, the charge turns black, showing complete vulcanization. If equal parts of vulcanized rubber (*a*) and sulphur be acted on, the product after heating to 200° is not dissolved nor soluble until the excess of sulphur is removed by washing (§§ 77, 89). Gas is often evolved (§§ 91, 93). In proportion as less sulphur relatively to the rubber is used, the product becomes more soluble and less gas is evolved. By adding about 20 or 25 % of dissolved sulphur to the vulcanized rubber (*a*) I obtained serviceable solutions of ebonite on treating at 200° either in CS₂ alone or in mixtures (§ 90) of this with gasoline or benzol, etc. In most cases these harden very quickly to a jet-black enamel. With less sulphur the color is brown in thin films.

90. Solution in mixtures of solvents, and solution of mixed gums.—By acting on vulcanized rubber with mixed solvents of the above kind, I obtained equally satisfactory results. All the rubbers mentioned

(*a* to *e*), ebonite excepted, pass into true solutions by aid of such treatment. Thus the gray elastic rubber (*b*) dissolves at once in a mixture of CS_2 and gasoline; and the gray nonelastic rubber (*c*) dissolves with like ease in mixtures of CS_2 with gasoline, or with benzol, or with ether, etc.; or of benzol and toluol; or, less easily, in mixtures of gasoline and benzol. Ebonite is partially devulcanized, and would probably be dissolved in large excess of solvent. No gas was evolved in any case, and this constituted an advantage of this method, § 93. In all cases the solution hardens at once on exposure to air, yielding the rubber if the solution be shaken, or a purer residue if the sediment be removed by subsidence and decantation.

Equally feasible is the solution of mixed gums, at 200° . Thus I made liquid mixtures of vulcanized rubber and gutta-percha in CS_2 , which hardened at once on exposure to air; liquid mixtures of rubber and shellac dissolved in CS_2 , hardening more slowly; liquid mixtures of vulcanized rubber and rosin in CS_2 , and in gasoline, which dried only in thin films after much time, etc.

91. Direct devulcanization.—When by aid of any of the above methods a true solution of vulcanized rubber is obtainable, direct devulcanization may be attempted by mixing the charge with some sulphur absorbent. Preferably such material should be chosen, which at 200° reacts neither on the rubber nor the solvent. Metallic filings do not appear to be available at high temperature. Treating ebonite with CS_2 , gasoline, or benzol to which copper filings had been added, I found the charge after exposing to 200° to be disintegrated, while an enormous amount of gas was evolved. Scarcely any solvent remained in the liquid tube. From direct experiments made on copper and on sulphur in carbon disulphide at 200° , I inferred that these reactions are insufficient to account for the gas evolved, although copper is superficially coated with sulphide. The gas must, therefore, be produced either at the expense of the rubber or of the reagent in presence of ebonite, and since all the solvents used behave alike, probably out of the rubber. Steel is scarcely attacked¹. I mention this, since the identification of the gas may throw some clew on the chemical character of the rubber. Decomposition frequently sets in on exposure of a highly vulcanized solution at ordinary room temperatures, whereas at 0° and under slight pressures (1 or 2 atmospheres) the gas remains in combination.

92. Fusion of impregnated rubber.—If vulcanized India rubber be impregnated or saturated by digesting it with the cold reagent or solvent for a suitable time (a few minutes to many hours), the swollen mass not only shows a relatively low melting point, but it remains liquid after cooling, provided, of course, the solvent is not allowed to

¹ Fortunately, therefore, steel apparatus is available. An interesting question occurs here, as to what becomes of the carbon in the case where mercury, sodium, copper, etc. are attacked by hot CS_2 , under pressure, and not by cold CS_2 .

escape. This is an observation of practical importance, since the retorts can thus be charged with solid or dry rubber, a minimum of solvent be sacrificed in treating, or by evaporation, and concentrated solutions be obtained often fit to be worked at once. The rubber so melted hardens on exposure to its original quality. Finally, the pressure necessary in this place is the smallest possible, and may be even below the data above given for the divers solvents.

Experiments may be cited as follows: Nonimpregnated vulcanized rubbers (samples *a* to *e*) do not melt if exposed in a closed tube to 210°. Only in a case of very slightly vulcanized pure rubber gum is there a trace of fusion perceptible at the edges, and here it may even be due to a stain of dirt (oil) accidentally deposited there. Gray rubber with a superficial film of exuded sulphur turns black, due to the formation of a film of ebonite.

All the samples of rubber (*a* to *e*) fuse at 210° when previously saturated, or nearly so, with cold carbon disulphide and exposed in a close-fitting closed glass tube. If the pressure be lowered by a capillary hole at one end of the closed glass tube, or if the tube be only partially filled and the empty end kept cool, the solvent is merely distilled off, and no fusion takes place. Whereas at 160° fusion scarcely occurs, melting seems to be complete at 175°. There is, therefore, an approximate coincidence of temperature in the present and in the above paragraphs. Similar results are obtained with benzol, with gasoline, and higher petroleum oils, etc. Fusion is absent or only incipient at 160°, and more than complete at 210°, provided only the solvent used be not too volatile. The gray rubbers (*b*, *c*) fuse to a more viscous or pasty mass than the gum rubbers (*a*), the consistency of the clear cold solution in the latter case being about that of treacle. In general the occurrences of this paragraph resembles the fusion of a salt in its water of crystallization, with this exception, that impregnated vulcanized rubber after fusion retains a consistence which is liquid relatively to the original impregnated charge.

The analogy with starch or gluten solutions is much more perfect. All of these substances swell up when submerged in the solvent. To effect solution or quasi solution, temperature must be raised to below 100° in the former cases, and considerable above 150° in case of rubber. Thus the only real difference in the process is an apparent one; for starch, the solvent water is still a liquid at the solution temperature, whereas for rubber the usual solvents, under atmospheric pressure, are vaporized at the solution temperature. It is interesting to note that a similarly detailed analogy in the thermodynamic behavior of rubber and of soft gelatins has recently been pursued at length by Bjernken¹. Under sufficient longitudinal stress, both these substances contract on heating, and they are, therefore, heated on further extension, as was proved by Thomson. Bjernken concludes that water

¹ Bjernken.

in the gelatins occurs as water and is not in a state of solution or combination.

To account for the behavior of rubber toward solvents, I have supposed coherence to be due to cohesive affinities, forces capable of being saturated like the ordinary chemical affinities, but of smaller intensity and probably greater number. If, therefore, rubber is impregnated with the solvent, a part of the cohesive affinities of the rubber combines with similar affinities of the solvent, and the result is so decided a decrease of the tenacity of the sample that it may now be triturated. If the impregnated material is to be liquid, the residual cohesive affinities of the rubber must be withdrawn from action. This may be done by heat (dissociation). The liquid thus obtained I do not conceive to be a true solution, i. e., one in which the division of solid has reached a definite molecule, but rather consisting of a suspension of excessively small rubber particles in the solvent. Conditions under which this takes place I have already discussed elsewhere¹, and the probable size of the ultimate particles is there indicated. Hence on cooling the solution need not at once become solid again. Diffusion, if occurring at all, is now an excessively slow process. Hence the aggregation of particles takes place gradually, until at length the whole body forms one coherent mass. In other words, all rubber solutions coagulate, and the solid structure in this case is probably that of a network or sponge holding solvent in its interstices.

If the coagulated solution be again heated (under pressure) a thin viscid liquid is again obtained which in its turn coagulates, etc. Hence even if the original rubber be chemically different from the dissolved product (polymerization) my reasoning would hold for the coagulated material.

Finally, I may add that the rubber deposited from any of the above solutions presents a curious case of slowly reacting elasticity. If a thread (say 1^{mm} in diameter) be twisted and then let go on a frictionless surface, it will squirm like a live worm for some minutes after. If it be stretched, the original length is regained with visible slowness. The internal changes probably take place along lines of very nearly neutral equilibrium.

93. Behavior of reagents and solvents.—Owing to the frequent occurrence of gaseous products in the above experiments I made special investigations on the decomposition of the reagents. Benzole and gasoline were found stable at 210°, and often above this temperature, whether mixed with water or with sulphur. Cf. § 95. Carbon disulphide, however, in addition to relatively slight decompositions noted in § 91, is decomposed by sodium and by mercury at 210°, although it remains stable in presence of bright steel or of sulphur. It is also stable in presence of zinc white (rubber pigment) at 210°. Violent double decomposition, however, occurs at this temperature in mixtures of water and CS₂, with the

¹ Barus; Am. Jour., Sci., vol. 37, 1889, pp. 126-128.

evolution of much gas, presumably $2\text{H}_2\text{S}$ and CO_2 . Thus it appears that a thread of mercury to shut off the experimental tubes § 76 is generally objectionable, as is also a thread of water in case of CS_2 . For this reason, moreover, the absence of gaseous reaction in case of mixed solvents, § 90, is to be attributed to the fact that CS_2 and water are not immediately in contact but separated by layers of benzole or gasoline.

An interesting question is suggested here, as to whether it be possible to express affinity on a scale of temperatures. For instance, let it be required to determine the affinity of a metal for sulphur. At ordinary temperatures not even sodium decomposes carbon disulphide, whereas such decomposition occurs in case of many metals if the temperature be sufficiently high. Hence the temperature at which such decomposition definitely sets in (for copper sooner than for iron, etc.) is to some extent a reciprocal expression of the affinity of the given metal for sulphur, bearing always in mind that the stability of the solid metallic molecule also enters into the consideration. Thus the arbitrary reagent CS_2 , in its relations to all the metals to be examined, fulfills a similar purpose to an arbitrary spring balance in measuring gravitational forces. Cf. § 95.

94. *Summary of the results.*—In the above paragraphs I have therefore indicated a method by aid of which vulcanized india rubber of any quality or character whatever, as well as the undecomposed or reclaimable part of rubber waste, may be dissolved or liquefied in a reasonably short time¹, and into solutions of any desirable degree of viscosity or diluteness—into solutions, moreover, from which india rubber may be regained on evaporation of the solvent. I have also indicated methods for passing from dissolved vulcanized rubber toward pure rubber, though I see little use for such a step.

I have elsewhere described divers forms of apparatus by which any of the above operations may be carried out on a large scale. They are of no interest here, but I mention them since it is only from such experiments that a full insight into the quality of the rubber deposited from any given solution may be obtained. Throughout my work the constancy of the dissociation temperature has been a marked feature. Thus, in the case of CS_2 , of turpentine, of the vulcanization of dissolved pure rubber, etc., no action took place below 160° . It may be noted that even this temperature is higher than where vulcanization is effected in the dry way, where 110° to 140° are deemed sufficient. Moreover, solution of vulcanized rubber takes place at 185° , quite as easily under 700 atmospheres as under the minimum admissible—say 20 atmospheres.

95. *Presumable conditions regarding the solution of carbon, etc.*—From the above paragraphs I inferred that the difficulty encountered in dissolving carbon is probably attributable to the relatively high dissociation

¹Practically at once, if the material is not too bulky.

temperature of the solid carbon molecule. I made many experiments to test this view, in all of which I failed to obtain solution even at low red heat and 600 atmospheres. My work thus corroborates the negative results of Hannay¹ on the direct solution of carbon. My experiments were made with gasoline, water, chloroform, benzole, and carbon disulphide, usually at 500° and 500 atmospheres. In case of gasoline I went as far as low red heat and 600 atmospheres. In most cases the reagents were decomposed (particularly carbon disulphide, benzole, chloroform) to gaseous products, while the carbon remained unaltered. Decomposition by metals if they yielded carbon (copper corroded by CS₂ and gasoline acted on by palladium) showed sooty deposits only. It appears therefore that the dissociation temperature of the amorphous carbon molecule must be looked for in the region of red heat.

In conclusion, I may state that experiments were also made with wood. This material swells up in water, and the inference is, compatibly with the above text, § 92, that if the temperature be sufficiently raised woody tissue must pass into solution. Many tests made upon cellulose in this way showed that the material is decomposed before solution sets in. The phenomena seems to be an ordinary dry distillation in spite of the presence of water under pressure. This is unfortunate, for if it were possible to dissolve wood, our forests would be digestible. At least, any such successful process must contribute essentially to the food products of the race.

¹Hannay: Proc. Roy. Soc., vol. 80, 1880, p. 188; Chem. News, vol. 41, 1880, p. 106. Cf. Hannay and Hogarth: Chem. News, vol. 41, 1880, p. 103; Mallet and Hannay: Nature, vol. 22, 1880, p. 192.

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