THE JOULE-THOMPSON EFFECT FOR AIR AT MODERATE TEMPERATURES AND PRESSURES.

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SYNOPSIS.—In the experiments as described air was pumped first through a set of tubes designed to remove carbon dioxide and moisture, then through the throttling device or "porous plug" and finally back to the pump. The plug and tubing immediately leading to it were immersed in an oil bath thermostat. The bath temperatures, for the most part, lay between 0° and 100° C., the mean pressures, from 4.5 to 6.4 meters of mercury, while the pressure-drop varied between 0.25 and 0.80 meters of mercury. The temperature-drop was measured by platinum resistance thermometers differentially connected. The plug was of the radial flow type originated by Regnault, roughly cylindrical in form, through the walls of which the air flowed toward the axis, escaping finally through one end. The accidental errors were apparently of an order under one per cent.

The Joule-Thomson coefficient (μ) was found to have a decreasing linear variation with increasing mean pressures. Its dependence upon both temperature and pressure are embodied in either of two empirical formulas, namely,

$$\mu = +0.3935 - 0.00691p - 0.001835t + 0.00000134t^2 + 0.0000325pt$$

$$\mu = -0.2599 + 182.0\frac{1}{\tau} - 552.4\frac{p}{\tau^2},$$

all pressures being measures in meters of mercury, t in degrees C., while $\tau = 273 + t$.

These formulas are applied to calculate the temperature of the ice point on the thermodynamic scale, to reduce to the same scale the readings of the constant pressure air thermometer and to discuss the variations of c_p with pressure. Good agreement with the results of other work is found in the second and third cases, while in the first, the result, in common with that found from other Joule-Thomson data, is higher than the result found from the characteristic gas equations.

The paper includes a brief historical summary of previous experimental work, a discussion of several theoretical points and of sources of error, especially heat leakage.

CONTENTS.

INTRODUCTION.

A NEED for new determinations of the Joule-Thomson effect has long been recognized by students of thermodynamics, and it has found expression occasionally in the literature touching this subject.

Such data, as is well known, still preserve their original importance for the study of molecular attractions in gases and for the establishment of the thermodynamic scale of temperatures. More recently they have acquired interest for the engineer, namely for the computation of steam tables, ammonia tables and the like. The latter aspect has been discussed by Davis.[1]

Aside from the desirability of experimenting over a wide range, increased accuracy is obviously one of the first improvements in the data that is needed. The published results have been considered too uncertain on the whole, and in many cases too difficult of interpretation to be of great value. The present paper is devoted largely to the latter phase of the problem and is therefore somewhat limited in scope.

At first it was planned to work with several gases and cover a considerable extent of temperatures and pressures. However, a year's experimentation at the Johns Hopkins University with carbon dioxide disclosed many difficulties in the way of obtaining results at all consistent with one another. It was decided, therefore, to confine the work for the time being to an attempt to develop a reliable method and to proceed to this end by ways that seemed the most direct. Side problems were to be avoided wherever possible. Hence the range of temperatures and pressures were restricted within the limitations of the resources already at hand. Air was chosen as the gas to be experimented upon, chiefly because of its availability and the small amount of attention to contamination and slow leaks in the apparatus that its use would entail. Results from pure gases are, of course, to be preferred in general, yet those obtained from air are not without interest as regards thermometry and for comparison with work on air in this and related fields.

It is hoped that in the experiments to be herein described, most of the larger sources of error have been overcome. The accidental errors are small for work of this kind, being of an order considerably under one per cent. Perhaps there is a systematic error outstanding, indicated possibly by the relatively large value computed for the thermodynamic temperature of melting ice. The sources of such error, if existent, have so far not been found. Further experiments with other gases should throw light upon this matter, especially those gases whose expansion coefficients have been determined with great care by Chappuis, namely, nitrogen, hydrogen and carbon dioxide. The author would welcome, in the meantime, any suggestions occurring to the minds of those interested in this subject.

Historical Outline.—Although a historical summary of experimental work down to 1905 has been given by Kester, in a paper to be taken up later, a complete outline would seem desirable here, first to supply a few omissions and secondly to include a considerable amount of new material.

After the original classical experiments of Joule and Thomson,[2] carried out in the years 1852 to 1862 on air, nitrogen, oxygen, carbon dioxide and hydrogen, whose work is too well known to need further comment, one of the early experimenters to enter this field was Regnault.[3] His work has often been overlooked. The most interesting feature of his apparatus is the ingenious design of its porous wall or throttling partition, which was not in the form of a "plug." It was a hollow enclosure through the wall of which the gas flowed from the outside to the interior. A hole in the wall was provided for the continuous escape of this gas. The obvious purpose of this design was to provide thermal protection. In this respect it seems greatly superior to the plug form used by Joule and Thomson. Yet Regnault abandoned the work as futile with an expression of regret at the waste of time spent on a research so "sterile." He found that the temperature readings within the enclosure were too uncertain to have any meaning. In the light of subsequent advances in methods of measurement, several possible causes for these troubles might be assigned, but, especially since his descriptions are not full in detail, their discussion here might not be profitable.

The forms of throttling device or "plug" introduced in these two investigations are typical. Most of the subsequent experimenters have employed the form used by Joule and Thomson, possibly because the work of Regnault, as far as it went, has had little attention directed to it. In 1910 Burnett and Roebuck,[4] in a paper entitled "On a Radial Flow Porous Plug and Calorimeter," proposed a plug on the Regnault principle adding improvements in detail. Their work, however, was entirely independent. Later Roebuck[5] used apparatus of this type on liquid water in order to determine the mechanical equivalent of heat. Only two other experimenters so far have published work with similar apparatus with gases, namely, Trueblood[6] and the present author. Following the usage of Trueblood the term "axial flow" will be applied to the plug form used by Joule and Thomson to distinguish it from the other or "radial flow" type.

One should not fail to note in this connection that certain protective features of the radial flow principle have come into use more or less generally in continuous flow calorimetry, as for example, in the work on C_p by Swann[7] and by Scheel and Heuse.[8]

Hirn[9] carried out throttling experiments upon steam, using an orifice. Work of others on steam, namely, Griessmann,[10] Grindley,[11] Peake[12] and Dodge,[13] has been discussed by Davis.[14] As Davis states, the first named used a porous plug very much like that of Joule and Thomson, while the others used a throttling calorimeter, their work being undertaken for the "purpose of determining the variation of the specific heat of steam with pressure and temperature, an investigation which has since been more satisfactorily accomplished in other ways."

Cazin[15] in 1870 published an account of experiments which were essentially modifications of the Gay-Lussac free-expansion experiment. His apparatus was complicated, and, as he admits, his results were qualitative.

Natanson[16] in 1887 described porous plug experiments on carbon dioxide at 20° C. only. His pressure-drop was about one atmosphere and his highest absolute pressure 25 atm.; and between the lowest and highest pressures he found a decided dependence of the cooling effect upon pressure, whereas Joule and Thomson had not noted (up to 6 atm.) any such effect. This dependence does not agree with that found later by Kester and is in the opposite sense from that found for air in the present paper.

Mention is made here of work reported by Witkowski,[17] who carried out experiments on air at high pressures, passed through a succession of porous plugs. Only a brief abstract of his paper has been available, which contains no quantitative results. There is no obvious theoretical advantage to be gained by employing a succession of plugs. All the data could be had from a single plug by properly varying the pressures and bath temperatures.

Kester[18] in 1905 extended the work of Natanson on carbon dioxide to temperatures between 0° and 100° C. finding also a dependence upon pressure. The results of the two observers are not in agreement, Kester's results at the same temperature (20° C.) being independent of pressure up to the highest pressure employed at that temperature, namely, 41 atm., while the work of Natanson yielded a positive pressure coefficient. At one pressure, 26.4 atm., Kester found an indication of a positive coefficient.

Olszewski[19] performed experiments (using not a porous plug but a throttle valve) on hydrogen in order to determine its "inversion temperature" as bearing upon the problem of its liquefaction. The high pressure of the experiment varied from 117 to 170 atm. and the low pressure was uniformly one atmosphere. The one datum of this experiment was − 80.°5 for the inversion temperature under these conditions. The effect observed was, of course, an integrated one and leaves much to be desired for application of thermodynamic equations.

Five years later[20] (1907) he did the same thing for nitrogen and air, finding a series of inversion points for magnitudes of the pressure-drop varying from 160 atm. to 30 atm.

Rudge[21] carried out (1909) a few experiments on carbon dioxide supplied on the market in the form of "sparklets" for making carbonated water. The duration of each experiment was but a few minutes and their author does not attach great importance to the results, but offers them in view of the scanty known data. It would seem that the ideal conditions for continuous-flow methods could hardly be realized in so short a time.

Bradley and Hale[22] in the same year carried out experiments upon "the nozzle expansion of air at high pressure," *i. e.*, from initial pressures of 70 to 200 atm. to final pressures of 1 atm. Their temperatures extended from 0° C. to − 120° C. approximately.

Their apparatus was a liquefier of the Hampson type and the air expanded through a specially constructed "nozzle." Their particular problem was the process of liquefaction; and their results were in qualitative agreement with those of Joule and Thomson. These experiments would seem subject to error from heat leakage.

Again in the same year (1909) Dalton[23] carried out at the Leyden laboratory similar nozzle experiments in air at 0° C. only and for pressure drops from about 5 to 40 atm. His results agree with the Joule and Thomson figures at 0° C., and he notices no pressure effect, although his curve would indicate an extremely slight negative coefficient.

Vogel,[24] whose original papers have been unavailable, carried out porous plug experiments in the Laboratory of Technical Physics of the Techniche Hochschule in Munich. He was looking for a pressure effect and found a negative coefficient. The temperature of his experiments was 10° C.

Noell,[25] whose original paper likewise has been unavailable but an abstract[26] of which is at hand, continued the work of Vogel in the same laboratory. His pressure-drops were 6 and 8 atmospheres while the arithmetic mean of the absolute high-side and low-side pressures varied from 25 to 150 atm. His high-side temperatures varied from − 55° C. to + 250° C. He worked with air only. He found a pressure as well as a temperature effect which he embodied in the interpolation formula:

$$\frac{\Delta T}{\Delta p} = \frac{50.1 + 0.0297\,p}{T} + \frac{14830 - 1.674\,p}{T^2} + \frac{366000 - 19093\,p}{T^3} - (0.122 + 0.0000157\,p).$$

This is evidently an empirical expansion in descending powers of T, whose coefficients are linear functions of p.

The pressure units seem to be kg. per cm.[2] in the left-hand member and atmospheres on the right. The difference in any case would not be more than about 3 per cent., but the author does not make it clear. The deviations of his observed values from those calculated by this formula vary from 2 per cent. to 6 per cent. at the lower temperatures, to 50 per cent., and over at the highest temperatures. Nevertheless his work seems to be more systematic and satisfactory than that of his predecessors, certainly for air.

Cuts of the apparatus of Vogel and Noell may be found in Jellineks' Lehrb. d. Ph. Chem., Vol. I., 1914. They show two forms of plug, the earlier being of the axial flow type, the later, a combination of the axial and radial flow types in which an inner axial flow plug was surrounded by a jacket containing the inflowing high side air at bath temperature.

Buckingham[27] has proposed a modified form of the porous plug experiment in which the process is to be rendered isothermal by supplying heat, say electrically, to the plug in just the sufficient amount to prevent the temperature-drop. If there should be a heating effect, as with hydrogen, there would have to be devised some way of abstracting heat from the plug. No extended experiments by this method have been published.

Trueblood[6] carried out experiments at about the same time as those of the present author, which are described in a paper entitled "The Joule-Thomson Effect in Superheated Steam; I. Experimental Study of Heat Leakage." He limited the work to a single temperature and pressure and carried out a thorough and effective study of the heat leakage. Extensive tests, under varying conditions, were made upon a number of different plugs of the axial and radial flow types. He concluded the latter to be the superior and that it is capable of yielding reliable results. A remarkable form of indirect heat leak was found for the radial flow type, which he named the "regeneration effect." This matter will come up later under a separate head.

The experimental work in this field, thus briefly summarized, lends itself only in small measure to the application of thermodynamic equations owing to the difficulty or impossibility of attaching a definite meaning to a large part of it. Thus the only work found available for the calculation of the thermodynamic scale of temperatures hitherto published[28, 29, 30, 31] has been that of Joule and Thomson principally, with later computations including the results of Natanson, Kester and, in one instance, of Olszewski.

It has seemed to the author that in some cases the programs of experimentation have been, perhaps, too ambitious in the direction of extreme temperatures and pressures with the result that an oversight of vital details affecting accuracy was quite possible. The intention to limit the present work in the way mentioned at the beginning was confirmed by considerations of this sort.

General Conditions of Present Experiment.—The range of temperatures was confined approximately to the fundamental interval—actually from 15° C. to 90° C., although experiments had been started at 110° C. when the apparatus called for repair. The term "pressure" in the title of this paper refers to the arithmetic mean of the absolute pressures on the two sides of the plug. The range lay from about 6 to 8½ atmospheres, or more precisely, from 4.5 to 6.4 meters of mercury. The pressure-drop ranged from 0.25 to 0.80 meter of mercury. Pressures throughout this paper will be expressed in meters of mercury. For the immediate purpose of these experiments outlined above, the obvious gas to be chosen was, of course, air.

Remarks on Theory.

The general theory of the plug experiment has been given so often in treatises and in journal articles that a full treatment of it here would be out of place. As much, however, should be given as is sufficient to define the necessary symbols and to develop such special formulæ as are needed in the computation of results.

The function $u + pv$, the "total heat" or so-called "*enthalpy*" of Kamerlingh Onnes, is supposed to be the same in the regions of equilibrium above and below the plug. Let us call it H. Then the Joule-Thomson coefficient (μ) is defined as the limiting value of the ratio of the temperature-drop to the pressure-drop, when these each approach zero, under the condition $H = const.$, that is,

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \qquad (1)$$ [1]

Graphically represented this is the slope of the tangent to the curve $H = const.$ on the (p, T) diagram. From (1), through the application of the second law of thermodynamics, follows the general relation always associated with the porous plug experiment, namely,

[1] It may be worth while to note, in passing, that inasmuch as one often finds confusion of statement between the free expansion or Gay-Lussac effect and the Joule-Thomson effect, the distinction between the two may be brought out by expressing the two as

$$\left(\frac{\partial T}{\partial p}\right)_u \quad \text{and} \quad \left(\frac{\partial T}{\partial p}\right)_H$$

respectively.

$$T\left(\frac{\partial v}{\partial T}\right)_p = v + \mu c_p.^1 \qquad (2)$$

It will be shown later that μ was found experimentally to be a function of temperature and pressure. In the search for an empirical formula to express this relation and one which would have a little more rational basis than a mere power series, resort was had to the equation of van der Waals. While this equation does not strictly fit the measurements on isotherms, yet the author is in accord with Berthelot[32] in thinking of it as a valuable index to broad features of the properties of gases and as being something more than an empirical interpolation formula.

Applying to van der Waals' equation, namely

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

the relation (2) above, we get, keeping only terms of the *second order* in the small quantities a and b, the relation

$$\mu c_p = -b + \frac{2a}{RT} - \left(\frac{6ab}{R^2T^2} - \frac{4a^2}{R^3T^3}\right)p. \qquad (3)^2$$

[1] Thus calling s the entropy

$$Tds = du + pdv = dH - vdp,$$

or, putting T = constant,

$$T\left(\frac{\partial s}{\partial p}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T - v.$$

But

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \text{ ("thermodynamic relation")}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_H = -c_p\mu.$$

$$\therefore \quad T\left(\frac{\partial v}{\partial T}\right)_p = v + \mu c_p. \qquad (2)$$

A short proof quite similar to this has been given by Callendar.[29]

[2] Expanding van der Waals's equation,

$$pv + \frac{a}{v} - bp - \frac{ab}{v^2} = RT,$$

and applying the operator $(\partial/\partial T)_p$ to both sides,

$$\left[p - \frac{a}{v^2} + \frac{2ab}{v^3}\right]\left(\frac{\partial v}{\partial T}\right)_p = R.$$

$$\therefore \mu c_p = T\left(\frac{\partial v}{\partial T}\right)_p - v = RT\left[p - \frac{a}{v^2} + \frac{2ab}{v^3}\right]^{-1} - v$$

$$= \left[RT - pv + \frac{a}{v} - \frac{2ab}{v^2}\right]\left[p - \frac{a}{v^2} + \frac{2ab}{v^3}\right]^{-1}$$

$$= \left[-b + \frac{2a}{pv} - \frac{3ab}{pv^2}\right]\left[1 - \frac{a}{pv^2} + \frac{2ab}{pv^3}\right]^{-1},$$

on substituting the value of $RT - pv$ from the expanded equation of van der Walas and

Now the variation in c_p within the limits of the present investigation is small or at most may be considered a linear function of p. If then we neglect the term in T^3, μ should be a function of the form

$$\mu = A + \frac{B}{\tau} + p\frac{C}{\tau^2}, \tag{4}$$

where $\tau = 273 + t$.

The first two terms are those of the complete formula of Rose-Innes.[30] It will be noted that the pressure effect is linear and even then only comes in if we retain second order terms. Later this formula as well as a five-constant power series linear in p and of the second degree in $t°$ C. will be fitted to the observations. Obviously the second power of τ in (4) could be replaced by the first power and the adjustment be empirically just about as good within the small range of observed temperatures, but the second power is retained to keep closer to the original basis.

Description of Apparatus.

The Air Circuit.—The air-circuit and the disposition of the various parts are shown in Fig. 1. Air is drawn in by the compressor at the intake A which is kept open all the time in order to replenish the supply of air lost by slow leakage. The air then passes upward through the driers D and D', the former containing a column of about a meter of calcium chloride, the latter about half a meter of soda-lime to remove carbon dioxide, followed by a half meter of calcium chloride to remove the water put in by the reaction of the carbon dioxide with the soda-lime. Water trapped in the lower end of D from the air under compression is

factoring out p. Let us now expand the right hand bracket and in all expressions retain no order in a and b higher than the second. Then

$$\mu c_p = \left[-b + \frac{2a}{pv} - \frac{3ab}{pv^2}\right]\left[1 + \frac{a}{pv^2} - \frac{2ab}{v^3} + \cdots\right]$$

$$= -b + \frac{2a}{pv} - \frac{4ab}{pv^2} + \frac{2a^2}{p^2v^3} + \cdots.$$

Now, in the second order terms, pv may be replaced by RT alone. In the first order term we must put $pv = RT - a/v + bp$.

$$\therefore \frac{2a}{pv} = \frac{2a}{RT}\left[1 - \frac{a}{vRT} + \frac{b}{RT}p\right]^{-1}$$

$$= \frac{2a}{RT} + \frac{2a^2}{vR^2T^2} - \frac{2ab}{R^2T^2}p + \cdots$$

$$= \frac{2a}{RT} + \frac{2a^2}{R^3T^3}p - \frac{2ab}{R^2T^2}p + \cdots$$

$$\therefore \mu c_p = -b + \frac{2a}{RT} - \frac{6ab}{R^2T^2}p + \frac{4a^2}{R^3T^3}p \cdots$$

Q. E. D.

drawn off by the valve B. This was done usually once during a run which lasted some four or five hours.

From the driers the air is carried through a quarter-inch gas pipe to the plug apparatus proper in a neighboring room. Here it passes first through a series of throttling needle-valves t, then through a third drying tube D'' containing phosphorus pentoxide. From this it passes

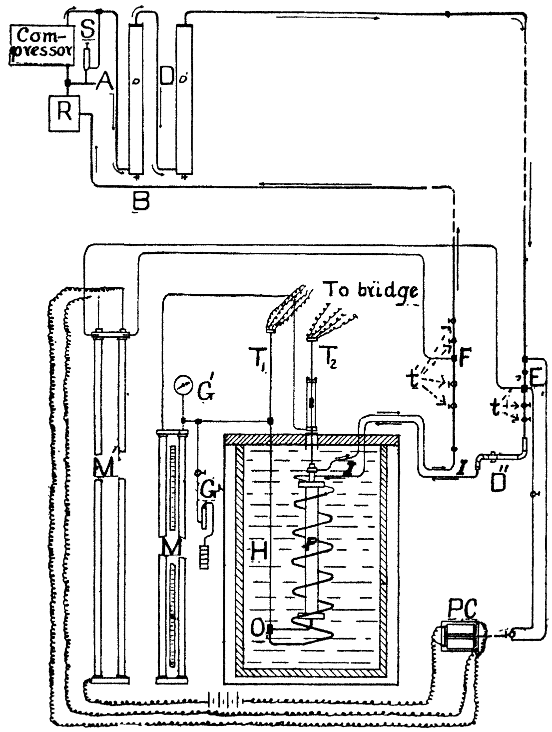

Fig. 1.

through copper "automobile tubing" of about 5 mm. outside diameter, into the bath, under the surface of which the automobile tubing continues for about two meters, connecting thence with a coil of larger pipe of brass and about one cm. internal diameter and 6 meters in length. This coil terminates in the plug casing P. After passing through the porous plug, the air leaves the casing by way of another length of automobile tubing much shorter than the first and soldered parallel with it for a purpose stated below.

Interchanger.—For a length I, I of about a meter the tubes are soldered together side by side, forming thus a heat interchanger, so that when the bath and the room were at considerably differing temperatures the air leaving the bath would be brought to approximately room temperature and the air entering the bath would be brought to approximately the bath temperature in advance. This device was found to be necessary for two reasons: first, it conserved the heat of the bath and improved its temperature regulation, and secondly, it prevented the throttles t' in the return line from progressively warming, a condition which was found seriously to interfere with pressure regulation. This warming of the valves would gradually change their opening and hence change the rate of flow of air through them.

After leaving the low pressure throttles t' the air returns to the compressor by way of a receiver R of about 10 liters capacity. Curiously enough, this receiver, when placed on the low-pressure side, was quite effective in reducing the pulsations in the air-circuit produced by the intermittent action of the compressor while no receiver was needed at all on the high pressure side.

Pressure Regulation.—It is obviously necessary to provide means to keep constant the pressures at all points, and especially the pressure-drop in passing through the plug. The heat of compression liberated here might quite mask the Joule-Thomson effect. It was observed, for instance, on one occasion, that a fluctuation in the pressure-drop of 0.1 per cent. resulted in a fluctuation of about 5 per cent. in the temperature-drop and consequently by 5 per cent. in the observed Joule-Thomson effect. Special precautions therefore were necessary to provide good pressure regulation. Further, this had to be automatic on account of the necessity for the observer to work alone. Fluctuations of 20 per cent. in the power service had to be cared for.

Rough pressure regulation was attained as a preliminary by placing an adjustable spring safety-valve S (Fig. 1) in a by-pass from the high pressure to the low pressure lines near the compressor. This was usually set so that the difference on the two sides of the valve would be from 80 to 160 lbs., gauge reading, depending upon the pressure drop at the plug.

Superposed upon this was a finer method of regulation which was designed to control the pressure drop between the points E and F. This was carried out by means of an electrically controlled valve mechanism actuated through contacts in a mercury manometer M', which was connected in at the points E and F. The valve mechanism is indicated at PC which is connected as a by-pass to the first or upper throttle t so that when opened the flow of gas is increased.

The two electrical contact-points of the manometer M' are set at any desired difference of level such that the tops of the mercury columns play just under them when the device is functioning properly. If for some reason the pressure difference decreases, the lower contact will be made, and this will actuate one of the electromagnets at *PC*, which, through setting in motion a train of gears will open the by-pass needle-valve at *PC* very slowly, thus supplying an increased flow of air and bringing the pressure difference back to its proper value. A similar action in the reverse direction will take place if the pressure drop exceeds the limits set by the positions of the contact points. When the pressure is at its proper value, the valve at *PC* is at rest.

There were, of course, small fluctuations in pressure remaining, even though this device gave much finer regulation than did the safety-valve *S*. These residual fluctuations were practically damped out by the throttles *t* and *t′* lying between the points *EF* and the plug. The greatest variations in the pressure drop at the plug were of the order of 0.1 mm. of mercury and usually too small to be observed.

The throttles *t* and *t′* together with the safety-valve *S* served, in addition, as a means of setting the absolute pressures in the system to any desired values.

Mounting of Thermometers.—T_1 and T_2 (Fig. 1) are brass tubes housing the stems of platinum resistance thermometers, one of which is situated in the elbow *O*, on the high-pressure side of the plug, and the second in the interior of the plug casing *P*. Emerging from the tops of these tubes and passing through sealed joints in appropriate hard rubber insulation are the leads which connect through heavy lamp-cords to the bridge. Into the latter they are connected differentially as will be described later. Thermometer tube T_2 has a telescoping joint indicated in the diagram whose purpose is to permit one to shift vertically the thermometer and so to explore the region on the low-pressure side of the plug in order to study the distribution of temperature therein.

The Differential Manometer.—From the sides of the stems of the thermometers T_1 and T_2 lead two small tubes connected to the manometer *M* as shown in Fig. 1. The latter is thus put in communication with the spaces occupied by the thermometer coils themselves and is intended to measure the pressure-drop between the high and low pressure sides of the plug. The manometer was somewhat over a meter in height and was furnished with a brass meter-bar of the "H" form made by the Société Genèvoise. This was placed between the tubes and read by a micrometer telescope from a distance of about one meter, the tube and scale being in the same field of view at one time. The crosshair was leveled by setting on the image of the level surface of mercury placed in a glass cell with plane sides at the same distance from the telescope as the manometer. The heights of meniscus were read off in order to supply data for the capillary correction which never exceeded 1 mm., and if omitted, would not have introduced an error exceeding 1/500 of the observed pressure drop, and even that would be within the accuracy demanded, for errors somewhat less than one per cent. in the Joule-Thomson effect came in from other sources. The corrections, however, were applied making use of the tables given in Kohlrausch, "Physical Measurements," 3d edition (English), p. 440. The internal diameters of the tubes varied from 5.0 mm. to 5.7 mm. along the portions where readings were made.

The readings were likewise reduced to 0° C., making use of tables given in Landolt and Börnstein's "Tabellen," 3d Aufl., pp. 34 and 35. Pressures throughout this paper are expressed in meters of mercury at 0° C. at the University of Virginia. The value for g (980 cm./sec^2) is needed only in final computations.

Pressure Gauges.—To the high-pressure side of the differential manometer were connected a piston gauge and a dial gauge, G and G' (Fig. 1) respectively. The latter was used for setting to the desired absolute pressures; while the former yielded their correct measure. The piston was of 3/8″ drill rod mounted in a snugly fitting brass cylinder provided with a leather packing at the top, so curved as to become tighter as the pressure increased. This also insured that the effective area of the piston was its own cross section and not a compromise between this and that of the bore of the cylinder. Provision was made for rotating the piston, in a manner similar to that carried out by Amagat, in order to eliminate the static friction.

The diameter of the piston measured by two micrometer calipers came to 0.9536 cm. giving an area of 0.7142 sq. cm. Thus 1 kg. on the piston corresponded to a pressure of 1.030 meters of mercury at 0° C. and at the same locality.

The weights were adjusted by a set of platinum plated weights furnished by Rüprecht of Vienna, and brought to within 0.02 per cent. of accuracy or about one fiftieth of the errors of reading of the gauge when in use. Great accuracy was not needed, for it will be seen that the effect of pressure on the Joule-Thomson coefficient is small.

Bath and Thermostat.—The bath was about 90 cm. deep and 30 cm. in diameter with triple walls of sheet brass. The space between the middle and inner walls was filled with asbestos, and that between the middle and outer was designed for the circulation of steam, but not so used. The outer wall was lagged with asbestos. The cover was lagged with about 10 cm. thickness of cotton waste which has been all that was necessary for temperatures up to 130° C. "Renown engine oil" made by the Standard Oil Co. was used to fill the bath and, on account of its great thermal expansion, a siphon overflow had to be provided. Rapid circulation was provided by two motor-driven propellers on one vertical shaft rotating in a well. The stirrer and heating coils are not shown in the diagram.

Heating was applied electrically from a 220-volt D.C. circuit, through four coils totaling a capacity of one kilowatt. These could be cut in independently in series or in parallel, various combinations being used, including auxiliary resistances, according to the temperature of the bath.

Thermostatic control was obtained by keeping a steady current in some of the resistances and varying the current in the remainder. This was done automatically by the wheatstone bridge type of thermostat similar in principle to that described by Darwin[33] and by Randall[34] and later made use of by the Leeds and Northrup Co. Its performance was quite good, keeping the bath, under the best working conditions,

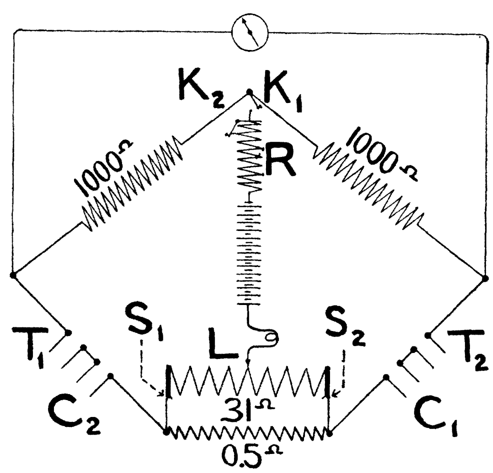

Fig. 2.

constant to 0°.001 C.; and in but few instances was the fluctuation more than 0°.004 C. It is a remarkably convenient form of apparatus for setting at any desired temperature.

The use of a 220-volt D.C. supply is perhaps open to criticism; but with care in insulation, trouble from leakage through the galvanometers from this source was avoided. It was, moreover, the only kind of power-supply at hand.

The Wheatstone Bridge.—Resistance measurements were made in terms of a decade resistance box manufactured by the Leeds and Northrup Co. of Philadelphia. The coils needed (from 30 ohms down) were calibrated twice, two years apart, and found to remain constant to well within the required accuracy.

The thermometers on the high and low-pressure sides of the plug were connected into the bridge differentially as shown in Fig. 2, where T_1 and T_2 represent the wires leading to the thermometer coils and C_1 and C_2 the compensation leads which will be described below.

The quantity desired is the difference in the effective resistances of the two thermometers. The Carey-Foster[35] method was employed because it measures directly the difference between resistances and eliminates all fixed contact- and lead-resistances. The mercury commutator for effecting the transposal of the resistances to be compared, which in this case are $T_1 + C_2$ and $T_2 + C_1$ is omitted from the diagram.

It will be noted that the arrangement of battery and galvanometer is not that usually published in the text-books. By putting, as indicated, the battery instead of the galvanometer in series with the sliding contact and by having no key in series with the galvanometer the error of thermal E.M.F.'s was eliminated. This arrangement follows the practice of the Bureau of Standards. It has worked admirably and obviated the necessity of reversing the battery current.

The slide wire S_1LS_2 was a "Students' Potentiometer" manufactured by W. G. Pye & Co., of Cambridge, England, and consists of a wire wound in a helix on a slate drum and with sliding contacts S_1S_2 at the ends. It has 10,000 divisions from end to end and a resistance of 31 ohms approximately. This being too high for direct use, it was shunted by a resistance of about half an ohm made of manganin wire. With this arrangement and by repeated tests at different dates the value of one division was determined to be 0.00005666 ohms or, in terms of the particular thermometers used, equivalent to about 0.0005° C. The precise conversion of bridge readings into degrees will be given later.

The errors due to the variability of the sliding contact resistances S_1 and S_2, being connected in series with a resistance as high as 31 ohms, proved to be negligible. For, by test, the uncertainty was not over 0.12 division (0.00006° C.) while, in the final readings, only the nearest whole division was taken into account. All other junctions in the four arms were either amalgamated or soldered. The wire S_1LS_2 was calibrated several times and was found uniform to a small fraction of a division.

For resistance thermometry, and with the battery connected between the thermometers as shown, the more sensitive arrangement is to have high-resistance ratio-arms; hence a high value for these, namely, 1,000 ohms, was employed.

The key K_1 opened and closed the battery circuit while K_2 in conjunction with the resistance R, permitted the observer to vary the battery current for the purpose of obtaining corrections due to the heating effect of the measuring current in each thermometer.

The Platinum Resistance Thermometers.—These were of the four-lead compensated type introduced by Callendar.[36] The ends of the compensating leads were united by a short length, about 1 cm., of the same sort of wire as that used for the thermometer coils. The thermometers were connected differentially into the bridge, thermometer No. 1 and compensating-lead No. 2, being connected in series on one side, while thermometer No. 2 and compensating lead No. 1 were in series on the other side. These connections (Fig. 2) are lettered T_1, C_2 on the left, T_2 and C_1 on the right. In differential connections, the need for the compensation leads is very much reduced, but, in the present instance, they were kept in to be on the safe side, especially in view of the fact that the depth of immersion of the two thermometers was not quite the same.

The wire for these thermometers was obtained from the Cambridge Scientific Instrument Co., Ltd., very pure and recommended by them for thermometer work, in which they make a specialty. The diameter of the wire was about 0.03 mm., and its length such as to give a change in resistance of about 11 ohms for a change in temperature from 0° C. to 100° C. It was wound upon the usual crossed mica frames in the form of a compact cube approximately 5 mm. each way. The fineness of the wire and the compactness of its mounting was for the purpose of allowing exploration of the space on the low-pressure side of the plug.

The four leads were sealed into the ends of a glass tube as appears at T_1 or T_2, Fig. 3, and passed thence up the tube and out through a wax-sealed joint into the room whence they were connected to the bridge by heavy No. 14 lamp-cord about 3 meters long each.

The thermometer coils were exposed to the flowing air in some of the preliminary experiments, but later, copper foil caps indicated by the dotted lines at T_1 and T_2 were slipped on. This made the galvanometer considerably steadier and did not introduce an objectionable lag because the copper caps should take the temperature of the gas before the walls of the enclosure.

The glass tubes containing the leads, after emerging from the air channels, were enclosed in larger brass tubes of 1/8″ pipe size (the brass tube for T_1 shown in the diagram is larger than natural size), which came in contact with the bath and allowed air-connection to the differential manometer. The immersion of T_1 was about 44 cm. and that of T_2

about 34 cm. under the bath. The latter immersion was extended by a lagged air-space above the bath's surface by about 12 cm. This was thought sufficient to eliminate the effect of heat conduction along the leads inside the glass tubes in spite of the stagnant air-space by which the leads were surrounded.

The electrical insulation proved sufficient at all times. Repeated tests were made; in fact, the bridge wiring was arranged so that the thermometer insulations between pairs of leads could be coupled in parallel and the combination thrown in series with the galvanometer and a battery of 30 volts. This test, as a matter of precaution, was made a part of the routine of observation. In dry weather the galvanometer was not sensibly deflected, while in one or two instances in damp weather a film seemed to form on the outside insulation whose resistance was of the order 20 megohms. This obviously would not affect the measurements.

Several tests were made for a possible effect of pressure on the resistance of the thermometers but none was found.

Application of Callendar's Formulæ.—These were adapted to the work in hand, as embodied in equation (8) below, in the following manner, beginning with the formulæ themselves, namely:

$$t_p = 100\frac{R - R_0}{R_{100} - R_0} \text{ (defining the ``platinum scale'')} \qquad (5)$$

and

$$t - t_p = \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} \text{ (correcting to the hydrogen scale)}, \qquad (6)$$

where δ is a quantity to be determined by experiment for the sample of platinum wire used.

Now, if Δt is a small temperature change, we get from (6)

$$\Delta t = \Delta t_p\left\{1 - \frac{2\delta}{10000}(t - 50)\right\}^{-1}$$

$$= \Delta t_p\{1 + 0.0003(t - 50)\} \qquad (7)$$

to the first order of approximation, if we put $\delta = 1.50$. This value, given by the Cambridge Scientific Company who furnished the wire, was accepted as sufficiently accurate. For it is evident that its omission altogether could not alter the right hand member of (7) by more than 1.5 per cent. in the range from 0° to 100° C. covered in these experiments.

If μ_{t_p} therefore, is the value of the Joule-Thomson coefficient observed in terms of the platinum scale and μ in terms of the hydrogen scale, then we have

$$\mu = \mu_{t_p}\{1 + 0.0003(t - 50)\}, \qquad (8)$$

where μ_{tp} is the observed Joule-Thomson coefficient in terms of platinum degrees, and μ this coefficient calculated in terms of the gas-scale. (The distinction between the hydrogen and nitrogen scales need not be drawn for these measurements.)

The values of the fundamental intervals, i. e., $R_{100} - R_0$:

	Thermometer T_1	Thermometer T_2
May 12, 1915............	10.952 ohms.	10.930 ohms.
" 14, "	10.963 "	10.932 "

Accurate knowledge of the fundamental interval of thermometer T_2 is all that is necessary, a matter that will come up later. The weighted mean for T_2 is 10.932 ohms.

The above tests were made with currents of air flowing past the coil at two speeds and likewise with the air stagnant. No variation of consequence occurred. The thermometers, moreover, showed themselves more than sufficiently stable during tests covering a year previous. The actual data then obtained cannot be used, however, on account of subsequent slight alteration in the thermometers.

Correction for Heating Due to Current.—The bridge current, of course, heats to some extent the thermometer coils themselves and this must be allowed for. Since the liberation of heat is proportional to the square of the current, the resulting small rise in temperature should follow the same law. Callendar's method is to double the bridge current and subtract one third the difference of the two corresponding settings from the first setting. The author found it a little more convenient to increase the bridge current in the ratio $1 : \sqrt{2}$. Thus the correction is immediately the difference in the two bridge settings.

Moreover, in order to make certain that this rule held under the present conditions a direct test was made with bridge currents in the ratio $1 : 2 : 2.5 : 4$. The linear relation between the bridge readings and the square of the current was satisfactory. This held also in varying currents of air. Thus, where the rates of flow were 0, 2.9, 19, 36, 80, 132 and 250 cc./sec. the corrected bridge readings were 0.°016, 0.°018, 0.°015, 0.°015, 0.°015, 0.°015, 0.°014 respectively (reckoning from an arbitrary zero).

The order of magnitude of the heating correction in the final runs was 0.°01 C. The lower value of the battery current was 6 milliamperes.

Incidentally, the above data show that the length of the coil of pipe in the bath was sufficient to give the gas the temperature of the bath before it reached the plug.

Conversion of Bridge Readings to Degrees.—After the heating correction has been applied, the differential reading may be converted into degrees by a multiplying factor which was obtained as follows:

The unit for reading off settings was taken as one revolution of the slide wire drum and is called the "bridge unit" hereafter. Repeated standardizations of the wire at four different dates in terms of the calibrated ohm gave the value 0.005666 ohms per bridge unit.

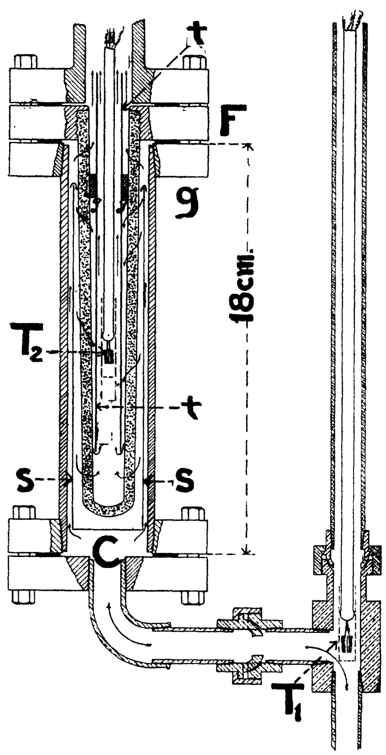

Fig. 3.

Combining this with the figure just given of 10.932 ohms per 100° C. we get the factor 0.05178 degrees per bridge unit.

The values for μ obtained from the observations in terms of bridge units per meter of mercury are convertible into their proper values in terms of degrees per meter of mercury by the application of first this factor and then formula (8).

The Porous Plug.—The form of plug finally adopted was suggested by the research of Regnault already alluded to. Its longitudinal section is shown in Fig. 3 (dotted shading) the material being earthenware—a Pasteur filter. As may be seen, the flow of gas through the plug is radial toward an axis, and after passing through the plug wall its outflow takes place parallel to the axis. The purpose of this construction, as already pointed out, is to furnish thermal protection.

The whole apparatus shown in Fig. 3 is immersed in the bath, whose surface is 44 cm. above the point T_1. Air after traversing about 8 meters of pipe, in the bath, passes T_1, enters the plug casing at C and travels upward between the wall of the casing and a bright tinned radiation shield *ss*, as is indicated by the arrows. After passing over the top of the radiation shield it fills the space immediately outside the wall of the plug, through which it flows in two streams, divided by the "guard ring" *gg*. Within the plug is a glass tube *tt* which constrains the lower of these two streams to pass, all of it, past the thermometer T_2 while the upper stream is kept from passing the thermometer. Both streams pass out finally at the top.

The purpose of the guard ring is to avoid errors arising from conduction of heat along the material of the plug from its mounting F and ultimately reaching the thermometer inside.

The temperature of the plug in general is different from that of the casing. Radiation between the two would introduce an error. The radiation shield is to prevent this. As will be seen later, the radiation shield proved to be unnecessary but it was retained as a precaution, and is free from objection.

The construction of the plug casing (Fig. 3) permits the use of the principle of interchangeable parts. It may be seen that different plugs may be bolted in and that different sizes of casing as well may be employed. This proved a valuable feature in the preliminary experiments.

Preliminary Experiments.

Early Experiments with the Axial Flow Plug.—A number of experiments were carried out at the Johns Hopkins University in 1905–6, on carbon dioxide with a straight-flow plug of the type used in the Joule-Thomson experiments. Platinum resistance thermometers were used and so arranged as to be movable. The pressure-drops were of the order of one atmosphere. Plugs of various materials were tried, eider down, cotton, silk and paper. A vacuum-jacket was attempted and, what seemed better, the guard ring principle contained in a suggestion by Buckingham[27] was carried out. The porous plug was coaxial with a second annular plug designed to eliminate lateral temperature gradients.

The last arrangement improved things somewhat, giving one result in agreement with those of Joule and Thomson, but the general characteristic of the experiments was their lack of reproducibility.

On displacing the low-side thermometer, for instance, a steep temperature gradient along the axis was observed. The observed cooling effect continually fell off as the thermometer was further withdrawn. A shift, for instance, from 1 to 4 and 6 cm. distances cut the effect to about one half and one third respectively.

With varying rates of flow also the effect varied, but with a tendency toward a limit for the higher speeds. Natanson observed a variation with flow also. Perhaps we can thus account for the partiality of observers for high flows and plenty of gas. This feature and the ample dimensions of the apparatus of Joule and Thomson undoubtedly contributed to the accuracy of their results.

In addition, an enormous amount of time had to be consumed before a steady state could be attained, amounting to an hour and a half before a reading could be taken. Apart from other considerations, this would lead to a large chance for error unless the pressure regulation were watched very closely. A damped oscillation in the cooling-effect similar to that in the Joule-Thomson experiments was also observed.

It was decided, then, as already mentioned, to narrow the field and to concentrate on developing a method for the attainment of reliable results. What was to be desired was thermal protection, fine pressure regulation, and good temperature control. These problems have been taken up in the manner already described. The later experiments have been carried out in the Rouss Physical Laboratory of the University of Virginia.

Preliminary Experiments with Radial Flow Plug—Exploration.—Referring to Fig. 3, it will be remembered that the thermometer T_2 was capable of being shifted throughout the entire length of the plug. In the initial explorations the inner tube *tt* had not been introduced. The temperature distribution was fairly uniform except above the middle, and the correction for the heating of the thermometers due to the bridge current was much larger at the bottom of the plug, where the air-flow was slow, than at the top where the air-flow was faster. This led to the introduction of the tube and guard ring with the result that it not only reduced this heating correction but rendered the temperature distribution along the tube uniform to the order of 0.°001 C. Closer tests than this were not pressing nor possible, for time-fluctuations due to bath and pressure fluctuations were of this order of magnitude.

The final arrangement of the plug with tube and guard ring is almost identical with the arrangement published by Burnett and Roebuck (*loc. cit.*).

Rate of Flow.—This was separately measured by collecting the air over a pneumatic trough. Roughly the linear speed was found to be directly proportional to the pressure drop and independent of the absolute pressures, and hence of density. The result can therefore be simply expressed by a single number, namely 2.3 cm. per sec. per cm. drop of mercury. In the final runs this would mean a maximum speed within the tube *tt* of 180 cm. per sec., a little more than this at the bottom of *tt* (Fig. 3) and about double this around the thermometer caps. In the coil leading into the plug-housing, the speed was about the same.

Velocity Cooling.—The upper limit of the possible errors arising from the change in kinetic energy involved in the above variation of speeds was computed to be of the order of magnitude of 0.°004 C. Actually none was observable. For, in a run with the plug removed and with speeds of flow in the ratios 50 : 100 : 200 : 330 the bridge readings (with reference to an arbitrary zero) were 0.°037, 0.°038, 0.°038, 0.°038 respectively. The fastest flow exceeded the greatest speed of the air in the final runs. This run, moreover, was taken with the thermometer caps on, when the error from velocity cooling should be a maximum, as is plain from a glance at Fig. 3. For, when the caps are removed, the speed of air past the thermometers would be less.

The formula used in this computation, namely,

$$c_p(T_1 - T_2) = \tfrac{1}{2}(w_2^2 - w_1^2) + g(h_2 - h_1)$$

was not strictly applicable, for, as in all deductions of this sort the temperatures could be given only by thermometers *moving with the gas.* Stationary thermometers would be expected to indicate smaller temperature differences. The preliminary experiments of Joule and Thomson, as well as those just outlined, are in agreement with this idea.

Aspirator Effect.—This is an effect cognate with velocity cooling. For to measure the pressure of a stream of fluid the manometer likewise should be moving with the fluid, strictly speaking. A test for error arising from this cause was made by taking readings on the differential manometer with the plug removed while the air was run through at velocities higher than those employed in the runs. The manometer showed zero reading throughout.

Effect of Varying Rates of Flow upon the Observed Temperature Drop.—These observations are depicted graphically in Fig. 4. Curve 2 was taken with the plug whose characteristic rate of flow has just been given,

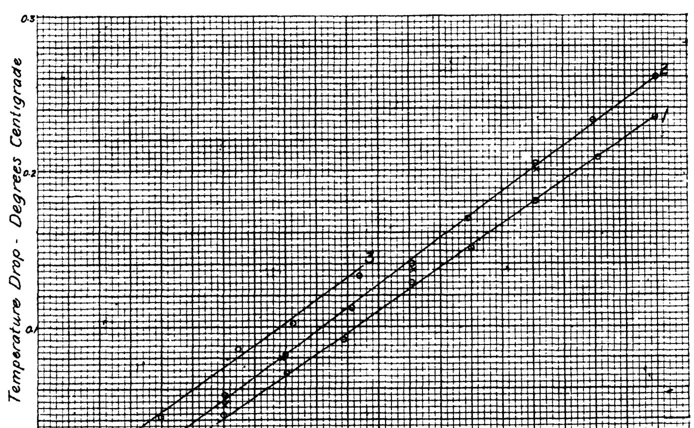

Fig. 4.

Preliminary Experiments, Varying Rate of Flow and Position of Guard Ring.

Curve 1: Relative Flow 0.7—Slope 0.28

" 2: " " 1.0— " 0.30

" 3: " " 3.0— " 0.29

Crosses: Guard Ring shifted 4 cm.—flow as in 2.

namely, 2.3 cm. per sec. per cm. of Hg pressure drop. Curve 1 applies to the same plug wrapped with rubber bands till its flow was 0.7 as great, while curve 3 is for a plaster of Paris plug whose flow was three times as great.

The first essential feature of these curves is that they are straight lines within the error of experiment, except near the origin. (This is true not only in the preliminary but in the final runs.) Near the origin the points were so irregularly distributed that they have been omitted from the diagram.

The second essential feature is that the more rapid the flow the nearer the curve approaches to a limiting line passing through the origin. A third feature to be noted is that these lines are sensibly parallel. These features will be taken up later, in discussing the effects of a residual heat leakage.

Heat Leakage by Conduction.—The nature of this residual heat leakage was sought in conduction, radiation and convection. Conduction through the gas does not seem probable. The only remaining path would be along the material of the plug. This point was tested by shifting

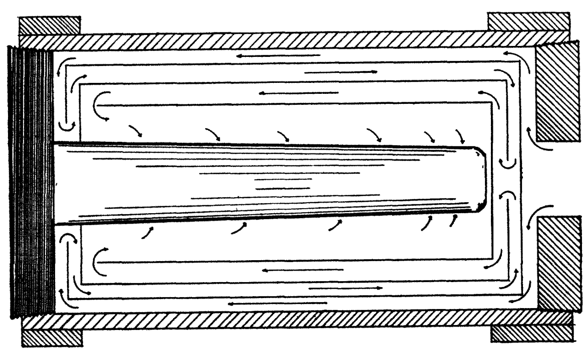

Fig. 5.

the guard-ring from a position 1.5 cm. from the plug flange F (Fig. 3) to a point 5.5 cm. therefrom. The results as shown by the rings and crosses (Fig. 4) rule out this source of error, the curves (No. 2) in these two cases being indistinguishable.

Heat Leakage by Radiation.—Since the surface of the plug must be at a different temperature (lower in case of air) from that of the walls of the plug casing, heat may pass by radiation across the annular space between them and thus reach the interior without first being absorbed by the gas itself, and so an error may be introduced. This was first tested by comparing runs with the dark iron casing walls lined with bright tin and then without the tin. There was no systematic difference. Again a trial was made with three radiation shields on the one hand, disposed as in Fig. 5, in a large casing and on the other, with no radiation shields at all (the casing being that shown in Fig. 3). Fig. 6 shows that

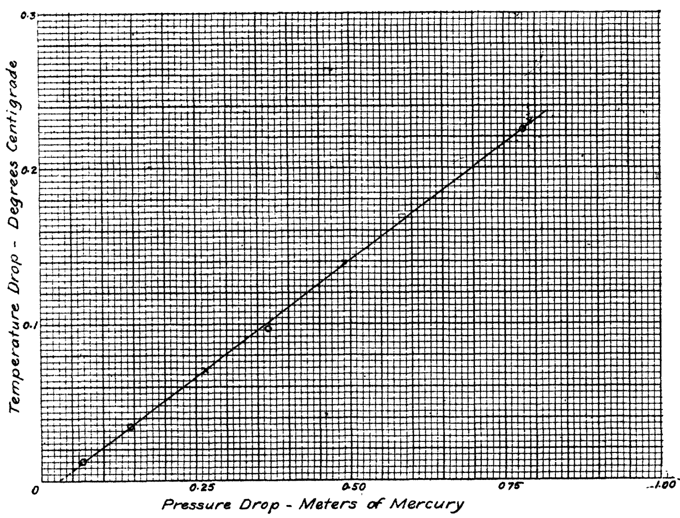

Fig. 6.

Preliminary Experiments, Effect of Radiation Shields.

Circles: No radiation shields
Crosses: 3 " "

these results also are indistinguishable. Radiation, then, is not to be looked for to explain the depression of these lines nor as a serious source of error.

Heat Leakage by Convection.—A turbulent motion of the gas surrounding the plug could possibly convey heat across from the walls of the casing without permanent absorption. If so, an increase in the inside diameter of the casing should reduce this error and shift the lines nearer to the origin. Now in the experiments of Fig. 6 (no shield), the annular space between the walls and the plug was about 6 mm. thick or about twice as thick as for the experiments of Fig. 4. The curve of Fig. 6 passes much nearer to the origin. Consequently convection must play a part.

It was not thought worth while to push these experiments further, the practical limit being apparently reached in the experiments of Fig. 6.

Influence of Density.—Where the mean density of the air is increased by operating at increased mean pressures, one should expect a minimizing effect upon the errors in the temperature readings, owing to the increased volumetric thermal capacity of the gas and the fact that the heat leakage should not increase in the same ratio, if at all. This was verified by experimental runs, whose results are shown in Fig. 7, where it will be seen that curves corresponding to the higher pressures pass nearer the origin. Further confirmation in the final results were found and will be noted when these come up.

A second effect is observable here. The slopes of the lines fall off with increasing pressure. This again more properly comes up later, where the diminishing effect of increased mean pressure upon the Joule-Thomson coefficient is discussed.

Derivation of the Joule-Thomson Coefficient from the Observations.—We are now in a position to discuss the relation of μ to these preliminary data. It is seen from what has gone before, that the continual reduction

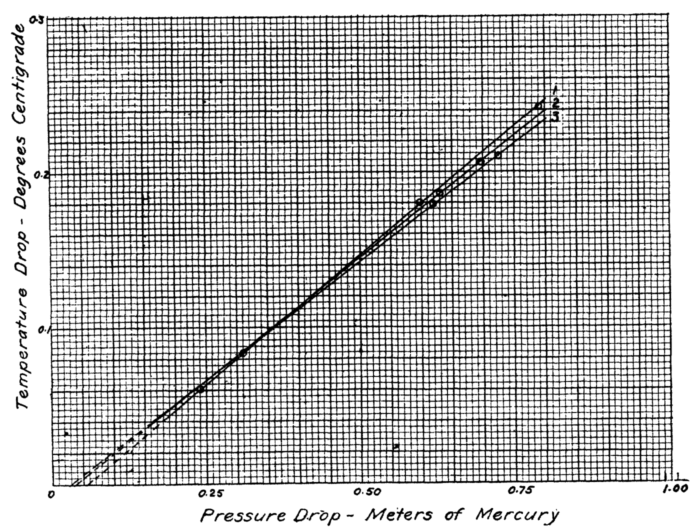

Fig. 7.

Preliminary Experiments, Varying Densities.

Curve 1: Mean pressure 2.5 meters mercury
" 2: " " 4.5 " "
" 3: " " 6.4 " "

of error by first reducing the heat-leak in obvious ways and secondly by increasing the mass of gas affected, has led in the main to the shifting of the curves of the type shown in Figs. 4, 6 and 7 so that their rectilinear portions (produced) are made to pass nearer to the origin without, however, changing their directions sensibly (exclusive, of course, of the pressure effect, which is entirely independent). The limiting ideal case, therefore, would be represented by a straight line passing through the origin, whose slope would be the true value of μ. The obvious step then to take is to make the actual runs under conditions as nearly ideal as feasible; and for the values of μ adopt the values of the slopes of these straight lines without reference to their position. These values are taken to be as near the truth as the data are capable of yielding it.

The question may now be asked: Can anything be said as to the constancy of $u + pv$ or H along these plots? It will be remembered that after the gas has passed through the plug the increment in the function H is equal to the gain of heat per gram of gas during its passage. Now it is conceivable that the heat-leak (measured in calories per second) might be of such magnitude as to make the slope of the plots too steep for a locus of constant H, or again, such as to make it too flat.

Start, for example, with one of the smaller pressure drops and suppose there is a small heat leak. The resulting temperature drop will be too small. Let this observation be represented by a point on the (p, t) diagram, say, near the origin on a plot like that of Fig. 6. The value of H for this point will be greater than its value, H_0, for the origin, which represents the state of the gas on the high pressure side of the plug. A straight line, then, drawn from the origin to a point A, say, when there is a heat leak, will pass from regions of lower to regions of higher H and will be too flat. Now suppose that the experiment be carried to a higher pressure drop and a second point B is determined. As a different and an extreme case of heat-leak, let us suppose, for the moment, that from the point A onward it remains constant. Then, since the rate of flow has been increased, due to the increased pressure-drop after we leave A, the gain per gram falls off. The line AB, therefore, passes from higher to lower values of H and is too steep. Now let us try another hypothetical law for the heat-leak, namely, that from the point A onward, it is proportional to the rate of flow of gas. Then the gain in heat per gram remains fixed and the two points A and B are characterized by the same value of H. A line plotted under this condition would be, therefore, a line of constant H, although this value would be greater than H_0. In general, then, starting from the point A: if the heat-leak varies more rapidly than the first power of the rate of flow of gas, the plot is too flat; if, less rapidly, the plot is too steep. In call cases the plot will lie under the line $H_0 =$ const.

The hypothesis that the heat-leak is proportional to the rate of flow of the gas seems a reasonable one to make for actual Joule-Thomson experiments, at least as a first approximation. For, as has been seen, the rate of flow is approximately proportional to the pressure-drop, which in turn is very closely proportional to the temperature-drop, and the latter again in turn would be expected to be proportional to the heat-leak, certainly as far as conduction and radiation are concerned, and possibly convection too. In the case of convection, however, there seems to be a possibility that the leak would be speeded up in the case of turbulent motion and cut down in the case of stream-line motion, thus producing deviations from the proportionality relation on one side or the other. At present there is no way of deciding this point but the deviation in any case should be small.

If, then, the total heat-leak be small and if its deviation from being proportional to the rate of flow be likewise small, the deviations of our plots from true curves $H =$ const. should be small to quantities of the second order of errors. It is hoped that this may be reasonably claimed for the final runs described in this paper.

In the light of what has just been developed, the actual plots are now susceptible of a further interpretation. The curve of Fig. 6, if completed by connecting up with the origin by the experimental determination of the requisite further points would of course curve upward in this region. This was actually done in some instances although some of the points were uncertain. This curvilinear portion of the plot, then, would represent a heat-leak varying more rapidly than a direct proportion of the flow-rate, while the remainder would represent a heat-leak proportional to this rate. Both the excess heat-leak and the uncertainty of the points near the origin are to be expected on account of the very slow, almost stagnant, flow of the air in experiments with such small pressure-drops.

As a matter of fact it is physically impossible for anything but an excess heat-leak to occur for this region. Otherwis we should have two curves, H and H_0 say, for which $H - H_0$ is finite, approaching intersection as a limit at an arbitrary point, namely, the origin of the diagram. We have, then, in other words, the surprising inference that it is impossible, in a throttling process, for a heat-leak to be continuously proportional to the rate of flow of gas below a finite limit of the flow and, likewise, of the pressure drop, although this would seem quite possible otherwise.

Referring now to Fig. 4, where the rate of flow of the air has been varied, other things being unchanged, by altering the porosity of the plug, the plots are explicable on the ground that the heat-leak is proportional to the rate of flow of the air in each case but that the constant of proportionality is smaller the greater the porosity of the plug.

Zeros of the Differential Thermometers.—In the determination of the slope of the lines just discussed, it is obviously unnecessary to know the precise value of the bridge setting when the pressure-drop is zero. This knowledge was useful in the preliminary experiments in affording an index of the magnitude of the heat-leak. In the final run, therefore, the determinations of the zeros were discontinued. For they required time and at best were uncertain. The conditions for accuracy in a body of stagnant air in the pocket-like interior of the plug in the position shown in Fig. 3 are obviously unfavorable. The only way to put this accuracy on a par with the other readings would be to provide a way of opening the plug and sending a current of air through.

A matter well worth noting here is that, when this method of observation is employed, one is relieved of the necessity of a close adjustment to equality of the differential thermometers. The high side thermometer serves in reality merely as a sort of compensator for error due to fluctuations in the bath temperature, and an accurate knowledge of it even is unnecessary. For example the fundamental intervals of the two thermometers T_1 and T_2 differed by 0.3 per cent. Now suppose the temperature of the bath during a run changed by as much as 0.01 degree. Then the differential reading, after the steady state had been reached, would be changed by 0.00003 degree.

Values given for the Temperatures and Absolute Pressures.—In what follows μ will be discussed as a function of temperatures and pressures. The pressures will be the means of the pressures above and below the plug. On the diagram they will be represented by the mid-points of the limited straight lines there plotted. As to temperatures, the variations are too small to make it worth while to correct the bath temperatures.

Error from Moisture.—Tests made at a fixed temperature and pressure, in which the air from the room was passed through long-used calcium chloride first; then the drying material was omitted; finally fresh calcium chloride was put in. The values obtained for μ were 0.35, 0.34, and 0.33 degrees per meter respectively, showing a small increase due to moisture (and the poor quality of old calcium chloride). One should expect, then, that a final drying with phosphorus pentoxide would suffice. In the final runs this was used, with the exception of those at 30° C., and these, in spite of that, seem to fit well into the empirical formula derived from all the observations, as will appear later. The phosphorus pentoxide could be continually observed from the outside during the runs, and it was only at the ends of the longer ones that it had a gummy appearance.

Conduction of Heat along the Thermometer Leads.—After the final runs had been made, it was suspected that there might be an error arising from this cause. A new set of runs with the thermometer caps removed, exposing the thermometer wire to the stream of gas would test this point.

A number of observations were, therefore, made covering the same range of temperature and pressure. The galvanometer, of course, was quite unsteady under these conditions, but the agreement between the new and the old data was satisfactory. Thus the mean of ten runs with the caps off gave for μ a value 0.265 while the mean of ten runs at the same temperatures and pressures with the caps on gave 0.267 degrees C. per meter of mercury pressure-drop. This was well within the accidental error of the runs with caps off.

Regeneration Effect.—After the experiments described in this paper had been completed, the paper by Trueblood, referred to in the beginning, appeared, in which is described a form of heat-leak arising from the peculiar geometry of the radial flow apparatus. The nature of this regeneration effect can best be described by quoting from Trueblood's paper: "At its open end, the plug is necessarily brought, for purposes of mechanical support, into good thermal contact with the metal walls of the case. As a result, fluid which has passed the low side thermometer is provided with a thermally short path of communication with fluid which has not yet passed through the plug. This results in a depression of the temperature of the latter, which, joining the low side fluid at at a temperature therefore lower than then exists there, contributes to a still further depression of the temperature of the fluid which has not yet passed. This cumulative action, similar in principle to that taking place in certain types of liquid air machines, is limited by the ability of the bath to supply heat to the low side fluid. . . . The effect of the action just described on the observed temperature drop is indirect, since the fluid directly affected does not pass the low side thermometer. But the temperature depression produced in the neighborhood of the open end produces indirectly, by conduction through the walls of the plug, the walls of the case, the inside lagging and, doubtless, to some extent through the fluid itself, a depression of the temperature of fluid which does pass the low side thermometer; that is, there is an outward leak of heat from fluid between thermometers to fluid which has passed the low side thermometer with the result that the observed temperature drop is too high."

In the author's apparatus the regeneration effect, he believes, was negligible, although, as a matter of fact, its possibility was not foreseen. For, under the heading *heat leakage by conduction*, it was shown that a shift in position of the guard ring did not lead to a change in reading. Now since the temperature depression of the low side gas is due to the "regeneration" process should be manifest in greater and greater degree at points nearer and nearer to the mechanical support, it should have been shown up by the test in question, which, as has just been seen, was not the case. This result may have been due to the unusually long and narrow proportions of the plug used. A natural remedy for the regeneration effect or any effect arising from conduction would seem to be the employment of a long plug.

Final Results.

Between August, 1915, and January, 1916, fourteen determinations of the Joule-Thomson coefficient (μ) were made at five temperatures between 0° C. and 100° C. and at mean pressures of 2.5, 4.5 and 6.4 meters of mercury.

In Table I. are collected the data summarized from each run. The first four columns need no comment. The "bridge readings" of column 5 correspond to the temperature-drop, without being reduced to degrees.

Table I.

1. Date.	2. Bath Temp.	3. Pressure (Meters).	4. Pressure Drop (Meters).	5. Bridge Readings.	6. Slope (Bridge Units per Meter).	Residuals. 7. Bridge Units.	Residuals. 8. Degrees.	9. Wt.	10. Intercepts (Bridge Units).
1916									
Jan. 10	15°.9	2.45	.763	14.26	0.698	—	—	0.2	
			.260	10.75					
" "		6.50	.694	13.53	0.622	—	—	0.3	
			.263	10.85					
1915									
Aug. 20	30°.0	2.49	.792	4.67	0.635	−0.01	−0.0005	1.0	−0.34
			.599	3.48		+0.02	+0.001		
			.311	1.63		0.00	.0000		
			.241	1.18		−0.01	−0.0005		
" 23	"	4.48	.697	3.98	0.607	−0.01	−0.0005	1.0	−0.24
			.631	3.59		0.00	0.0000		
			.298	1.60		+0.03	+0.0015		
			.199	0.94		−0.03	−0.0015		
" 26	"	6.40	.726	4.07	0.588	−0.01	−0.0005	1.0	−0.19
			.620	3.46		−0.02	−0.001		
			.310	1.63		0.00	0.0000		
			.255	1.32		0.01	+0.0005		
Nov. 24	50°.0	2.50	.747	4.12	0.560	+0.02	+0.001	1.0	−0.08
			.653	3.54		−0.03	−0.0015		
			.343	1.84		+0.01	+0.0005		
			.264	1.39		0.00	0.0000		
Nov. 29	"	4.50	.820	4.37	0.535	−0.05	−0.0025	0.5	+0.03
			.689	3.77		+0.05	+0.0025		
			.309	1.71		+0.03	+0.0015		
			.193	1.03		−0.03	−0.0015		
Dec. 1	"	6.33	.790	4.28	0.529	−0.02	−0.001	1.0	+0.12
			.711	3.90		+0.02	+0.001		
			.307	1.74		0.00	0.0000		
			.193	1.14		+0.01	+0.0005		

TABLE I. (*Continued*).

1. Date.	2. Bath Temp.	3. Pressure (Meters).	4. Pressure Drop (Meters).	5. Bridge Readings.	6. Slope (Bridge Units per Meter).	Residuals. 7. Bridge Units.	8. Degrees.	9. Wt.	10. Intercepts (Bridge Units).
1915									
Dec. 6	70°.0	2.53	.769	3.93	0.496	+0.02	+0.001	1.0	+0.1
			.500	2.54		−0.04	−0.002		
			.259	1.41		+0.02	+0.001		
Dec. 8	"	4.36	.747	3.84	0.480	−0.01	−0.0005	1.0	+0.26
			.497	2.66		+0.01	+0.0005		
			.247	1.44		−0.01	−0.0005		
Dec. 13	"	6.40	.718	3.72	0.468	0.00	0.0000	1.0	+0.36
			.498	2.70		+0.01	+0.0005		
			.255	1.55		0.00	0.0000		
Dec. 16	90°.0	2.44	.746	4.87	0.441	0.00	0.0000	1.0	+1.57
			.509	3.83		0.00	0.0000		
			.257	2.71		0.00	0.0000		
" "	"	4.52	.747	4.91	0.421	−0.01	−0.0005	1.0	+1.78
			.495	3.88		+0.02	+0.001		
			.248	2.81		−0.01	−0.0005		
Dec. 15	"	6.35	.743	3.51	0.406	−0.02	−0.001	1.0	+0.51
			.506	2.60		+0.04	+0.002		
			.253	1.52		−0.02	−0.001		

This reduction is more simply done later. Column 6 gives the slope of the straight line that would be formed by plotting after the manner of Figs. 6 and 7, but actually they have been calculated by the method of least squares. The residuals in temperature, shown in column 8, give no evidence of a systematic deviation from the straight line and, moreover, the order of their magnitude is seldom over 0°.001 C. The weights (column 9) assigned to the several runs are the same for all except three, where experimental difficulties of a temporary sort turned up during the respective runs. In the two runs of January 10 it was impractical to get more than two points for each straight line, so there was no least square reduction. That carried out on November 29 suffered from a derangement of the pressure controlling apparatus. The later runs included one less point each but the gain in observing experience about balanced the omission of one point, and so the weights for these were kept at unity. The "intercepts" (column 10) on the temperature axis, are known to within additive constants only, except for the runs at 30° C., where zero readings of the differential thermometers were taken. The only purpose these data serve here is to furnish further evidence for the conclusions stated under the head "*influence of density*." It will be seen that with ascending pressures, hence increasing densities, the intercepts progressively rise along the temperature axis, with one exception.

The Joule-Thomson Coefficient Expressed as a Function of Temperature and Pressure.—The values of the slopes (column 6) reduced to the proper units are taken as the values of μ for reasons already given. This reduction is now made by the use of the multiplying factor 0.5178 together with formula (8). μ is then expressed in degrees C., hydrogen scale, temperature-drop per meter of mercury pressure-drop.

The fourteen values of μ thus obtained are classified in Table II.

Table II.

Approximate Pressure. (Meters.)	15° C.	30° C.	50° C.	70° C.	90° C.
	.358	.327	.290	.258	.232
2.50	(+.008)	(+.002)	(−.002)	(−.002)	(+.002)
	(+.002)	(+.001)	(.000)	(−.001)	(+.001)
		.312	.277	.250	.220
4.50		(−.001)	(.000)	(−.001)	(−.001)
		(−.002)	(−.002)	(.000)	(−.002)
	.319	.302	.274	.244	.213
6.40	(−.006)	(.000)	(+.002)	(+.002)	(−.001)
	(−.010)	(.000)	(+.004)	(+.003)	(−.002)

Upper line of residuals—five-constant formula.
Lower line of residuals—three-constant formula.

according to temperature and pressure. To these values were fitted, by least square computation, two empirical formulas, one a five-constant formula in t, the other a three-constant formula in $t + 273$ or τ. In the same table are included in parentheses, under each observed value of μ, the residuals (obs.-calc.) obtained with each of these formulas, the upper one applying to the former, the lower, to the latter formula.

The five-constant formula was tried following upon an initial inspection of the observations, which showed that the variations of μ were linear in p but not linear in t. Consequently a second degree term in t was included. The formula is

$$\mu = +0.3935 - 0.00691p - 0.001835t + 0.00000134t^2 + 0.0000325pt, \tag{9}$$

the units being as above specified.

Five constants make an unwieldy formula and seemed quite too many for the limited range of temperatures and pressures here employed. Resort was then had to the three-constant formula (4) suggested by the use of the equation of van der Waals. The least square reduction for this gave

$$\mu = -0.2599 + 181.96\frac{1}{\tau} - 552.4\frac{p}{\tau^2}, \tag{10}$$

where $\tau = 273 + t$. This formula is plotted in Fig. 8, which shows likewise the observed points.

The five-constant formula agrees a trifle more closely with the observations than does the other, as should be expected, having two more constants, but there is little to choose between them in this respect. All things considered, the three-constant formula is to be preferred; it is more rational and is simpler.

The computations of these formulæ were subjected to the standard

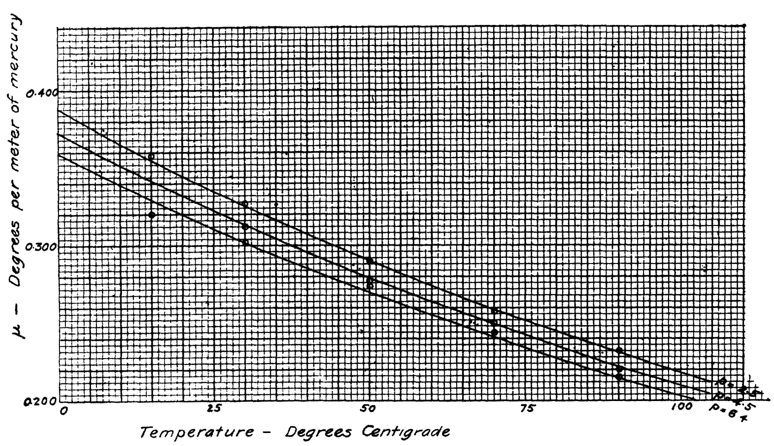

Fig. 8.

Joule-Thomson Coefficient, as a Function of Temperature and Pressure.

Curves are graphs of the formula:

$$\mu = -0.2599 + 181.96\frac{1}{\tau} - 552.42\frac{p}{\tau^2}$$

Circles are observed values.

numerical checks throughout. The smallness of the residuals, being on the whole less than one per cent. would indicate, at least for the present observations, that a better formula is not worth looking for.

Comparison with Other Results.—Joule and Thomson gave as their formula for air

$$\mu = 0.92\left(\frac{273.7}{T}\right)^2 \text{ degrees C. per 100 inches of mercury,}$$

which, by reduction, is

$$\mu = 0.362\left(\frac{273.7}{T}\right)^2 \text{ degree C. per meter of mercury.}$$

Their data have been embodied by Rose-Innes (*loc. cit.*) in the formula

$$\mu = -0.275 + 178\frac{1}{T} \text{reduced to degs. C. per meter of mercury,}$$

which resembles (10) omitting the pressure term. The observations of Joule and Thomson, it will be remembered, did not indicate an effect of pressure.

Buckingham, by making use of the results of Kester on carbon dioxide and of Joule and Thomson on oxygen, air, nitrogen, and hydrogen, applied the law of corresponding states and found two formulas of similar type, one of which is

$$\mu = \frac{a_1}{\tau - b_1} - d_1, \qquad \tau = 273 + t.$$

A few numerical values calculated by the aid of this formula and the values given for the constants, will be found further on in Table III.

The only experiments published showing a pressure effect for air are those of Vogel and of Noell. The latter, being performed subsequently in the same laboratory may be considered as superseding the former. However, it is well to state Vogel's formula, namely,

$$\mu = 0.268 - 0.00086p \quad \text{(pressures in kg. per cm}^2\text{)},$$

which holds for the fixed temperature only.

The lengthy formula of Noell is quoted near the beginning of this paper. The pressure coefficient at 10° C. is practically the same in both cases. At 0° C. Noell's pressure coefficient is -0.0015 while that found by the author is -0.0074 the units in both figures being degrees C. and meters of mercury. The agreement here leaves something to be desired but it is well to note that the greater portion of the data to which Noell's formula was adjusted lay in a range of much higher temperatures and pressures than the temperatures and pressures of the present paper. It is interesting to note that Noell's formula is also linear in p and that both coefficients are negative.

Further corroborative evidence as to the negative sign may be found in the calculations of Dalton (*loc. cit.*) for hydrogen based on the empirical equations of state of Kamerlingh-Onnes. He plots numerous curves of the integrated Joule-Thomson effect, or in other words curves $H =$ const. over a wide range in temperature and pressure, *i. e.*, from 1 to 100 atm. and $-215°$ C. to $+17°$ C. These curves in the (p, t) plane were all concave downward, showing a negative pressure coefficient of μ for hydrogen, over the whole field, which covered some inversion points and both positive and negative values of μ. One would expect that an application of the law of corresponding states might lead to the same thing for all gases, although a general statement of this sort could not be made. In fact, accepting van der Waals' equation for the moment, a glance at equation (3) shows that the sign of the expression

$$\left(6b - \frac{4a}{RT}\right)$$

determines the sign of the pressure coefficient. In regard to carbon dioxide, Natanson found a positive coefficient, and Kester found no dependence upon pressure except at 26.4 atm. and here an increase in μ over its value at lower pressures was indicated. The matter on the whole for carbon dioxide seems undecided.

In Table III. are set forth for comparison a few numerical values for μ calculated from the formulæ of other observers above quoted (omitting those of Vogel and Rose-Innes). In general the values of the present paper exceed the other values. The former, at 4.5 meters pressure are in closest agreement with those of Buckingham. It is of interest to note, however, that, choosing a temperature of 0° C. for example, the integrated cooling effect over a drop of about 7 atmospheres calculated by the author's formula agrees with that set down for "corresponding states." This was roughly the pressure-drop in the experiments of Joule and Thomson.

TABLE III.

t° C.	Joule and Thomson.	Corresponding States. (Buckingham.)	Noell $p = 1m.$	Present Paper.		
				$p = 1m.$	$p = 4.5m.$	$p = 6.4m.$
0	.362	.374	.365	.399	.373	.359
50	.259	.270	.244	.298	.278	.270
100	.194	.212	.165	.224	.210	.203

Calculation of the Temperature of the Ice Point on the Thermodynamic Scale.—The general relations are

$$\frac{v_{100}}{T_{100}} - \frac{v}{T_0} = \int_{T_0}^{T_{100}} \frac{\mu c_p}{T^2} dT \quad \text{(pressure = const.)}, \tag{11}$$

$$v_{100} = v_0(1 + 100\,\alpha),$$

$$T_{100} - T_0 = 100.$$

The first of these is one of the two ways of integrating equation (2); the second equation defines, in terms of experiment, the mean temperature coefficient at constant pressure of the gas used in the experiment; while the last is a mathematical definition. The limits of integration are the two temperatures of the ice point and the steam point.

If we factor out a mean value of c_p (which varies but slightly within these limits) calling it $\bar{C}_p$ and call the value of the remaining definite integral $(I_{100} - I_0)$, noting that $1/v_0 = \rho_0$ the density of the gas at the given constant pressure and at the ice point, then the combination of these three relations results in

$$T_0 = \frac{1}{\alpha} + \frac{T_0(T_0 + 100)}{100\alpha}\,\rho_0 \bar{C}_p(I_{100} - I_0)$$

without approximation.

The first term on the right is the temperature of the ice point on the scale of the gas in question. The second term is the quantity that must be added thereto in order to derive the same temperature on the thermodynamic scale. It is small and may be called a "correction." Its relative magnitude will be seen to come out only about 0.0037 times the first term.

Now the accuracy of this term is limited by that of the determinations of μ, namely an order somewhat under one per cent. Expressed in degrees this would come to about 0°.01 C. The following two approximations therefore are permissible: First, T_0 may be replaced by 273; secondly, the evaluation of the integral

$$\int_{T_0}^{T_{100}} \frac{\mu}{T^2}\,dT,$$

in which formula (9) or formula (10) must be used, t may be treated as if it were $T - 273$ in formula (9) and in formula (10) τ may be treated as if it were T. Further, or successive approximations are unnecessary. The above formula, with these approximations, then becomes

$$T_0 = \frac{1}{\alpha} + \frac{273 \times 373}{100\alpha}\,\rho_0 \bar{C}_p(I_{100} - I_0). \tag{12}$$

The value of $(I_{100} - I_0)$ has been computed and found to be

$+ 0.000306$ by (10), the three-constant formula for μ,

and

$+ 0.000308$ by (9), the five-constant formula for μ,

the unit of pressure still being one meter of mercury at 0° C. in this locality.

The expression of this result in terms of absolute units and the calculation of the remainder of the formula were carried out by means of the following data:

$$\begin{aligned} \text{density of mercury} &= 13.595 \text{ gm. per cm}^3, \\ g &= 980 \text{ cm. per sec}^2, \\ \bar{C}_p &= 241 \text{ cal per gm. per deg.}, \\ 1 \text{ cal.} &= 4.187 \times 10^7 \text{ ergs.} \\ \rho_0 &= 0.001293 \frac{100}{76} \text{ gm. per cm}^3, \\ \alpha &= 0.00367282. \end{aligned}$$

The value for g is rounded off from 979.937, the figure given as determined in this locality by the U. S. C. and G.S.; that for $\bar{C}_p$ is a mean taken from the papers of Swann and Scheel and Heuse already mentioned. The value for α was determined with great care and precision by Chappuis[37] at the standard thermometric pressure of one meter of mercury. The reciprocal of this is 272.270.

The correction term in (12) obtained by use of these data are

1.093 by the three-constant formula

and

1.100 by the five-constant formula,

whence, for the thermodynamic temperature of melting ice, we get

$T_0 = 273°.36$ by the three-constant formula

and

$T_0 = 273°.37$ by the five-constant formula.

The other most recent calculations are by Buckingham (1908) using the Joule-Thomson coefficient for various gases adjusted into a single reduced formula by the "law of corresponding states," and by Berthelot (1907) using the characteristic equation. Previously in 1903, he had computed values on the basis of the Joule-Thomson effect. These results are collected in Table IV.

TABLE IV.

Author.	T_0.	Gas.	Method.	Reference Used Here.
Buckingham (1908)	273 273	Air	J-T effect	Buckingham[31] (1908)
	273.286	N_2	"	"
	273.049	H_2	"	"
	273.267	CO_2	"	"
Berthelot (1903)	273.13	H_2	"	Buckingham[31] (1907)
		N_2		
		CO_2		
		Air		
Bertholet (1907)	273.04	H_2 in Pt-Ir (1)	Characteristic equation	Berthelot[32] (1907)
	273.07	" " " (2)		
	273.10	" in *verre dur*		
	273.09	N_2		

The value arrived at in this paper is higher than any of these; and, further, it will be noted that the method by the Joule-Thomson effect gives higher values than does the method using the characteristic equation of the gas. This fact has been noted by Buckingham and others but has not been considered to be satisfactorily explained. Rose-Innes and Berthelot (the latter while discussing his values obtained from hydrogen) have suggested the possibility of a surface action at the walls of the containing bulb, such as the formation of a layer of gas whose density is different from that to be found in the interior. This, of course, affects the main term $1/\alpha$.

Pressure Coefficient of α.—A partial comparison may be made here by taking into consideration the pressure coefficient of α found by Chappuis[37] for nitrogen and that deducible for air from the results of this paper. Reference to equation (12) will show that the correction term is proportional to the density ρ_0 (neglecting the pressure effect in μ, an influence of the second order) and hence proportional to the pressure, which, in the present units, has the value 1. T_0, being a constant, this term is, therefore, the pressure coefficient of the reciprocal of α. The pressure coefficient for α, then, is computed to be 0.0000147 for air, while Chappuis finds the value 0.0000119 for nitrogen, or about four fifths as much, an agreement which, at least, is qualitative.

Correction to the Constant-pressure Air Thermometer between the Ice and Steam Points.—Here, since by definition, the centigrade gas and centigrade thermodynamic scales must agree at both end-points, a closer agreement among the results from various sources is to be expected.

We have, as before, the general relations

$$\frac{v}{T} - \frac{v_0}{T_0} = \int_{T_0}^{T} \frac{\mu c_p}{T^2} dT \equiv \bar{c}_p(I - I_0)$$

and

$$v = v_0(1 + \alpha t),$$

defining t on the gas scale in question.

Now let

$$T - T_0 = t_a$$

defining t_a on the thermodynamic scale and

$$T_0 = \frac{1}{\alpha} + \eta$$

where η stands for the correction term in (12).

Therefore, since $v_0 = 1/\rho_0$,

$$T_0(1 + \alpha t) - T = TT_0\rho_0\bar{c}_p(I - I_0).$$

The left-hand member becomes

$$- t_a + T_0\alpha t = - t_a + t + \alpha\eta t.$$

Therefore the formula at once reduces to

$$t_a - t = \alpha\eta t - TT_0\rho_0\bar{c}_p(I - I_0),$$

in which $t_a - t$ is the correction sought.

Replacing η now by its expression in (12) and noting that, for the same reasons as before it is permissible, in the right-hand member, to identify t with t_a, c_p with C_p, and to replace T_0 and $1/\alpha$ by 273, the equation finally becomes

$$t_a - t = 273\rho_0\bar{c}_p\{3.73(I_{100} - I_0)t - (I - I_0)(t + 273)\}, \qquad (13)$$

which, inspection shows, vanishes at both the ice and steam points, as, of course, it should. The values of $\bar{C}_p$ and ρ_0 are the same as those given for the computation of (12). $\bar{C}_p$ and $\bar{c}_p$, strictly speaking, are not identical, owing to the differing limits of their respective integrals, but it is obvious that their difference is not sufficient to affect the computations.

Corrections $(t_a - t)$ calculated by this formula for every 10° C. are to be found in the last column of Table V. The other columns are copied from Buckingham's article in the Phil. Mag., 1908.[31] The corrections are negative, that is, the numbers in the table are to be subtracted from the constant-pressure readings. The new values and those of Berthelot in this instance are seen to be practically identical. Chappius (*loc. cit.*), moreover, states that the air and nitrogen scales are sensibly the same in this interval; so that we have here a real basis for comparison. This is agreement within the accuracy of gas thermometry.

TABLE V.

Thermodynamic Corrections to the Constant Pressure Nitrogen Scale Obtained by Various Writers, Compared with the Corrections to the Constant Pressure Air Scale Deduced from the Joule-Thomson Effect. 1,000 mm. = pressure.

t°C.	Rose-Innes, 1901.	Callendar, 1903.	Berthelot, 1903.	Buckingham, 1907.	Mean.	This Paper (Air), 1916.
10	0.0120	0.0109	0.010	0.0078	0.010	0.0100
20	0.0205	0.0188	0.017	0.0137	0.017	0.0170
30	0.0261	0.0236	0.022	0.0179	0.022	0.0212
40	0.0288	0.0260	0.024	0.0203	0.025	0.0235
50	0.0289	0.0260	0.024	0.0209	0.025	0.0238
60	0.0269	0.0240	0.022	0.0198	0.023	0.0218
70	0.0228	0.0204	0.019	0.0172	0.020	0.0189
80	0.0168	0.0151	0.014	0.0129	0.015	0.0141
90	0.0092	0.0081	0.007	0.0071	0.008	0.0068

Variation of c_p with Pressure.—Recent work of Holborn and Jacob[38] on c_p for air at 60° C. and at pressures from 1 to 200 atmospheres affords a further comparison of the present work with that of other observers in that the Joule-Thomson effect can be utilized to evaluate the pressure coefficient of c_p.

Writing equation (2) in the form

$$\mu c_p = T\left(\frac{\partial v}{\partial T}\right)_p - v$$

and differentiating with respect to T at constant p, we get

$$\mu\left(\frac{\partial c_p}{\partial T}\right)_p + c_p\left(\frac{\partial \mu}{\partial T}\right)_p = T\left(\frac{\partial^2 v}{\partial T^2}\right)_p = -\left(\frac{\partial c_p}{\partial p}\right)_T, \tag{14}$$

the last member following directly from a well-known equation in thermodynamics.

Now the left-hand member can be evaluated by using either formula (9) or (10) for μ and (say) Swann's values (*loc. cit.*) of c_p and $(\partial c_p/\partial T)_p$. It should be noted that, in regard to units, c_p may be expressed in calories per gm. per deg., since the equation is homogeneous in that physical quantity. Also since μ is here expressed in degrees per meter of mercury and since the data of Holborn and Jacob for $(\partial c_p/\partial p)_T$ are expressed in atmospheres for the pressure unit, the left hand member must be multiplied by 0.76 to make the two sets of results comparable. Finally T must be put equal to $273 + 60 = 333$, the temperature of Holborn and Jacobs' experiments.

Now Swann gives at one atmosphere,

$$c_p = 0.241 \quad \text{and} \quad \left(\frac{\partial c_p}{\partial T}\right)_p = 0.000016,$$

then by the 3-constant formula (10) also at 1 atmosphere

$$\mu\left(\frac{\partial c_p}{\partial T}\right)_p = 0.0000047,$$

$$\text{and} \quad c_p\left(\frac{\partial \mu}{\partial T}\right)_p = -\,0.0003901.$$

The sum of these two (of which the first is almost negligible) is $-\,0.0003854$. Multiplying by 0.76 we get

$$\left(\frac{\partial c_p}{\partial p}\right)_T = 0.000293 \text{ cal. per gm. per deg. per atm.}$$

The value of this quantity from Holborn and Jacobs' empirical interpolation formula, namely,

$$10^4 c_p = 2413 + 2.86p + 0.0005p^2 - 0.00001p^3,$$

is

0.000286 cal. per gm. per deg. per atm.

and from their observations at their lowest range of pressures alone (namely 1 to 25 atmospheres) it is

0.000312 cal. per gm. per deg. per atm.

The agreement here is about as good as would be expected. Moreover it is corroborative as regards a comparison between two widely different forms of continuous flow experiments.

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