THE JOULE–THOMSON EFFECT IN CARBON-DIOXIDE. I. EXPERIMENTAL.

BY FREDERICK E. KESTER.

HISTORICAL SUMMARY.

THE original Joule experiments, the aim of which was the determination of the amount of work done against the forces of intermolecular attraction when a gas expands without doing external work, were performed in 1844.[1] The apparatus, used by him, consisted of two copper flasks, each of about 2.2 liters capacity, joined by a pipe and a stop-cock, which opened or closed the connection between them ; the whole was submerged in a water calorimeter. The air having been removed from one of the flasks by pumping to a very low pressure and the test gas having been pumped into the other to a high pressure, it is evident that, upon opening the stop-cock, the expansion of the gas to twice its original volume, took place without the performance of external work. Any fall or rise in the temperature of the gas as a whole must have meant a decrease or an increase in the kinetic energy of its molecular motions with an equal increase or decrease in the potential energy of molecular separation. But, in spite of the facts that initial pressures as high as 22 atm. were used and that the calorimeter was so shaped that the water used was reduced to the smallest allowable amount, no noticeable change in the temperature of the bath occurred. It must be regretted that this apparatus cannot be made sensitive enough to measure the amount of energy changed from one form into the other during the expansion, for here the effect sought is a pure one — no part of the internal energy is expended in external work — an advantage which no other form of apparatus possesses.

It was during a report by Joule, upon these experiments, before the Royal Society in 1844, that Thomson became interested in the

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[1] J. P. Joule, Phil. Mag. (3), **26**, 369, 1845 ; Joule's Scientific Papers, I., 172.

problem ; to him is due the porous plug form of apparatus. With it the method employed is to maintain constant gas pressures on the two sides of a plug of porous material, packed tightly into a short length of the gas path. The flow through the plug is then a steady one, of such character that practically no work is done in giving the gas a kinetic energy due to an increase in its stream velocity — the flow is a diffusion process. Here, however, the thermal effect obtained is no longer a pure one ; the difference in the temperatures of the gas before it enters and after it leaves the plug is due both to the work done against molecular attractions and to the difference between the values of the product $p \cdot v$ ($p =$ pressure ; $v =$ specific volume) which exist on the two sides of the plug. This difference is the difference between the amount of work done upon one gram of the gas in forcing it into the porous plug and the amount done by one gram of the gas as it leaves the plug. The product $p \cdot v$ will have different values on the two sides of the plug, not only because the particular gas in use does not follow Boyle's law ; the difference in temperature, caused by the change in the potential energy of the molecules, will of itself establish a difference between the values of the product. Just how large a fraction of the total thermal effect this external factor may become in special cases will be shown later in a discussion of experimental results. I speak of it here at some length in order to make as clear as possible the errors which are liable to affect any theoretical discussion involving (implicitly or explicitly) a separation of the total observed thermal effect into its component parts ; although the whole may have been measured with considerable accuracy, it may not be possible to make this separation with the same nicety.

The series of researches carried on by Joule and Thomson,[1] with the porous-plug form of apparatus, extended through the years from 1852 to 1862, and included work on air, oxygen, nitrogen, carbon dioxide, hydrogen and mixtures of two or more of these.

Following the same principle which underlies the porous-plug experiment, Hirn[2] made a series of observations upon the cooling

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[1] Joule and Thomson, Phil. Mag. (4), 4, 481, 1852 ; Phil. Trans., **143**, 357, 1853 ; Phil. Trans., **144**, 321, 1854 ; Phil, Trans., **152**, 579, 1862 ; Joule's Sci. Pap., II., 216 ; Kelvin's Math. and Phys. Pap., I., 333.

[2] G. A. Hirn, Théorie Mech. de la chaleur (3 ed.), II., 387.

effect experienced by steam (in both the saturated and superheated states) when it expands from various pressures to atmospheric pressure. The expansion in these experiments did not take place through a porous-plug, but through a small opening into a large, well-jacketed space; in order to destroy (partially at least) the high stream velocity resulting from the free expansion, the steam was made to impinge upon a flat surface placed only a short distance in front of the opening through which it expanded.

Then, returning to the original form of apparatus used by Joule — that of the double flask — Cazin[1] performed a number of experiments upon air, carbon dioxide and hydrogen. In his work, although the form of apparatus was essentially the same as Joule's, the method of experiment was very different and much more complicated. In its main features the method was as follows: With the large stop-cock between the flasks open, the pressure of the contained gas was measured by suitable manometers, and the temperature, brought to the same value in the two chambers, was observed. The stop-cock was closed, a *part* of the gas was pumped from one flask into the other and the flasks and contained gas were brought to the original temperature, under which conditions the new pressures were measured. Then with the stop-cock wide open, the gas was allowed to expand suddenly from the one flask into the other; as soon as the pressures had become equal the cock was closed, and a series of pressure and time readings were taken while the temperatures were brought again to the original value. Finally the stop-cock was opened, the temperatures were brought a fourth time to the same original value and the common pressure was measured. By this last step any loss of gas, which may have occurred during the pumping or expansion, could have been detected. The pressure and time readings were used to indicate the value of the common pressure at the time of opening the stop-cock; the knowledge of this pressure completed the data, from which the state of the gas at each step was determined. The whole process could then be subjected to thermo-dynamic analysis. The relation between this method of procedure and that of Joule's will be readily understood by observing that Cazin measured (implicitly)

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[1] A. Cazin; Ann. de Chim. et de Phys. (4), 19, 5, 1870.

the changes in temperature of the gas by means of the pressure changes. On account of numerous complications the results of these experiments are open to serious criticism, and in the later discussion of the results of the various researches they will not be considered.

From the time of Cazin's work no other experimental results upon this problem appeared until those of Natanson[1] were published in 1887. His work was done with the porous-plug form of apparatus, the same in all important features as that of Joule and Thomson. Natanson's observations were made upon only one gas, CO_2, and at room temperature. The method of procedure was to keep the difference of the pressures on the two sides of the plug very nearly the same (about one atmosphere) in all of his experiments and to vary the initial pressure of the gas at will, whereas in the Joule-Thomson researches the pressure behind the plug was kept the same (barometric pressure) and the pressure in front varied. The highest pressure used by Natanson was nearly 25 atm., and between the lowest and this highest pressure he found a decided dependence of the cooling effect of CO_2 upon pressure, whereas Joule and Thomson had been unable to detect (up to 6 atm.) any such dependence in the case of any gas. Natanson, in the report on his work, lays special emphasis upon the remarkable purity of the gas used in his experiments, and criticises the Joule-Thomson results on this ground, though the criticism as made is not a fair one.

In 1898 Witkowski[2] published a report on the determination of the cooling effects in air when it was allowed to expand through a series of porous plugs spaced along a considerable length of tube. Nothing but a review of this article has been available in the libraries consulted; consequently no judgment can be given here concerning the value of the results.

More recently a very interesting determination of the inversion temperature of the Joule-Thomson effect in hydrogen was made by Olszewski.[3] The expansion in this case took place through a small

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[1] E. Natanson, Wied. Ann., **31**, 502, 1887.

[2] A. W. Witkowski, Rozprawy der Krakauer Akad., math-naturw. Klasse, **35**, 282, 1898; Beiblätter, **23**, 411, 1899.

[3] K. Olszewski, Ann. d. Phys., **7**, 818, 1902.

opening into a large space in which the jets and eddies were dissipated into thermal (molecular) motions, as in Hirn's experiments. In the expansion chamber was placed a delicately constructed platinum thermometer coil, and this chamber together with the spiral tube which led the hydrogen to the small jet-opening was submerged in a cooling bath. The temperature of the bath was so adjusted that, after all parts of the apparatus had reached the proper thermal condition and the jet was opened, no change in the resistance of the platinum coil could be detected.

The present research, the results of which are to be described in this paper, was undertaken at the suggestion of Professor Nichols. It was started in the past academic year (1903–4) in Professor Voigt's division of the Physical Laboratory in Göttingen and the results of this preliminary part of the work were published in January of this year.[1] The general arrangement of apparatus, both in Göttingen and in Ithaca, has been in principle the same as that of Joule and Thomson and of Natanson. One essential difference lies in the use of thermo-electric junctions placed in the gas path, instead of thermometers, for the measurement of the temperature changes. Various important alterations, in the present apparatus, from the design and from the method of manipulation of last year will be mentioned below.

I shall express here my sincere thanks for the valuable suggestions and for the kindly encouragement and direction given to me by Professor Nichols and Professor Merritt. I wish also to thank Professor Moler for many suggestions as to the construction of apparatus. Nothing in my work has been more pleasant than the uniformly courteous treatment which I have found throughout the department.

Description of Apparatus.

A general diagram of the apparatus is given in Fig. 1. The gas was obtained in the usual CO_2 cylinders which contain about 20 pounds of liquid CO_2. This quantity is equivalent to 4,500 or 4,600 liters of gas under normal conditions. The great advantages of such a source lies in the high pressures and in the steadiness of the pressure under which the gas is delivered from them: at room tem-

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[1] F. E. Kester, Phys. Zeitschr., 6, 44, 1905.

perature the vapor pressure of CO_2 is 55–60 atm. In order to avoid a great decrease in the temperature of the liquid, due to evaporation, the cylinders were placed in a water bath while in use; this was especially necessary when the determinations were made at high pressures, for then the quantity of gas delivered to the apparatus was very great.

The water vapor, carried along with the gas, was removed by calcium chloride contained in the U-shaped drying tube. Examination of the drying material, when it was thought advisable to inspect the condition of the tube, left no doubt as to the thoroughness of its action; the chloride in the last branch of the tube seemed perfectly dry, and was easily shaken out; that in the first branch (at least that in the top part) was somewhat moist; how far down this state of affairs extended could not be discovered for the material could not be shaken out. The tube was washed out, thoroughly dried and refilled with fresh chloride.

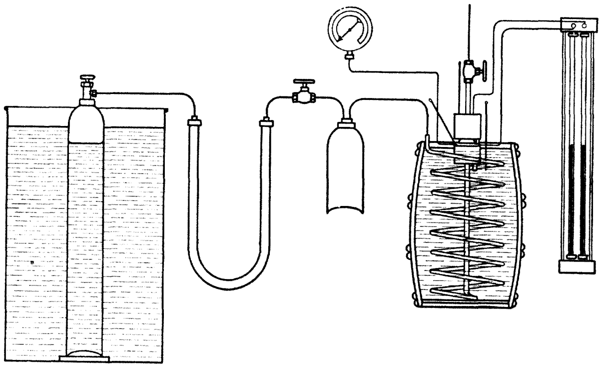

Fig. 1.

The control valve through which the gas next passed is well adapted, by its form of construction, to this use. Its needle is small — about 2.5 mm. in mean diameter — and only slightly conical. The regulation of the pressure in the part of the apparatus beyond it could be made with considerable nicety by means of a short lever arm attached to the hand-grip of the valve.

From the valve, the gas next passed into the small cylinder which served as a pressure equalizing reservoir. Its capacity is 4.3 liters; the volume of this part of the apparatus — from valve to valve — is very nearly 5 liters.

The copper tube, which led the gas from the equalizing chamber up to the porous plug is 10 mm. in inner diameter, 1.25 mm. in wall thickness and about 8 m. long. Before it was wound into spiral form its complete length was threaded with long, spiral, steel lathe-turnings. This was done to break up the possible formation of any well defined stream lines, which would prevent the gas from coming thoroughly into contact with the walls of the tube. The mass of water in which the spiral was submerged was about 100 kg.

After passing through the plug the gas escaped through the second needle valve into the open.

The construction of the nozzle, in the middle of which the porous plug is held, is shown in detail by Fig. 2. The same plug was used for all the experiments of this year's work; it contains 3.4 g. of clean cotton fiber, compressed between two thin perforated disks of steel into a space 15 mm. in diameter and 24 mm. in height. The material immediately surrounding it is the red "vulcanized fiber" which is found so useful in electrical construction. It is inferior to hard rubber in heat insulation, but rubber could not be considered for this purpose because it becomes semiplastic long before it reaches the temperature of boiling water. The small tube which holds the upper steel disk in place is also of this same material. The steel cylinder, which surrounds the vulcanized fiber nozzle, is provided with screw caps as shown; lead washers are used in packing the joints. The thermo-electric junctions are made of steel and constantan wires 0.18 mm. in diameter and are carried by plugs of vulcanized fiber. The wires are cemented in place with a mixture of litharge and glycerine — a cement which serves remarkably well for such purposes. The plugs themselves are held hard upon the seats, cut for them in the steel cylinder, by means of steel encircling rings, each of which is provided with a slot on one side and a set screw diametrically opposite. Pressure tubes lead into the gas path at points indicated in the drawing; one is joined to the pressure gauge (see Fig. 1); the others to the mercury pressure-differenee manometer. Finally the two oil cups, one surrounding the lower part of the nozzle, the other the upper part, are held in place as shown. Each of these baths as well as the large water bath is provided with a stirrer; a small motor furnishes power for all of them.

Electrical heating coils were used in the various baths to maintain constant temperatures when determinations were made above room temperature ; ice, in the large water bath, and copper tubes, in the oil baths, through which cold salt-water flowed, were used in the determinations at 0° C.

This part of the apparatus is in design quite different from the nozzle used last year in the preliminary part of this research. The changes were made in order to accomplish (1) observations at higher temperatures than would have been possible of attainment with hard rubber ; (2) the insertion of the thermal junctions into place without the necessity of unsoldering and resoldering after they had been calibrated ; (3) a definite control of temperatures about the two parts of the nozzle.

The whole apparatus was designed to work up to a pressure of 50 atm. with a factor of safety of at least 2 in all parts. The highest pressure at which determinations were made was 41 atm.

A set of the usual gas analysis pieces was used to determine the amount of impurity in samples of the gas taken from the apparatus after a determination was finished. A solution of KOH was used to absorb the CO_2 and the residue was then measured.

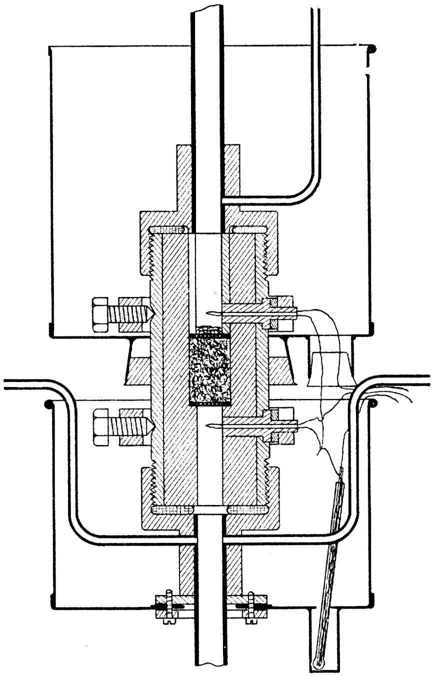

Fig. 2.

The electrical circuits are shown diagrammatically in Fig. 3. The method involved is that of the potentiometer somewhat modified. The two thermo-electric junctions in the gas path constitute a couple for the measurement of the difference of temperatures above and below the porous-plug ; the junction in the bath and one of the others serve to measure the difference between the bath temperature and the gas temperature. The steel wires *I* are brought to a common junction; the constantan wires *C* are joined one to each of the three wires which lead to the switch *S* and to the potentiometer wire *AB*. To avoid, as far as possible, junctions between dissimilar metals all lead wires and the wire *AB* are of constantan; an important advantage results also from the fact that the resistance of *AB* remains constant even though the room temperature vary considerably.

The closed circuit, of which the potentiometer wire is a part, consists of a dry cell as a source of current, a variable resistance (part of which is a liquid resistance for fine adjustment of current strength), the potentiometer wire *AB* and a Weston voltmeter used as an ammeter. The sensitiveness of this instrument is such that a full scale deflection is caused by a current somewhat less than 0.01 amp. In order to use it in the circuit, a connection is inserted so that the current flows through only the moving coil (of about 70 ohms resist.).

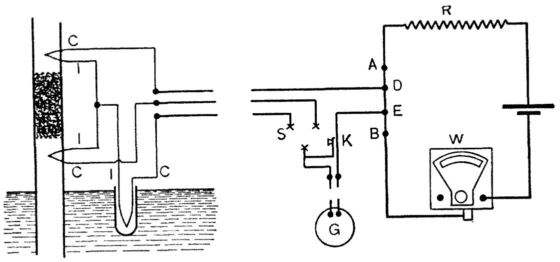

Fig. 3.

The switch *S* deserves special notice. In circuits where the electromotive forces are as small as those which are handled here (the greatest value of the e.m.f. in this part of the circuit during observations was about 0.00007 v., and the aim, during the construction of the circuits, was to keep the stray e.m.f.'s within one five-hundredth of this maxim) no ordinary form of switch can be used satisfactorily even when extreme care is taken in the thermal isolation of the working parts. The construction of the switch is shown in Fig. 4; an ordinary three-way glass stop-cock was used for the purpose, and mercury serves as the conducting material.

No description will be necessary to make the drawing clear, unless it be such as will call attention to the precaution of sealing thin-walled glass tubes onto the heavy ones where they entered the mercury jacket. The three constantan wires which lead to the switch enter the tubes from above and dip into the mercury. This use of stop-cocks as electrical commutators and switches is due to des Coudres.[1]

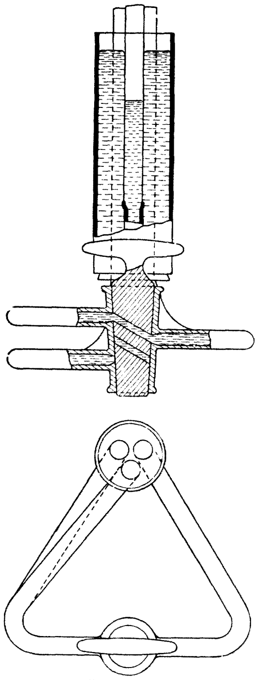

Fig. 4.

The galvanometer G is of the moving coil type, It is the one which was constructed in this laboratory by White and was fully described by him last year in this REVIEW.[2] At all soldered junctions, even where wires of the same metal joined and especially where dissimilar metals joined, precautions were taken to keep corresponding junctions at the same temperature. But in the galvanometer different materials were used in the various parts, and this precaution could not readily be taken. Trouble from this source was avoided by using a piece of constantan wire as a short-circuiting key K. With S open and K closed, a deflection of the galvanometer needle usually occurred; the steady reading of the galvanometer with S and K in these positions was taken as the zero point of the apparatus at the time. A long study of the circuits showed that, with a pair of the steel-constantan junctions submerged in the same bath of mercury as near each other as possible, with no current flowing in the potentiometer wire AB and with S properly closed, the galvanometer deflection never differed from that obtained by opening S and closing K as much as the maximum error, mentioned above, would allow. This method of taking the zero point was, therefore, justified.

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[1] Th. des Coudres, Wied. Ann., 43, 673, 1891.

[2] W. P. White, PHYS. REV., 19, 305, 904.

CALIBRATION. MANIPULATION. SOURCES OF ERROR.

No great amount of care was necessary in order to measure gas pressures and pressure differences with sufficient accuracy. The observations of last year upon CO_2 at room temperature, showed that the dependence, if any, of the thermal effect upon pressure is so slight that the use of a pressure gauge with even tolerably large scale errors would have been allowable, provided that the mechanism be delicate enough to indicate small changes in pressure. The instrument used in the present apparatus has a range of 1,000 lbs. per sq. in. and a least count of 4 lbs.; motions of the pointer corresponding to pressure changes of 0.5 lb. could readily be detected and slight tappings on the gauge insured a corresponding freedom of motion of the mechanism.

The mercury pressure-difference manometer was read by means of clips which fit nicely to the glass tubes and reach over to a wooden meter bar between the tubes. An error of as much as 1 mm. in the determination of a total height of mercury of 700 or 800 mm. would have been less serious than the errors which could not be avoided in the temperature measurements.

Each of the three baths was provided with a Baudin thermometer of 100° range subdivided to fifths of a degree; readings to fiftieths could easily be made. The stem of each one was calibrated throughout its length and corrections were calculated from this calibration and from determinations of the fixed points. The thermometer in the large bath was always submerged to a point only a little below the top of the mercury thread; therefore no stem correction (due to a difference between the temperature of the stem and that of the bath) was necessary for this one. Auxiliary thermometers were tied to the stems of the other bath thermometers and stem corrections, calculated from the readings of the auxiliaries and from the lengths of mercury threads out of the baths, were applied.

The first step made in the calibration of the electrical part of the apparatus was to check the accuracy of the Weston instrument scale at small intervals. This was done with the aid of a potentiometer. The departures of the ammeter readings from a proportionality to the strengths of current which produced them was in no case greater than 0.2 of a scale division.

In the calibration of the thermal junctions three Baudin thermometers, each of 12° range, subdivided to fiftieths of a degree, and a Golaz thermometer, of similar construction, were used. The Baudin thermometers (0°–13°, 12°–23°, 22°–33°) were sent to the National Bureau of Standards for comparison with the standard thermometers of that institution. After their return to this laboratory the Golaz was carefully compared with the Baudin of 12°–23° range and these two were used in the actual calibration of the working thermal junctions. By means of a magnifying eye-piece, which was made for this purpose, thermometer readings were estimated to 0°.001 ; errors due to jumping of the mercury threads were avoided as far as possible by taking readings while the temperatures were slowly rising.

It was, of course, not to be expected that accuracy such as this could be attained in baths when the temperatures were far from that of the room, and as the junctions were to be used in determinations at temperatures from 0° to 100° some method was necessary by which a careful calibration at room temperature could be extended. This was done by use of an auxiliary thermal couple (the working junctions could not be used on account of the length of wires necessary). One junction of the couple was kept at 0° C. while the other was carried over the range of temperatures from 0° to 100°. For this part of the calibration the potentiometer wire (*AB* of Fig. 3) was made of such length that the points *D* and *E* were 100 cm. apart. The resistance of this length of wire having been measured and the constant of the ammeter being known, it was possible to reduce the ammeter readings to micro-volts. The parabola

$$e = a \cdot t + b \cdot t^2$$

was then fitted to the observations. The third column of the following table gives the e.m.f.'s calculated from this equation with $a = 50.8_4$ and $b = 0.021_9$. The significance of the columns of residuals will be better understood when it is stated that one tenth of an ammeter division is equivalent to about 4 micro-volts of thermo-electromotive force.

Temperature (Degrees).	E.M.F. (Microvolts).		
	Observed.	Calculated.	Residuals.
18.78	965	962	+3
0.08	3.0 (?)	4	−1
2.07	101	105	−4
2.14	102	108	−6
7.23	364	369	−5
7.29	367	372	−5
7.40	375	377	−2
11.77	596	601	−5
11.80	601	603	−2
11.81	601	603	−2
21.27	1,091	1,091	
21.24	1,087	1,089	−2
21.20	1,087	1,087	
26.03	1,337	1,339	−2
25.96	1,336	1,335	+1
25.91	1,335	1,332	+3
31.91	1,644	1,645	−1
31.72	1,635	1,636	−1
31.59	1,625	1,629	−4
99.52	5,276	5,276	

From the above equation we have as the thermo-electric power of this particular steel and constantan

$$de/dt = a + 2bt = 50.8_4 + 0.043_8 \cdot t = 50.8_4 (1 + 0.00086_2 \cdot t)$$

The determination of the "temperature coefficient" (0.00086_2) of thermo-electric power of these metals was the aim of this part of the work.

The actual calibration of the working junctions at room temperature was next made. Two mercury baths were used for this purpose; the mercury was contained in two small, cylindrical Dewar bulbs submerged side by side, nearly to their tops in the same bath of water. The thermal junctions were protected with thin coatings of collodion and one was placed in each of the mercury baths close to the bulb of one of the two thermometers mentioned above. The long potentiometer wire was replaced by a short constantan wire 1 mm. in diameter, and *DE* was made 14 mm. (resistance about 0.009 ohm).

Fig. 5 shows the results of a calibration, made before determinations on the thermal effect had been begun. Only one calibration was made before the determinations because this one checked so closely two calibrations of a couple, which was broken before it could be used, that more were considered unnecessary. The intention was to make a second calibration after all determinations had been finished, but in removing the junctions from their places, one of the small plugs was broken ; recalibration was therefore impossible. The fact that the curve does not pass through the origin of coördinates is easily explained by a change in the thermometer corrections after comparison ; with both junctions in the same mercury bath, with no current in the potentiometer and with the switch *S* properly closed no deflection of the galvanometer occurred. The working curve was therefore drawn to the same slope as the calibration curve and made to pass through the origin.

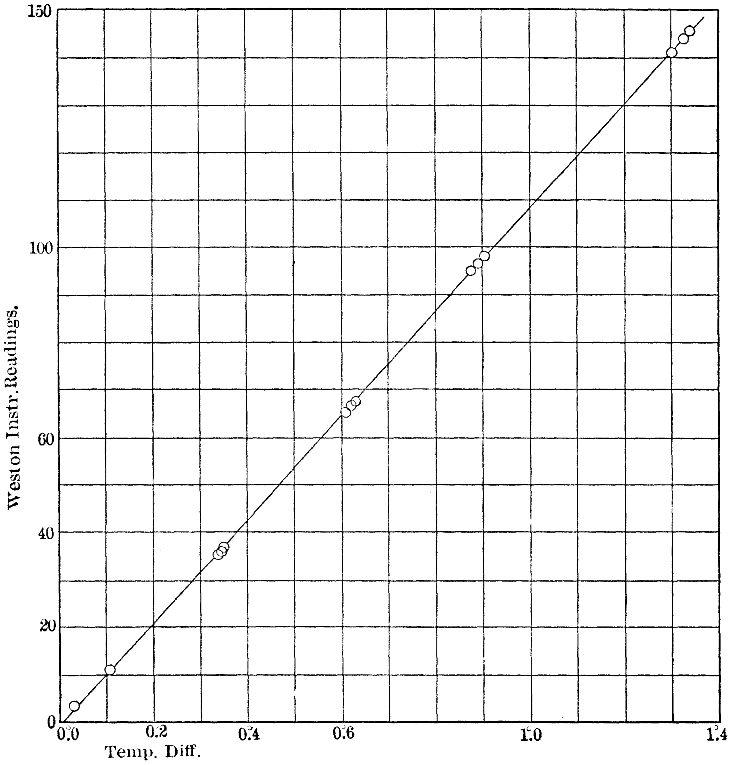

Fig. 5.

If w be used to represent the ammeter reading and τ the *difference* in the temperatures of the thermal junctions, the working curve is given by the equation

$$\tau = 0.00925 \cdot w$$

when the mean temperature, t, is 20°.3 C. Then from the work on the auxiliary couple we have

$$\left(\frac{w}{\tau}\right)_t = \left(\frac{w}{\tau}\right)_o (1 + 0.00086_2 \cdot t).$$

From these we find that

$$\left(\frac{\tau}{w}\right)_o = 0.00941$$

and therefore that

$$\left(\frac{\tau}{w}\right)_t = \frac{0.00941}{1 + 0.00086_2 \cdot t},$$

which enables us to transfer ammeter readings into temperature differences for any mean temperature. The sensitiveness of the ammeter, immediately after the calibration was completed, was found to be $5.83_6 \times 10^{-5}$ amp. per division. The sensitiveness was afterwards taken at intervals of several days; changes could be noticed (due apparently to weakening of the magnetic field) but they were so slight as not to affect the calibration.

After the calibration the collodion was dissolved from the junctions and these were put into their places in the nozzle.

In the manipulation of the apparatus three persons were necessary. It was the duty of the first to attend the control valve and by careful adjustment to maintain a constant pressure in the part beyond; the second person controlled the bath temperatures and read the thermometers and the pressure difference manometer; the third attended the galvanometer and ammeter readings.

In order to make a determination the baths were put into the proper condition, the pressure was brought to the desired value and the exit valve was opened until the pressure difference was about one atmosphere. The large water bath was kept as nearly as possible at constant temperature and the oil baths were brought to temperatures which were indicated from time to time by the electrical readings. The time necessary for a determination varied from fifteen minutes to an hour; in several cases even a longer time elapsed before steady conditions were attained.

In general the pressure difference, under which a determination was made, was not exactly one atmosphere. Correction was made to this unit by assuming a proportionality of the thermal effect to pressure difference — a law firmly established by the work of Joule and Thomson and again by that of Natanson.

The control of temperatures of the oil baths was a source of difficulty — especially in the determination at 0° C., for at this temperature it was necessary to use a flow of cold salt water through copper tubes submerged in the oil and the control was not an easy one. However, a determination was continued until the proper temperature control had been maintained sufficiently long to insure either a negligible or a calculable error due to this source. To obtain data from which approximate errors could be estimated from known errors in the bath temperatures, large changes in these temperatures were intentionally made from time to time and the resulting effects upon the temperatures of the gas stream were noted.

Of all the determinations which were made, two or three were discarded because the necessary corrections would have been too serious; four of the others were corrected, one to the extent of 0°.015, the other three by amounts not exceeding 0°.010.

It might seem, on first thought, that serious error would be caused by conduction of heat through the porous plug and around the plug through the material of the nozzle. But this transfer is at most only a small thing, and moreover is of such character as to eliminate itself; for the heat given up by the gas stream between the lower thermal junction and the plug will be almost exactly equal to that taken up by the stream in the corresponding region above the plug (the symmetry is broken only by the thin layer of gas between the main body of the nozzle and the small tube of vulcanized fiber which holds the upper steel disk in place).

During the determinations at high temperatures it was necessary to heat the gas before it reached the large spiral in order that it might enter the nozzle at, or very nearly at, the temperature of the bath. The heating was accomplished by applying a Bunsen flame, protected from air drafts, to the copper tube between the pressure equalizing cylinder and the bath. This method of heating cannot be made a very steady one and some fluctuations of temperature remained after the gas had passed through the spiral. The potentiometer settings were made more difficult on this account, but a steady watch was kept on the galvanometer behavior and it was found that the ammeter readings taken when the fluctuations were small were consistent with each other and also that at these times the difference between the temperature of the bath and that of the gas as it entered the nozzle was small.

RESULTS.

Determinations were first made at room temperature, the gas pressure being changed from one determination to another with the intention of finding the law of dependence of the thermal effect upon pressure. The results, as plotted from time to time, began to trace, with more or less certainty, a line parallel to the axis of pressures. The line was very nearly a verification of the results of last year, except that there was no indication of a decrease of pressure until a pressure of 41 atm. was reached. Here the result was considerably lower than those preceding. It was noticed however that the gas analysis, which was made at the end of the determination, indicated a higher percentage of impurity than any of the previous analyses had shown (see determination X. in the table below). It was then decided to delay the experiments and to make a search for purer gas.

The gas, which had been used up to this time, showed amounts of impurity varying from 4 or 5 per cent. (by volume), when taken from a full cylinder, to about 0.2 per cent. when from an empty one; the amount of impurity *gradually* decreased as the gas was used from the cylinders. Complete analyses of the gas were not made, but delicate tests for H_2S and for SO_2 gave negative results. These were considered possible components — the gas came from natural springs — and tests for them were essential because, if present, they would have been absorbed by KOH and would not have appeared as impurities in the partial analyses. Also a test for oxygen gave negative results, showing that the impurity was not air.

No better gas was found, however, and it was decided so to choose the cylinder, which was to furnish the gas for any determination, that two or more results could be obtained, at a given pressure and temperature, with amounts of impurity differing as widely from each other as possible. By this procedure a dependence of the thermal effect upon impurity could be determined, and the thermal effect for pure CO_2 could be found by extending the curves back to the axis of no impurity (see Fig. 6).

This was done and the results of the observations at various pressures and temperatures are contained in the following table. The gas

No.	Date.	Percentage Impurity.	Mean Pressure (atm.).	Mean Temperature.	Pressure Difference (cm. Hg).	Temperature Difference.	Same Corrected on Account of Bath Temperatures.	Temperature Difference per Atmosphere Pressure Difference.
XVI.	5/17	0.32	7.6	$-0^\circ.5$	68.6_6	$1^\circ.31_6$	$1^\circ.32_6$	$1^\circ.46_7$
XV.	5/11	0.32	7.6	$-0\ .6$	71.1_7	$1\ .37_1$		$1\ .46_4$
XI	5/4	2.1	7.6	$+0\ .8$	73.2_0	$1\ .32_8$		$1\ .37_9$
								1.39_6 at -0.6
XII.	5/9	0.28	14.4	$-0\ .4$	69.6_0	$1\ .34_6$		$1\ .47_0$
XIV.	5/11	0.75	14.4	$-0\ .6$	69.4_8	$1\ .34_3$	$1\ .32_8$	$1\ .45_5$
XVII.	5/17	0.20	21.2	$-0\ .6$	69.1_5	$1\ .33_2$		$1\ .46_4$
XIII.	5/9	0.72	21.2	$-0\ .6$	72.7_0	$1\ .36_9$		$1\ .43_1$
XVIII	5/18	1.7	26.4	$-0\ .5$	71.2_0	$1\ .36_3$	$1\ .36_7$	$1\ .45_0$
II.	4/19		7.6	20 .4	76.7_3	$1\ .19_9$		$1\ .18_8$
VII.	4/20	1.5	7.6	20 .4	74.5_8	$1\ .14_0$		$1\ .16_1$
VIII.	4/25	0.23	10.8	20 .5	73.6_9	$1\ .16_1$		$1\ .19_7$
III.	4/19		14.4	20 .4	76.1_7	$1\ .17_0$		$1\ .16_7$
IV.	4/19	0.20	21.2	20 .4	76.5_8	$1\ .17_7$		$1\ .16_8$
V.	4/19		25.2	20 .4	75.7_6	$1\ .18_6$		$1\ .19_0$
IX.	4/25	0.89	27.4	20 .4	76.1_2	$1\ .16_4$		$1\ .16_2$
XXI.	5/19	0.24	34.2	20 .4	71.1_3	$1\ .11_8$		$1\ .19_4$
XIX.	5/19	1.1	34.2	20 .4	76.8_8	$1\ .16_4$	$1\ .17_1$	$1\ .15_7$
XX.	5/19	0.45	41.0	20 .4	75.3_6	$1\ .17_4$		$1\ .18_4$
X.	4/25	2.2	41.0	20 .4	75.8_8	$1\ .13_2$		$1\ .13_4$
XXII.	5/24	0.17	7.6	39 .5	75.2_4	$1\ .03_3$ (?)	(Empty Cyl.)	$1\ .04_1$ (?)
XXIV.	5/24	0.24	7.6	39 .5	76.3_0	$1\ .04_8$		$1\ .04_4$
XXIII.	5/24	2.1	7.6	39 .5	75.5_0	$1\ .02_0$		$1\ .02_7$
XXX.	6/2	0.22	14.4	59 .5	76.2_5	$0\ .95_6$		$0\ .95_3$
XXVI.	5/26	1.3	14.4	59 .5	75.1_4	$0\ .93_3$		$0\ .94_4$
XXIX.	6/2	1.3	14.4	59 .5	76.1_6	$0\ .95_0$		$0\ .94_8$
XXXI.	6/15	0.42	14.4	79 .5	74.3_9	$0\ .85_0$		$0\ .86_8$
XXXIII.	6/16	0.20	14.4	96 .6	74.0_0	$0\ .74_7$		$0\ .76_7$
XXXII.	6/16	1.8	14.4	96 .5	77.1_4	$0\ .82_2$		$0\ .80_6$

presures and temperatures tabulated in it are the averages of the two values of each on the two sides of the porous plug. The last column gives the corrected thermal effects — corrected where necessary, on account of errors in one or the other of the bath temperatures, and also on account of the pressure-differences. These corrected values are plotted as ordinates of Fig. 6 with corresponding percentages of impurity as abscissas. The values of the thermal effect for pure CO_2 as indicated by the lines of Fig. 6 are then plotted as ordinates in Fig. 7, with corresponding temperatures as abscissas.

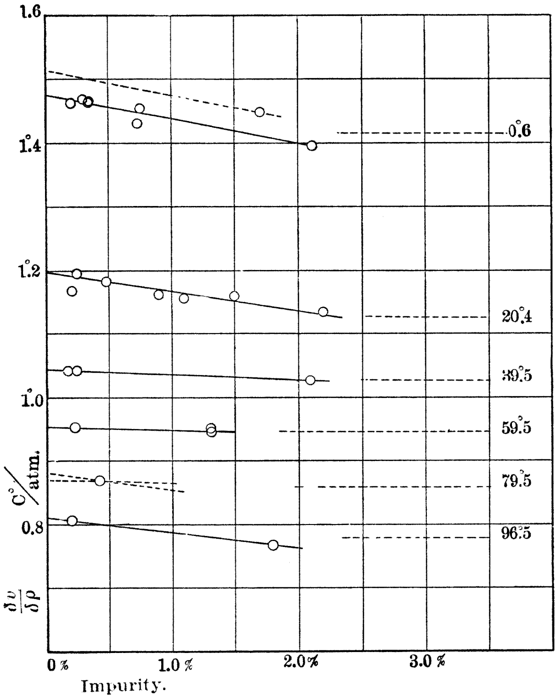

Fig. 6.

For the results obtained at 20° C. the lines of Fig. 6 intersect the axis of no impurity at nearly the same point for all pressures, 41 atm. being the highest pressure reached at this temperature. All except three of the results obtained at 20° are plotted in Fig. 6. No analyses of the gas were made for them (they were obtained before any serious dependence upon impurity was suspected). The determination at 0° C. exhibited the same peculiarity until a pressure of 26 atm. was reached. The result at this pressure gives a point on the impurity diagram considerably above the line which shows the dependence of the thermal effect upon impurity. In the results taken, both at 20° C. and 0° C., there seemed to be no regular dependence of the effect of impurity (upon the observed thermal effect) upon pressure. Accordingly the thermal effect for pure gas at 26 atm. pressure was assumed to be that indicated by a line drawn parallel to the line which represents the other results at the same temperature.

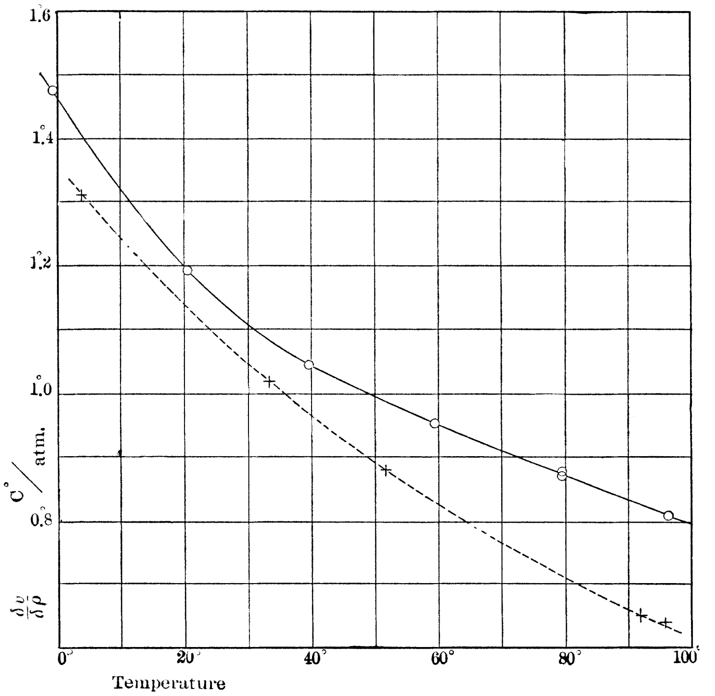

Fig. 7.

Several trials were made at 0° C. to reach higher pressures than this. CO_2 condenses at about 35 atm. when its temperature is 0°, and it had been hoped that determinations could be carried to within 3 or 4 atm. of this point. The behavior of the electrical circuits seemed to indicate that condensation of the gas occurred at the control valve, due to the severe cooling there. If this did occur it was, of course, present also in the case of determinations under high pressures at 20° C.; but at 20° the large copper spiral was able, probably, to cause a complete re-evaporation of the small globules of liquid. The determination at 26 atm. was made possible only by the application of a Bunsen flame to the copper tube just in front of the valve. Very likely the use of a spiral heating tube at this point would have made work at higher pressures possible, but, with the determinations at higher temperatures still to be made, there was no time for the necessary changes.

Of the three results obtained at 80° C. only the last one was kept. The other two were obtained under such unfavorable heating conditions that the behavior of the electrical part of the apparatus did not insure a great amount of confidence in them. The simple application of a Bunsen flame to the small copper tube just in front of the large water bath was found to be quite satisfactory in the determinations at 40° and at 60°, but when the heating became as vigorous as was necessary at 80°, this alone was not satisfactory. The behavior of the apparatus indicated serious irregularities in the effect of the flame, due perhaps to the fact that the gas in passing through the tube came more and less thoroughly into contact with the heated walls. With this explanation in view a corresponding remedy was applied. A length of 25 or 30 cm. of the tube at this place was filled with lathe turnings which served to stir the gas as it passed through the heated portion. With this precaution the observations at 80° and at 97° were fully as satisfactory as those at 60° had been.

An attempt was made, after the determinations at 97° were obtained, to add others at 80°, but a series of mishaps rendered these impossible. The most serious was the development of leaks at the nozzle, caused by the change from a high temperature to a lower one — the lead packing has a much greater coefficient of expansion than the steel of the nozzle. A repair of the leaks made necessary the removal of the thermo-electric junctions, but the plugs which carried them had become so firmly fixed in their places by the action of the high temperatures upon the packing materials that one of them was broken. This made even a recalibration of the junctions impossible. Determinations were discontinued. I may state here — merely as a fact of observation — that all of these accidents occurred while I was using the thirteenth cylinder of gas.

Since only one satisfactory determination was obtained at 80° the best indication, obtainable from it as to the magnitude of the thermal effect for pure gas at this temperature, is that given by the pair of dotted lines, drawn through the point which represents it in Fig. 6, one parallel to the line of results at 60° the other parallel to that at 97°. With this treatment the absence of other results at 80° increases the uncertainty (already present on account of errors of observation and of control) by an amount less than 0°.01.

The variations in the slope of the impurity lines from one temperature to another is a source of considerable concern. The indication of the results up to 60° is that the effect of the impurity becomes less as the temperature increases, but the line of results at 97° does not fulfil this indication. An interpretation of the variation of slope of the lines is offered by the results at 0° and at 20°. At either of these temperatures the determinations which were obtained with the purest gas are fairly consistent with one another — there is only one exception to this statement; result IV., taken at 20°, falls low. On the other hand the results at higher percentages of impurity are not consistent; especially is this true at 0°. So far as records of the determinations are concerned the latter results are just as trustworthy as the others. An attempt to represent the effect of impurity at each of the various pressures, say at 0° C., results in a series of lines whose slopes differ almost as much as do the slopes of the lines from one temperature to another. The only interpretation, then, which the results warrant, is that the impurity is not the same gas or gases in the various determinations. Unfortunately a complete analysis of the impurities was not made for each sample of gas taken from the apparatus. It is fortunate, however, that for almost all temperatures, results were obtained with very pure gas; the distance over which extrapolation is necessary in order to determine the thermal effects for pure gas is not a great one; the errors introduced by the uncertainty in the slope of the lines are, therefore, not serious.

The dependence of the thermal effect upon impurity is a part of an entirely separate problem — that of the Joule-Thomson effect in mixtures of gases — upon which some work was done by Joule and Thomson themselves. I hope to be able to take up this problem, with such modifications of the present apparatus as will be necessary, in order to verify and to make more complete the experimental results at present available. Recent developments in the theory of gas mixtures have made work in this region even more important scientifically than it was in the past century.

In a discussion of the results of the present research it is necessary to call attention to discrepancies between them and the results of previous researches. The preliminary results of last year are not wholly in accord with those of this year. The line

$$\frac{\partial\vartheta}{\partial p} = 1^\circ.19 - 0.0015 \cdot p$$

which was found to represent those obtained last year at 22° C. indicates values for low pressures which are tolerably consistent with the indication of the curve of Fig. 7 for the same temperature. For high pressures the discrepancies are serious and in view of the facts that, in the preliminary work, the amounts of impurity in the gas were not followed closely and that it was impossible to maintain proper temperature control about the nozzle, it is necessary to discard the results of last year in comparison with the present ones.

Considering then the work of Natanson, whose determinations were all made at room temperature (20° C.) and at pressures ranging from 1.5 atm. to nearly 25 atm., it is to be noticed first that the equation, given by him as a representation of his results,

$$\frac{\partial\vartheta}{\partial p} = 1^\circ.18 + 0.0126 \cdot p_m$$

where p_m is the average value of the pressures on the two sides of the porous plug, really does not represent them fairly. The values of the thermal effect plotted as ordinates, with corresponding values of p_m as abscissas, trace with considerable certainty a curved line which starts at about 1°.23 and rises, with steadily increasing slope as the pressure increases, to a value of about 1°.50 at 25 atm.

This very marked dependence upon pressure is not verified by the results of the present research. In the determinations made this year no dependence upon pressure was shown by the results at 20° although the pressure was carried as high as 41 atm.; and at 0° no dependence was found until a pressure of 26 atm. was reached; here the result indicated an increase in the thermal effect over the values at lower pressures. The result just mentioned is isolated and was, moreover, obtained under considerable difficulty; its indications must therefore, in all fairness, be rated as somewhat doubtful. However, in another paper further experimental evidence, deduced from Andrews' work on the compressibility of CO_2, will be given, which will tend to indicate again that such a change is altogether probable at this pressure.

To account for the discrepancy between Natanson's results and my own is not easy. There appears to be only one explanation and that is not entirely satisfactory; it rests upon the fact that, in his apparatus, the large copper tube, through which the gas passed before reaching the porous plug, was closely packed with lathe turnings in order to provide greater surface with which the gas would be brought into contact. The use of more turnings than are sufficient to bring the gas thoroughly into contact with the wall of the tube would seem, however, to be detrimental; there is very little chance for conduction of heat into the interior of the tube by the turnings for they touch the walls and each other only in small points; moreover, if the packing of these turnings was as close as Natanson's description indicates, it is to be expected that a fall of pressure would result from the obstruction offered to the flow of gas, and a fall of pressure means a Joule-Thomson effect of corresponding magnitude. If, therefore, some cooling of the gas, due to this cause, did occur, in all probability the gas entered the plug at a temperature lower than that of the bath, for it is not to be expected that the bath could remove the effects of the fall of pressure which occurred in the last end of the tube. Whether or not such an explanation will account for the total apparent increase in the thermal effect observed by Natanson and for the form of curve, which his results trace, cannot be determined.

In order to compare more readily the results obtained by Joule and Thomson with those of the present piece of work I have copied theirs in the following table ; the results are corrected, however, to the basis of 1 atm. difference in pressure above and below the porous plug. The corrections, which had already been made by them, covered errors due to influence of the bath upon the gas stream and reduced the observed thermal effects to the basis of pure CO_2. The latter was made on the assumption that each component of the mixture maintained its own individual thermal effect and was entirely independent of the other component ; this assumption was not considered by them to be a correct one — in fact it had been proven experimentally to be false — consequently the last column of the table cannot be considered to be completely corrected. The dotted line of Fig. 7 represents these results.

The Joule-Thomson Results.

Gas Components.		Bath Temp.	Press Diff. in. (Hg).	Obs. Cooling Effect.	Mean Temp.	Corrected Cooling Effect. (1 atm.)
CO_2.	Air.					
96.5 %	3.5 %	7°.4	164.1	6°.72	4°.0	1°.31
98.2	1.8	35 .6	127.5	4 .19	33 .5	1 .02
99.2	0.8	54 .0	146.0	4 .18	51 .9	0 .88
97.9	2.1	93 .5	167.2	3 .42	91 .8	0 .65
98.3	1.7	97 .5	151.0	3 .11	95 .9	0 .64

The discrepancies between these results and my own are very pronounced throughout the range of temperatures used, but are especially so at the higher temperatures. It is at once evident that the incompleteness of the corrections for impurity cannot explain such differences ; if, however, data for completing these corrections were available the gap would be narrowed by the process.

In the present apparatus there seems to be only one possible explanation of the discrepancies. There is a possibility of a flow of gas from the region below the porous plug to that above by another path than the porous plug itself. A screw packing (not shown in Fig. 2 on account of complication of the drawing) was provided around the middle of the vulcanized fiber nozzle — between it and the surrounding steel cylinder — in order to prevent any gas from leaving the lower region by flowing outward along the plug which carries the lower thermal junction, then upward between the fiber nozzle and the steel cylinder, and into the main gas stream again, along the plug, which carries the upper junction. Any flow of gas through this packing would be a diffusion process and, if adiabatic, would not affect the accuracy of results; however there is danger that such a flow may be far from adiabatic in character. At high temperatures that part of the steel cylinder between the two oil baths is exposed to air which is lower in temperature than the baths; the error would, therefore, increase the observed cooling effect. This explanation will not account for the discrepancies between the two curves at low temperatures. Moreover the danger here is not as great as it seemed, at first glance, to be. The part of the apparatus from the top rim of the barrel to a point above the upper oil bath was enclosed in heavy wrappings of cloth and the air temperatures in this enclosure, even at points some distance from the baths, were only ten or fifteen degrees below the bath temperatures. The protection of this part of the steel cylinder from the surrounding air is better than the drawing of Fig. 2 indicates; the flange on the bottom of the upper oil cup is deeper than is there shown; it extended, in the determinations at low temperatures, to within a short distance of the oil in the lower bath, and in those at 80° and 97° the hot oil softened the rubber ring, which supports the upper cup, so that it moved down and rested on the steel ring which holds the lower thermal junction in place. Furthermore there is considerable experimental evidence leading to the conclusion that errors from this source were not serious; *e. g.*, when the results were compared and this source of error was under consideration, it was thought that an explanation could be found here for the change in slope of the impurity line at 97° (Fig. 6). Errors in temperature of the oil baths would have had considerable influence upon that part of the gas which may have flowed along this by-path. But the records of the observations at this temperature show that such errors in bath temperatures as were present and also the change in temperature of the air in the enclosure under the cloth wrappings would have had a tendency to decrease the slope of this line rather than to increase it. Finally an examination of the packing, described above, after the apparatus was dismounted, showed that it was hard and firm, and, although it is impossible to say that no gas leaked around by this path, all available facts indicate that the amount was not such as would seriously affect the results.

On the other hand, there are, in the Joule-Thomson determinations, two possible sources of error which may account for the discrepancies between the two sets of results. A study of the descriptions and drawings of their apparatus shows a possibility that the gas pressure above the porous plug was not barometric pressure as they assumed it to be; the gas, after it escaped from the plug, passed through a pipe into a gas holder. The dimensions of this pipe are not given, but from the drawings of their apparatus and from descriptions of other parts I judge that it was a 2-in. pipe; the length is altogether uncertain. There was, moreover, at one point of the pipe a large stop-cock — dimensions uncertain. In view of the fact that the stream velocities varied from 2 to 3 feet per second (assuming the pipe 2 inches in diameter) it seems possible that some appreciable fall in pressure occurred in this pipe and stop-cock. An excess over barometric pressure would have made the pressure difference, under which an experiment was performed, less than that which their mercury pressure gauge indicated. A more serious error would result from the effect of pressure upon the reading of the thermometer which was placed in the gas path just above the porous plug. Each of the errors resulting from this cause would make the apparent thermal effect (reduced to a pressure difference of 1 atm.) smaller than the true value. The other possible source of error is brought to one's notice by the fact that Joule and Thomson make no mention of having applied a stem correction to the readings of the thermometer which measured the temperature of the large water bath. This bath temperature was assumed by them (correctly, since in their apparatus the large copper tube in the bath was 60 feet long and 2 inches in diameter) to be the temperature of the gas as it entered the porous plug. But the thermometer, which measured the bath temperature, was so placed that its bulb was near the nozzle and in the observations at high temperatures must have had a considerable length of its stem and of mercury thread exposed to air at a temperature far below that of the bath. The thermometer would have read too low and, if no stem corrections were applied, the observed thermal effect would have been too small. None of the discrepancies between their results and mine is too large to be accounted for by reasonable assumptions as to the magnitude of these two possible errors in their observations.

In addition to the acknowledgments in the introduction of this paper I wish to acknowledge my hearty thanks to Dr. S. R. Cook, Mr. C. W. Waggoner, Mr. L. Howe and especially to Mr. H. J. Lathrop for help in taking observations during the work of this year.

In a later paper I shall show that it is possible to separate the thermal effects, measured in this research, into the two essential parts, one due to the external work which is done by the gas, the other — the pure Joule effect — due to the work done against the forces of intermolecular attraction ; for this separation the available data on the compressibility of CO_2 will be used. The theoretical treatment of the results — their bearing upon the various characteristic gas equations, the possible development of such an equation for this gas, the deduction of a law of molecular attraction — will also be given in that paper.

SUMMARY.

The porous plug form of apparatus was used in this piece of work. The difference between the pressures on the two sides of the plug was about 1 atm. for all of the determinations. The differences in temperatures, (1) of the gas before and after passing through the plug, (2) of the gas and of the large water bath, which surrounded the copper heating (or cooling) tube, were measured by thermo-electric junctions ; the thermo-electro-motive forces were measured by a modified potentiometer method.

In order to obtain the magnitude of the cooling effect for pure CO_2, determinations were made at a given temperature and at a given pressure with gas containing various percentages of impurity and these results were then extrapolated for pure CO_2. At 0° C. the results of such extrapolation show no dependence of the thermal effect upon pressure until a pressure of 26.4 atm. is reached ; the one result obtained here indicates an increase over the values observed at lower pressures. At 20° C. the thermal effect

is independent of pressure as far as observations were carried; 41 atm. was the highest pressure reached at this temperature. The dependence of the cooling effect upon temperature is shown by the full line of Fig. 7; for purposes of comparison the results of the Joule-Thomson determinations for CO_2 are also represented in this figure, by the dotted line.

PHYSICAL LABORATORY, CORNELL UNIVERSITY,
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