The Joule-Thomson Effect in Helium

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Important changes in the apparatus previously used in the measurement of the porous plug coefficient, μ, for air are described in some detail. The effect of air as an impurity in helium has been investigated by direct experiment and shown to be quite negligible even at 10 percent of air but increasing rapidly thereafter with increasing proportion of air. It appears that an experimental study of μ in mixtures of N_2 and He is desirable. The helium was purified by contact with activated charcoal at liquid air temperatures. μ for helium has been measured from -190 to $300°C$ and from 1 to 200 atm. In this range μ is negative, is independent of pressure except at the lowest temperatures, and is small both in magnitude and in variation. Significant trends of μ at the two temperature extremes have been observed. Applications to theory and to other physical properties will follow in later articles. Reasons are given for supposing that helium will not approximate with high accuracy to a perfect gas at any temperature.

IN preceding papers[1,2] will be found in detail the description of the methods, apparatus, and data for the work on the Joule-Thomson effect in air. These methods and apparatus, with some modifications, have been used in the work here reported on helium. The present article will be limited to a description of the changes introduced into the apparatus and methods, and to the presentation of the helium data, reserving their analysis and application for later publication.

GENERAL FLOW SYSTEM

A comprehensive view of the whole flow system is given in Fig. 1.

During measurements at low temperatures the helium circulates from the compressor (5), to the water trap (6), the sodium hydrate driers (7, 8, 9), the manifold (44), the automatic valve (45), the first exchanger coil (13), the carbon dioxide boiler coil (14), the second exchanger coil (15), the plug chamber, the valves A, B, and C, the two exchangers (15) and (13), the low-pressure reservoir (19), and back to the compressor. The compressed air, providing the major part of the bath cooling, passes the exchanger coils (20, 21, 22), and expands at the valve (46) before passing through the coiled copper pipe (23) brazed to the outer wall of the thermostat tank. For work above room temperature, air and carbon dioxide cooling is discarded, and the helium passes directly from coil (13) into coil (15).

The pressure at the compressor outlet is called p_0: beyond the high-pressure regulating valve p_1: inside the plug p_2: and in the low-pressure reservoir p_3. T_1 and p_1 are the temperature and pressure at entry to the plug, and T_2 and p_2 at exit from it.

The helium is stored in the high-pressure cylinders 1, 2, 3, and 4. Each has a volume of about 2700 cubic inches, while the volume of the high-pressure part of the system is about 500 cubic inches. These cylinders and other parts of
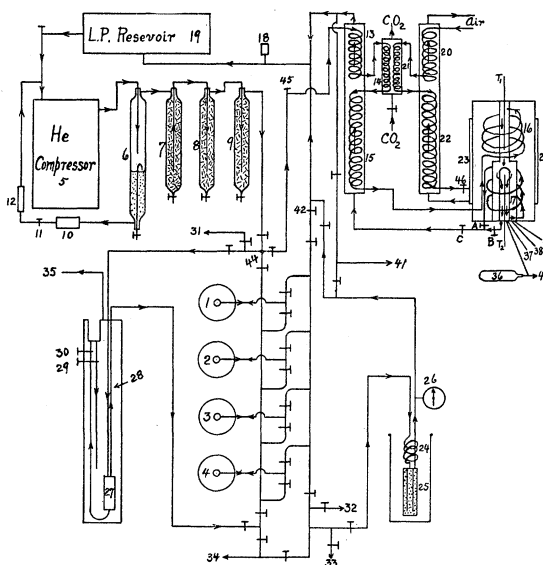

FIG. 1. Flow diagram.

[1] Roebuck, Proc. Am. Acad. **64**, 287 (1930).

[2] Roebuck, Proc. Am. Acad. **60**, 537 (1925).

the flow system are interconnected through a "valve switchboard" of 25 valves, whose bodies are immersed in oil to reveal leaks.

The charcoal and liquefier purifiers are shown as (25) and (27). (33) and (34) are openings for filling and evacuating. The P_1 and P_2 barostats are connected at (39) and (40) respectively; the gauges and manometer at (37) and (38). (36) is an extra volume added to the low-pressure side of the plug. The He analyzer is connected at (41).

In the prevention of loss and contamination of helium due to leakage, it has been found most effective to silver solder all fixed joints and to employ unions with carefully ground joints of steel.

<center>COMPRESSOR</center>

After two-thirds of the helium data had been obtained, the worn-out cylindrical block of the old compressor was replaced by another re-designed as experience had suggested. All inlet and outlet valves, of the light leaf type, were built into the heads. The water jacket was cast so as to immerse both compressor heads and also that part of the piston rod lying between the long packing box in the head and the shorter one
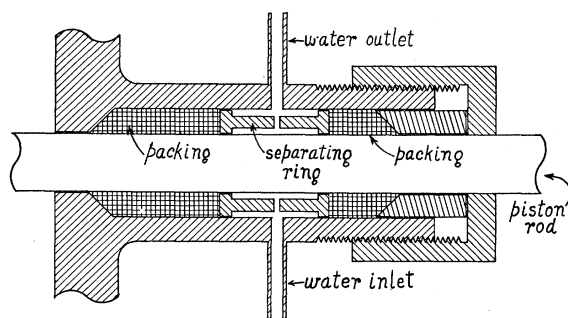

FIG. 2. Piston rod packing box.

in the wall of the water jacket. This served primarily to exclude leakage of helium by cooling and lubricating the piston rod and its packing, and secondly to advertise such leakage.

The latter purpose was accomplished in the old compressor by an ingenious packing box used at Leiden.[3] A short description of this device (Fig. 2) is called for, since the successful operation of the barostat valves depended upon its use. The packing is divided by a separating ring cut and

placed to permit the circulation of water about the piston rod. The water outlet was provided with a trap for catching any escaping helium.

The wood fiber piston packing must be kept wet. To avoid the introduction of fresh water with its impurities and the pressure disturbances caused by its discharge, it is circulated (Fig. 1) through the compressor intake, water trap (6), filter (10), control valve (11), and the observing glass (12).

By this arrangement oil and its decomposition products resulting from high compression temperatures are almost eliminated, the only internal source of oil being the piston rod packing.

<center>LOW-PRESSURE RESERVOIR</center>

Since the flow through the system changes with every change in the pressure difference, $p_1 - p_2$, the compressor has to handle a great variety of flows. A closed, fixed volume, low-pressure system allows the compressor to adjust its intake pressure automatically to suit the flow sent to it. Moreover, the maximum value of the high pressure, p_0, is limited by the amount of gas put in the flow system, and dangerous values are readily avoided. A galvanized steel, double extra heavy, domestic hot-water boiler, of about 180 liters volume is used as the low-pressure reservoir (19 in Fig. 1). It limits the pressure fluctuations from the compressor to about 4 percent, and its charge of gas at atmospheric pressure would raise the high pressure 6 atm. at 200 atm. It is connected to the compressor so that the pulsations have to go through it to get to the plug apparatus. It is built to carry 13 atm., but since a sudden stoppage of the compressor might expose the low side to more than this, a special safety valve (18) following the design described by Ernst,[4] was built. This is provided with internal and external reservoirs for castor oil which has to escape before the helium. The ring seat, ground to fit the flat disk, is tight to castor oil if turned gently into contact.

<center>BAROSTATS</center>

A number of changes have been made in the arrangements previously described. The sliding contact used to actuate the valve-operating

[3] Leiden Laboratory Comm. No. 83, p. 20 and Plate IV, or No. 54, Plate VII, Fig. 3.

[4] Ernst, J. Ind. and Eng. Chem. 18, 664 (1926).

motor has been replaced by a reversing mercury[5] switch illustrated in Fig. 3. The four mercury carrying glass tubes, A, B, C, D, are mounted on a board which is supported at one end by a horizontal shaft carried by the barostat load tank, and at the other end by a cord from the cylinder on the valve stem. By the use of supporting cords at E and F, pulleys are avoided and the ratio between the motions of the ends of
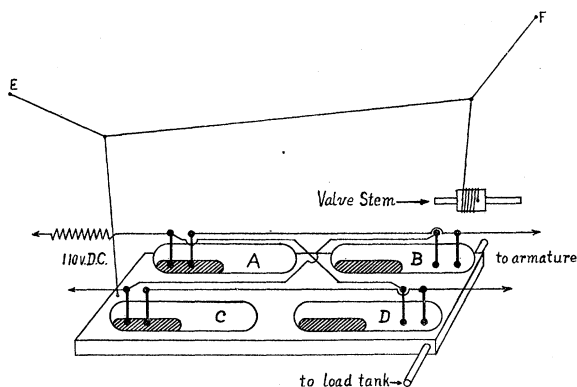

FIG. 3. Reversing switch and connections.

the cord may be varied. A rise of the load tank tilts the board throwing the mercury to the left against the terminals, so energizing the motor which rotates the valve stem and winds up the cord until the board is again horizontal. The four tubes of two terminals each are preferred to two tubes of four terminals each, since with four tubes the right and left pairs may be tilted toward each other. By varying this tilt and the motor speed, continuous overshooting may be avoided and the motor allowed to rest except for needed adjustment. The control resistance should be placed on the power side of the switch to protect the tubes during a chance shorting. Four condensers connected across the breaks are mounted on the under side of the board.

A second alteration is the provision of contacts like spark plugs in the U tubes of the barostats where the pressure is transmitted from mercury to oil, to permit of checking the position of the mercury surface. When necessary, new castor oil may be forced in with the aid of a small pump. These U tubes were previously operated until

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[5] Minneapolis-Honeywell Regulator Company, Minneapolis, Minnesota.

some obvious trouble appeared, when they had to be dismantled and refilled.

The packing boxes on each of the three valves A, B, and C were originally built into the steel base of the apparatus. The lubricant in the packing distilled out at the high bath temperatures and froze at the low. Only very small leaks could be tolerated with the helium, so the valve packing boxes were moved out about 20 cm from the base. They were provided with a copper tube wound around and soldered to the extension tube close to the stuffing box. A stream of warm water through this tube dominated the stuffing box temperatures at all bath temperatures.

Ordinary packings on the stems of the barostat valves (45 and A, Fig. 1) sufficiently tight to prevent helium leakage are too tight for successful operation by the motor. They were consequently provided with a packing separator ring (Fig. 2). A single hole through the packing box wall served as an inlet for castor oil from the bottom of a small strong reservoir. Helium under the same or greater pressure than that at the valve is admitted above the castor oil through a check valve which, by allowing only slow escape of the helium, prevents the oil from frothing through the whole apparatus. Any tendency of the oil to leak inward past the inner section of the packing is now small, on account of the small pressure drop, and only moderate tightness is required to prevent the oil leaking outward past the outer section. The lesser tightness now required for the complete absence of leak of helium and the better lubrication due to the oil made it possible to use these barostats for helium.

The most important change concerns only the barostat controlling p_1. Previously the compressor delivered the air directly at the controlled pressure p_1 which was maintained constant by wasting some compressed air through the barostat valve. This put all irregularities in the compressor performance instantly on the barostat. In the new arrangement the pressure p_0 at the compressor delivery is dropped to p_1 through the control valve (45, Fig. 1). Compressor irregularities now affect p_1 only as they influence the flow through the valve, and the resulting lag

allows their slow and smooth correction by a slight motion of the valve stem.

It was quickly observed that if $p_0 - p_1$ did not exceed about 300 lbs., hunting ceased, the barostat tank set itself at a remarkably steady position, and p_1 became the steadiest we have ever had.

In the routine measurements of the points for an isenthalpic curve, p_2 is successively shifted to new values, each shift involving a shift of the amount of gas at the pressure p_2. The resulting change in $(p_1 - p_2)$ alters the flow, and hence p_3 shifts also. Both of these demands must be met from the supply in p_0. It is therefore necessary during these changes of p_2 to watch p_0 carefully and to shift gas between the system and the storage cylinders as required.

The control of p_2 offers now a more difficult problem than that of p_1, largely on account of the range of values for which p_2 must be set. The helium escaping from the plug chamber is checked by the valves A, B, and C (Fig. 1). If B is closed, the gas has to flow through the coil in the lower part of the bath, which lessens the temperature adjustment in the interchanger. Valve B is open only when it is desired to keep the escape pressure p_2 as low as possible, for which the passage through B provides a shorter, freer path. Valve A is automatically controlled by the p_2 barostat and valve C manually by a 40 cm handle, which tends to offset the difficulty of setting because of its large seat.

To prevent hunting, the barostat valve A must control only a small part of the pressure difference $(p_2 - p_3)$. With valve B closed, valve C is set so that p_2 is 10–20 percent below that desired. Valve A is then closed slowly by rotating the wooden cylinder with respect to the valve stem, and allowing the motor to shift the valve. With p_2 small, the barostat takes up the regulation easily. As p_2 is set at higher values, A and C must be more and more nearly closed. If valve A be allowed to close entirely, violent hunting starts immediately. The barostat load is supported weakly by a coiled door spring to vary the pressure slightly with load position to aid the balancing. The final adjustment has often to be made by slight shifts of the regulator load. This regulator adjustment is the most difficult manipulation of the experiments.

MANOMETER

Except for the provision of electrical contacts to adjust the position of the mercury surfaces in the U tubes, there was no change in the rotating piston differential manometer used in the previous work.

FLOW METER

The variation in p_3 made the Venturi meter almost useless. The needed rough values of the mass flow are given by the values of p_3 since the compressor is run at almost constant speed.

THERMOSTAT BATH

For the work above room temperature, a new steel cylinder for the outside case of the bath is substituted for the one on which the copper tubes had been brazed. A set of heating coils wound on this new cylinder aids in the maintenance of uniform temperature in the circulating bath fluid by providing heat supply over approximately two-thirds of the area from which heat is lost.

In the previous work the Russian mineral oil used as bath liquid vaporized badly at 300°C. It was a relief to find that "Stanolind 200" of the Standard Oil Company would stand this temperature much better.

When the lower temperature work began to indicate the expected change in μ, it was decided to try using liquid air as bath liquid. The thermostat bath was consequently made the collecting chamber at the foot of a Hampson type air liquefier. With the help of carbon dioxide precooling, liquid air could be accumulated in the tank. A stock of liquid air was prepared in advance, and it was forced into the bath after liquid was already appearing there.

The temperature of the bath depends on the composition of the liquid air and on the pressure. The escaping vapor was led back to the compressor for reliquefying, which apparently held the composition sufficiently constant. The first successful run (-184.3°C) was made this way, but in all later attempts the temperature of the bath varied so much, most probably from pressure variation, that no reasonable data could be taken. It would seem that in the successful run everything worked remarkably smoothly. Finally we tried keeping the bath full by pouring in liquid

with the bath open and the liquefier shut down. If the additions were practically continuous, the temperature stayed constant enough for reasonable data, as in the run at $-192.3°C$. It would seem better, however, to add a balanced escape valve[6] to hold the bath pressure constant in the first plan. These two runs cost an inordinate amount of work, many attempts failing from blocked valves, frozen valve stems, and so on.

TEMPERATURE CONTROL

Only one important change has been introduced in the thermostat and heater. A device equivalent to that mentioned in the first paper on air[1] (p. 547) has been put into service and has justified the expectations. It has been described in detail in a separate publication[7] and need only be sketched here.

A tube rheostat in the heater circuit is provided with a long screw on which a nut carries the contact springs. The screw is rotated by a gear and a worm on a d.c. motor. Current from the thermostat trip operates a mercury reversing switch in the armature circuit of this motor. The rheostat contact is thus moved up and down as the "on" and "off" mechanism of the thermostat operates. If the on and off intervals are unequal, the slider progresses in a direction so chosen that for too high bath temperatures, resistance is added to the heater circuit and the on and off intervals shifted to equality. This device substitutes continuous adjustment for the previous haphazard hand adjustment to meet changes in the heat demand. Since the thermostat galvanometer deflection is continually restored to the same place, the bath temperature changes are small and transient. This has also allowed of lower galvanometer sensitivity, so that the whole arrangement is exceedingly stable. The violent changes in heat demand resulting from the adjustments during the measurements are smoothed out quickly.

THERMOMETERS

The platinum resistance thermometers and the bridge are the same as used in the previous work, except as accident made it necessary to repair both thermometers. The opportunity was used to replace the brass cases with steel, and to replace the copper lead wires with silver. The constants of the thermometers were changed very little by this work.

PLUGS

The tubular form of porous plug (radial flow) was used here as in all the previous work.[1, 2] The general theory has been also discussed[8] but should be applied to this special case.

In all the measurements taken with pure helium, the temperature rises with the fall of pressure through the plug wall. The temperature gradient hence requires that heat should flow up the gas stream, which is the condition for the most perfect exclusion of heat leaks. The plug chamber was filled with cotton for the low temperatures and with long fiber asbestos for the high. Any heat escaping from the plug surface into this insulation is carried back immediately by the gas flow. The guard ring at the base of the plug excludes exchanges with the plug support, and all the rest of the gas is taken by the internal flow guide past the thermometer coil. The substitution of a steel tube for the brass thermometer case lessens the conductivity loss there. There has been very little erratic data, or evidence of heat leaks, or of kinetic energy of flow in all the data taken. Duplicate runs almost invariably checked excellently.

Since the copper plating on graphite came loose occasionally, silver put on from an ordinary silvering bath was substituted for the graphite. The penetration of the silvering and copper solutions into the porcelain was lessened by first filling the pores with pure water and keeping them full by filling the tube with water and corking the open end. The copper coated tube was then lead soldered or lead-tin soldered into the steel holder.

The porcelain tubes were all part of the set made by the Montgomery Porcelain Products Company and paid for by a grant from the Rumford Fund of the American Academy. Some of the tubes had been used in the air work.

ANALYSIS

The helium was stated to contain about 2 percent of nitrogen. During the experiments air

[6] Leiden Laboratory Comm. No. 87.
[7] Roebuck, Rev. Sci. Inst. 3, 93 (1932).
[8] Burnett and Roebuck, Phys. Rev. 30, 529 (1910).

could not be entirely excluded. Slow passage over activated charcoal cooled by liquid air will take out all these gases as completely as desired, while absorbing very little helium. The only gases not so absorbed are hydrogen and neon, which are hardly to be feared.

An all-glass apparatus, for connection at (41) of Fig. 1, was built to pass a measured volume of helium through activated charcoal cooled by liquid air. The charcoal was evacuated and on warming to room temperature gave off the absorbed gases. The gas was collected by a Toepler[9] pump and measured over kerosene above mercury. No analysis of this gas was made, and it is simply recorded as volume percent.

PURIFICATION OF HELIUM

The first attempt at purification was to liquefy the nitrogen,[10] but this apparatus (25 of Fig. 1) would not reduce the impurity below $1\frac{1}{4}$ percent. Consequently, charcoal absorption was tried.

A cylinder of copper (25 of Fig. 1) 10 cm in diameter and 38 cm long was divided into two equal volumes by another coaxial cylinder. The whole was filled with 1.5 kilos of granular activated charcoal and immersed in liquid air. The helium was passed through an interchanger, through a pipe immersed in the liquid air, down the outer cylinder, and back the inner one, at 15 L/min. under 2 atm. pressure. One passage reduced the impurity to 0.25 percent and a second passage to below 0.1 percent.

EFFECT OF IMPURITY

Any judgment as to the effect of impurity must be based on direct measurements of its effect. Air is the most probable impurity, so a set of experiments to determine its effect up to a few percent of air, was carried out. The results proved so surprising that the proportions were extended to cover the whole range to pure air. The bath temperature is 51.63°C. The data from the measurements are plotted in Fig. 4, as it seems hardly necessary to give the numerical data in detail. Each isenthalp is marked with the volume percent of air.

The curve for pure helium is straight so that μ,

[9] M. Travers, *Experimental Study of Gases*.
[10] Leiden Laboratory Comm. No. 94-f, p. 51 and Plate IV.

the slope, is a constant over the whole pressure range. Up to about 10 percent of air the curves fall closely upon each other, but a marked shift occurs at 20 percent of air. From this percentage on, the shift grows more rapidly than the percentage of air, the greatest effect of a 1 percent change being at the air end. There is thus no simple additive rule, nor are the roles of
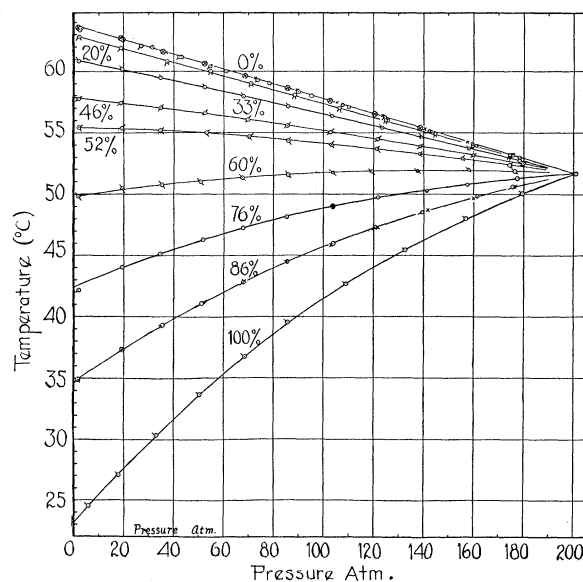

FIG. 4. Helium-air mixtures. Isenthalpic curves. Bath 51.6°C. percent air by volume.

the two gases at all alike. 1 percent of air in the helium produces no measurable change, while 1 percent helium in air produces the largest effect of any 1 percent change. To emphasize this extraordinary behavior, the ΔT for the pressure drop from 200 to 15 atm. is plotted in Fig. 5 against the composition as indicated. The curve leaves the helium side horizontally and enters the air side with the steepest slope.

If one could assume that here the Joule-Thomson effect arises mainly from the molecular forces in the gas, then this behavior could be interpreted to mean that the helium-air forces are like the helium-helium forces and are small or even repulsive, while the air-air forces are relatively large and attractive. Then the introduction of a small proportion of air into the helium separates the air molecules from each other, and the mixture acts essentially like helium. On the other hand, the addition of a
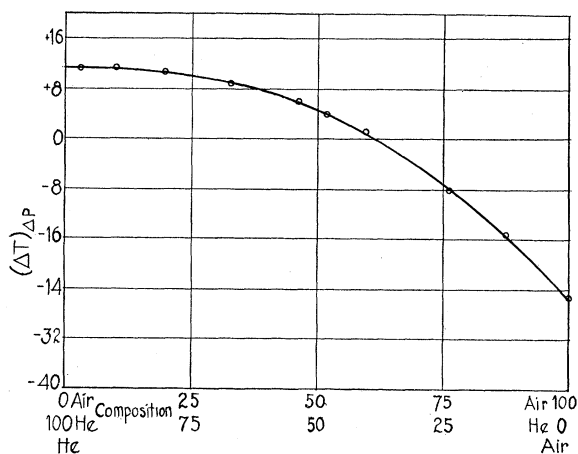
FIG. 5. Helium-air mixtures. ΔT (for $\Delta p = 200 - 15$ atm.) vs. composition. Bath 51.6°C.

small proportion of helium to air also separates the air molecules and the mixture shifts rapidly from the air character. This, of course, neglects the effect of the external work on μ. Before any quantitative deductions can be drawn, pv data must be taken into consideration.

Any likely air impurity has a quite negligible effect on the helium data, except when the temperature and partial pressure of the air present may possibly condense some of it to liquid in the neighborhood of the porous plug.

EXPERIMENTAL DATA. ISENTHALPS

The data for the series of temperatures are plotted in Figs. 6a and 6b. The continuous abscissa is the pressure expressed in atmospheres (76 cm of mercury at 0°C) measured from zero pressure. The ordinate is the temperature in the centigrade hydrogen scale, and since the measured change of temperature is small the scale is broken and the curves crowded together.

The practice followed fairly consistently in the air work, of duplicating each run with a different plug of different permeability, was not so necessary here, since the virtue of the methods may be considered as established and since helium presents a simpler problem than air. Some of the curves were duplicated and some were taken once with plugs whose performance was already tested. These curves all fit smoothly into the general picture. This seemed sufficient to prove that the data were not a function of the rate of flow and that heat leaks were negligibly

small. The changing of plugs involves much labor and material losses of helium.

The outstanding features of the curves are their straightness (except the lowest two) and their negative slope. While it has been generally inferred from related properties[11] that helium would show a rise in temperature on dropping in pressure through a porous plug, this is the first direct experimental evidence of it. The amount of this rise of temperature for a 200 atm. drop is only 12°C, as compared with 30° fall for air. This drop with air is a much more rapid function of the temperature than the helium rise. On casual observation, the slopes of the helium curves appear alike.

The points generally fall almost exactly on the straight line. Since the run may be summarized so completely by the slope of the curve, it has not been considered necessary to publish the data in detail. The precision with which the individual points fall on a curve is slightly higher than the precision with which the slope can be duplicated experimentally.

The bending of the two lowest curves is in agreement with the general picture presented later. But the slope of the right-hand end of the lowest curve is steeper than that of the straight lines above. This does not fit the picture, but seeing the difficulty of the measurements at this temperature, it may for the present reasonably be attributed to experimental error.

JOULE-THOMSON COEFFICIENT, $\mu = (dT/dp)_h$

When the accumulating data showed that the isenthalpic curves were straight lines, it became evident that the values of this coefficient could be measured with greater precision than with the corresponding curved lines for air. The group of points from one run were divided into two groups at opposite halves of the line; the coordinates of the first point in one group were subtracted from those of the first point in the second group to give a ΔT and a Δp whose quotient is μ, and so on through the group. This gave up to six or seven independent readings of μ from one experiment. These values were averaged to give μ for the run.

As with air, the highest pressure point on the curve is the most unsatisfactory of the group.

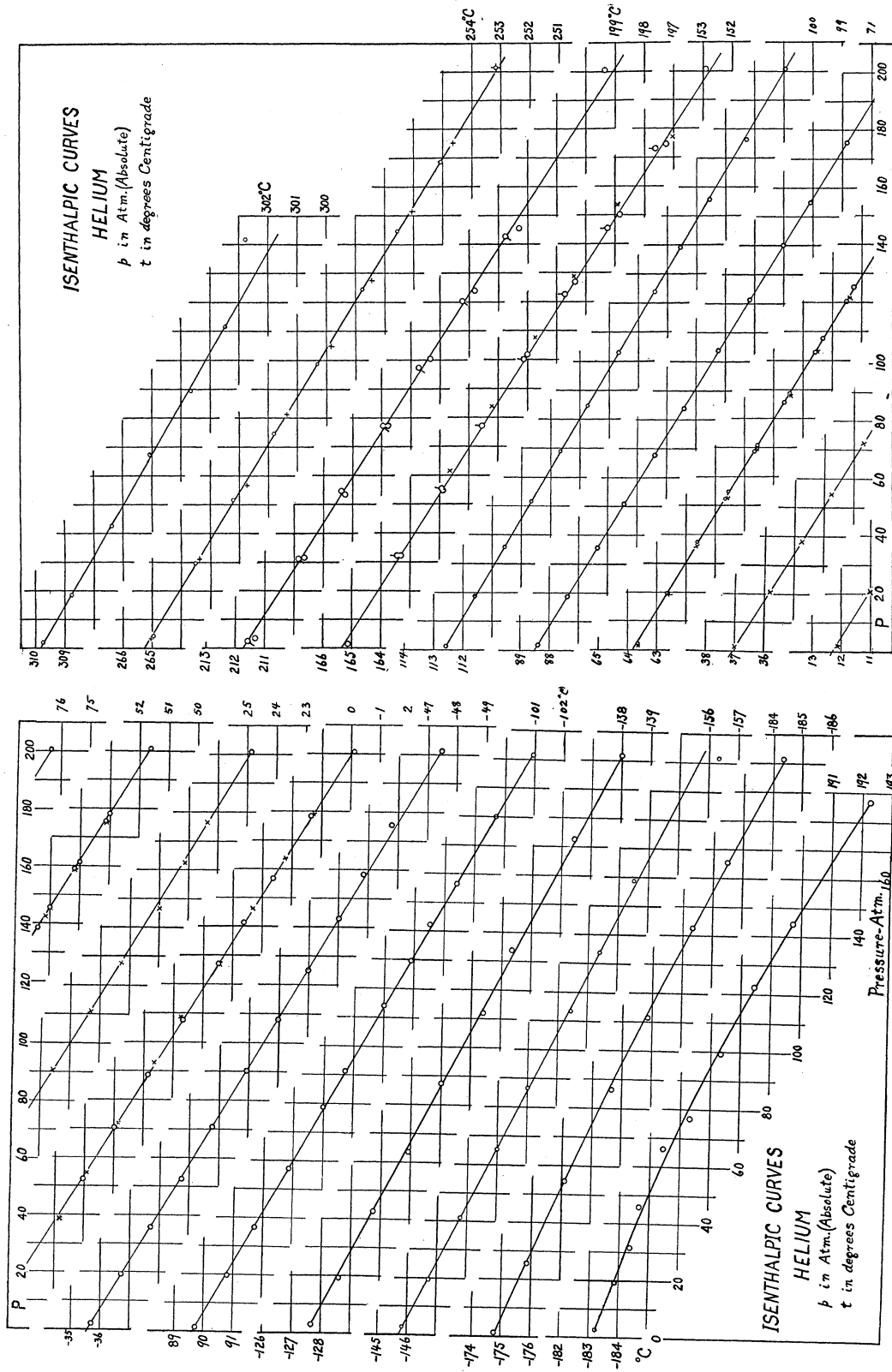[11] J. H. Perry, J. Phys. Chem. **28**, 1108 (1924).

FIG. 6a. Isenthalpic curves helium. p in atm. (absolute) t in °C.

b. Isenthalpic curves helium. p in atm. (absolute) t in °C.

This results mainly from uncertainty as to the difference of resistance of the two thermometers at the bath temperature. To measure this at the bath temperatures would have involved undue labor and loss of helium. The effect of this uncertainty is only to displace the high-pressure point. Irregularity in bath temperature[1] may also contribute to this uncertainty, though this was lessened at the high temperatures by special heating of the plug support. The highest pressure point has been neglected in the computation of μ.

The values of μ are collected in Table I with the other related data, and they are plotted against the temperature in Fig. 7. One is impressed first by the small absolute value of μ even at its largest, 0.0628°C/atm.; then secondly by the small range of the variation—the smallest value is 58 percent of the largest. Over this same range of temperature μ for air goes from about +1°/atm. through zero to −0.01. For helium between 0 and 250°C the minimum value is 95
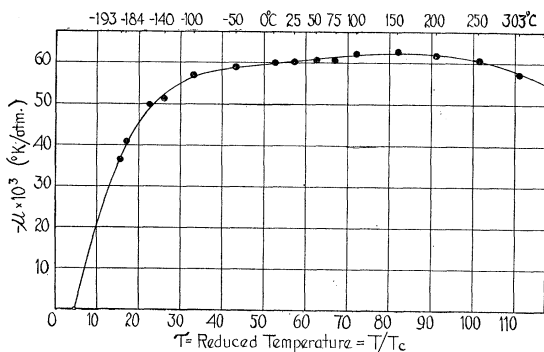

FIG. 7. Helium $-\mu \times 10^3$ vs. t and T.

percent of the maximum, while over the range 0° to 100°C the variation is only slightly larger than the experimental error.

The curve in Fig. 7 shows these relationships even more strikingly. μ is ordinate. Temperature is abscissa and is put on in °C across the top of the plot and in reduced units across the bottom. For this the critical temperature of helium is taken as 5.19°K[12] and $T_{ice} = 273.15$°K. The figures are listed in the fourth column of Table I. The measurements extend when expressed in reduced temperature units over a much greater temperature range than is possible for any other gas. For comparison, the Kelvin scale temperatures for

[12] Onnes, Leiden Laboratory Comm. No. 147-b.

TABLE I. *Values of μ.*

		$\mu = (dT/dp)_h$ in °C/atm.				$-\mu \times 10^2$ from curve
Curve	Bath (°C)	T(°K)	T/T_c	T_H	$-\mu \times 10^2$	
300	302.76	575.9	111.0	3682	5.68	5.78
250	253.16	526.3	101.4	3364	6.07	6.09
200	199.36	472.6	91.1	3023	6.16	6.21
150	152.91	425.1	81.9	2717	6.28	6.24
100	100.96	374.2	72.1	2392	6.21	6.18
75	75.74	348.9	67.2	2230	6.07	6.15
50	51.36	324.8	62.6	2077	6.07 } 6.07	6.11 } 6.09
25	24.28	297.5	57.3	1901	6.01	6.04
0	− 0.11	273.1	52.6	1745	5.99	5.96
− 50	− 48.17	225.0	43.4	1440	5.88	5.86
−100	−100.96	172.1	33.2	1101	5.57	5.65
−140	−138.01	135.2	26.1	866	5.11	5.23
−155	−156.3	116.8	22.5	750	4.97	4.87
−180	−184.3	88.9	17.1	567	4.10	3.99
−190	−192.3	80.9	15.6	518	3.65	3.68
(From air)		23.6	4.55	151	0	

hydrogen of these reduced temperatures are given in column 5 under T_H.

The point[13] $\mu = 0$, $T = 23.6$°K, is computed from the reduced temperature (4.55) at which air[1] has $\mu = 0$ for $p \gtreqless 1$. Helium has been liquefied by the use of a regenerator so that it must cool itself on expansion at temperatures obtainable by hydrogen boiling under reduced pressure. Hydrogen boils at 20.39°K at $p = 1$ atm. and freezes at 13.95°K at $p = 54.1$ mm.[14] The temperature at entry to the regenerator falls at about 15°K[6] in the Leiden arrangement. That is, 23.6°K as the inversion temperature at 1 atm. leaves sufficient margin for producing liquid. To judge from the behavior of air, the inversion curve will fall to lower temperatures at higher pressures. Mr. Flim of the Leiden Laboratory expressed the opinion that if the inlet pressure to the helium liquefier was raised to 200 atm., for example, no liquid helium would be obtained. Their usual inlet pressure is 25 atm.[15] It might easily follow from the above that with increased pressure drop the integrated cooling effect would decrease enough to prevent the formation of liquid.

[13] Kirkwood and Keyes' (Phys. Rev. 37, 839 (1931)) estimate of 54°K from an equation of state is very high when compared with the considerations given here. It is quite out of agreement with the corresponding state considerations for air and hydrogen.

[14] Van Laar, *L'Hydrogen et les Gas Nobles.*

[15] W. H. Keesom, *Rapport et Comm. du 5ème Congres Int. du froid*, Rome, 1928, p. 144; and Leiden Laboratory Comm. Sup. No. 45, p. 28.

On the other hand, the point $\mu=0$, $T=23.6°$K falls readily on the extension of the curve through the other points in Fig. 7. The part of this curve falling below liquid air temperature would be exceedingly difficult to obtain, as, for example, air would have to be kept from contact with the apparatus. It is hoped, however, to cover this region by the use of hydrogen. Table II

TABLE II. *Temperature range of experiments.*

	°K	°C	Reduced temps. He	H	Air
Min. temp. of exps.	83	−190	16	2.5	0.59
Max. temp. of exps.	573	300	110	17.3	4.1

shows that hydrogen falls, fortunately, over the gap in reduced temperature between the helium and the air data. In terms of corresponding states, this will map out the field from below, to 110 times, the critical temperature.

The rapid fall in the value of μ with falling temperature shows first at about −75°C. Above −75°C μ increases slowly and very steadily to about 150°C, where again it begins to fall. The steady part covers the range about room temperature and simplifies materially the temperature scale application.

The high temperature decrease of μ was first definitely evident at the 250°C reading, so the temperature of the bath was pushed up to 300°C and the value of p_1 reduced to 142 atm. The value of μ so obtained confirms the downward trend.

The value of μ being independent of pressure except at the two lowest temperatures, these conclusions hold over the pressure range, 1–200 atmospheres, of our experiments.

The definition of a perfect gas [$(pv)_T=$const. and $u=f(T)$ only] requires that $\mu=0$. Since 0.06°C/atm. is a small quantity, helium is a good approximation in this particular to a perfect gas. The downward trend in the $\mu-T$ curve above indicates that this approximation is improving with temperature rise. The $pv-p$ curves for helium[16] are straight lines of positive slope, α, which falls steadily with temperature up to 400°C. These two trends, the fall of both μ and α, suggest that at a sufficiently high temperature helium might become a perfect gas. Calculation of η, the free-expansion coefficient, from these data however shows that at 200°C η is negative and increasing numerically. Theoretical considerations, as will be shown later, also suggest that η will not go to zero at any high temperature. One must conclude that there is no warrant for expecting helium to become a perfect gas at any temperature.

A general picture of the isenthalpic curves, some physical properties of helium, and corrections to the helium and air thermometers will be presented in succeeding articles. Meanwhile, experimental work will proceed on nitrogen and mixtures of nitrogen and helium.

This work has been greatly assisted by several grants from the Wisconsin Alumni Research Foundation, and it is a pleasure to acknowledge our indebtedness.

[16] Holborn and Otto, Zeits. f. Physik 30, 320 (1924).