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THE VARIATION OF THE SPECIFIC HEATS (C_p) OF OXYGEN, NITROGEN AND HYDROGEN WITH PRESSURE

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Abstract

The specific heats, C_p of oxygen at 26° and 60°C, nitrogen at 26° and 60°C and hydrogen at 50°C have been measured as a function of pressure over the pressure range 10 to 130 kg/cm^2. A continuous flow method is used, by which the ratio of C_p at a pressure p to $(C_p)_0$ of the same gas at a pressure of one atmosphere is measured. The theory of the method shows that the experimental results are practically independent of the usual errors arising from heat leakage and the Joule-Thomson effect. Complete experimental curves as well as tabulated values are shown for $C_p/(C_p)_0$ as a function of pressure. Details of construction and use of the apparatus are given.

In a previous paper[1] the author has described an experimental method for determining the variation of the specific heat C_p of a gas with pressure. A method of continuous flow calorimetry was used whereby the ratio of C_p at a pressure p to $(C_p)_0$ at a pressure of one atmosphere was measured. The present paper presents values of this ratio obtained by the use of improved apparatus over the pressure range of 10 to 130 kg/cm^2, for oxygen at 26° and 60°C, nitrogen at 26° and 60°C and hydrogen at 50°C.

I. Theory of the Method.

A schematic representation of the new apparatus is given in Fig. 1. A gas at a high pressure enters a temperature-controlled bath at *a* where it comes to a fixed temperature. From the bath the gas in conducted through a *heat interchanger* and then to a *pressure reduction valve* where the pressure is reduced to approximately one atmosphere. At the low pressure the gas passes through a second bath, (different in temperature by 10° from the first) and again passes through the *heat interchanger* and escapes. In the interchanger the two gas streams are in such intimate thermal contact that they emerge at approximately the same temperature. The temperature of each gas stream is measured just before it enters and leaves the interchanger at T_1, T_2, T_3 and T_4 where $T_2 - T_1 = \Delta t$ and $T_4 - T_3 = \Delta t_0$ are the temperature changes in the high and low pressure streams respectively.

After passing through the region where the interchange of heat takes place both gas streams are thermally connected to some conducting *base* (*for wall*) on which is mounted a conducting surface (*interchanger wall*) which encloses the entire *interchanger* including some length of the gas conduits with their respective radiation-convection shields S_1, S_2, S_3 and S_4. With this construction it is possible to regulate the temperature of the heavy copper

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[1] E. J. Workman, Phys. Rev. **36**, 1083 (1930).

heater guard in such a way that the *interchanger wall* will be an isothermal enclosure equal in temperature to the *heater guard.* The conduits leading to and from the interchanger are of low thermal conductivity and arranged with the view of minimizing the net heat leakage through the wall of the interchanger.

If we assume that a steady state of gas flow and temperature distribution has been attained, we see that there is an interchange of heat between the two gas streams, and that a simple relation exists between C_p for each gas stream and the four measured temperatures indicated above. The resistance to the flow of gas between the points where their temperatures are measured will give rise to a small Joule-Thomson temperature change in each stream. Let us indicate these temperature changes by $\mu\Delta p$ and $\mu_0\Delta p_0$ in the high and low pressure lines respectively. Also let q be a net amount of heat per gram of gas gained through leakage by the two gas streams. Since the pressure and temperature differences over each gas stream in the interchanger are small we can now write

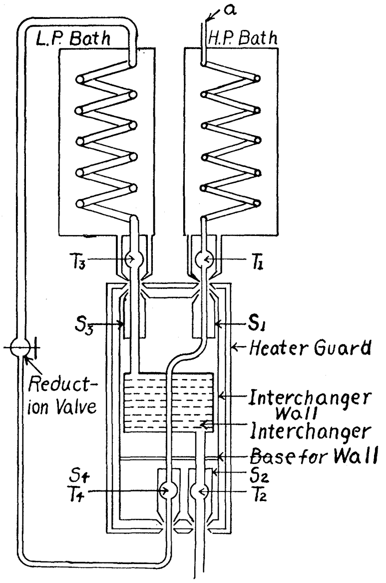

Fig. 1. Schematic diagram of apparatus.

$$q = \bar{C}_p[\Delta t + \mu\Delta p] - (\bar{C}_p)_0[\Delta t_0 + \mu_0\Delta p_0] \tag{1}$$

where C_p and $(C_p)_0$ are average values over the temperature intervals indicated by Δt and Δt_0 respectively. Solving (1) for $\bar{C}_p/(\bar{C}_p)_0$ we have

$$\frac{\bar{C}_p}{(\bar{C}_p)_0} = -\frac{\Delta t + \mu_0\Delta p_0 - q/(\bar{C}_p)_0}{\Delta t + \mu\Delta p}\,. \tag{2}$$

Expanding the right hand number of Eq. (2) we have

$$\frac{\bar{C}_p}{(\bar{C}_p)_0} = -\frac{\Delta t_0}{\Delta t} - \phi \tag{3}$$

where ϕ is a correction term, given by the relation

$$\phi = \left[\frac{\mu\Delta p\Delta t_0}{\Delta t} - \mu_0\Delta p_0 - \frac{q}{(\bar{C}_p)_0}\right]\left[\frac{1}{\Delta t} - \frac{\mu\Delta p}{\Delta t^2}\cdots\right] \tag{4}$$

With the usual methods of flow calorimetry it is difficult to deal with correction terms of the type of ϕ in Eq. (3). It seems therefore that perhaps the greatest virtue of the method, outlined above, rests on the fact that it is possible to eliminate, almost completely, errors of this kind by interchanging the bath temperatures and taking the mean value of the two results thus obtained. If a set of temperature readings be taken when, for example $T_1 = 45°\text{C}$ and $T_3 = 55°$ and a similar set taken for the reverse arrangement $T_1 = 55°$ and $T_3 = 45°$ we see, when applying these readings toward the determination of $\bar{C}_p/(\bar{C}_p)_0$ in Eq. (3) that the correction term is changed in sign but not appreciably in value in going from one arrangement to the other. This result is apparent from Eq. (4) if we bear in mind the fact that $\mu\Delta p$ does not differ greatly from $\mu_0\Delta p_0$ and that they are both small in comparison to the measured temperature intervals. Furthermore q is small in comparison to the amount of heat available for transfer between the two gas streams in passing through the interchanger and is approximately the same in each arrangement of bath temperatures. The fact that in either case, T_2 and T_4 do not differ much from the mean of T_1 and T_3 justifies the assumption that the factors which determine the magnitude of q will be about the same in these two experiments.

These arguments indicate that it is possible to conduct a set of experiments whereby a value of $\bar{C}_p/(\bar{C}_p)_0$ is obtained which, to a very high degree of approximation will be independent of the Joule-Thomson effect and small heat leakages of the type q. Moreover, if we assume that the values of the specific heats here involved have a linear variation with temperature over the small range T_1 to T_3, we see that $\bar{C}_p/(\bar{C}_p)_0$ becomes simply the value of $C_p/(C_p)_0$ at the mean temperature $(T_1+T_2)/2$.

RESULTS

With apparatus designed with the aim of meeting the requirements set forth in the foregoing paragraphs, values for $C_p/(C_p)_0$ have been determined for oxygen at 26° and 60°C, nitrogen at 26° and 60°C and hydrogen at 50°C over the pressure range of 10 to 130 kg/cm^2. In all cases the temperature difference in the two gas streams as they enter the interchanger (T_1-T_3) has been $\pm 10°\text{C}$.

The results of the measurements are shown graphically in Fig. 2 where $(T_4-T_3)/(T_1-T_2)$ are plotted as ordinates against the pressure in kg/cm^2 as abscissae. In all these cases the upper curves are obtained when the bath temperatures are arranged such that $T_1 < T_3$ i.e. when the high pressure gas is warmed and the low pressure gas is cooled in the interchanger. The lower curves represent the data for the reverse arrangement of bath temperatures. The mean curves in Fig. 2a, b, c, d and e give the values of $C_p/(C_p)_0$ as a function of pressure.

In Table I values of the ratio $C_p/(C_p)_0$ for the gases studied are given with their corresponding pressures and molecular density ratios. The density

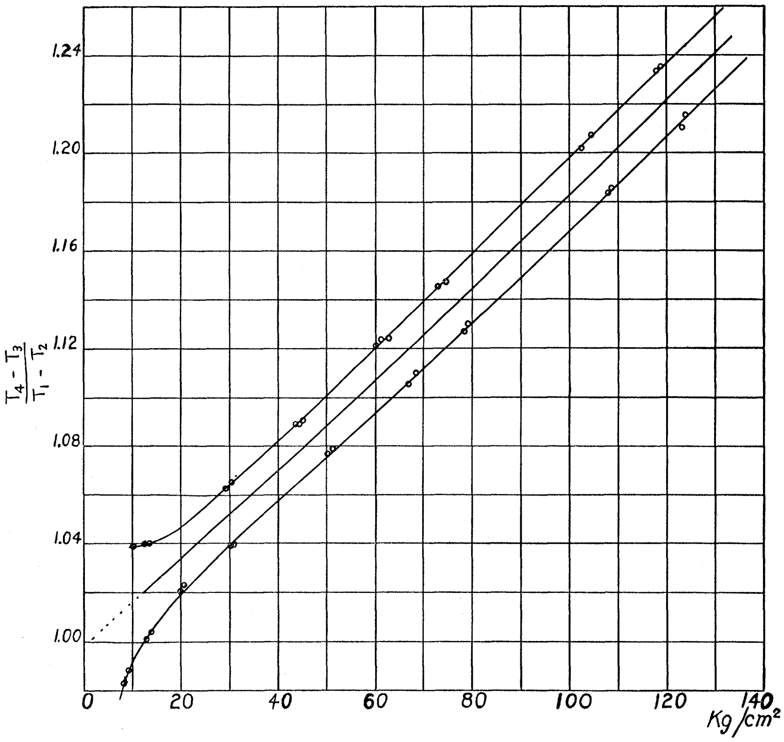

Fig. 2*a*. O_2 at 26°C.

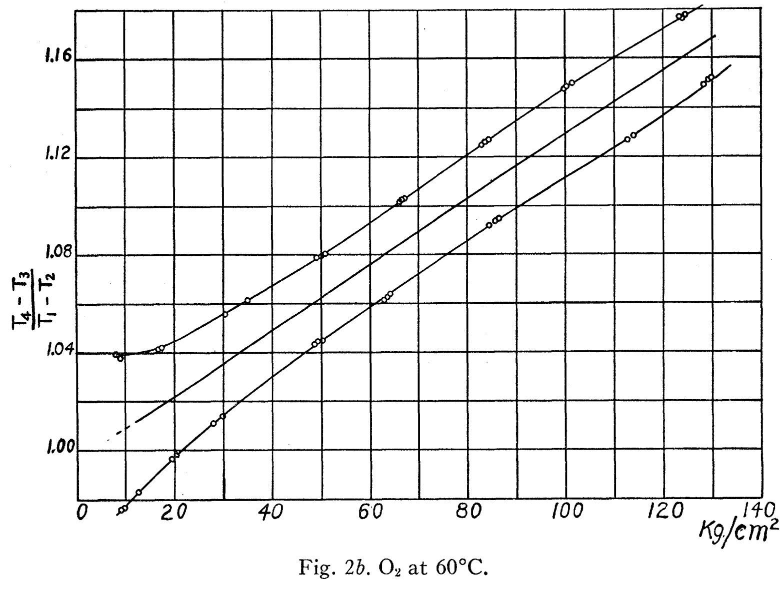

Fig. 2*b*. O_2 at 60°C.

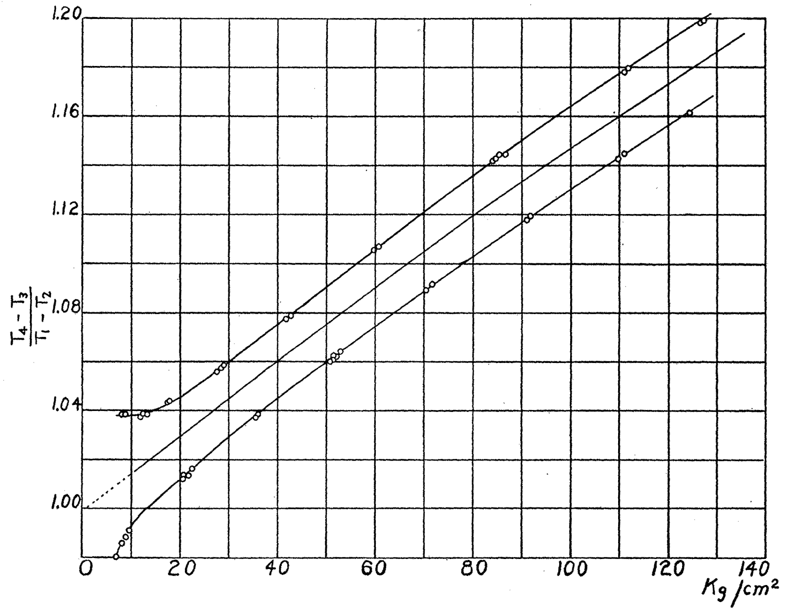

Fig. 2*c*. N_2 at 26°C.

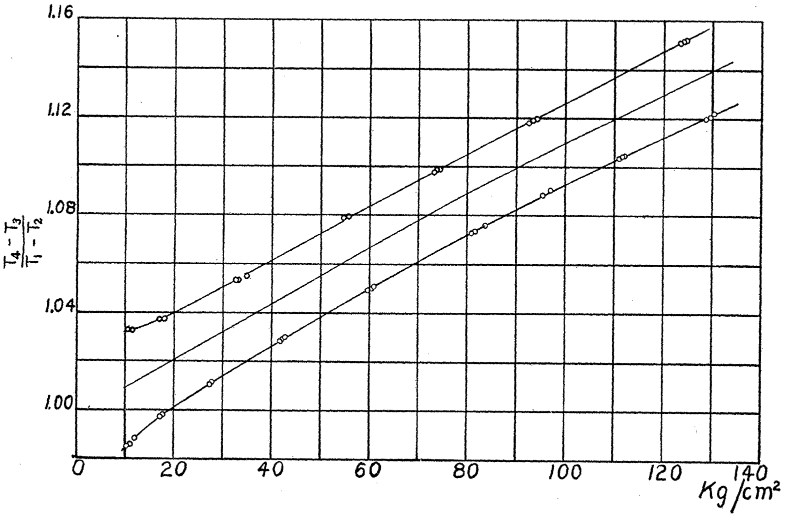

Fig. 2*d*. N_2 at 60°C.

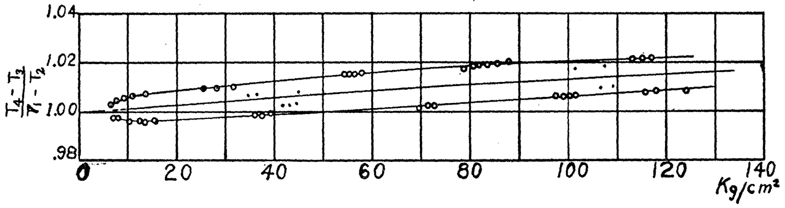

Fig. 2*e*. H_2 at 50°C.

TABLE I. *Values of* $C_p/(C_p)_0$.

Pressure in kg/cm^2	$O_2-26°$	$O_2-60°$	$N_2-26°$	$N_2-60°$	$H_2-50°C$
10	1.0160 (9.6)	1.0090 (9.6)	1.0137 (9.7)	1.0097 (9.7)	1.0013 (9.7)
30	1.0520 (28.5)	1.0355 (28.8)	1.0443 (28.9)	1.0322 (29.1)	1.0041 (29.5)
50	1.0880 (47.1)	1.0632 (47.8)	1.0746 (48.3)	1.0551 (48.7)	1.0072 (49.7)
70	1.1255 (65.4)	1.0901 (66.6)	1.1050 (76.7)	1.0780 (68.5)	1.0098 (70.3)
90	1.1637 (83.5)	1.1162 (85.4)	1.1332 (87.4)	1.0991 (88.6)	1.0120 (91.4)
110	1.2020 (101.2)	1.1420 (104.2)	1.1597 (107.2)	1.1194 (109.1)	1.0142 (112.9)
130	1.2410	1.1680	1.1860	1.1390	

ratios (number of molecules per unit volume at a pressure p over the number at a pressure of one atmosphere) are given in parentheses.[2] The values of the

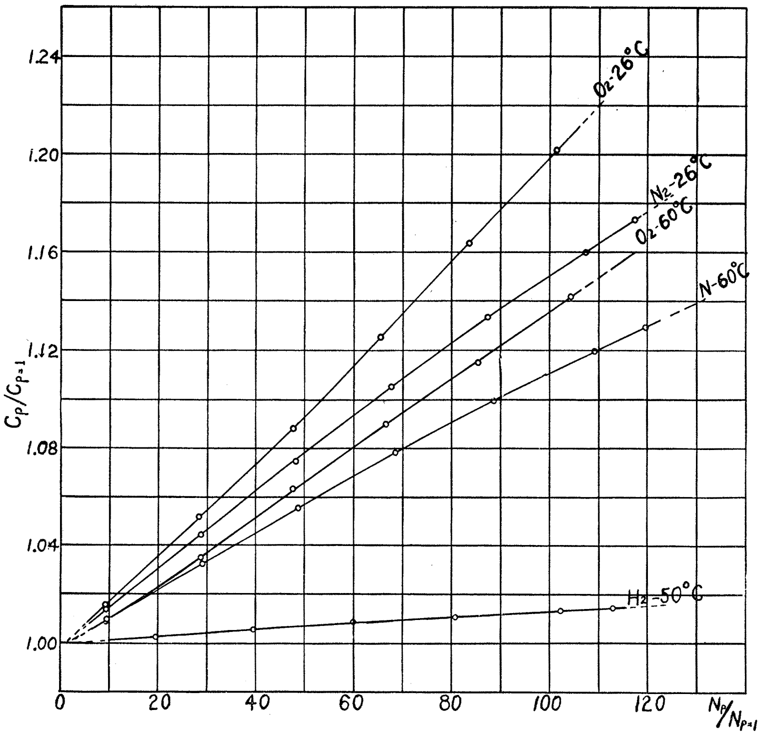

Fig. 3. $C_p/(C_p)_0$ as a function of the molecular density.

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[2] In making this transformation the PV values of Holborn and Otto have been used. Holborn and Otto, Zeits. f. Physik, **33**, 1 (1925).

specific heat ratios were obtained from the carefully drawn mean curves. The probable error is less than 0.2 percent. The curves in Fig. 3 show $C_p/(C_p)_0$ as a function of the molecular density.

DISCUSSION OF RESULTS.

In the first part of this paper it is shown that the separation of the two experimental curves for each case given in Fig. 2 a, b, c, d, and e is due to the existence of a correction term ϕ (Eq. 3). Although this term involves, as well as the Joule-Thomson effect, a small heat leakage q, it is of interest to consider the Joule-Thomson effect alone.[3]

With oxygen and nitrogen the Joule-Thomson effect is a cooling effect under these conditions of temperature and pressure. In the series of experiments where $T_1 < T_3$ this cooling would therefore have the effect of decreasing the magnitude of $T_1 - T_2$ and increasing that of $T_4 - T_3$. As a result the values of $C_p/(C_p)_0$ calculated by the relation $C_p/(C_p)_0 = (T_4 - T_3)/(T_1 - T_2)$ would be too large. By similar reasoning we see that corresponding values would be too small when the reverse arrangement of bath temperatures is used. i.e. when $T_1 > T_3$. A separation in this direction is observed in the cases of oxygen and nitrogen. With hydrogen, however, we expect the Joule-Thomson effect to warm the gases slightly under the conditions of this experiment. It is in this case where a large Joule-Thomson effect does not predominate in producing a separation of the curves that we see most clearly the effect of a small heat leakage. A further study of heat leakage in the case of hydrogen was made by increasing the flow of gas to double the normal rate. The increased flow of gas may alter the relationship between q and the regular interchange of heat. This would be shown by a change in the interval between the two curves. The dotted points of Fig. 2e show the effect of the increased flow for hydrogen, where the points above the mean curve are associated with conditions which produced the upper curve and the other points result from the inverse arrangement of bath temperatures. *The symmetry in the position of the "dotted" points, with respect to the mean curve, gives additional proof that the mean value curve is independent of the term* ϕ *in Eq.* (3).

It is of interest to examine the curves for evidence of the Joule-Thomson effect in the region of lower pressures. If the rate of gas flow in grams per second remains constant, it is apparent that the volume of gas passed per second in the high pressure line of the interchanger will increase at the lower pressures with the result that the Joule-Thomson effect will come more and more into effect in this region. This is shown with remarkable certainty in all three gases. The behavior of hydrogen in this region is of peculiar interest because the Joule-Thomson effect is observed as a warming effect instead of cooling as in oxygen and nitrogen.

In passing the discussion of the curves presented here, it should be stated

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[3] In this treatment we have not considered the effect of temperature on the specific heats of gases in relation to the interval between the curves. It is easy to show that such a consideration would give rise to a second term in Eq. (3) which, like ϕ, almost completely vanishes in the mean curve.

that in general, care should be taken in attaching any particular significance to the shape of the upper and lower curves except in so far as the mean curve is affected. It must be remembered that the conditions of gas flow in the high pressure stream are different for all values of the pressure. As a consequence the temperature gradients along the conduit leading to the interchanger may change in such a way as to change the magnitude of the heat leakage. Indeed it has been possible in the case of nitrogen at 60°C to change the flow over such a wide range that q changed in sign. In connection with limitations just mentioned it may be of equal importance to say that to one using this method to study the specific heat of gases, the character as well as the position of the individual curves may point to the imperfections of the apparatus at hand. For example, we can be reasonably certain that in the present apparatus the net heat transfer q arises from an excessive heat conduction along the line leading from the low pressure bath to the heat interchanger.

The data indicate that the heat leakage and the Joule-Thomson temperature effect are both within the allowable magnitude specified in the theory of the method. The intercepts of the mean curves on the pressure axis indicate that there is no trouble in measuring temperatures as was certainly the case in the work previously reported by the author.[1] The errors in this earlier work were due to the fact that the temperature gradients which gave rise to an error in temperature measurements in one region of pressure differed more in another region than was expected at that time. In the light of further work, however, it is made clear that this variation is to be expected when temperatures are measured as in the earlier work.

The oxygen and hydrogen used in this work was obtained from the Philadelphia plant of the Paschall Oxygen Company, and the nitrogen from the Linde Air Products Company of New York City. By special analysis at the respective plants these gases were shown to be better than 99.5 percent pure. The gas was dried over phosphorus pentoxide before it was passed through the apparatus.

Details of Construction and Use of the Apparatus.

A simple scale drawing of the apparatus is difficult to realize because of its compactness and lack of symmetry in a single plane. Fig. 4 is a "sectional" drawing which may serve to show the actual construction of the several parts as well as the complete gas circuit. The scale is distorted but dimensions of the interchanger parts may be estimated if the various parts (thermometer tubes, shields etc.) are considered as drawn to scale, connected as shown but spread out laterally in the plane of the paper. The cylindrical boundary of the interchanger must therefore be thought of as being 2.25 inches in diameter and 5 inches long rather than 4.5 inches in diameter and 5 inches long as the scale might indicate. The same consideration must be made for the heater guard w which is 3 inches in diameter and 7 inches long. The high pressure gas conduits, where low thermal conductivity is desired, are nickel silver tubes 0.063 inches outside diameter with 0.010 inches wall. The corresponding low pressure tubes are of nickel silver with 0.125 inches outside diameter and 0.005

wall. Other tubes are drawn to a corresponding scale. All nickel silver parts are thinly gold plated.

The gas circuit is as follows: Gas from the high pressure reservoir is conducted to the tube *c* through which it passes to the temperature controlled bath *b*. The inner bath *ib*, being heat insulated from *b* serves to smooth out temperature fluctuations due to slight periodic changes in the heating current applied to the outer bath, which surrounds it. The gas stream now passes through the nickel silver tube *e* which conducts it through the boundary of the interchanger *h* to *q* where the light walled tube turns back sharply and is soldered, for thermal contact, to the copper radiation shield *r*. From *m* to *j* the conduit is developed into the form of a spiral helix which terminates at *j* where another shield *i* is attached. The circuit passes from *j* to the chamber *s* where nearly all the interchange of heat between the two gas streams takes place. From this enclosure the high pressure gas passes into a copper tube at *u* which winds about between the two copper walls *v*, to which it is soldered for thermal contact, leading to the nickel silver tube *l* which passes the gas through the outlet thermometer tube *o*. A radiation convection shield *n* is soldered to *l* as shown. From the outlet thermometer tube the gas passes, along the path indicated, to the reduction valve *f* where the pressure is re-

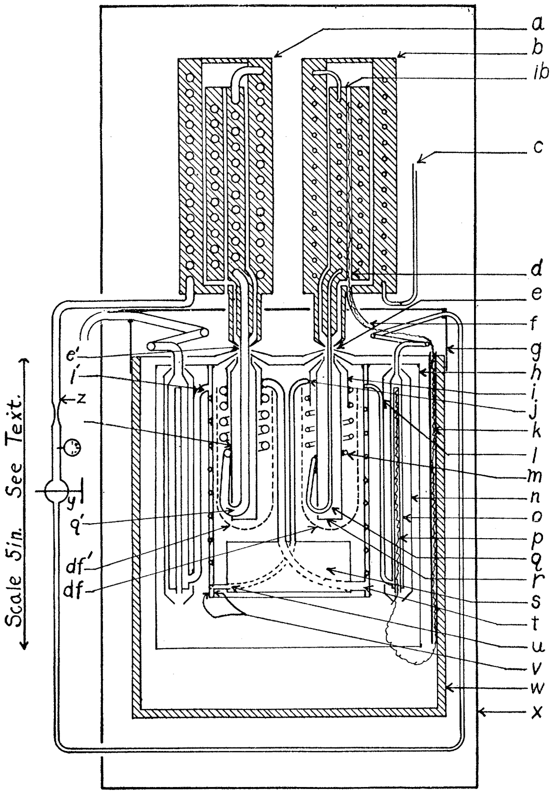

Fig. 4. Sectional diagram which shows the actual construction of the several parts of the apparatus as well as the complete gas circuit.

duced. After passing the point *z* the gas at a pressure of approximately one atmosphere is conducted to a second temperature controlled bath *a*. The course of the low pressure gas through the apparatus is exactly similar to that of the high pressure stream except that in the region between *t* and *l* the low pressure stream is constrained to move in a spiral path through the duct formed by the high pressure line and the two copper walls *v*. From the point *g′* the low pressure gas escapes into the air.

The temperature controlled baths are made by machining thick-walled copper tubes in such a way that one fits snugly inside an outer tube. Helical grooves cut on the smaller tube serve as a conduit for the gas streams. The two baths thus constructed consist essentially of a solid block of copper about 5 inches long and 2.5 inches in diameter. The outer baths are equipped with electrical heating coils for maintaining constant temperatures while the inner baths are allowed to "float" at a temperature determined by the temperature of the gas which flows through them. The relative sizes of the outer and inner baths are represented approximately in the drawing.

The interchanger, as will be seen, is constructed in such a way that the regions of large temperature differences are in its inner folds while the outside is very nearly equal in temperature to the temperature of the two gas streams as they leave the interchanger. With this arrangement it is possible to have an isothermal surface *h* on the interchanger which can be thermally protected by keeping the temperature of the surroundings equal to the temperature of the surface. This is accomplished by means of the heavy copper heater guard *w* which is kept at the same temperature as the surface of the interchanger by maintaining a zero reading on a five junction copper-constantan thermocouple connected to their respective surfaces.

The thermocouple which measures temperature change on the high pressure line has one end inserted in the hole *d* in the inner bath. It passes through a german silver tube *e*, a copper tube *k* and terminates in the thermometer tube *p*. Since the thermometer tube is very nearly equal in temperature to the interchanger surface and the heater guard, conduction from the interchanger along the thermocouple wire is minimized by passing the thermocouple wires through the tube *k* which is soldered to the heater guard. Practically the entire temperature gradient along the thermocouple wires exists along the length between the bath and the wall of the heater guard. Tube *f* is a thin-walled nickel silver tube which is soldered to *b* and extends through the first heater guard wall, having the purpose of protecting the wires and smoothing out the temperature gradient along them. Other thermocouples measure the temperatures of *ib* and the heater guard to an ice bath. The temperatures on the low pressure side are measured by exactly similar methods.

The temperature difference between the two baths is maintained at 10°C. Temperature gradients therefore exist between the points where the inlet temperatures are measured and some point inside the interchanger where the interchange of heat between the two gas streams starts. In order to minimize the net transfer of heat along the entrance tubes, it is desirable to prevent the interchange of heat for some distance after the gas streams pass through the boundary of the interchanger. To accomplish this, the tubes in addition to being poor heat conductors are gold plated to give a surface of low emissivity to radiation at these temperatures. The radiation-convection shields *i* and *r* are of copper thinly gold plated. Small dewar flasks *df* and *df′* further serve to isolate these regions. It is found by direct measurement that with these precautions the temperature changes along the tubes from *e* to *q* and the corresponding length *e′* to *q′* are of the order of 1 percent of the total changes. The thermal conductivity per unit length of the two inlet tubes is approximately the same and since the temperature changes are in all cases almost equal and opposite, a compensating effect should reduce the net transfer of heat along them.

On the outlet side little trouble with heat conduction is met, because the temperatures to be measured are so nearly equal to the surrounding temperatures. The interchange of heat between the two gas streams has been made as complete as is easily possible in order to produce this condition of temperature equality at the outlet side. The amount of interchange is somewhat dependent upon the gas used and the condition of flow but for all conditions the difficiency in interchange does not exceed 0.2 percent.

The enclosure defined by the walls *v* and *h* will therefore be at about the same temperature as the outlet thermometers and the shielding here represented is considered adequate for the purpose of isolating the region where the temperatures are measured. Measurements are carried out at different temperatures and since it is desired to have similar conditions for each experiment the entire assembly is enclosed by a constant temperature boundary which in all cases is maintained at a temperature 10° lower than the mean of the two bath temperatures. This boundary is a temperature controlled cylindrical shell about 18 inches long and 6 and 8 inches inside and outside diameters. Since the difference in bath temperatures is always 10°C one will be five degrees and the other 15°C above the temperature of the enclosure. To prevent this temperature distribution from producing dissimilar conditions when the bath temperatures are interchanged the shield *g* which is thermally connected to *w* is provided.

The temperature of enclosure *x* is controlled by a thermostat while the two bath temperatures are controlled manually by the observer. All temperature measurements are made by the use of five-junction constantan-copper thermocouples, used with a White double potentiometer and the usual auxiliary equipment.

The flow of gas is controlled by producing a constant rate of delivery to the low pressure bath. This is accomplished by maintaining a constant pressure on a capillary leak *z* (Fig. 2). In general the flow of gas on the low pressure side was maintained at 70 cc/sec. for oxygen, 80 for nitrogen and 160 for hydrogen.

Pressure measurements were made with a high class Bourdon spring gauge developed for this work, in the shops of this laboratory. It was calibrated against a dead weight gauge.

The author is indebted to the staff of the Bartol Research Foundation for providing facilities for this work, and the United States Gauge Company for calibrating pressure gauge.