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A NEW METHOD OF MEASURING THE VARIATION OF THE SPECIFIC HEATS (c_p) OF GASES WITH PRESSURE

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Abstract

A method is described whereby the ratio of c_p at a high pressure to c_p for the same gas at a pressure of one atmosphere taken as a standard is determined. The continuous flow principle is used in such a way that the necessity for measuring gas flow and heat input is avoided. A stream of gas at high pressure is brought to a temperature t_1 and passed through a heat interchanger acquiring there a temperature t_2, after which it is throttled to atmospheric pressure, brought to a temperature t_3 and returned to the heat interchanger, where its temperature again becomes t_2. The ratio of c_p at a high pressure to that at atmospheric pressure is equal then to $(t_3-t_2)/(t_2-t_1)$ plus certain small corrections. Measurements on commercial oxygen taken at a mean temperature of 26° C and pressures ranging from 15 to 100 atmospheres indicate a pressure coefficient of this ratio of 0.00165 ± 0.00005 per atmosphere.

IN CONSIDERATION of the need for further data on the specific heats of gases the present work was undertaken with the object of developing a method of determining the variation of c_p with pressure for a number of gases over a large range of pressure and temperature. Air[1,2] and ammonia[3] are the only gases on which direct measurements on c_p have been made over a considerable range of pressure. Indirect determinations follow from data on the Joule-Thomson effect. Here we note the work of Burnett[4] on CO_2 and Roebuck[5] on air. Recently Beattie[6] and Bridgeman[7] using the Beattie-Bridgeman equation of state have calculated c_p as a function of pressure and temperature for air and ammonia.*

The method of measurement to be described in this paper is of value because of its simplicity and the fact that the usual calorimetric errors are easily detected and in most cases eliminated. It possesses the advantage of avoiding the measurement of quantities of matter and of energy. On the other hand relative values only are determined.

A schematic arrangement of the apparatus is shown in Fig. 1. B and B' are constant temperature baths and I is a heat interchanger. The gas at high

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[1] Lussana, Nuov. Cim. 1894 to 1908.

[2] Holborn and Jacob, Berl. Ber. **1**, 213 (1914); also Zeit. Inst. **31**, 116 (1911).

[3] Osborne, Stimson, Sligh and Cragoe, Sci. Papers Bureau of Standards **20**, 65 (1924).

[4] Burnett, Phys. Rev. **22**, 590 (1923).

[5] Roebuck, Proc. Amer. Acad. Arts and Sciences **60**, 537 (1925).

[6] Beattie, Phys. Rev. **34**, 1615, (1929).

[7] Bridgeman, Phys. Rev. **34**, 527, (1929).

* For a review of the earlier work on this subject, see Partington and Shilling, "Specific Heats of Gases," London, 1924.

pressure passes through the tube *a* in the bath *B* where it comes to a fixed temperature. It then passes through the interchanger where its temperatures on entering and leaving are measured. After leaving the interchanger the pressure is reduced almost to one atmosphere by the reduction valve *V*. It now passes through a second constant temperature bath *B'*, back through the interchanger, and escapes. The temperatures at entrance and exit are measured as before.

The interchanger is so constructed that the two gas streams, after passing through a region where their entrance temperature are measured, are brought into such intimate thermal contact that they leave the interchanger at approximately the same temperature.

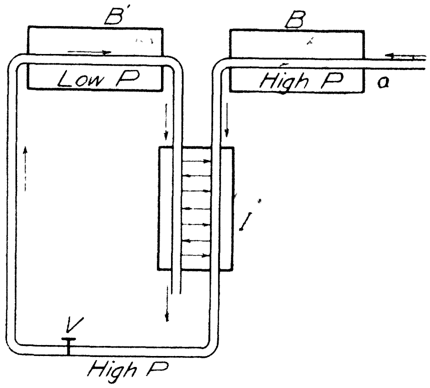

Fig. 1. Schematic arrangement of apparatus.

If there is no net passage of heat from the interchanger to the surroundings, then the amount of heat gained by one stream is equal to that lost by the other. Further, since these streams are equal, it follows that the ratio of the two specific heats are inversely as the temperature changes in their respective lines; i.e. $(c_p)/(c_p)_0 = (t_3 - t_2)/(t_2 - t_1)$[†]. Methods of applying small corrections to values thus obtained will be discussed later.

During the course of this work three different types of interchangers were constructed and used. The third and best will be described in detail. Fig. 2 shows a sectional drawing of the third interchanger. For convenience it is made schematic to the extent that only one gas line (low pressure) is shown entering and leaving. Except for a smaller diameter and a greater wall thickness the construction of the high pressure line where it enters and leaves is the same. In general the heavy lines represent polished copper an the light lines German silver, thinly copper-plated. The low pressure gas enters at *a* from the bath, its line of flow being protected by the heavy copper shield S_1 which is thermally coupled to the bath and the tube *a* within the bath.

[†] Recently attention has been directed to the work of Callendar (Roy. Soc. Phil. Trans. **212,** 1 (1912) and of Romberg Amer. Acad. Proc. **57,** 377–387 (1912) where the variation with temperature of the specific heat of water was determined by a similar method of flow calorimetry.

At *b* the gas is stirred by a small tuft of steel wool and passes along the thermometer tube *c* where it is further stirred in its path by small fins soldered to *c* (not shown).

At *d* the gas passes out through a copper tube which bends back sharply (not shown in drawing) and passes to *e* along the length of the shield S_2, to which it is soldered for thermal contact. The section *gg'* is interposed between the thermometer cell and the point *g* beyond which interchange begins, in order to minimize errors arising from heat conduction. Both this section and the corresponding section *uu'* of the high pressure line pass parallel to each other in a dead air space bounded by the tube *f*.

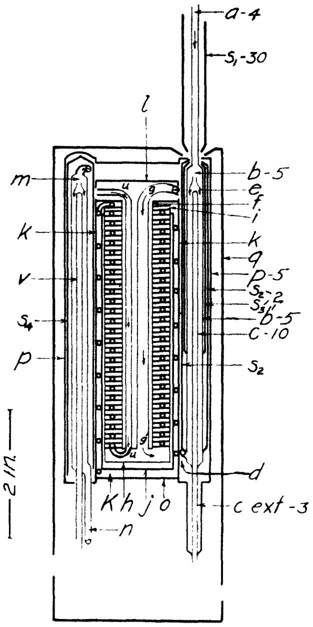

Fig. 2. Sectional drawing of interchanger. Copper in heavy lines, German silver in light lines. Letters refer to text; numbers indicate thickness of the walls in thousandths of an inch.

About the tube *f* are two thin copper ribbons wound helically and spaced as shown. To these are tin soldered the high pressure line shown by the small circles. Fitting snugly over this helical ribbon is a cylinder *h* closed at lower end. The two gas streams are therefore constrained to spiral around an axis (twenty-four times) in passing from *g'* to *i*, both being closely coupled thermally.

The cylinder *h* above referred to has a double wall, the outside of which *j* is of copper with an intervening dead air space. The high pressure line is wound on the outside of the cup as shown, soldered in place, and closed over with a thin copper cylinder *k* which makes a tight enclosure and extends across the upper end to provide the shield *l*. The two gas streams flow around seven or eight times before reaching the end chamber *K*. From *k* the low pressure gas enters a copper tube, which is soldered, as in the case of the inlet tube, to a shield S_4 and leads to the tube *m* which is exactly similar in size and arrangement to the inlet tube *b*. The gas leaves by way of the tube *n* (shown in part) and passes out into the room.

After the interchange of heat and before the exit temperatures are measured, both exit streams are put in good and approximately equal thermal contact with the end plate *o* as a means of making a base for the external shield *p* which surrounds the interchanger and provides it with an equal temperature boundary. A heavy copper cylinder *q* provided with a heating coil acts as a heater guard and is kept at the same temperature as the surface of the interchanger. This is accomplished by adjusting the heater current to maintain a zero reading on a five-junction copper-constantan thermocouple connected differentially between the constant temperature boundary (near its base) and the inside of the heater guard.

The thermal capacity of the interchanger, including the four thermometer tubes is equivalent to approximately 18 grams of water and requires on the average about 35 minutes to attain a steady state with a flow of 50 cc/sec. at atmospheric pressure.

The two baths are exactly similar, each consisting of an outer bath which contained an electric heating coil and thermostat as well as a large coil through which the gas flows, and an inner bath without heating or cooling coils which served to smooth out temperature fluctuations due to the heater current in the outer bath which surrounds it. The bath liquid was kerosene. The similarity of the baths and their thermostat mountings made it possible quickly to reverse the order of the bath temperatures.

All temperature measurements were made with copper-constantan, thermocouples, used differentially. The tubes *c* and *v* (Fig. 2) were provided for the insertion of a five-junction thermocouple to read the temperature change in the low pressure line. A similar arrangement was used for the high pressure line. In addition, for the purpose of checking, a two-junction couple was provided for the two inlet temperatures and a similar one for the two outlet temperatures. Only the copper lead wires were permitted outside the heater guard. Potential differences were measured with a White single poteniometer using the usual auxiliary equipment.

The similarity of the thermoelectric properties of the thermocouples was established by standardization and the formula of Adams[8] was used in obtaining the temperature intervals from the bridge readings in microvolts.

Pressure readings were taken on a spring gauge, devised by combining an optical indicating arrangement (telescope, mirror and sale) with a high class Bourdon spring of the type used in hydraulic gauges. This arrangement gave approximately 530 scale divisions for a pressure of 100 kg/cm^2. The gauge was calibrated against a Pratt and Whitney dead-weight gauge.

Commercial oxygen gas (water free) with a flow of approximately 50 cc/sec. was used. Two cylinders connected in parallel provided a reservoir sufficiently large to permit the taking of temperature and pressure readings continuously, thus eliminating the necessity of pressure control on the high

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[8] Adams, J. Wash. Acad. **3**, 469 (1913).

pressure side. The flow of gas was controlled from the low pressure side by adjusting an ordinary pressure reduction valve in such a way as to maintain a constant pressure (11 pounds/sq. in.) on a glass capillary leak.

The bath temperatures were controlled by mercury-in-glass thermostats so as to maintain one gas inlet stream at approximately 33.2°C and the other at approximately 18.8°C.

In making a run the baths were brought to steady state of temperature regulation and the gas started through the interchanger. The heater guard temperature was then adjusted until it was the same as the surface of the interchanger. After the steady state had been reached a zero reading on the heater guard thermocouple was maintained for about 15 minutes before taking calorimetric measurements. In regulating the guard temperature the observer also gave attention to the room temperature. It was thought desirable that the room temperature should be kept fairly constant with respect to the outside temperature of the interchanger, which differed from the arithmetic mean of the bath temperatures depending upon the pressure of the high pressure gas and the order of the bath temperatures. This was accomplished by keeping the room temperature such that the heater guard temperature could be regulated by limiting its power input to the small range 0 to 0.35 watt. After the heater guard thermocouple had indicated zero for 15 to 20 minutes, readings were taken on the pressure gauge and the four thermocouples. From two to four sets of readings were taken in a given pressure range. The bath thermostats were then interchanged thus reversing the order of the bath temperatures and another group of readings taken at a somewhat lower pressure.

Let the subscript 1 be applied to the state of the high pressure gas upon entering the interchanger and the subscript 2, to that upon leaving. Similarly let the subscripts 3 and 4 apply to the low pressure line entering and leaving respectively. Further, let i stand for the function $u+pv$. Now if q is the heat from various outside sources gained per gram for both streams, we have

$$q = i_2 - i_1 + i_4 - i_3. \tag{1}$$

Now it is reasonable to assume that the variation of these functions is linear over the small range of temperature and pressure in each gas line. We then get

$$q = c_p[T_2 - T_1 + \mu(p_1 - p_2)] + (c_p)_0[T_4 - T_3 + \mu_0(p_3 - p_4)] \tag{2}$$

where the subscript 0 applies to conditions at atmospheric pressure and μ is the Joule-Thomson coefficient. It finally follows that

$$\frac{c_p}{(c_p)_0} = -\frac{T_4 - T_3 + \mu_0(p_3 - p_4)}{T_2 - T_1 + \mu(p_1 - p_2)} + \frac{q}{(c_p)_0[T_2 - T_1 + \mu(p_1 - p_2)]} \tag{3}$$

Since we measure $(T_4 - T_3)/(T_1 - T_2)$ we write Eq. (3) in the form:

$$\frac{T_4 - T_3}{T_1 - T_2} = \frac{c_p}{(c_p)_0} + \phi(\mu, q) \tag{4}$$

where $\phi(\mu, q)$ is a correction term. The sign of this term is changed, but not its value if we interchange the bath temperatures; so that these corrections can be eliminated. The whole problem thus centers on the accurate measurement of the various temperatures. With an ideal interchanger in which pressure drops and thermal leakages are negligible we see from what has been said before that the last term in Eq. (4) would vanish.

The mean values of the ratio on the left of Eq. (4) for each group of readings were calculated and they are shown plotted against the corresponding mean pressures in Fig. 3. Curve 1 represents values obtained when the high pressure bath was maintained at 33.2°C and the low pressure bath at 18.8°C; while curve 2 gives the values obtained with the reverse order of bath temperatures. The fact that curves 1 and 2 do not coincide and pass through the point $p=1$ atmosphere and $(t_4-t_3)/(t_1-t_2)=1$ gives evidence that we are not dealing with the ideal calorimeter just referred to.

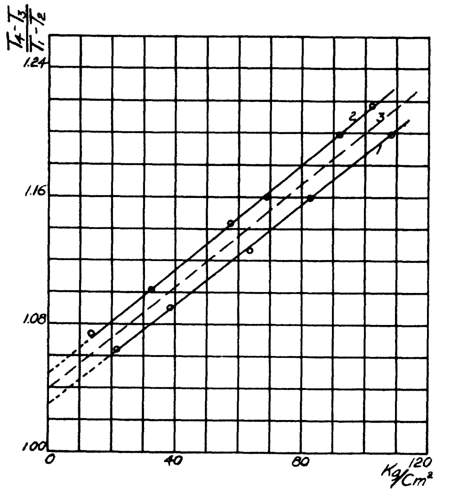

Fig. 3.

In order that the difficulties might have further study a set of observations was taken with both baths set at 26°C and a flow of 50 cc/sec. A cooling effect in each gas stream as it passes through the interchanger was observed. The magnitude of the effect for three different pressure regions is shown in Table I.

If corrections of the type given in the last column of Table I were to be applied along the length of the two curves the general effect would be to change the shape of each slightly and bring them somewhat closer together. Since the proposed corrections would not affect in any sense the mean curve 3 of 1 and 2 they are not applied. These corrections include the Joule-Thomson effect, velocity cooling and possible index errors; and we conclude that the mean curve is independent of the Joule-Thomson effect and heat leakage q.

A part of the separation between curves 1 and 2 might be attributed to temperature effects upon the specific heat c_p of oxygen. Since there is considerable evidence to show that c_p at atmospheric pressure changes very slightly with temperature in the region in which we are interested, we shall consider it as constant. On the other hand, c_p at pressures of 60 and 100 kg/cm^2 decreases quite considerably with temperature increase between 0 and 50°C. Data of this type on oxygen are lacking but if we adopt values calculated by Beattie[6] or by Bridgeman[7] for air and make corrections to curves 1 and 2, assuming air and O_2 to be alike in these respects, we find that the correction is more than sufficient to bring them together at 100 kg/cm^2 pressure. If, on the other hand, we use observed values quoted by Beattie, the corrections so obtained are not sufficient to reduce the divergence between 1 and 2 at 100 kg/cm^2 by more than 50 percent. If we make similar corrections at lower pressures, 0 to 20 kg/cm^2, it is seen that the effect almost vanishes. It should be observed, however, that the corrections listed in Table I for this region are almost sufficient to bring the two curves together.

TABLE I

High pressure kg/cm^2	High Pressure line cooling °C	Low Pressure line cooling °C	Calculated correction factor for corresponding points on 1 and 2, Fig. 3.	
13	0.023	0.020	Curve 1	1.008
			Curve 2	0.992
64	0.008	0.008	Curve 1	1.002
			Curve 2	0.998
83	0.015	0.012	Curve 1	1.003
			Curve 2	0.997

It is apparent therefore, that uncorrected curves obtained in the manner that 1 and 2 were obtained will never coincide for the large temperature intervals here used and may have slopes such that the divergence between them will increase slightly with increases in pressure. It is equally apparent however, that we are justified in drawing a mean curve 3.

The residual errors giving the effect of moving the mean curve 3 upward by approximately 4 percent must be due to difficulties in measuring temperature changes in one of the thermometer tubes. The difficulty doubtless lies in the fact that heat is conducted along the high pressure entrance thermometer tube. An examination of the entrance thermometers in the interchanger gives evidence of the possibility of some interchange of heat between the two gas streams before the temperatures are determined. The effect of this is to induce a temperature gradient in the thermometer cells and therefore an uncertainty in meaning of the temperature readings. The results indicate that this effect is larger in the case of the high pressure line as might be expected from the construction. It also appears in this connection that errors of this type depend only on the general temperature distribution in the apparatus to a high degree of approximation. The slopes of the curves in Fig. 3, therefore, are not affected appreciably. It is of especial interest to note that with the first (and very faulty) apparatus curves were obtained intersecting the horizontal axis at about 30 kg/cm^2 having, however, appproximately the same slope as the mean curve here given.

The apparatus was designed to work in the region from 20 to 200 atmospheres and therefore too much confidence should not be placed in measurements taken at pressures lower than 20 atmospheres.

The mean value of the slope between 30 and 100 kg/cm^2 is 0.00160 per unit of pressure here used, or 0.00165 per atmosphere. The value obtained from the first apparatus mentioned above is 0.00176 per atmosphere and that from a second apparatus is 0.00171 per atmosphere. The two earlier sets of apparatus, moreover, embodied a radically different method of measuring temperatures, namely that the thermometer tubes and their respective shields for measuring t_1 and t_3 were located in the baths B and B' (Fig. 1).

Although the present work has been done on oxygen, it is not without interest to compare results with those already obtained for air. The experimental work of Roebuck gives 0.00140 per atmosphere, while the calculations of Beattie from the Beattie-Bridgeman equation of state yield, 0.00166 per atmosphere. The experiments of Holborn and Jacob while performed at 59°C (where the value 0.00119 emerges) may be reduced to the temperatures of these experiments by using the calculations of Beattie, resulting in the value 0.00162 per atmosphere.

The agreement in the values for $(d/dp)\ [c_p/(c_p)_0]$ as obtained by the use of three calorimeters is considered sufficient evidence for establishing the validity of the method for precise work. This point could be made more impressive if space could be taken to describe in detail the great differences in type and quality of the three sets of apparatus. The arrangement of the apparatus last used possesses many defects, many of which can be almost completely eliminated by more careful design and construction. Perhaps the most important feature of the method over and above its simplicity is the fact that the sources of error speak their presence in the nature of the results which it yields.

Plans to investigate gases other than oxygen and to extend the readings over a range of temperature were brought to a halt by the development of a leak in the interchanger. This, together with the fact that designs for an improved apparatus were in mind, made it seem wiser to publish the results already obtained and defer the general survey until the new designs could be realized.

In conclusion the author wishes to express thanks to Professor L. G. Hoxton who proposed the method for his interest during the progress of the work.