

MEASUREMENT OF THE JOULE-THOMSON COEFFICIENT¹

A Laboratory Experiment

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SINCE the properties of gases, real and ideal, are used extensively as illustrations in elementary thermodynamics, there has seemed to be a need for more quantitative laboratory experiments involving gases. Measuring the Joule-Thomson coefficient, μ , of a gas would seem to be the most practical and direct method of studying deviations of a real gas from ideal behavior, and of illustrating some of the simple thermodynamic relationships. The simple apparatus described below was assembled in a relatively short time from items usually available in a college laboratory, the only expensive item being a sensitive, low-resistance, d.-c. galvanometer.² For CO₂ and N₂, values of μ have been obtained which agree with the accepted values to within the experimental uncertainty of ± 3 per cent of the present results. It is interesting to note that the original "porous plug" experiments of Joule and Thomson (*J*), which were carried out exactly 100 years ago, yielded remarkably accurate results for the same gases. It is a worth-while experience for students to read the original papers of Joule and Thomson; the two scientists become much less names in a textbook and much more the great experimentalists and thinkers who helped to build the science of thermodynamics. In what follows it is assumed that the reader is familiar with the nature of the "porous plug" experiment and the basic principles involved.³

DESCRIPTION OF THE EXPERIMENT

The apparatus used is shown schematically in Figures 1 and 2. The porous plug consists of a fine-grained, sintered, Pyrex glass disc *A* sealed into a tube *B* of 30-

mm. diameter.⁴ Gas at the higher pressure, P_2 (say 1 atm. $< P_2 < 2$ atm.) flows in at *C*, passes through the plug *A*, and finally passes out to the atmosphere through the holes *D*⁵ in the outer jacket *E*, which serves mainly to minimize the heat transfer through the walls of *B*. The outer jacket is supported by asbestos or cork rings (cross-hatched) and serves also to support the lower thermocouple.

The difference in temperature, ΔT , between the high pressure gas directly above the plug *A* and the low pressure gas below is measured by a single-junction copper-Constantan thermocouple *F*, *F'*⁶ as shown. The wires used were small enough to minimize heat conduction down the wire to the junctions, but stiff enough to support the junctions in the positions shown. The wires were sealed into the capillary tubes by sucking into the capillary hot liquid Apiezon W wax.⁷ As shown in Figure 1, the leads (copper) were connected directly to the galvanometer,² the reading of which was directly proportional to ΔT . The proportionality constant was obtained by direct calibration against Beckmann thermometers (before assembly) and also from accurate knowledge of the resistances in the circuit. The galvanometer sensitivity was reduced when necessary by using an accurate resistance box as a shunt. With no shunt one mm. deflection corresponded to 0.0053°C. difference in temperature.

The whole assembly shown in Figure 2 was packed into the container, *G*, with vermiculite (for thermal insulation) and the container *G* immersed, as shown, in a constant-temperature water bath. It was found essential to control carefully the initial temperature of the entering gas by passing it through the long copper spiral *H*, also immersed in the bath. The gases came

¹ These experiments were carried out mainly in the physical chemistry department of the Massachusetts Institute of Technology, Cambridge, Massachusetts.

² A Leeds and Northrup No. 2430-D d.-c. galvanometer was used. The resistance was rather high, but actually the voltage sensitivity is the important factor. The characteristics were: current sensitivity, 0.000411 amp./mm. deflection; resistance, 534 ohms.

³ See any good textbook of physical chemistry or thermodynamics, *e. g.*, GLASSSTONE, "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co., Inc., New York, 1946, pp. 286 and 292.

⁴ This (*A* and *B*) is a standard item manufactured by the Corning Glass Co., item No. 39570, diameter 30 mm., porosity F, in Catalogue No. LB-31.

⁵ There are six holes equally spaced around the tube at the position shown.

⁶ No. 36 insulated copper wire and No. 30 insulated Constantan wire.

⁷ A low vapor pressure sealing wax obtainable from J. G. Biddle Co., Philadelphia, Pennsylvania.

from commercial cylinders and were cooled considerably⁸ on passing through the pressure regulator attached to the cylinder. The high pressure is maintained sufficiently constant by using the standard commercial pressure regulators, and the difference in pressure, ΔP , was measured accurately by connecting the high pressure side to a mercury manometer open to the atmosphere on the low pressure side. The apparatus is designed so that no significant differences in pressure exist except across the plug A.

After the system has come to thermal equilibrium (no gas flowing), the gas flow is started and the high pressure adjusted to a given value. On the average it was necessary to take readings of ΔT over a period of about 30 minutes under constant pressure conditions to make sure that ΔT had become sufficiently independent of time (say, less than 0.01° change in five minutes). In this manner values of ΔT corresponding to various high pressures (therefore ΔP 's) are obtained. Since μ is to a good approximation independent of pressure over a range of a few atmospheres, a plot of ΔT against ΔP should be a straight line passing through the origin and with the slope μ ; for a single determination we can write $\mu = \Delta T / \Delta P$. Figure 3 shows data obtained by us and by students in the undergraduate physical chemistry laboratory at Bryn Mawr College for CO_2 and N_2 and also by Joule and Thomson for CO_2 and air⁹ for comparison. Our values for 20°C . of 1.06 ± 0.03 for CO_2 and 0.23 ± 0.01 deg./atm. for N_2 compare satisfac-

⁸ In the case of CO_2 the Joule-Thomson cooling in the pressure regulator is so great that, over a period of time, heat must be supplied to the regulator to prevent solid CO_2 from plugging the throttling valve in the regulator. Recall the well known demonstration of making solid CO_2 "snow" by the rapid expansion from a cylinder through a porous bag.

⁹ Oxygen and air have a Joule-Thomson coefficient very close to that of nitrogen at low pressures; actually Joule and Thomson used a mixture of CO_2 and air (obtained from fermentation!) and calculated the value of μ for pure CO_2 by using a somewhat arbitrary assumption concerning mixtures of gases.

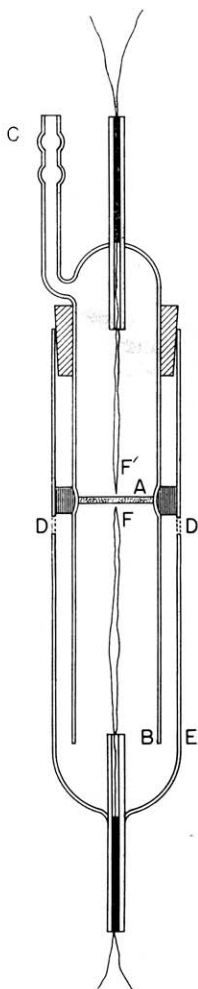


Figure 1

A, Porous (sintered glass) plug
B, Inner glass tube
C, Inlet for high-pressure gas
D, Outlets for low-pressure gas
E, Outer glass tube
F, Thermocouple junctions

torily with the accepted values (2,3) of 1.10 for CO_2 and 0.23 for N_2 under the same conditions of pressure and temperature. The uncertainties are estimated from those in the individual ΔT measurements.

It seems clear that the apparatus described represents only one of a number of possible (and equally simple) designs, many of which would give results as good or better than those presented. In addition to Joule and Thomson's paper, those of Roebuck and collaborators (4-7) can be consulted in designing an apparatus. The sources of systematic experimental errors boil down mainly to unwanted transfers of heat by radiation and by conduction across the plug and walls of the vessel and down the thermocouple wires. For the apparatus described above, the error in temperature measurement owing to the nonrandomness of the molecular velocities introduced by the bulk flow of the gas can be shown easily to be negligibly small.¹⁰ If mercury-in-glass thermometers are used, a method similar to that of Joule and Thomson (1) could be used to avoid errors resulting from the effect of pressure on the thermometer readings.

TREATMENT OF THE DATA

Since μ values for a gas provide quantitative information concerning the gas imperfections, it is interesting, as an exercise, to see how μ is related to other properties of the gas and of the individual gas molecules. Below are listed some suggestions for calculations of possible

¹⁰ The extra kinetic energy corresponding to the component of velocity introduced by the bulk (Poiseuille) flow of the gas is very small compared to the average kinetic energy of random motion.

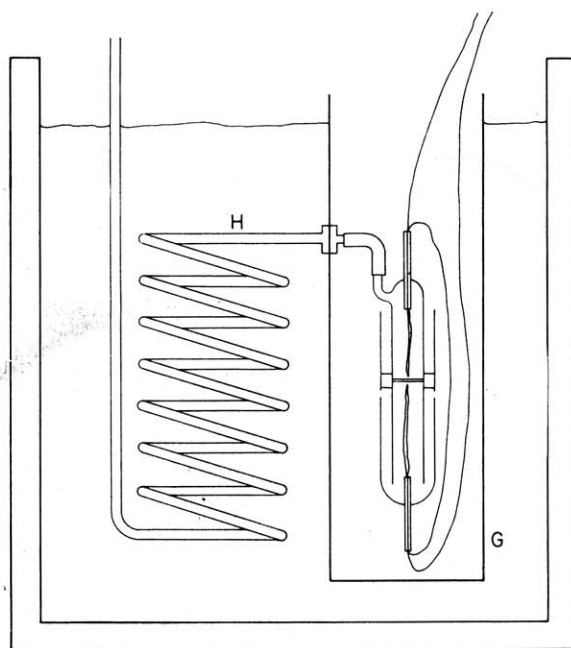


Figure 2

G, Metal can in thermostat
H, Copper coil in thermostat

interest involving μ ; in the table are given numerical values for CO_2 and N_2 .

(1) Check the exact thermodynamic relation,³ $\mu C_p = T(\partial V/\partial T)_p - V$, by using good experimental values for C_p (see the table (II)) and by calculating the other quantities from the Beattie-Bridgeman equation of state (2). The slight discrepancy in the table must imply inadequate experimental values or (as probably in this case) the slight inadequacy of the empirical equation of state. (V stands for volume per mole.)

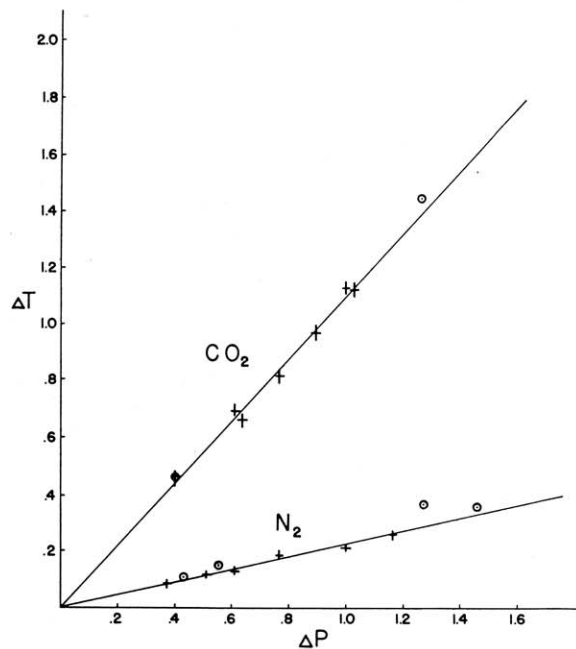


Figure 3

+ = points obtained by students
o = Joule and Thomson's original data

(2) If the van der Waals equation of state is assumed, the following equation can be shown to be a good approximation: $\mu C_p = (2a/RT - b)$, where a and b are the van der Waals constants. Check the validity of this assumption. This equation relates μ to the van der Waals constants (III in the table).

(3) Using the equation of state data (from, say, the Beattie-Bridgeman equation) calculate the "internal pressure," $(\partial E/\partial V)_T$ (IV). In the van der Waals equation this is represented as the correction to be applied to the external (measured) pressure, and hence should be approximately equal to the correction term, a/V^2 (V).

(4) Calculate the heat absorbed, $q = \Delta E$, for the expansion of 1 mole of gas, initially at 2 atmospheres, into a vacuum to give a final pressure of 1 atmosphere, and at a constant temperature of 298°K. This corresponds to Joule's earlier experiment (9) on free expansion, and it is easy to see why the effect was too small to detect. For CO_2 , q is 6.5 cal., and if the water bath involved contained several liters of water, the temperature change

Numerical Data for CO_2 and N_2 ^a		
Equation of state data	CO_2	N_2
Coefficients of Beattie-Bridgeman equation (2)		
β	-3.0598	-0.1497
γ	+0.35706	+0.03518
δ	+0.00466	-0.00004
V_i (ideal volume = RT/P)	24.4539	24.4539
Calculated from B.-B. equation		
V (actual)	24.3290	24.4478
$(\partial V/\partial T)_p$	+0.08290	+0.08225
$(\partial(PV)/\partial P)_T$	-0.1247	-0.0061
Coefficients of van der Waals equation (2)		
a	+3.61	+1.31
b	+0.0428	+0.0373
Heat capacity data (8)		
C_p	+0.366	+0.287
C_v	+0.285	+0.205
Joule-Thomson coefficients (2, 3)		
Derived quantities		
I $C_p\mu$ (experimental)	+0.392	+0.064
II $C_p\mu$ (calculated from B.-B. equation)	+0.375	+0.063
III $C_p\mu$ (calculated from v.d.W. equation)	+0.252	+0.069
IV $(\partial E/\partial V)_T$ ("internal pressure")	+0.011	+0.0024
V a/V^2 (van der Waals correction term)	+0.0061	+0.0022
VI $(\partial E/\partial P)_T$	-0.268	-0.060
VII $(\partial T/\partial P)_E$	-0.95	-0.29
Change in energy for various processes (kg.-cal./mole)		
VIII Increasing average intermolecular distance from 27 Å. (at 2 atm.) to 34 Å. (at 1 atm.)	+0.0065	+0.0015
IX Evaporation of condensed phase (av. intermolecular distance = 4 Å.) at 1 atm. equilibrium pressure (2)	+5.6	+1.2
X Breaking one chemical bond (av. for CO_2) (dissociation to ground states of atoms) (10)	+163	+85

^a $P = 1$ atm., $T = 298^\circ\text{K}$. Unless otherwise noted, the units are liters, atmospheres, moles, degrees K.

to be observed would be of the order of 0.001°. Note, also, that q provides us with a quantitative measure of the average force between the molecules under normal conditions; for q represents the increase in potential energy (per Avogadro's number of molecules) when the average distance of separation of the molecules is increased by 7 Å. (from 27 Å. at 2 atm. to 34 Å. at 1 atm.) (VIII). This quantity may be compared with similar values for evaporation of the condensed phase (IX), and breaking a chemical bond (X). It is of interest also to calculate the change in temperature of the gas if the free expansion from 2 to 1 atm. is carried out (in our imaginations) under conditions where the gas is thermally isolated, *i. e.*, exchanges no heat with the container (VII).

For the examples chosen, the table provides a quantitative expression of the fact that CO_2 deviates much more than N_2 from ideality. We feel that carrying out the experimental measurement of the Joule-Thomson

coefficient and performing some of the suggested calculations make more tangible, and give more concrete significance to, the physical picture of a real gas.

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