work of Dyas and Hill, and that $\Delta F_0^{\ddagger}$ agrees very well. The anomalous behavior of the former quantities previously found in 60% methanol was not found in the present experiments.

Discussion

Although the isomeric change accompanying the mutarotation of glucose is structurally a simple one, the mechanism by which it is brought about by various catalysts is not clear. While it is possible that the increased association of acetic acid which would be expected as methanol is added to the solution, might explain the unexpected constancy of the rate if the true catalyst were the dimer, there are no data on the extent of the dimerization in these solvents to support such a theory. Further work involving other catalysts, and an elucidation of the mechanism of the isomerization is needed.

Summary

The mutarotation of glucose has been studied using acetic acid as the catalyst in three mixtures of methanol and water at 35 and 45°. The catalytic coefficients for the solvent and for acetic acid have been evaluated. The ionization of acetic acid in the solvent mixtures used has been measured, and the ionization constants evaluated by extrapolation.

The catalytic constant for acetic acid has been found to be independent of the MeOH concentration, and thus of the dielectric constant of the medium.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE OHIO STATE UNIVERSITY]

An Apparatus for Measuring Joule–Thomson Effects in Gases by Direct Expansion Through a Valve[1]

BY HERRICK L. JOHNSTON

Introduction

A valve was used in the first experiment of Joule and Thomson[1a] but was abandoned by them in favor of a porous clay plug with "axial" flow because of the lesser difficulty with heat flow between the high and low pressure sides. A valve was used again by Olszewski[2] in determining inversion points for hydrogen, nitrogen and air. In 1909 both Bradley and Hale[3] and Dalton[4] the latter working in the Leiden Laboratory—published the results of throttle experiments with air. Since then the valve method has been abandoned in favor of apparatus built on the porous plug principle. The most extensive and most accurate determinations of Joule–Thomson coefficients have been made by Roebuck and co-workers,[5] at the University of Wisconsin, who used an unglazed porcelain cup with radial flow of gas through its walls as "porous plug." This type of plug was also used by Hoxton,[6] who gives in his paper an historical outline of Joule–Thomson work prior to 1919.

The use of a porcelain plug—and particularly of the cup shape with radial flow of gas—appears to possess a distinct advantage over other types of Joule–Thomson apparatus because of the low thermal conductivity of porcelain and the possibility of reducing errors resulting from heat leak between the low pressure and high pressure sides. However, an apparatus of the throttling type offers advantages in simplicity of design and operation. Its practicability depends upon ability to eliminate significant error from heat leak.

The measurements of Bradley and Hale,[3] and those of Dalton,[4] revealed clearly the principal sources of error in Joule–Thomson measurements. Bradley and Hale obtained direct evidence of the thermal effect of "jet kinetic energy" noticed originally in the early work of Joule and Thomson.[1a] By this is meant the conversion of disordered thermal energy into ordered kinetic energy in the high velocity jet. The effect is to lower the temperature of the gas in the jet and is greatest where the cross section of the gas stream is least—such as between stem and seat of the valve. It disappears a few centimeters beyond the nozzle, when the motion of the gas molecules has again become random. The effect may amount to several degrees adjacent to the nozzle and, presumably, may amount to several tens of degrees in the region of greatest constriction. This effect may introduce error into the measurement of Joule–Thomson effects in two ways: (1) the temperature measured in the low pressure gas stream may be too low if measured too near to the nozzle; (2) heat leak to the cold gas will be increased as

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(1a) Joule and Thomson, *Phil. Mag.*, **4**, 481 (1852).

(2) K. Olszewski, *Ann. phys.*, **7**, 818 (1902); *Phil. Mag.*, **13**, 722 (1907).

(3) W. P. Bradley and C. F. Hale, *Phys. Rev.*, **29**, 258 (1909).

(4) J. P. Dalton, Leiden Comm. No. 109c (1909).

(5) (a) Burnett and Roebuck, *Phys. Rev.*, **30**, 529 (1910); (b) Burnett, *ibid.*, **22**, 590 (1923); (c) Roebuck, *Proc. Am. Acad. Arts Sci.*, **60**, 537 (1925); *ibid.*, **64**, 287 (1930); (d) Roebuck and Osterburg, *Phys. Rev.*, **43**, 60 (1933); **45**, 332 (1934); **46**, 785 (1934); **48**, 450 (1935).

(6) L. G. Hoxton, *Phys. Rev.*, **13**, 438 (1919).

the gas passes between stem and seat. This heat leak may even be so large as to reverse the sign of the apparent Joule–Thomson effect in some cases as was observed, in fact, by Dalton[4] in his first series of experiments with a brass valve. In one experiment air expanded, at 0°, from 20 atmospheres down to 1 atmosphere was actually warmed although its normal Joule–Thomson effect is 5.4° of cooling. This large error was somewhat reduced when the gas flow through the brass valve was increased by working with a wider opening of the valve. It was removed, for flow rates greater than 11 liters per minute, when a glass valve with a wooden stem was substituted for the brass valve. The glass valve withstood pressures up to about 70 atmospheres.

We have designed and constructed an apparatus with which we have been able to measure Joule–Thomson effects without significant error from either "jet kinetic energy" influence on measured temperatures or thermal conduction. An essential feature of the apparatus is a specially constructed valve with a thin monel body, an ebony valve stem and a valve seat of either lignum vitae or lucite. We have used the apparatus between 60 and 300°K and for pressures up to 200 atmospheres.

Joule–Thomson Apparatus

Figure 1 is a general plan of the apparatus. High pressure hydrogen which has already exchanged its heat with low pressure return hydrogen enters at A; passes downward through the coils of the interchanger B, where it exchanges heat with the vapor from boiling liquid air; goes to the bottom of coil C, which is immersed in liquid air; passes through liquid air trap D, which is made of thick walled copper; passes downward through coil E and enters the expansion valve at point F. A gage line at G leads to a calibrated test gage which records the pressure above the valve seat in the valve H.

The expansion chamber is a glass dewar 38 cm. long by 7.6 cm. i.d. enclosed in a brass cylinder 41 cm. long. The valve body H is soldered into the lid of this cylinder so that almost the entire two inch portion with 1.19 mm. wall (*cf.* Fig. 2) is below the lid. The entire upper portion of the dewar, and the inch of cylinder above the top of the dewar is packed with fiber glass insulation to make conditions within the dewar as nearly adiabatic as possible.

The gas stream from the orifice is conducted through a 2.22 cm. o.d., cylinder 10 cm. in length, formed from Monel metal sheet 0.254 mm. thick, and passes out at the bottom through a copper screen soldered to a copper thermocouple ring I. The lower half of this 2.22 cm. cylinder is filled with loose copper turnings J, to produce eddies in the flowing gas. The 2.22 cm. cylinder is held in place by a fiber cross piece which is anchored to the 9.52 mm. o.d. monel tubes K,K. A few small holes are drilled in the thin monel cylinder just

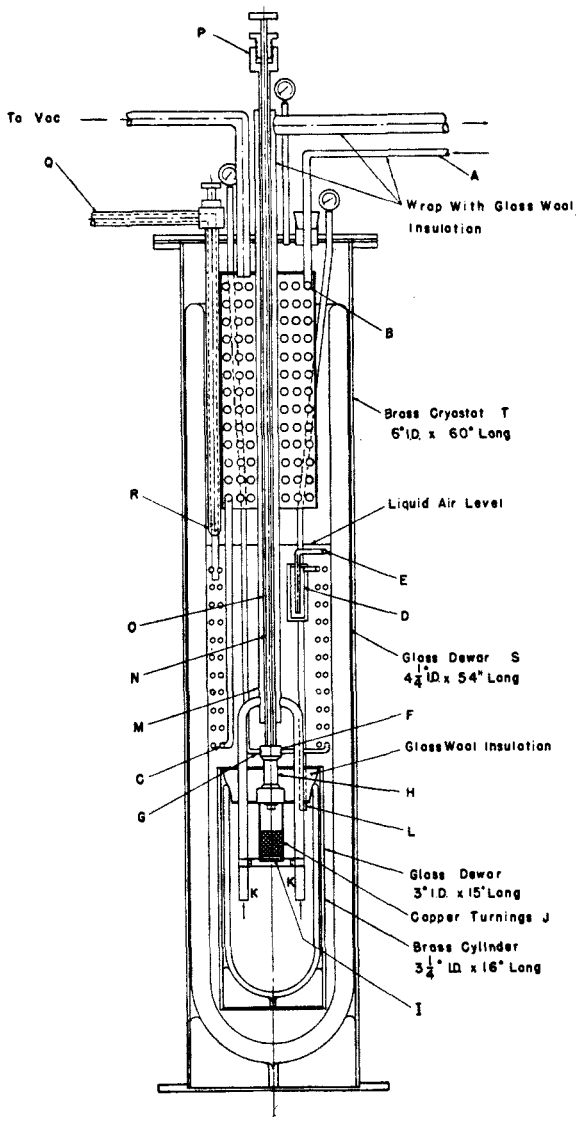

Fig. 1.—Joule–Thomson apparatus: vertical scale 10″ = 1′; horizontal scale 20″ = 1′.

above the thermocouple ring to bleed off a portion of the gas into the dewar and so prevent direct heat conduction from a layer of quiet gas near the top of the expansion chamber. To avoid a quiet pocket of gas below the thermocouple ring the two tubes K,K which conduct the expanded gas out of the expansion chamber extend to about the middle of the dewar (*i.e.*, to a point about 7.5 cm. below the thermocouple ring). A gage line, L, communicates with a low pressure gage which registers the pressure in the expansion chamber.

Standard thermocouples are soldered to the high pressure copper tubing at F and into a well in the copper ring I. The thermocouple from the expansion chamber passes up through one of the 9.52 mm. tubes K,K.

The return hydrogen passes upward through K,K into the 1.90 cm. brass tube M. The 5.55

mm. monel rod N that turns the valve is enclosed in the 9.52 mm. o.d. × 0.89 mm. wall monel tube O that is silver soldered to the valve body at the bottom and provided with a packing gland P at the top. O passes up through the center of the brass tube M. This arrangement has the advantage that heat exchange with the cold return hydrogen compensates for heat leak down N and O.

Liquid air enters the apparatus through the vacuum jacketed siphon tube Q and the control valve R. The flow of liquid air is regulated so as to maintain a constant level above the coils C,E, during runs. The level is observed through windows in the 138 cm. Pyrex dewar S (10.9 cm. i.d.) that encloses the apparatus, and in the brass cryostat vessel T. The temperature of the boiling liquid air was controlled by means of manually controlled vacuum evaporation.

Valve Design

Details of the valve construction are shown in Fig. 2. The valve body was turned down from a piece of monel bar 8.32 cm. in length. The ends were turned down to 1.90 cm. o.d. and drilled out and shaped to accommodate an interchangeable valve stem and an interchangeable valve seat, respectively. The two-inch middle portion of the valve body was turned to 1.27 cm. o.d. and given a 1.19 mm. wall, to reduce heat flow to the seat and to the orifice beyond the seat. The interchangeable stem, 31.8 mm. in length, was attached to 6.35 mm. monel rod, that carried the threads for adjusting the valve. After some preliminary experimentation ebony was adopted for the valve stem.

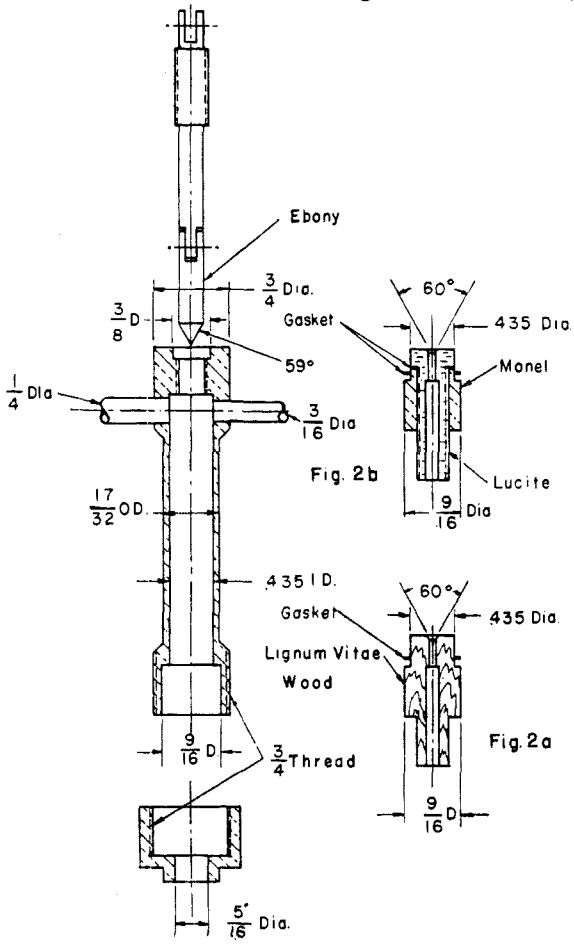

Fig. 2.—Valve detail: scale, 2 = 1 inches.

The valve seat, and orifice, were machined out of suitable nonconducting materials shaped so as to fit into the lower recess of the valve body, as shown in the diagram. In the initial design this cylindrical seat block was in one piece and was held in place by a flanged nut, as shown in Fig. 2a. A thin lead gasket on the upper shoulder of the valve seat was intended to prevent leakage around the valve seat block. This design proved satisfactory with wooden valve seats since most woods possess thermal expansion coefficients along the grain that are less than that of monel, so that the gasket tightens when the valve is cooled. However, the design was unsatisfactory for plastic materials which we used in most of our work, because thermal expansion coefficients for plastics are generally less than that for monel. As a result, there was bad leakage past the gasket with all plastic valve seat blocks, when the valve was cooled to liquid air temperature.

This defect with plastic valve seats was remedied by redesigning the valve seat block, as illustrated in Fig. 2b. In this design the block is made in two parts, an inner cylinder of plastic threaded into an outer cylinder of monel. The combination block is held in place by the same flanged nut employed in the original design. The original lead gasket seal, which leaked at low temperatures with an all-plastic block, is now held between two monel surfaces, and holds satisfactorily. A new gasket was necessary between the two parts of the combination block, as is shown in the diagram. However, the shrinkage of the plastic inner cylinder, at low temperatures, tightens the gasket seal and prevents leakage.

We originally discarded glass as a valve seat material because of its fragility and because of the difficulty of machining it, or of molding it to a machine fit. We experimented with several kinds of hard wood. With most of these results were unsatisfactory due either to softness, which made machining difficult, or to leakage of high pressure gas along the grain. Eventually we had success with heart wood from a museum specimen of lignum vitae. This valve seat proved satisfactory at both room temperature and liquid air temperature for about 40 runs. In time, however, the seat channelled, from mechanical action of the high velocity gas stream. Efforts to duplicate the valve seat from another piece of lignum vitae (taken from the center of a bowling ball) failed due to the tendency of this sample to either buckle or split under tension.

Among plastics, we experimented first with several of the phenolic-aldehyde type. These proved mechanically unsatisfactory in initial tests. Finally, we experimented with lucite, which machines well and gives excellent results at both room and liquid air temperatures (design 2b). Our first lucite valve seat was broken through an accident after about 60 runs; but was replaced, and this second one has now given good service for more than 200 runs.

Operating Procedure

High pressure gas is delivered to the Joule–Thomson apparatus by means of a compressor which withdraws gas from a gas holder sealed with oil. The compressed gas passes through a coil immersed in a refrigerant bath on its way to the expansion apparatus, to remove oil and water (the liquid air trap within the apparatus is a second, and more efficient step in freezing out condensable impurities). The low pressure gas that emerges from the expansion chamber and passes up through the 1.90 cm. brass tube passes through a heat interchanger, where it receives heat from the incoming, high pressure gas; then passes through a gas meter, which measures the flow; and returns to the gasholder, where it is ready to repeat the cycle.

The pressures at the expansion valve were controlled manually in runs taken to date, although a barostat of the type used by Roebuck[5] would appear to be an advantage. We have constructed such a barostat but have had some difficulty in getting it to operate satisfactorily within the desired limits of pressure control. This is no doubt a purely mechanical difficulty, that we hope to correct later.

The flow of gas was controlled either by varying the speed of the motor that drives the compressor or by "spilling" a portion of the high pressure gas back to the compressor intake by means of a bypass valve near the compressor. We have varied the flow rate, in the course of our runs, between 55 and 1700 liters per minute. The apparatus has given good results at either extreme and the measured Joule–Thomson effects have been independent of flow rate. This indicates that we have been successful in reducing heat leak, as well as "jet velocity" effect, to below significant limits.

Pressures and temperatures are measured simultaneously during the runs. Full readings are taken on the copper–constantan thermocouple soldered to the inlet tube at F (Fig. 1), which indicates the temperature from which expansion occurs and difference readings between the couple at F and the couple at I. The difference readings are used to compute the Joule–Thomson effect. Small corrections to these measured ΔT's are applied for: (1) small changes in the temperature at F and (2) small changes in pressure during the run. These corrections are applied by reference to: (1) isobars and (2) isotherms, constructed from the data. A Wenner thermocouple potentiometer is used for the thermocouple measurements. The thermocouples that we employ were compared, at about 5° intervals, with one which was standardized by the U.S. Bureau of Standards between 18 and 300°K.

Performance

As we have already mentioned, we have obtained results which are independent of flow rate between wide limits of 60 and 1700 liters per minute, which serve to indicate that our data are not influenced by significant amounts of heat flow to the jet, or to the expansion chamber.

In our early runs (which were made with hydrogen at room temperature and with 1700 liters per minute) we were gratified to observe that there was rapid response between variations in pressure and the temperature difference between the thermocouples. This is illustrated in Fig. 3 for a run made, with hydrogen, at room temperature. This run was made at a pressure of 170 atm. and a flow rate of 1700 liters per minute. The pressure was allowed to drift between valve settings, and the variations in ΔT were noted. These data were taken with the lignum vitae valve seat, but results with lucite were similar.

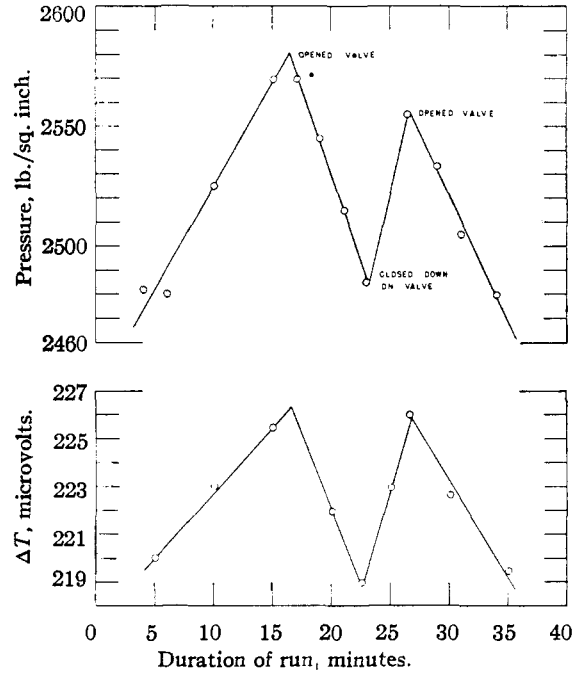

Fig. 3.—Correlation between observed ΔT's and variations in pressure.

Good temperature control of the inlet gas is important. Sudden changes in the inlet temperature are accompanied by equally sudden changes in the measured ΔT's which are to be attributed either to: (1) failure of the ingoing gas to reach thermal equilibrium with the wall of the copper tubing, immediately, or (2) lag in the response of the out-

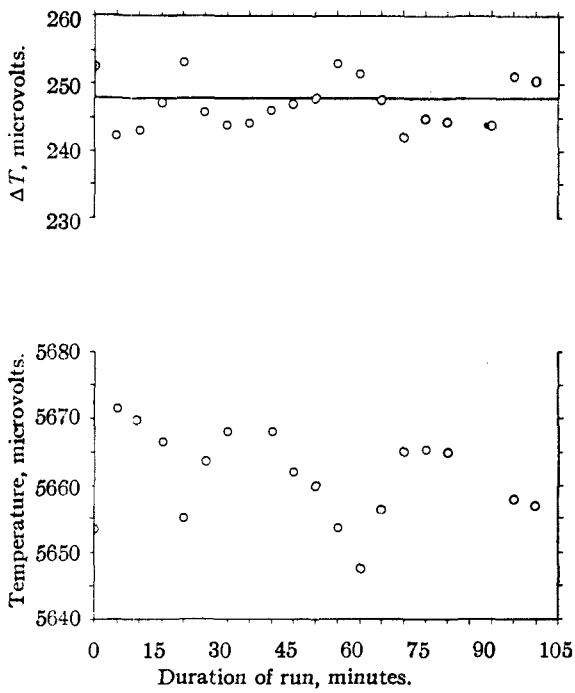

Fig. 4.—Lag in adjustment of ΔT's following adjustment of inlet temperatures.

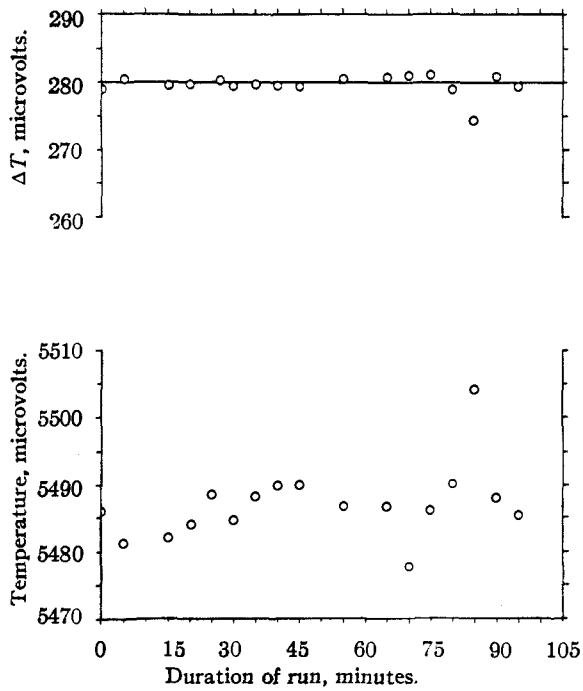

Fig. 5.—A representative run with good temperature control for the first hour followed by poor temperature control for thirty minutes.

let thermocouple due probably to the buffering effect of the copper turnings, J, and perhaps the walls of the expansion chamber dewar. Due to one or both of these causes any drift in the inlet temperature is accompanied by a drift of opposite sign in the apparent Joule–Thomson effect. This is clearly illustrated in Fig. 4, for a run with hydrogen at 64°K. (pressure = 68 atmospheres and flow rate 80 liters per minute) in which the temperature control on the boiling liquid air was especially poor.

Figure 5, which shows a run made with hydrogen at 75°K. (136 atm. pressure and 1275 liters per minute rate of flow), illustrates, for one run, the difference between good and bad temperature control.

With good temperature and pressure control (inlet temperature constant to within $\pm 0.3°$ and pressure constant to within 0.3 atm.) equilibrium was usually attained within five or ten minutes except for very small flow rates. With flow rates of 90 or 120 liters per minute, fifteen to twenty minutes were sometimes required to reach steady readings of ΔT. After some early experimentation we adopted a policy of extending runs until we obtained at least thirty minutes of good temperature and pressure control.

Data obtained with this apparatus will be given in subsequent papers.

Acknowledgment.—We wish to acknowledge the assistance of Mr. L. E. Cox, our chief mechanic, in designing the lucite valve.

Summary

An apparatus is described for measuring Joule–Thomson effects in gases by expansion through a valve designed to minimize errors from thermal conduction. Satisfactory results are obtained with valves having valve stems of ebony and valve seats of either lucite or lignum vitae. Provision is also made to eliminate the "jet kinetic energy effect" in measuring the temperature of the expanded gas.

Results obtained with hydrogen show that the measured effect is independent of flow rate, between 60 and 1700 liters per minute CFM, which indicates that thermal conduction and "jet kinetic energy effect" are absent. They also show a rapid response to variations in pressure, of the correct magnitude and sign, but show some lag in attaining thermal equilibrium when the inlet temperature of the gas changes rapidly. Equilibrium is attained within five to ten minutes at high flow rates and within fifteen minutes to half an hour at low flow rates, under conditions of good pressure and temperature control.

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