THE JOULE-THOMSON EXPERIMENT

OBJECTIVE: Measure the Joule-Thomson coefficient of carbon dioxide. Compare the calculated value with that calculated from the equation of state.

1. INTRODUCTION:

One of the fundamental assumptions of the Kinetic Theory of Gases is that there is no attraction between molecules of the gas. An ideal gas may be regarded as one for which the molecular attraction is negligible. The fact that gases may be liquefied implies that the molecules of a gas attract one another. This attraction was studied by J. L. Gay-Lussac (1807) and J. P. Joule (1843) who investigated the dependence of energy of gases on pressure using the apparatus shown in Fig. 1. Copper bulb A was filled with air under pressure, isolated from an evacuated similar bulb B by a valve, V. The bulbs were immersed in a well-stirred water bath equipped with a sensitive thermometer. After thermal equilibrium had been established, valve V was opened to allow the gas to expand into bulb B.
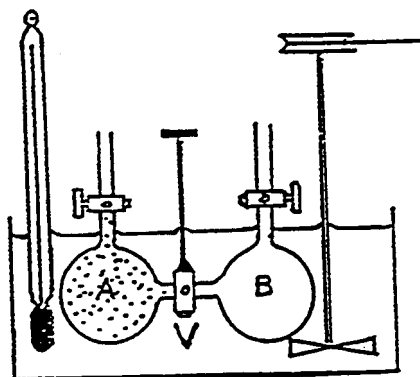

Figure 1 Joule Apparatus

No change in temperature was detected. In Joule's words, "no change of temperature occurs when air is allowed to expand in such a manner as not to develop mechanical power" (i.e. do no external work, w = 0). Since no change of temperature was observed, q = 0 and therefore

$$dU \ = \ dq \ = \ dw \ = \ 0 \tag{1}$$

(i.e. the expansion occurred at constant U). Now, for U = U(V,T) it can be shown

that

$$\left(\frac{\delta U}{\delta V}\right)_T = -\left(\frac{\delta U}{\delta T}\right)_V \left(\frac{\delta T}{\delta V}\right)_U \qquad (2)$$

Joule's observation that

$$\left(\frac{\delta T}{\delta V}\right)_U = 0$$

implies (from eqn. (2))

$$\left(\frac{\delta U}{\delta V}\right)_T = 0$$

or the energy of a gas is a function of temperature alone, independent of volume (and therefore of pressure) at constant temperature. Because the system used by Joule had a very large heat capacity compared with the heat capacity of air, the small change of temperature that took place was not observed. Actually the gas in A warmed up slightly and the one which had expanded into B was somewhat cooler and when thermal equilibrium was finally established the gas was at a slightly different temperature from that before the expansion. Thus

$$\left(\frac{\delta U}{\delta V}\right)_T \neq 0$$

It is only when the pressure of the gas before expansion is reduced that the temperature change becomes smaller and smaller. Thus we can deduce that in the limit of zero pressure the effect would be zero and the energy of the gas would be independent of volume. An ideal gas can be defined by

$$PV = nRT$$

$$\lim_{P \to 0}\left(\frac{\delta U}{\delta V}\right)_T = 0 \qquad (3)$$

In fact any of the following are valid for an ideal gas

$$\left(\frac{\delta U}{\delta V}\right)_T = \left(\frac{\delta U}{\delta P}\right)_T = \left(\frac{\delta H}{\delta V}\right)_T = \left(\frac{\delta H}{\delta P}\right)_T = 0 \qquad (4)$$

THE JOULE-THOMSON EXPERIMENT.

The study of the dependence of the energy and enthalpy of real gases on volume (pressure) was done by Joule in association with Thomson who devised a different procedure. They allowed gas to expand freely through a porous plug, or frit.
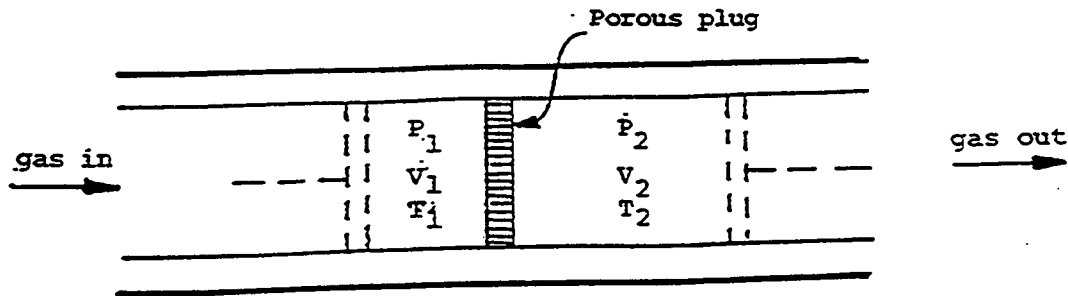
Figure 2 Principle of the Joule-Thomson apparatus

As shown in Fig. 2, the gas expands from a pressure P_1 to pressure P_2 by the throttling action of the porous plug. The entire system is thermally insulated so the expansion occurs adiabatically, i.e.

1
$$q = 0$$

Gas is allowed to flow continuously through the porous plug, and when steady state conditions have been reached the temperatures of the gas before and after expansion, T_1 and T_2, are measured directly with sensitive thermocouples. The following argument shows that this expansion occurs at constant enthalpy. Consider the expansion of a fixed mass of gas, through the frit. This may be treated by considering a system defined by the imaginary pistons shown in Fig. 2. The gas occupies a volume V_1 at a pressure P_1 and temperature T_1 before the expansion and a volume V_2 at P_2, T_2 after the expansion. What is the work done in this process? Compression of the imaginary piston on the LHS leads to work done (by the surroundings on the system) of

$$-p_1 \Delta V \text{ where } \Delta V = \int_{V_1}^{0} dV = -V_1 \text{ or } w_{LHS} = +P_1 V_1$$

Similarly, expansion of the imaginary piston on the RHS leads to work done on the system by the surroundings of

2
$$- P_2 \Delta V \text{ where } \Delta V = V_2 - 0 = V_2 \text{ or } w_{LHS} = - P_2 V_2$$

The total work done on the gas system during the expansion is then

3
$$w = w_{LHS} + w_{RHS} = + P_1 V_1 - P_2 V_2$$

The overall change in internal energy of the gas during the adiabatic expansion is then

4
$$\Delta U = q + w = 0 + w = + w$$

or

5
$$\Delta U = P_1 V_1 - P_2 V_2 = U_2 - U_1$$

Rearrangement gives

6
$$U_2 + P_2 V_2 = U_1 + P_1 V_1$$

but

7
$$H \equiv U + PV$$

so

8
$$H_2 = H_1$$

This is therefore an **ISOENTHALPIC** expansion and the experiment measures directly the change in temperature of a gas with pressure at constant enthalpy which is called the Joule-Thomson coefficient, μ_{JT}

$$\mu_{JT} = \left(\frac{\delta T}{\delta P}\right)_H = \lim_{P \to 0}\left(\frac{\Delta T}{\Delta P}\right)_H \tag{5}$$

For expansion, ΔP is negative and therefore a positive value for μ_{JT} corresponds to cooling on expansion and vice versa.

What is μ_{JT} for an ideal gas? Because the process is isoenthalpic, we can

write
$$\left(\frac{\delta H}{\delta P}\right)_T = -\left(\frac{\delta H}{\delta T}\right)_P\left(\frac{\delta T}{\delta P}\right)_H = -C_P\mu_{JT}$$

but
$$\left(\frac{\delta H}{\delta P}\right)_T = \left(\frac{(\delta U + PV)}{\delta P}\right)_T = \left(\frac{\delta U}{\delta P}\right)_T + \left(\frac{\delta (PV)}{\delta P}\right)_T = \left(\frac{\delta U}{\delta P}\right)_T$$

$$= 0 \text{ for an ideal gas (from eqn. 4)}$$

Since the heat capacity at constant pressure is not zero, the Joule-Thomson coefficient must be zero for an ideal gas.

For real gases, if a Joule-Thomson experiment is performed, corresponding pairs of values of pressures and temperatures, say P_1 and T_1, P_2 and T_2, P_3 and T_3 etc., determine a number of points on a pressure-temperature diagram, as in Fig. 3a, and since $H_1 = H_2 = H_3$ etc., the enthalpy is the same at all of these points, and a smooth curve drawn through the points is a curve of constant enthalpy (Fig. 3a). Note carefully that this curve does not represent the process executed by the gas in passing through the plug, since the process is irreversible and the gas does not pass through a series of equilibrium states. The final pressure and temperature must be measured at a sufficient distance from the plug for local non-uniformities in the stream to die out, and the gas passes by an irreversible process from one point on the curve to another.

By performing other series of experiments, again keeping the initial pressure and temperature the same in each series, but varying them from one series to another, a family of curves corresponding to different values of H can be obtained. Such a family is shown in Fig. 3b which is typical of all real gases.
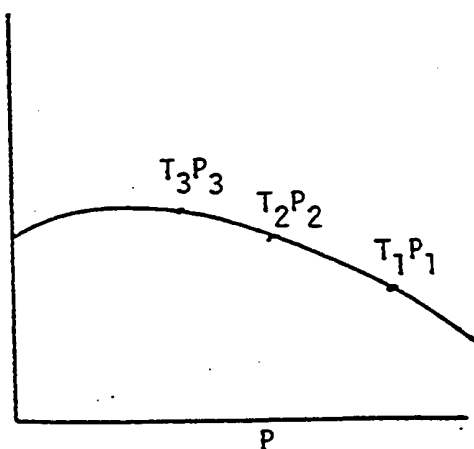

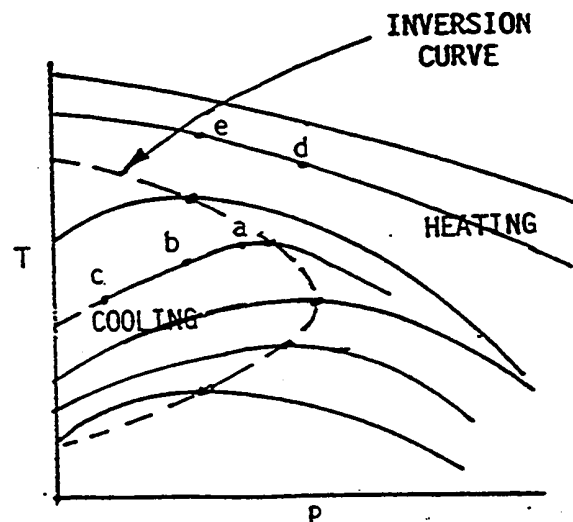**Fig. 3a Points of equal enthalpy**   **Fig. 3b Isenthalpic curves and the enthalpy. inversion curve.**

If the temperature is not too great the curves pass through a maximum called the inversion point. The locus of the inversion points is the inversion curve. The slope

of an isoenthalpic curve at any point is $(\frac{\partial T}{\partial P})_H$ and at the maximum of the curve, or

the inversion point, $\mu_{JT} = 0$. When the Joule-Thomson effect is to be used in the liquefaction of gases by expansion, it is evident that the conditions must be chosen so that the temperature will decrease. This is possible only if the initial pressure and temperature lie within the inversion curve. Thus a drop in temperature would be produced by an expansion from point a to point b to point c, but a temperature rise would result in an expansion from d to e.

Do not assume that any gas with $\mu_{JT} = 0$ must be ideal; from the above it should be obvious that real gases can have many temperatures at which $\mu_{JT} = 0$. Most gases at room temperature and reasonable pressures are within the "cooling" area of Fig. 3b; however hydrogen and helium are exceptional in having inversion temperatures well below room temperature, and at room temperature behave like the d to e transformation, i.e. warm on expansion. Can you explain why?

2.1. CALCULATION OF THE JOULE-THOMSON COEFFICIENT

The enthalpy is a definite property and its value depends on the state of the system, e.g. on temperature and pressure

$$H = H(P, T)$$

$$dH = \left(\frac{\delta H}{\delta P}\right)_T dP + \left(\frac{\delta H}{\delta T}\right)_P dT \tag{6}$$

In the Joule-Thomson experiment H is constant, i.e. dH = 0

$$\mu_{JT} = \left(\frac{\delta T}{\delta P}\right)_H = -\frac{\left(\frac{\delta H}{\delta P}\right)_T}{\left(\frac{\delta H}{\delta T}\right)_P} \tag{7}$$

Now $(\frac{\partial H}{\partial T})_P$ is C_p, the heat capacity at constant pressure. Also since

$$dH = TdS + VdP$$

$$\left(\frac{\delta H}{\delta P}\right)_T = T\left(\frac{\delta S}{\delta P}\right)_P + V$$

but the Maxwell's relation from

$$dG = VdP - SdT$$

is $\left(\frac{\delta S}{\delta P}\right)_T = \left(\frac{\delta V}{\delta T}\right)_P$

$$\therefore \quad \left(\frac{\delta H}{\delta P}\right)_T = V - T\left(\frac{\delta V}{\delta T}\right)_P \tag{8}$$

Thus

$$\mu_{JT} = \frac{T\left(\frac{\delta V}{\delta T}\right)_P - V}{C_P} \tag{9}$$

For a <u>real gas</u> $\left(\frac{\partial V}{\partial T}\right)_P$ may be obtained from any equation of state by differentiation as shown below for the van der Waals and Beattie-Bridgeman equations of state.

2.2 (a) THE van der WAALS EQUATION OF STATE:

$$PV = RT - \frac{a}{V} + bP + \frac{ab}{V^2} \tag{10}$$

can be written in the form given below, if the very small term $\frac{ab}{V^2}$ is neglected,

and the term $\frac{a}{PV}$ is replaced by $\frac{a}{RT}$

$$V = \frac{RT}{P} - \frac{a}{RT} + b \tag{11}$$

Differentiation w.r.t. T at constant P gives

$$\left(\frac{\delta V}{\delta T}\right)_P = \frac{R}{P} + \frac{a}{RT^2} \tag{12}$$

and from (11) above

$$\frac{R}{P} = \frac{V - b}{T} + \frac{a}{RT^2}$$

which, when substituted in (12), gives

$$T\left(\frac{\delta V}{\delta T}\right)_P - V = \frac{2a}{RT} - b \tag{13}$$

If this is finally substituted in (9) the value of U_{JT} is given by

$$\mu_{JT} = \frac{\left(\dfrac{2a}{RT}\right) - b}{C_P} \tag{14}$$

2.2   (b) **THE BEATTIE-BRIDGEMAN EQUATION OF STATE:**

$$PV = RT + \frac{\beta}{V} + \frac{\gamma}{V^2} + \frac{\delta}{V^3} \tag{15}$$

$$\beta = RTB_0 - A_0 - \frac{RC}{T^2}$$

$$\delta = RB_0 bc / T^2$$

has five adjustable constants A_o, B_o, a,b,c,compared with van der Waals two.

A similar procedure to that used for the van der Waals equation gives the Joule-Thompson coefficient for the Beattie-Bridgeman equation:-

$$\mu_{JT} = \frac{1}{C_P}\left\{ - B_o + \frac{2A_o}{RT} + \frac{4c}{T^3} + \left[\frac{2B_o b}{RT} - \frac{3A_o a}{(RT)^2} + \frac{5B_o c}{RT^4}\right]P \right\} \tag{16}$$

2.3   EXPERIMENTAL PROCEDURE:

The Joule-Thomson apparatus is shown in Fig. 4. This apparatus will be set up for you and initial adjustments will not be necessary. Because it takes a long time for the porous frit to come to a steady thermal state, the gas will be turned on some two hours prior to the start of the laboratory to ensure that the temperature difference across the porous frit has attained a constant value. This is indicated by the constancy of emf of the thermocouple.
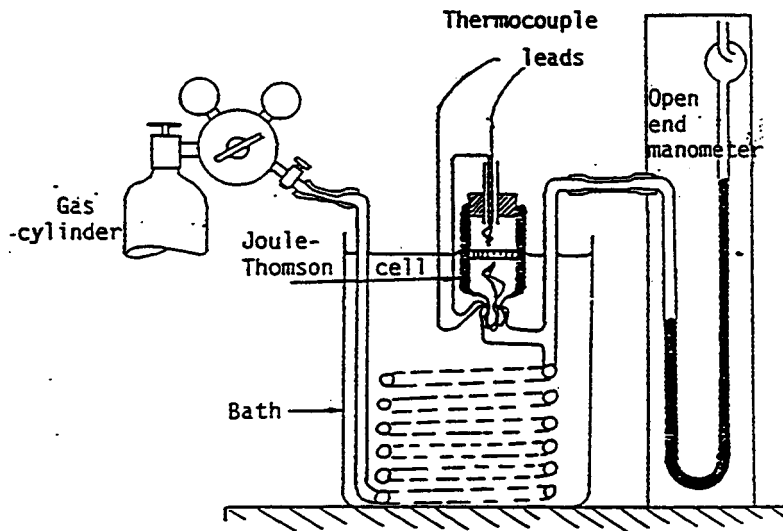

Figure 4. Joule-Thomson Apparatus

1) To use and make the digital pressure gauge work, you will need about 5 minutes. First, wait about 90 seconds for it to go to 780 Torr, then zero it by pressing and holding the zero button on the gauge for 2 seconds. Values will be changing for a few seconds, but in this case, it is not a big problem. Second, after zeroing it, you will be adjusting the desired pressure by **VERY SLOWLY** opening the needle on the gas cylinder and controlling the pressure of around 250 Torr and taking the reading off the voltmeter. The first set of readings (first experimental point) can be taken immediately after the start of the lab period or when instructed to do so by the T.A.

Note: Most digital voltmeters exhibit so called 'zero drift' at very low voltage measurements. TO correct this, the meter is shorted and the reading displayed on the panel is taken to be zero. This reading is then subtracted from the reading of the thermocouple and the difference is taken to be the emf generated by the thermocouple.

2) Take readings as described above at 5 min intervals until four (emf,ΔP) readings show no significant differences (i.e. no systematic drifts).

3) Take arithmetic mean of the four readings and assign to it a confidence limit.

4) **VERY SLOWLY** (for approx. 90 seconds) increase the pressure difference, ΔP, across the frit by about 100 Torr by opening very slowly the needle valve on the gas cylinder. Start taking readings 5 minutes after the change of pressure has been made and then at 5 min. intervals until, as before, four readings show no significant difference. In this manner, obtain 8 experimental points. Use the calibration graph provided in the lab to calculate ΔT, the temperature change across the porous frit.

2.4 CALCULATIONS:

For each point determine the average values of ΔP and ΔT. Determine the uncertainties in ΔP's and ΔT's and plot a graph of T versus P enclosing each point in an uncertainty box. Draw the best fitting line through the points and determine the slope of this line. Draw also lines of maximum and minimum slopes. Review the theory of Least Squares Analysis as outlined in the Error Analysis section and using

any spreadsheet calculate **m** and **b** for the line. Attach the spreadsheet print out to your report. Finally compute σ_m and σ_b and compare with your graphical analysis. From the slope determine the Joule-Thomson coefficient, μ_{JT}, in $^{\circ}$C/atm. and the uncertainty $\pm\mu_{JT}$. Calculate the Joule-Thomson coefficient for the gas from (a) the van der Waals and (b) Beattie-Bridgeman equations of state, using equations (14) and (16) respectively. Assume P = 1 atm.in equation (16). The pertinent values of the constants are given in Table 1.

Table 1. Values of constants for equations of state (in MKS units).

	CO_2	He	N_2
van der Waals			
a (j m^3 $mole^{-2}$)	0.364	3.457×10^{-3}	0.141
b (m^3 $mole^{-1}$)	4.267×10^{-5}	$2.370\ 10^{-5}$	3.913×10^{-5}
Beattie-Bridgeman			
A_o (j m^3 $mole^{-2}$)	0.50728	2.1886×10^{-3}	0.13623
B_o (m^3 $mole^{-1}$)	1.047×10^{-4}	1.409×10^{-5}	5.04×10^{-5}
a (m^3 $mole^{-1}$)	7.132×10^{-5}	5.984×10^{-5}	2.617×10^{-5}
b (m^3 $mole^{-1}$)	7.235×10^{-5}	0.00	-6.91×10^{-5}
c (m^3 deg^3 $mole^{-1}$)	6.60×10^2	$4.0\ 10^{-2}$	42.0
C_P (joule $mole^{-1}deg^{-1}$)	37.085	20.670	26.952

N.B. 1 atm / 760 mm Hg /760 Torr/ 101.32 kPa.

2.5 DISCUSSION:

Discuss the relative values of all μ_{JT}s coefficients, i.e. from the experiment, from the literature and the ones calculated from the equations of state. Include in your discussion a short explanation of why gases (usually) cool on free expansion.

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Single-Junction copper-constatan thermocouple emf/μV

Temperature difference between identical thermocouples at 25°C

ΔT/°C	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
0.0	0.00	0.41	0.81	1.22	1.63	2.03	2.44	2.85	3.25	3.66	4.07
0.1	4.07	4.47	4.88	5.29	5.69	6.10	6.51	6.92	7.32	7.73	8.14
0.2	8.14	8.54	8.95	9.36	9.76	10.17	10.58	10.98	11.39	11.80	12.21
0.3	12.21	12.61	13.02	13.43	13.83	14.24	14.65	15.05	15.46	15.87	16.28
0.4	16.28	16.68	17.09	17.50	17.90	18.31	18.72	19.12	19.53	19.94	20.35
0.5	20.35	20.75	21.16	21.57	21.97	22.38	22.79	23.20	23.60	24.01	24.42
0.6	24.42	24.83	25.23	25.64	26.05	26.45	26.86	27.27	27.68	28.08	28.49
0.7	28.49	28.90	29.31	29.71	30.12	30.53	30.93	31.34	31.75	32.16	32.56
0.8	32.56	32.97	33.38	33.79	34.19	34.60	35.01	35.42	35.82	36.23	36.64
0.9	36.64	37.05	37.45	37.86	38.27	38.68	39.08	39.49	39.90	40.31	40.71
1.0	40.71	41.12	41.53	41.94	42.34	42.75	43.16	43.57	43.97	44.38	44.79
1.1	44.79	45.20	45.60	46.01	46.42	46.83	47.24	47.64	48.05	48.46	48.87
1.2	48.87	49.27	49.68	50.09	50.50	50.90	51.31	51.72	52.13	52.54	52.94
1.3	52.94	53.35	53.76	54.17	54.58	54.98	55.39	55.80	56.21	56.61	57.02
1.4	57.02	57.43	57.84	58.25	58.65	59.06	59.47	59.88	60.29	60.69	61.10
1.5	61.10	61.51	61.92	62.33	62.73	63.14	63.55	63.96	64.37	64.77	65.18
1.6	65.18	65.59	66.00	66.41	66.81	67.22	67.63	68.04	68.45	68.85	69.26
1.7	69.26	69.67	70.08	70.49	70.90	71.30	71.71	72.12	72.53	72.94	73.34
1.8	73.34	73.75	74.16	74.57	74.98	75.39	75.79	76.20	76.61	77.02	77.43
1.9	77.43	77.84	78.24	78.65	79.06	79.47	79.88	80.29	80.69	81.10	81.51
2.0	81.51	81.92	82.33	82.74	83.14	83.55	83.96	84.37	84.78	85.19	85.60