

## B. Experiment #2, Measurement of Joule-Thomson Coefficient

### Objectives:

1. Measure the relationship between the change in enthalpy versus the change in temperature.
2. Experimentally determine the Joule-Thomson coefficient of CO<sub>2</sub>.
3. Investigate the relationship between potential energy and kinetic energy in a gas molecule.

### Background:

For an ideal gas, the  $PV$  behavior and energy,  $E$ , are functions of temperature alone. Since the enthalpy (equation 1), is the sum of  $PV$  and  $E$ , it is also true that the enthalpy is a function of temperature alone for an ideal gas.

$$H \equiv E + PV = h(T) \quad (1)$$

Since these vary exclusively with temperature, it must be that the partial derivatives holding temperature constant are equal to zero (equation 2).

$$\left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial E}{\partial P}\right)_T = \left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T = 0 \quad (2)$$

These equations show that the energy of an ideal gas is independent of the gas's volume. In other words, if you expanded a gas at a constant temperature its internal energy would be unchanged. This is true provided that the expansion is adiabatic and that the expansion happens without doing work. Non-ideal gases do experience a small temperature change on free expansion. This effect can be measured using a continuous flow setup

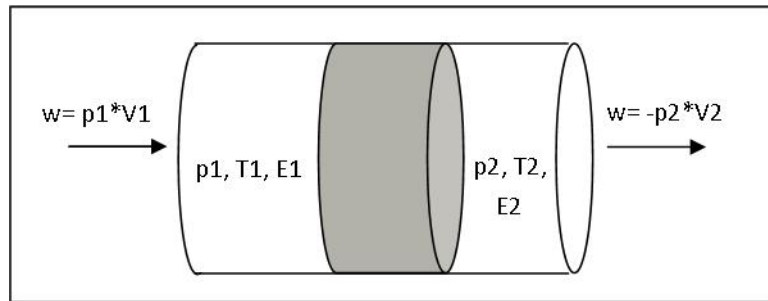


Figure 3. Schematic of the Joule-Thomson experiment.

through a porous plug so that the solid parts of the experimental apparatus come into thermal equilibrium with the gases. The pressures, temperatures, volumes, and total energies are defined as in figure 1.

Under these circumstances the work done on the system by the surroundings is given by equation 3.

$$w = p_1 V_1 - p_2 V_2 \quad (3)$$

If the whole apparatus is insulated, making it adiabatic, then the change in internal energy is given by equation 4, which can be combined with eqn. 4 to give equation 5.

$$\Delta E = E_2 - E_1 = q + w = w \quad (3)$$

$$E_1 + p_1 V_1 = E_2 + p_2 V_2 = H_1 = H_2 \quad (4)$$

Equation 5 states that the process takes place at constant enthalpy, which is the total energy of the system (with respect to vacuum) and the energy required to make room for it by displacing its surroundings. The first derivative of enthalpy is equation 6, which in this case equals zero.

$$dH = \left( \frac{\partial H}{\partial P} \right)_T dp + \left( \frac{\partial H}{\partial T} \right)_P dT = 0 \quad (5)$$

Rearranging eqn. 5 gives the Joule-Thomson coefficient, which describes the relationship between the change in pressure and the change in temperature (eqn. 7). The Joule-Thomson coefficient gives a measure of how much potential energy is converted into kinetic energy (or *vice versa*) as the average separation between gas molecules changes.

$$\mu \equiv - \frac{\left( \frac{\partial H}{\partial P} \right)_T}{\left( \frac{\partial H}{\partial T} \right)_P} = \left( \frac{\partial T}{\partial P} \right)_H = \lim_{\Delta P \rightarrow 0} \left( \frac{\Delta T}{\Delta P} \right)_H \quad (7)$$

## Procedure:

1. Set up apparatus as shown below.

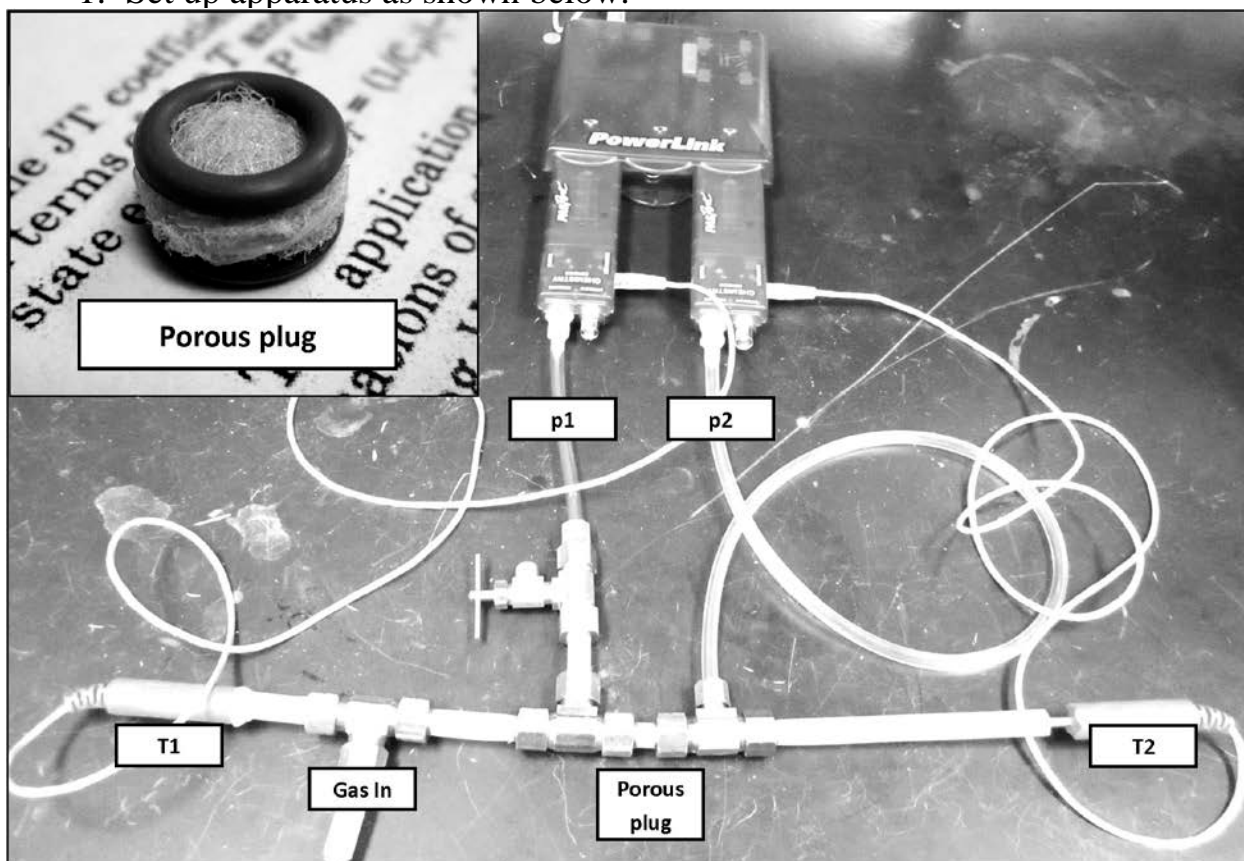


Figure 4. Experimental setup for the measurement of Joule-Thomson coefficients. The porous plug shown in the inset consists of two adhesive-backed felt pads intended for furniture with a piece of parafilm in between. A very small hole was poked through the parafilm using a pin.

2. Connect the using a 25 foot coil of high-pressure tubing, making sure to tighten the hose clamps. A long piece of tubing helps the incoming gas to remain at room temperature through the experiment.
3. Prepare the computer interface.
  - a. Connect the pressure and temperature sensors as shown in figure 2.
  - b. In Datastudio, setup the experiment so that the pressure is measured in atm and the temperature in Kelvin.
  - c. In Datastudio, setup a calculation so that the difference between the temperatures and pressures can be computed and plotted automatically.
  - d. Display the pressure difference and temperature difference together on a graph.

- e. Check the calibration of the temperature sensors by submersing them both in an ice water bath.
- 4. Prepare to take a measurement
  - f. You will be measuring very small differences in temperature ( $\sim 0.5$  to  $\sim 3$  K). When  $\Delta T$  is so small, the rate of heat flow is also small so it can take a long time for  $\Delta T = 0$ . This time can be reduced by touching the metal parts of the apparatus as little as possible, unless it is on purpose to adjust the temperature difference of the probes.
  - g. Open the valve on the apparatus, and flush the system with  $\text{CO}_2$ .
  - h. Close the valve and, using a low pressure difference, run gas through the setup up to try and bring the thermometers into equilibrium.
    - i. If  $T_2$  is too high, increase the pressure difference to  $\sim 2$  atm to cool it, then reduce the pressure difference to try and maintain  $T_2 = T_1$ .
    - ii. If  $T_2$  is too low, briefly touch the brass fitting close to the temperature probe to raise it.
  - i. With the two temperature probes in equilibrium, increase the pressure difference across the plug to 2 atm and wait for  $\Delta T$  to stabilize. Decrease the temperature in increments of 0.5 atm and let stabilize.

**Report:**

- 5. Plot  $\Delta T$  vs  $\Delta P$  (with the pressure in bar). Fit a line to the graph. From the slope, evaluate the Joule-Thomson coefficient in K/bar.
- 6. Calculate the Joule-Thomson coefficient using the van der Waals constants (see appendix).
- 7. Compare your measured and calculated values with those found in the literature, and comment on any differences.
- 8. For most gases,  $\mu$  is positive (that is, the gas cools on expansion) at room temperature. However, as the temperature is increased  $\mu$  decreases and eventually changes sign (the gas begins to heat on expansion), the temperature at which this happens is called the inversion temperature. Evaluate the inversion temperature using the van der Waals coefficients and equation (7) in the literature.