

JOULE-THOMSON COEFFICIENT

Apparatus

Before starting this experiment, read the following sections in GNS (7th ed.): Thermocouples (p.607); Cylinders, reducing valves, gas regulators (p.705); and Needle valves (p.706).

Our apparatus is very similar to that described in GNS (p.100-101). You should carefully open the black box and remove the thermal insulation to compare our set-up to that in GNS. Please be very careful with the thermocouple probes: **Never** move the box by pulling from the probes and do NOT bend them.

Procedure

The EMF generated by the *differential* T-type (Copper-Constantan) thermocouple is proportional to the temperature difference across the frit and it is measured with a Keithley-2000 multimeter, which directly produces a temperature reading that is recorded with the Lab View program. (The Voltage-Temperature conversion factor is the Seebeck coefficient mentioned in GNS, which is built in the Lab View program). The Pressure is measured with a digital handheld manometer and also recorded with the Lab View program. Press the Power and HOLD buttons simultaneously to turn this instrument on and disable the “auto power off” function (An “n” will appear in the middle of the screen at which time the HOLD button can be released, and then the power button).

The software should be started with the pressure set at zero bars, which would ideally produce a temperature reading that is also zero. If this is not the case, let the software run for a few minutes until the temperature reading is stable ($\pm 0.01^\circ\text{C}$) and then stop the program and re-start it. Then follow the procedure in GNS, using pressure steps anywhere from 0.1 to 0.5 bars, and do NOT go to pressures higher than 5 bars.

You will determine the Joule-Thomson coefficients of Nitrogen, Carbon Dioxide, Argon, and Helium. Compare your results to the literature values and suggest possible sources of error in your measurements. Explain the sign and relative magnitudes of the coefficients for the four different gases in terms of stored potential energy at high pressure. Also, calculate the value of μ for these gases at 298K by using the van der Waals equation presented in GNS, and both Virial Analyses, presented in the book and in this handout (below). *Be careful in handling units in calculating the van der Waals μ ; GNS gives a and b in non-SI units.* The Beattie-Bridgeman equation is rarely used and can be omitted.

For the CO₂ experiment, heating tape should be used over the regulator to avoid freezing of the gas (around the metallic part of the regulator ONLY). Remember to turn the Variac (that controls the heating tape) off after you are done with the CO₂ experiment, otherwise the Teflon tubing from the gas cylinder will melt.

Please, turn the digital manometer and the Keithley 2000 off after you are done

Virial Analysis

The *virial equation of state* is frequently used to represent the behavior of real gases. Unlike empirical equations of state, such as the van der Waals equation (which is, at best, very approximate) and the Beattie-Bridgeman equation (which is now rarely used) which are discussed in GNS, the virial equation can be derived from *exact* statistical mechanical theory.

One form of the virial equation is the *density series*:

$$p\tilde{V}/RT = 1 + B(T)/\tilde{V} + C(T)/\tilde{V}^2 + \dots, \quad (1)$$

where p is the pressure, $\tilde{V}$ is the molar volume, T is the absolute temperature and R is the gas constant. The quantities $B(T)$ and $C(T)$ are, respectively, the second and third virial coefficients and are functions of temperature only. While the constants in the van der Waals equation of state and some of the constants in the Beattie-Bridgeman equation have some qualitative relationship to intrinsic molecular properties of a real gas, the following expression can be derived rigorously by the methods of statistical mechanics:

$$B(T) = 2\pi N_A \int_0^\infty \{1 - \exp[-u(r)/k_B T]\} r^2 dr \quad (2)$$

where N_A is the Avogadro constant, k_B is the Boltzmann constant, and $u(r)$ is the intermolecular pair potential energy at an intermolecular separation r .

[H. Kamerlingh Onnes (1901); J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, (1954); W. J. Moore, *Physical Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, N.J. (1972), pp.26, 130, 926.]

An alternative virial equation, the *pressure series*, is also used:

$$p\tilde{V} = RT + B'(T)p + C'(T)p^2 + \dots \quad (3)$$

It is easy to show, by making the substitution

$$\tilde{V} = \frac{RT}{p} \left(1 + \frac{B}{\tilde{V}} + \frac{C}{\tilde{V}^2} + \dots \right) = \frac{RT}{p} \left(1 + \frac{B'p}{RT} + \frac{C'p^2}{RT} + \dots \right)$$

In the right-hand side of Eq.(1) and expanding the denominators [i.e., remembering that $1/(1+x+\dots) = (1+x+\dots)^{-1}$], that $B' = B$ and $C' = (C - B^2)/RT$.

An expression for the Joule-Thomson coefficient in terms of the virial coefficients is more easily derived from the pressure expansion since

$$\mu = \left(\frac{\partial T}{\partial p} \right)_H = - \frac{(\partial \tilde{H}/\partial p)_T}{(\partial \tilde{H}/\partial T)_p} \quad (4)$$

$$\begin{aligned} (\partial \tilde{H}/\partial p)_T &= \tilde{V} - T(\partial \tilde{V}/\partial T)_p = RT/p + B' + C'p - T[R/p + dB'/dT + (dC'/dT)p] + \dots \\ &= [B' - T(dB'/dT)] + [C' - T(dC'/dT)]p + \dots \end{aligned} \quad (5)$$

$\tilde{H}$ is also temperature dependent, so we integrate $(\partial \tilde{H}/\partial p)_T$ with respect to pressure obtaining

$$\tilde{H} = \tilde{H}^o + [B' - T(dB'/dT)]p + [C' - T(dC'/dT)]p^2/2 + \dots \quad (6)$$

Where $\tilde{H}^o$ is the molar enthalpy of the real gas at zero pressure (which is the same as that at the standard state of the ideal gas at the standard pressure p^o). Eq. (6) can now be differentiated with respect to temperature to obtain the heat capacity:

$$\tilde{C}_p = (\partial \tilde{H}/\partial T)_p = \tilde{C}_p^o + [(dB'/dT) - (dB'/dT) - T(d^2B/dT^2)]p + \dots = \tilde{C}_p^o - T(d^2B/dT^2)p + \dots \quad (7)$$

Substituting into Eq. (4) and substituting from B' and C' to the density coefficients B and C, we obtain an expression for the Joule-Thomson coefficient correct to the first power of the pressure

$$\mu = - \frac{[B - T(dB/dT)] + \{[2C - 2B^2 - T(dC/dT) + 2TB(dB/dT)]/(RT)\}p + \dots}{\tilde{C}_p^o - T(d^2B/dT^2)p + \dots} \quad (8)$$

Values of B and C for N₂, Ar, and CO₂ are given in Table 1 below. Values for other gases can be found in J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gases and Gas Mixtures* (Clarendon Press, Oxford, 1980) from which the values in Table 1 have been adapted. The uncertainties in B are of the order of $\pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ while the uncertainties in C are at least as large as $\pm 200 \text{ cm}^6 \text{ mol}^{-2}$.

TABLE 1 - Virial Coefficients

	T/K	B/(cm ³ mol ⁻¹)	C/(cm ⁶ mol ⁻²)
Ar	223.2	-37.8	1800
	273.2	-22.1	1700
	323.2	-11.0	1200
	373.2	-4.2	1000
N ₂	273.2	-10.3	1540
	298.2	-4.8	1380
	323.2	-0.3	1280
	348.2	3.3	1220
	373.2	6.4	1200
CO ₂	273.2	-151	5600
	298.2	-123	5300
	323.2	-104	4930
	348.2	-87	4430
	373.2	-74	4150