by how much must the precision of the pressure measurements be improved before gas imperfection corrections become significant? How does this depend on the choice of gas to be used?

SAFETY ISSUES

The ballast bulb must be taped to prevent flying glass fragments in the unlikely event of breakage. Safety glasses should be worn for all laboratory work. Gas cylinders must be chained securely to the wall or laboratory bench (see pp. 705–6 and Appendix C). Liquid nitrogen must be handled properly (see Appendix C).

APPARATUS

Closed-tube manometer; null manometer; properly taped and mounted ballast bulb; heavy-wall pressure tubing; Dewar flask; large ring stirrer; notched cover plate for Dewar with hole for mounting gas thermometer bulb; electrical heating mantle; steam generator with rubber connecting tubing; steam jacket; two ring stands; ring clamp; two clamp holders; one large and one medium clamp.

Cylinder of helium or dry nitrogen; pure ice (1 kg); ice grinder; liquid nitrogen (1 L); boiling chips; stopcock grease; vacuum pump or water aspirator.

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EXPERIMENT 2

Joule–Thomson Effect

The Joule–Thomson effect is a measure of the deviation of the behavior of a real gas from what is defined to be ideal-gas behavior. In this experiment a simple technique for measuring this effect will be applied to a few common gases.

THEORY

An ideal gas may be defined as one for which the following two conditions apply at all temperatures for a fixed quantity of the gas: (1) Boyle's law is obeyed; i.e.,

$$pV = f(T)$$

and (2) the internal energy E is independent of volume. Accordingly, E is independent of pressure as well, and in the absence of other pertinent variables (such as applied fields), E of an ideal gas is therefore a function of the temperature alone:

$$E = g(T)$$

It is apparent that the enthalpy H of an ideal gas is also a function of temperature alone:

$$H \equiv E + pV = h(T)$$

Accordingly, we can write for a definite quantity of an ideal gas at all temperatures

$$\left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial E}{\partial p}\right)_T = \left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T = 0 \tag{1}$$

The absence of any dependence of the internal energy of a gas on volume was suggested by the early experiments of Gay-Lussac and Joule. They found that, when a quantity of gas in a container initially at a given temperature was allowed to expand into another previously evacuated container without work or heat flow to or from the surroundings ($\Delta E = 0$), the final temperature (after the two containers came into equilibrium with each other) was the same as the initial temperature. However, that kind of experiment (known as the *Joule experiment*) is of limited sensitivity, because the heat capacity of the containers is large in comparison with that of the gases studied. Subsequently, Joule and Thomson[1] showed, in a different kind of experiment, that real gases do undergo small temperature changes upon free expansion. This experiment utilized continuous gas flow through a porous plug under adiabatic conditions. Because of the continuous flow, the solid parts of the apparatus come into thermal equilibrium with the flowing gas, and their heat capacities impose a much less serious limitation than in the case of the Joule experiment.

Let it be imagined that gas is flowing slowly from left to right through the porous plug in Fig. 1. To the left of the plug, the temperature and pressure of the gas are T_1 and p_1; and to the right of the plug, they are T_2 and p_2. The volume of a definite quantity of gas (say 1 mol) is V_1 on the left and V_2 on the right, and the internal energy is E_1 and E_2, respectively. When 1 mol of gas flows through the plug, the work done on the system by the surroundings is

$$w = p_1V_1 - p_2V_2$$

Since the process is adiabatic, the change in internal energy is

$$\Delta E = E_2 - E_1 = q + w = w$$

Combining these two equations we obtain

$$E_1 + p_1V_1 = E_2 + p_2V_2$$

or

$$H_1 = H_2 \tag{2}$$

Thus this process takes place at constant enthalpy.

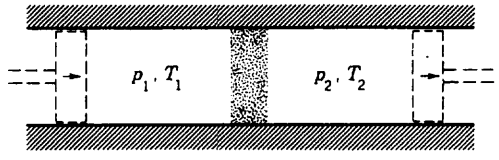

FIGURE 1
Schematic diagram of the Joule–Thomson experiment. The stippled area represents a porous plug.

For a process involving arbitrary infinitesimal changes in pressure and temperature, the change in enthalpy is

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT \tag{3}$$

In the present experiment dH is zero and dT and dp cannot be arbitrary but are related by

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

The quantity μ defined by this equation is known is the *Joule–Thomson coefficient.* It represents the limiting value of the experimental ratio of temperature difference to pressure difference as the pressure difference approaches zero:

$$\mu = \lim_{\Delta p \to 0}\left(\frac{\Delta T}{\Delta p}\right)_H \tag{5}$$

Experimentally, ΔT is found to be very nearly linear with Δp over a considerable range; this is in accord with expectations based on the theory given below.

The denominator on the right side of Eq. (4) is the heat capacity at constant pressure C_p. The numerator is zero for an ideal gas [see Eq. (1)]. Accordingly, for an ideal gas the Joule–Thomson coefficient is zero, and there should be no temperature difference across the porous plug. For a real gas, the Joule–Thomson coefficient is a measure of the quantity $(\partial H/\partial p)_T$ [which can be related thermodynamically to the quantity involved in the Joule experiment, $(\partial E/\partial V)_T$]. Using the general thermodynamic relation[2]

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V \tag{6}$$

it can be shown that, for an ideal gas satisfying the criteria already given,

$$pV = \text{const} \times T \tag{7}$$

where T is the absolute thermodynamic temperature. The coefficient $(\partial H/\partial p)_T$ is therefore a measure of the deviation from the behavior predicted by Eq. (7). On combining Eqs. (4) and (6), we obtain

$$\mu = \frac{T(\partial V/\partial T)_p - V}{C_p} \tag{8}$$

In order to predict the magnitude and behavior of the Joule–Thomson coefficient for a real gas, we can use the van der Waals equation of state,[2] which is

$$\left(p + \frac{a}{\tilde{V}^2}\right)(\tilde{V} - b) = RT \tag{9}$$

where $\tilde{V}$ is the molar volume. We can rearrange this equation (neglecting the very small second-order term $ab/\tilde{V}^2$ and substituting p/RT for $1/\tilde{V}$ in a first-order term) to obtain

$$p\tilde{V} = RT - \frac{ap}{RT} + bp$$

Thus,

$$\left(\frac{\partial \tilde{V}}{\partial T}\right)_p = \frac{R}{p} + \frac{a}{RT^2}$$

Combination of these two equations yields

$$\left(\frac{\partial \tilde{V}}{\partial T}\right)_p = \frac{\tilde{V} - b}{T} + \frac{2a}{RT^2} \tag{10}$$

which on substitution into Eq. (8) gives the expression

$$\mu = \frac{(2a/RT) - b}{\tilde{C}_p} \quad \text{(van der Waals)} \tag{11}$$

This expression does not contain p or $\tilde{V}$ explicitly, and the molar heat capacity $\tilde{C}_p$ may be considered essentially independent of these variables. The temperature dependence of $\tilde{C}_p$ is small, and accordingly that of μ is also small enough to be neglected over the ΔT obtainable with a Δp of about 1–5 bar (namely about 4 K or less for the gases considered here). Accordingly, we may expect that μ will be approximately independent of Δp over a wide range, as stated previously.

For most gases under ordinary conditions, $2a/RT > b$ (the attractive forces predominate over the repulsive forces in determining the nonideal behavior) and the Joule–Thomson coefficient is therefore positive (gas cools on expansion). At a sufficiently high temperature, the inequality is reversed, and the gas warms on expansion. The temperature at which the Joule–Thomson coefficient changes sign is called the *inversion temperature* T_I. For a van der Waals gas,

$$T_I = \frac{2a}{Rb} \tag{12}$$

This temperature is usually several hundred degrees above room temperature. However, hydrogen and helium are exceptional in having inversion temperatures that are well below room temperatures. This results from the very small attractive forces in these gases (see Table 1 for values of the van der Waals constant a).

TABLE 1 Values of constants in equations of state[a] and the Lennard-Jones potential

	He	H_2	N_2	CO_2
van der Waals[3]:				
a	0.03457	0.2476	1.408	3.640
b	0.02370	0.02661	0.03913	0.04267
Beattie–Bridgeman[4,5]:				
A_0	0.0219	0.2001	1.3623	5.0728
a	0.05984	−0.00506	0.02617	0.07132
B_0	0.01400	0.02096	0.05046	0.10476
b	0.0	−0.04359	−0.00691	0.07235
$10^{-4}c$	0.0040	0.0504	4.20	66.00
Lennard–Jones [6]:				
ε/k (K)	6.03	29.2	95.0	189
σ (nm)	0.263	0.287	0.370	0.449

[a] Units assumed are V in $dm^3\ mol^{-1} \equiv L\ mol^{-1}$, p in bar $\equiv 10^5$ Pa, T in K. ($R = 0.083145$ bar $dm^3\ K^{-1}\ mol^{-1}$.)

Other semiempirical equations of state can be used to predict Joule–Thomson coefficients. Perhaps the best of these is the Beattie–Bridgeman equation,[4,5] which can be written (for 1 mol) as

$$p = \frac{RT(1 - \epsilon)}{\tilde{V}^2}(\tilde{V} + B) - \frac{A}{\tilde{V}^2} \tag{13}$$

where $A = A_0(1 - a/\tilde{V})$, $B = B_0(1 - b/\tilde{V})$, and $\epsilon = c/\tilde{V}T^3$. In this equation of state, there are five constants which are characteristic of the particular gas: A_0, B_0, a, b, and c. In terms of these constants and the pressure and temperature, the Joule–Thomson coefficient is given[4] by

$$\mu = \frac{1}{\tilde{C}_p}\left\{-B_0 + \frac{2A_0}{RT} + \frac{4c}{T^3} + \left[\frac{2B_0b}{RT} - \frac{3A_0a}{(RT)^2} + \frac{5B_0c}{RT^4}\right]p\right\} \tag{14}$$

This equation predicts a small dependence on pressure not shown by Eq. (11), which is based on the van der Waals equation.

The most general of the equations of state is the *virial equation,* which is also the most fundamental since it has a direct theoretical connection to the intermolecular potential function. The virial equation of state expresses the deviation from ideality as a series expansion in density and, in terms of molar volume, can be written

$$\frac{p\tilde{V}}{RT} = 1 + \frac{B_2(T)}{\tilde{V}} + \frac{B_3(T)}{\tilde{V}^2} + \cdots \tag{15}$$

The virial coefficients B_2 and B_3 depend only on temperature and are determined by two- and three-body interactions between molecules, respectively. For pressures below about 10 bar, the B_3 term is very small and can be neglected. Solving Eq. (15) for $\tilde{V}$ and $(\partial\tilde{V}/\partial T)_p$ in a manner similar to that for the van der Waals case above gives

$$\mu = \frac{T(\partial B_2/\partial T)_p - B_2}{\tilde{C}_p} \tag{16}$$

From statistical mechanics,[6] $B_2(T)$ is given by

$$B_2(T) = N_0\int_0^\infty [1 - e^{-U(r)/kT}]2\pi r^2\, dr \tag{17}$$

and $(\partial B_2/\partial T)_p$ can be obtained by differentiation. $U(r)$ is the potential energy as a function of the separation of the molecules, taken to be spherical, and is important because it can be used to predict many of the transport and collisional properties of a molecule. One common choice for $U(r)$ is the so-called Lennard–Jones 6-12 potential, which has the form

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{18}$$

where ε is the well depth corresponding to the minimum in the potential and σ is the separation corresponding to $U(r) = 0$; see Fig. 47-1. Values for these parameters are included in Table 1 for the gases of interest in this experiment.

EXPERIMENTAL

The experimental apparatus shown in Fig. 2 is patterned after a design given in Ref. 7. The "porous plug" is a $\frac{3}{8}$-in.-OD stainless steel frit of 2 μm pore size and $\frac{1}{16}$-in. thickness pressed into a $\frac{3}{8}$-in. Swagelok tee made of nylon for reduced thermal conductivity. The

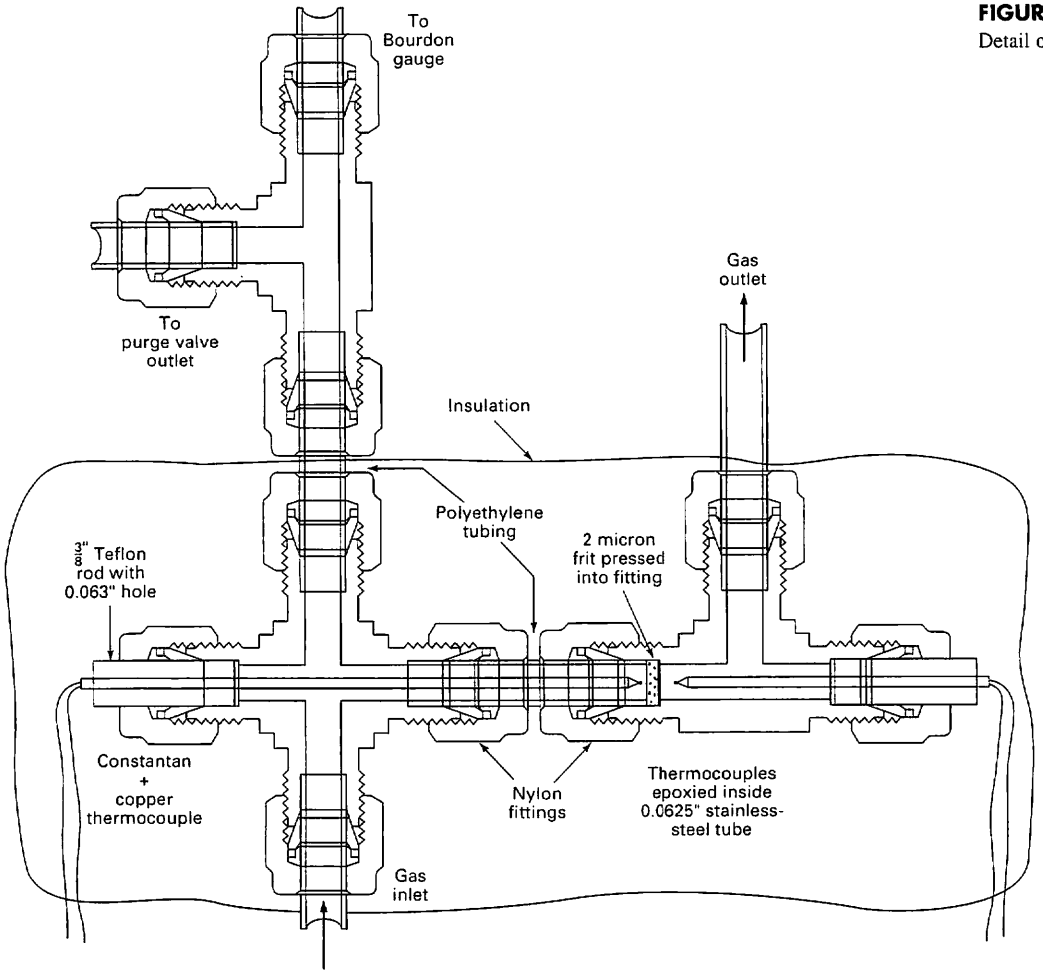

FIGURE 2
Detail of Joule–Thomson cell.

high-pressure inlet is attached to a $\frac{3}{8}$-in. cross to provide ports for gas introduction, pressure measurement, and thermocouple placement just in front of the frit. The Bourdon gauge (0–10 bar) should be connected via a tee to a purge valve to facilitate gas changes. Before use the assembly should be tested at 10 bar for leaks. Thermal insulation such as glass wool should be wrapped around the frit assembly to keep the expansion as adiabatic as possible.

The temperature difference ΔT across the frit is measured with two copper-Constantan (type T) thermocouples with wires of 0.010-in. diameter or less for reduced thermal conductivity. The thermocouples can be sealed with epoxy into a $\frac{1}{16}$-in. stainless-steel sheathing tube, which can be connected to the cross fitting by a $\frac{1}{16}$-in. to $\frac{3}{8}$-in. Swagelok adaptor, or more simply by swaging a $\frac{3}{8}$-in. Teflon rod with a 0.063-in. feedthrough hole for the thermocouple tube, as shown in Fig 2. A convenient 6-in., $\frac{1}{16}$-in.-OD sealed subminiature probe with an exposed thermocouple junction and external strain relief is available from Omega (e.g., probe TMTSS-062E-6). The 6-in. length is sufficient to allow the thermocouples to be positioned adjacent to the center of the frit, as shown in the figure.

Because the maximum temperature change will be only 0.5 to 4 K, a sensitive digital voltmeter (0.1 μV), null voltmeter, or potentiometer is desirable for accurate measurements. To obtain the temperature *difference* directly, the two Constantan leads of the thermocouples

should be clamped together and the copper leads should be attached to the measuring device.† For best absolute accuracy, the two thermocouples should be calibrated (e.g., using a standard thermometer) to determine their temperature coefficients (Seebeck coefficient) α. However, for a copper–Constantan thermocouple, α varies only slightly with temperature, from 39 to 43 μV K^{-1} from 0 to 50°C. At 25°C, α is 40.6 μV K^{-1} and the variation is small from one thermocouple to another. For small temperature differences, a linear relation $\Delta V_{TC} = \alpha \Delta T = \alpha(dT/dP)\Delta p$ is a good approximation for the thermocouple potential difference between the two junctions.‡ Thus, to the accuracy needed for this experiment, the slope of a plot of ΔV_{TC} versus Δp can be combined with an assumed value of $\alpha = 40.6$ μV K^{-1} to yield (dT/dp) and hence μ.

Procedure. Set up the apparatus shown in Fig. 2. The gas supply should be a cylinder or supply line equipped with a pressure regulator and a control valve. The supply pressure should be constant during the measurements. Because a significant temperature change occurs as gases go from high to low pressure through the pressure regulator itself, the gas should be passed through about 50 ft of $\frac{1}{4}$-in. coiled copper tubing contained in a water bath at 25 ± 1°C. A $\frac{1}{4}$-in.-to-$\frac{3}{8}$-in. adaptor can be used for a short, insulated polyethylene tubing connection to the expansion apparatus. Before initiating gas flow, record the bath temperature and determine any offset voltage between the two thermocouples.

Start the measurements with CO_2 with the pressure regulator set to minimum pressure. Open the control valve and purge the copper line and pressure gauge of air or any other gases with the purge valve open. Then close the purge valve and slowly increase the pressure to 4 bar. After this pressure is reached, record the thermocouple reading every 30 s, until the values become constant (typically a few minutes). Lower the regulator pressure by about 0.5 bar and again take readings every 30 s until a constant value is obtained. Continue this procedure down to a final pressure of 0.5 bar. Note that this is the excess pressure over the discharge pressure into the room (assumed to be at 1 bar).

Change the gas supply to N_2 and again purge the copper coil and pressure gauge with the purge valve open. Close this valve and bring the pressure slowly to 10 bar, a higher value than for CO_2 since the cooling is less. After the temperature has stabilized, repeat the sequence of measurements as for CO_2 but at 1-bar intervals. Finally, repeat the N_2 procedure using He gas. In this case, the temperature change will be much smaller and positive: i.e., the gas heats on expansion because it is above the so-called Joule–Thomson inversion point, the temperature at which the coefficient μ is zero. After completion of the experiment, make sure that all cylinder valves are closed.

CALCULATIONS

For each gas studied, do a linear regression to fit ΔV_{TC} (or ΔT) versus Δp so as to obtain the slope along with its standard error. On a single graph, show for each of the three gases the best-fit straight line along with the experimental data points. From the slopes, evaluate the Joule–Thomson coefficient μ in units of K bar^{-1}. Compare your results with literature values given in Ref. 7. Calculate μ for these gases at 25°C from the van der

†As an alternative to a thermocouple, one can use two sensitive thermistor probes and an appropriate resistance bridge circuit (see Chapters XVII and XVIII). A calibration to convert the bridge measurement to ΔT is required in this case.

‡In practice, one often finds that $\Delta V_{TC} = \alpha \Delta T + \delta V_{TC}$, where δV_{TC} is a small offset voltage (~1–3 μV) observed when both the reference and the measuring junction are at the same temperature. This "nonthermodynamic" result can occur if the thermocouple wire has regions of compositional variation or strain (e.g., from kinking) that are subject to a temperature gradient. δV_{TC} can be ignored in this experiment, since it affects only the intercept of the plot of ΔV_{TC} versus Δp and not the slope.

Waals and Beattie–Bridgeman constants given in Table 1. $\tilde{C}_p$ values for He, N_2, and CO_2 at 25°C are 20.79, 29.12, and 37.11 J K^{-1} mol^{-1}, respectively.

Plot the Lennard–Jones potentials for each of the gases studied. Obtain μ from Eqs. (16)–(18) by numerical integration and compare the values from this two-parameter potential with those from the van der Waals and Beattie–Bridgeman equations of state. [*Optional:* A simple square-well potential model can also be used to crudely represent the interaction of two molecules. In place of Eq. (18), use the square-well potential and parameters of Ref. 6 to calculate μ. Contrast with the results from the Lennard–Jones potential and comment on the sensitivity of the calculations to the form of the potential.]

DISCUSSION

The Joule–Thomson coefficient gives a measure of how much potential energy is converted into kinetic energy or vice versa as molecules in a dense gas change their average separation during an adiabatic expansion. As mentioned earlier, the magnitude and sign of μ are determined by the balance of attractive and repulsive interactions and, for most gases at room temperature, cooling occurs as molecules work against a net attractive force as they move apart. The exceptions are the weakly interacting species He and H_2, where μ is negative at 300 K and precooling below the inversion temperature is first necessary before cooling can occur on expansion. Calculate the inversion temperature for the gases of Table 1 using Eqs. (11), (14), and (16), neglecting the last, small pressure-dependent term in (14), and compare your values with experimental ones you find in the literature. Equations (14) and (16) can be most easily solved for T_l by iteration, using for example the Solve For function of spreadsheet programs, as discussed in Chapter III.

Joule–Thomson cooling is the basis for the Linde method of gas liquefaction, in which a gas is compressed, allowed to cool by heat exchange, and is then expanded to cool sufficiently that the gas liquefies. This effect is also important in the operation of refrigerators and heat pumps. Using cylinders of high-pressure gas, cooling can be achieved without power input in a device without moving parts, and hence the Joule–Thomson process has been used in cooling of small infrared and optical detectors on space probes. Discuss some of the design factors that might be important in achieving maximum cooling efficiency in the latter kind of a device.

For the more difficult Joule experiment, we can write

$$\eta \equiv -\left(\frac{\partial T}{\partial V}\right)_E = \frac{(\partial E/\partial V)_T}{(\partial E/\partial T)_V} = \frac{T(\partial p/\partial T)_V - p}{C_v} \tag{19}$$

This quantity is called the *Joule coefficient.* It is the limit of $-(\Delta T/\Delta V)_E$, corrected for the heat capacity of the containers as ΔV approaches zero. With the van der Waals equation of state, we obtain $\eta = a/\tilde{V}^2\tilde{C}_v$. The corrected temperature change when the two containers are of equal volume is found by integration to be $\Delta T = -a/2\tilde{V}\tilde{C}_v$, where $\tilde{V}$ is the initial molar volume and $\tilde{C}_v$ is the molar constant-volume heat capacity. It is instructive to calculate this ΔT for a gas such as CO_2. In addition, the student may consider the relative heat capacities of 10 L of the gas at a pressure of 1 bar and that of the quantity of copper required to construct two spheres of this volume with walls (say) 1 mm thick and then calculate the ΔT expected to be observed with such an experimental arrangement.

SAFETY ISSUES

Gas cylinders must be chained securely to the wall or laboratory bench (see pp. 705–6 and Appendix C).

APPARATUS

Insulated Joule–Thomson cell similar to that of Fig. 2 (suitable stainless steel frits can be obtained from chromatographic parts suppliers, e.g., Upchurch Scientific part C-414); metal or nylon tees, crosses, and reducers (available from Swagelok and other manufacturers); $\frac{3}{8}$-in. Teflon rod; type T insulated copper–Constantan thermocouples with 0.010-in.-diameter wires; voltmeter with 0.1-μV resolution (e.g., Keithley 196), null voltmeter (e.g., Hewlett Packard 419A or Keithley 155), or sensitive potentiometer (e.g., Keithley K-3). Cylinders of CO_2, N_2, and He with regulators and control valves; 50 ft of $\frac{1}{4}$-in. copper coil, $\frac{3}{8}$-in. and $\frac{1}{4}$-in. polyethylene tubing; 0- to 10-bar Bourdon gauge; 25°C water bath.

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EXPERIMENT 3

Heat-Capacity Ratios for Gases

The ratio C_p/C_v of the heat capacity of a gas at constant pressure to that at constant volume will be determined by either the method of adiabatic expansion or the sound velocity method. Several gases will be studied, and the results will be interpreted in terms of the contribution made to the specific heat by various molecular degrees of freedom.

THEORY

In considering the theoretical calculation of the heat capacities of gases, we shall be concerned only with perfect gases. Since $\tilde{C}_p = \tilde{C}_v + R$ for an ideal gas (where $\tilde{C}_p$ and $\tilde{C}_v$ are the molar quantities C_p/n and C_v/n), our discussion can be restricted to C_v.

The number of *degrees of freedom* for a molecule is the number of independent coordinates needed to specify its position and configuration. Hence a molecule of N atoms has $3N$ degrees of freedom. These could be taken as the three Cartesian coordinates of the N individual atoms, but it is more convenient to classify them as follows.

1. *Translational degrees of freedom:* Three independent coordinates are needed to specify the position of the center of mass of the molecule.
2. *Rotational degrees of freedom:* All molecules containing more than one atom require a specification of their orientation in space. As an example, consider a rigid diatomic molecule; such a model consists of two point masses (the atoms) connected by a rigid massless bar (the chemical bond). Through the center of mass, which lies on the rigid bar, independent rotation can take place about two axes mutually perpendicular to each other and to the rigid bar. (The rigid bar itself does not constitute a third axis of rotation under ordinary circumstances for reasons based on quantum theory, there being no appreciable moment of inertia about this axis.) Rotation of a *diatomic* molecule or any linear molecule can thus be described in terms of *two* rotational degrees of freedom. *Nonlinear* molecules for which the third axis has a moment of inertia of appreciable magnitude and constitutes another axis of rotation require *three* rotational degrees of freedom.
3. *Vibrational degrees of freedom:* One must also specify the displacements of the atoms from their equilibrium positions (vibrations). The number of vibrational degrees of freedom is $3N - 5$ for linear molecules and $3N - 6$ for nonlinear molecules. These values are determined by the fact that the total number of degrees of freedom must be $3N$. For each vibrational degree of freedom, there is a "normal mode" of vibration of the molecule, with characteristic symmetry properties and a characteristic harmonic frequency. The vibrational normal modes for CO_2 and H_2O are illustrated schematically in Fig. 1.

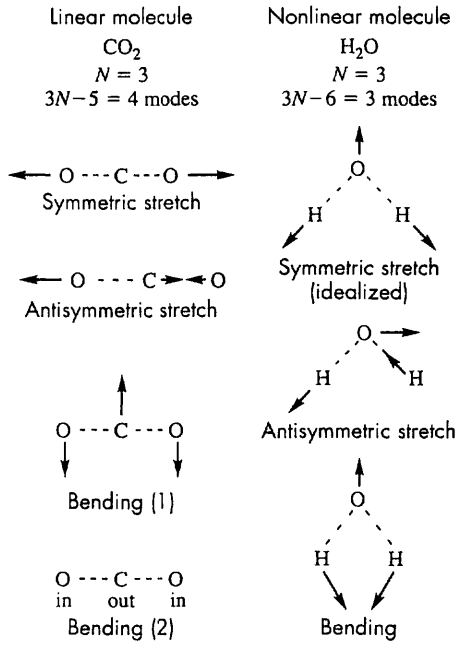

FIGURE 1
Schematic diagrams of the vibrational normal modes for CO_2, a linear molecule, and H_2O, a bent molecule.

range of −2 to +7°C with graduations of 0.01° is convenient. Such thermometers require careful handling. Not only are they relatively fragile, but they are susceptible to certain malfunctions (separation of the mercury column, bubbles in the bulb) arising principally from the extreme fineness of the thread. Whenever possible, keep these thermometers upright; *avoid overly rapid heating or cooling.* If the mercury thread separates (which often happens when thermometers are shipped), cool the bulb in an ice–salt mixture to bring the mercury entirely into the bulb and tap if necessary to bring any bubbles to the top of the bulb. Then allow the thermometer to warm to room temperature in an upright position.

Over the years, occasional news stories have stressed the potential health hazards of mercury thermometers when used for medical purposes. In fact, the risk of mercury poisoning from a broken mercury thermometer in a physical chemistry experiment is extremely low. The key safety rule if such a thermometer were to break is the prompt and efficient cleanup of any spilled mercury: see Appendix C for further details. Note that essentially no mercury will be spilled if the stem rather than the bulb is broken. In conclusion, mercury thermometers should be handled with reasonable care, but they are safe, useful, and precise scientific instruments of considerable value for research applications.

2. Special Liquid Thermometers. For temperatures below the freezing point of mercury (−39°C), one can use several kinds of liquid-in-glass thermometers. Toluene thermometers may be used down to −95°C, and pentane thermometers will operate as low as −130°C. Mercury thermometers constructed from special glasses may be used far above the normal boiling point of mercury (357°C). However, outside the ordinary mercury range it is usually more convenient, as well as more accurate, to use thermometric devices of other types, especially thermocouples or resistance thermometers.

Thermocouples.[2,9] Thermocouples provide one of the most convenient and versatile means of measuring temperatures over a wide range from very low (−250°C) to very high (2300°C) values. All that is required is two kinds of fine wire made from appropriate metals or alloys, a suitable precision voltage-measuring instrument (a good potentiometer or digital voltmeter), and a constant-temperature bath (almost always an ice–water bath) for the reference junction. Thermocouples are simple to use and, being small, have a rapid response to temperature changes. Although their sensitivity is limited, temperature resolution of 0.001 K can be achieved with very good voltmeters, and much better resolution is possible with multijunction thermocouples called thermopiles (see p. 688). The principal disadvantage of thermocouples is the need for very careful calibration to achieve good absolute accuracy and some tendency for the calibration to change with time, especially at high temperatures.

When two dissimilar metals are placed in contact, a transfer of electrons from one to the other takes place and a double charge layer forms at the junction surface. As in the case of a junction between a metal electrode and an electrolyte solution, the resulting electrical potential must be measured in the presence of a reference junction, which in the present instance is a junction of the same two metals at a known temperature. As shown in Fig. 2,

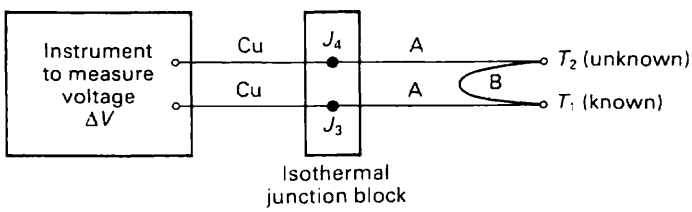

FIGURE 2
Schematic diagram of a two-junction thermocouple setup.

the thermoelectric potential difference ΔV is measured between the ends of two wires of the same kind. One wire of metal A leads to the junction at the reference temperature T_1, and the other wire of metal A leads to the junction at the unknown temperature T_2; these two junctions are connected directly by a wire of the second metal B, which completes the circuit. The potential drop ΔV is a measure of the temperature difference $\Delta T = T_2 - T_1$. In cases where ΔT is not too large, ΔV is roughly proportional to the difference between the unknown and the reference temperature:

$$\Delta V = \alpha \, \Delta T \tag{10}$$

where α is called the Seebeck coefficient in honor of Thomas Seebeck, who discovered the thermoelectric effect in 1821. In fact ΔV is not exactly a linear function of ΔT, since the sensitivity α varies slowly with temperature. Thus a well-known reference temperature T_1 and calibration tables are needed to obtain values of T_2 from measured ΔV values. It is common practice to use the ice point (0°C) as the reference temperature; in this case ΔT equals the value of T_2 in degrees Celsius.

The presence of an isothermal junction block in Fig. 2 should also be noted. Almost all high-quality voltage-measuring instruments have input terminals made of copper. Unless metal A of the thermocouple pair is also copper, connection of the thermocouple to the voltage instrument will create two new bimetallic junctions J_3 and J_4. The presence of any temperature difference between the input terminals would then generate an unwanted extra thermoelectric potential drop and cause an error in the determination of T_2. In practice, this error voltage is usually very small and can often be neglected. However, for high-precision measurements this source of error can be eliminated by using an isothermal junction block. This block is made from an electrical insulator with high thermal conductivity, which ensures that J_3 and J_4 are at the same temperature, T_{block}. The value of T_{block} has no effect on the measured ΔV values.

The isothermal junction block is also used in commercial thermocouple devices that utilize only a single junction. Since T_{block} can have any value, it is made equal to the reference temperature T_1, as shown in Fig. 3*a*. Another simplification is the elimination of wire A in the junction block, so that two junctions (Cu–A and A–B) at the same temperature T_1 are replaced by one (a Cu–B junction) as shown in Fig. 3*b*. It can be shown empirically that

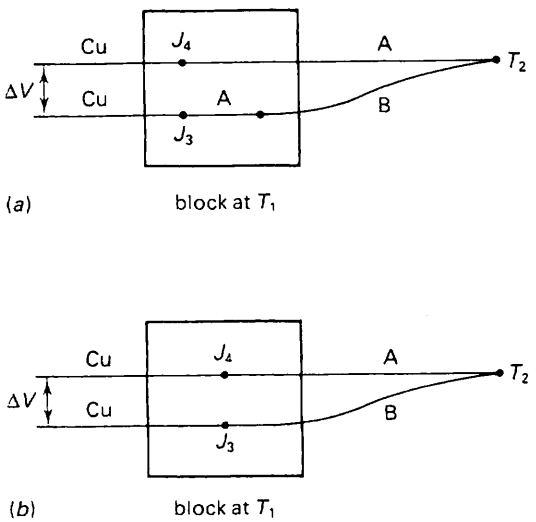

FIGURE 3
Configurations for a "one-junction" thermocouple arrangement utilizing an isothermal junction block held at a reference temperature T_1; see text for details.

TABLE 3 Thermocouple characteristics

ANSI type	Metals	Useful temperature range (°C)	Sensitivity (μV K^{-1}) −200°C	25°C	300°C	Notes
T	Copper Constantan	−200 to 370	15.8	40.7	58.1	*R, I, V,* *O* (mild)
J	Iron Constantan	0 to 750	21.8[a]	51.7	55.4	*R, I, V,* *O* (moderate *T*)
E	Chromel Constantan	−200 to 900	25.1	60.9	77.9	*I, O*
K	Chromel Alumel	−200 to 1250	15.2	40.5	41.5	*I, O, L*
N	Nicrosil Nisil	−200 to 1250	9.9	26.8	35.4	*I, O, L*
S	Platinum Pt + 10%Rh	0 to 1450	—	6.0	9.1	*I, O*

Notes: Atmospheres in which bare-wire thermocouples can be used: *R* = reducing, *O* = oxidizing, *I* = inert, *V* = vacuum, *L* = limited use in vacuum or reducing atmospheres.

[a] Not recommended for low temperatures.

this modification has very little effect on the measured value of ΔV. The isothermal junction block can be mounted in an ice–water bath so that $T_1 = 0°C$. Many commercial thermocouple systems (voltage-measuring instruments plus thermocouple assembly) do not utilize an ice bath but employ software or hardware compensation schemes so that the reference temperature T_1 can have an unregulated value equal to the ambient room temperature.[6] For high-precision work, a well-regulated ice bath should always be used.

The most useful thermocouples for general work are listed in Table 3.[10] Both pure metals and various alloys are used. Many of these alloys are nickel alloys. *Constantan* (sold under the trade names Advance and Cupron) is available in two different compositions: 60%Cu + 40%Ni is designed for use with type *J* thermocouples, and 55%Cu + 45%Ni is used for both type T and type E thermocouples.† *Chromel* is the trade name of a 90%Ni + 10%Cr alloy, and *Alumel* is the trade name of a 95%Ni + 2%Mn + 2%Al + 1%Co alloy. Two other nickel alloys with trade names are *Nicrosil* (84.4%Ni + 14.2%Cr + 1.4%Si) and *Nisil* (95.5%Ni + 4.4%Si + 0.1%Mg).

The *copper–Constantan* thermocouple, called type T, is widely used. This has the important advantage that one of the metals (metal A in Fig. 3) is copper. Thus an isothermal junction block is not needed, and no stray thermoelectric potentials can occur at the input terminals of the voltage instrument even if a temperature difference does occur there. Furthermore, if a thermocouple is to be used without calibration, the possible systematic errors are smaller for type T than for other types of thermocouples. However, Cu has a very high thermal conductivity and oxidizes above 350°C. *Iron–Constantan* (type J) thermocouples are popular because of their high sensitivity and the wide range of atmospheres in which they can be used (although Fe oxidizes at high temperatures). Individual thermocouples may show variations from the standard voltage–temperature conversion table values owing to trace impurities in the iron. Type J couples should never be used above 760°C, since a magnetic phase transition at that temperature can shift the calibration at

†The letter codes used for thermocouples have been established by the American National Standards Institute (ANSI).

lower temperatures after cycling above 760°C. A *Chromel–Constantan* (type E) thermocouple is attractive for low-temperature use owing to its high sensitivity and low thermal conductivity. The *Chromel–Alumel* (type K) couple is convenient because it can be used over a very wide temperature range and the sensitivity is almost constant above 25°C (e.g., $\alpha = 36\ \mu V\ K^{-1}$ at 1250°C). There is some calibration instability due to an order–disorder phase transition at ~500°C. The *Nicrosil–Nisil* (type N) thermocouple is a more recently developed couple for use at high temperatures. It is similar to type K with changes in the alloy composition to reduce problems associated with the order–disorder transition and to improve the resistance to oxidation at high temperatures. As a result, this couple has excellent long-term stability. *Platinum–platinum* + 10% *rhodium* (type S) thermocouples have low sensitivity but can be used at temperatures as high as 1700°C. The calibration stability is excellent, and the type S thermocouple was the standard device specified by IPTS-68 to measure temperatures in the range 630.74 to 1064.43°C. However, it was replaced in this role for ITS-90 by the platinum resistance thermometer.

Other thermocouples not listed in Table 3 include the Chromel–gold couple for cryogenic use below −200°C (useful range 4 K to above 100 K) and several tungsten–tungsten + rhenium couples that can be used up to 2300°C.

Although extensive tables are given in various handbooks for converting measured thermoelectric voltages into temperatures, the best tables are those published by the National Institute of Standards and Technology (NIST).[6,11] No matter what tables are used, thermocouple wires should be selected carefully and one or more specimens of each production lot (the spools are marked with this number) should be calibrated at a number of widely spaced temperatures. Such a calibration can be made using fixed points or by comparison with a "standard" thermometer; see p. 616. For very precise work, each individual thermocouple should be calibrated. Deviations between the reading of a given thermocouple and the entries in standard conversion tables are due to strains and small compositional variations that can occur during fabrication of the wires. Over the temperature range from −200 to +300°C, these systematic errors can vary from ±1°C to ±4°C for different thermocouples. As an example the uncertainty in the absolute accuracy of an uncalibrated type T thermocouple is the larger of ±0.8°C *or* ±0.75 percent of the Celsius temperature above 0°C (±1.5 percent of the Celsius temperature below 0°C). For type K, the analogous values are ±2.2°C or ±0.75 percent above 0°C (±2.0 percent below 0°C).

Junctions to be used only at low or moderate temperatures (below 170°C) may be joined with soft solder (be sure to use a noncorrosive flux such as rosin) or silver solder, but it is better to weld the two metals together with an electric arc or an oxygen–gas flame. The two wires are stripped of any insulating material and then twisted together tightly over a distance of ~0.5 cm. If a glass-blowing torch is used, the end of the junction should be dipped in paste flux and placed in the reducing region at the tip of the blue part of the flame. Remove the wires as soon as the metals melt and form a small bead at the end. This bead should be pinched with a pair of long-nosed pliers and examined carefully to make sure it is hard and metallic rather than a bead of oxide (which crumbles easily). The two wires must be electrically insulated from each other, and some consideration must be given to the temperature characteristics of the insulating materials. In particular, at high temperatures nothing should come into contact with the wires, particularly Chromel-P and Alumel, that will form a liquid flux (low-melting eutectic) with the protective oxide film.

Thermocouple wire is available commercially either as bare wire or as wire protected with a variety of insulators. The best choice of insulation for use up to 280°C is Teflon. Its resistance to abrasion, chemical reaction, solvents, and humidity is excellent, and its flexibility is good. Braided fiberglass is very good for use up to 480°C, but it has poor abrasion resistance and quite high porosity. Special braided ceramic fibers are available for use

as high as 1425°C. Bare wires and Alundum tubes can also be used above 450°C. The junctions of any thermocouple, and the wire itself when bare wire is used, must always be protected carefully from corrosion or mechanical damage. For use in liquids and solutions at moderate temperatures, a thermocouple is usually placed in a closed glass tube (~6 mm in diameter) with a small amount of nonvolatile oil or silicone grease at the bottom to improve the thermal contact. It is also possible to bond thermocouple junctions to a wide range of solid surfaces (metals, ceramics, glass, plastics) with high-thermal conductivity epoxy adhesives. Fully assembled thermocouple probes are also available commercially with both wires mounted in a stainless steel or Inconel protective sheath and insulated from each other with a compacted ceramic such as MgO, which is good up to 1650°C. The junctions can be obtained exposed as a bare butt weld or bare bead or enclosed in the sheath metal (grounded and ungrounded options are available).

A satisfactory environment for the 0°C reference junction is provided by a slushy mixture of ice and distilled water in a Dewar flask, with a ring stirrer and a monitoring mercury thermometer. Elaborate thermoelectric ice–water chambers are also available; these are convenient for prolonged periods of use but rather expensive. As mentioned previously many commercial thermocouple systems eliminate the ice bath by placing the cold junction on an isothermal block that is at room temperature and compensating for the resulting error. This is a convenient but less accurate procedure.

For ordinary work with thermocouple wires of large or medium diameter, the thermoelectric potential can be measured with a good digital voltmeter (DVM) or a dc potentiometer. If a continuous record of the temperature is required, the thermocouple can be connected to a millivolt strip-chart recorder; or a DVM with an interface to a computer can be used to store frequent periodic readings. For precision work a high-resolution ($6\frac{1}{2}$-digit) high-impedance DVM is required. Such equipment used with a calibrated copper–Constantan thermocouple having one measuring junction and one reference junction maintained carefully at the ice point permits one to measure the absolute temperature around room temperature with an uncertainty of about ± 0.01 K. However, the precision is much better than this, and temperature differences can be measured to within ± 0.002 K or better.

Several precautions should be observed in order to enhance the long-term stability of a thermocouple.

1. Use the largest diameter wire that is feasible without conducting too much heat away from the area of the measurement junction.
2. If very thin wires are required, use larger-diameter extension wires for regions where there is almost no temperature gradient (typically the room temperature leads that go to the voltage-measuring device).
3. Avoid mechanical stresses and vibrations that might cause strain distortions in the wires.
4. Avoid very large temperature gradients along the wire.
5. Operate the thermocouple only at temperatures below its design limit.
6. If operating in a hostile atmosphere, use an adequate external sheath to protect the wires.

Platinum Resistance Thermometers.[2,5,12] The platinum resistance thermometer (PRT) is capable of extremely high accuracy, owing to the high purity attainable for platinum and the high reproducibility of its temperature coefficient of resistivity. For a standard PRT used to determine absolute temperature values with the highest possible accuracy, the resistance element is a coil of pure platinum wire, carefully annealed both before and after winding and enclosed in a sealed sheath (glass or thin-walled metal tube) containing dry air or helium as a heat-transfer gas. The design of standard PRTs is aimed

Other Procedures. It is seldom necessary in physical chemistry laboratory work to purify chemical compounds beyond the purity attainable commercially. For special purposes, such techniques as recrystallization, fractional distillation, chromatographic separation, and zone refining may be used.[3]

GAS-HANDLING PROCEDURES

Many physical chemistry experiments involve the use of one or more gases such as oxygen, nitrogen, hydrogen, helium, argon, and carbon dioxide. We shall be concerned here with procedures for handling these gases.

Cylinders, Gas Regulators, Reducing Valves. Although some gases can be prepared in chemical generators, see for example Exps. 37 and 43, it is far more convenient and desirable to obtain gases commercially in steel cylinders. These cylinders are available in several types and sizes. The large size is 51 in. in height and 9 in. in diameter; at 2200 psi and 70°F it contains approximately 280 moles of gas (~7000 L at STP). In addition, smaller cylinders and very small lecture bottles are useful for supplying special gases such as hydrogen chloride and acetylene. Note that most gas pressure gauges read in psi (pounds/square inch), and that 14.7 psi equals 1 atm.

Each cylinder is delivered with a protective cap, which should be removed only when the cylinder has been chained against a laboratory table or a wall. **Cylinders should always be chained** to prevent upset, which has been known to cause violent release of the gas or even bursting of the cylinder, with serious consequences.

At the top of the cylinder are a needle valve and a threaded outlet. To clear the outlet of dust, the needle valve should be barely opened for an instant and reclosed. In most laboratory work a *regulator* is attached to the cylinder. This usually comprises a Bourdon gauge to indicate the cylinder pressure (up to 4000 psi), another gauge to indicate outlet pressure (ordinarily up to 60 psi), an adjustable diaphragm valve to regulate the outlet pressure, and an outlet needle valve to control the flow rate. In the diaphragm valve, the needle of a needle valve is attached to a flexible diaphragm. When the outlet pressure exceeds the desired value (controlled by a spring between the diaphragm and an adjusting screw), the motion of the diaphragm is such as to close this needle valve, shutting off the flow of gas from the high-pressure side; when the outlet pressure is too low, the diaphragm opens this needle valve.

The fittings and threads on the cylinder outlet are of several types, depending on the kind of gas, in order to prevent the wrong regulator or other fitting from being used with a given cylinder—e.g., an H_2 regulator on an O_2 cylinder.

The regulator fastens to the cylinder with a metal-to-metal contact, no gasket ordinarily being required except in the case of CO_2 cylinders. The connection is made tight with a large wrench. To verify that the seal is gas-tight, close the diaphragm valve, then open and close the cylinder valve and watch the cylinder pressure gauge for a few minutes.

Regulator Operation. When it is desired to use gas from a cylinder, follow the procedure given below:

1. Close the outlet needle valve and the diaphragm valve (turn the screw handle counterclockwise until it rotates freely).
2. Open the cylinder valve fully and check the cylinder pressure gauge to make sure that the cylinder is not empty.

3. *Make sure that the outlet needle value is closed,* and then slowly turn the handle on the diaphragm valve clockwise until the outlet gauge reads about 2 psi. Keep in mind that the outlet pressure gauge reads overpressure, i.e., psi *above* atmospheric pressure. 1 psi = 0.068 atm = 51.7 Torr.
4. In order to purge the system and the regulator chamber of air, open a vent valve and then *very slowly* open the outlet needle valve enough to achieve a reasonable flow rate. (If the gas is toxic or expensive, one can connect a vacuum pump to the vent valve and pump out the system and regulator.) After a brief purge period, close the vent valve, allow the system to fill, and then close the outlet needle valve. When one wishes to fill the system to an overpressure greater than 2 psi, *slowly* turn the diaphragm valve handle until the outlet pressure rises to the desired value.
5. When gas is no longer needed, close the outlet needle valve and the cylinder valve.

Do not allow a cylinder to be emptied down to 1 atm; there should be some overpressure left when the cylinder is returned. Unneeded cylinders should be returned to the supplier to avoid needless demurrage (cylinder rental) charges.

A simple *reducing valve,* consisting of a needle valve with fittings to match the cylinder and a hose connector for the low-pressure side, can be used in place of a regulator for some purposes when gas flow through an open system is desired. This device is less expensive than a regulator, but its use requires more care because, if the system should accidentally be closed, the pressure will build up to whatever is required to burst it at its weakest point if this is less than the full cylinder pressure. It is advisable to connect the system to the reducing valve with a lightweight rubber tube that will easily blow off the hose connector if the pressure becomes too high, or to provide some other safety valve near the inlet end of the system.

Warning: Never connect a gas cylinder directly to a closed system that is not specially designed to withstand high pressures (such as a "combustion bomb" for heats of combustion). Even when a regulator is used, remember that the diaphragm valve may slowly leak; arrange for some kind of safety pressure release, if only a rubber tubing connection that can be easily blown off.

Most gases undergo a Joule–Thomson cooling when they expand in a regulator or reducing valve. In the case of CO_2, the cooling at high flow rates is often large enough to be troublesome, causing frosting of apparatus or even clogging of the regulator or the reducing valve with solid. In addition to this effect, there may be a compressional heating of the gas if a significant pressure is built up quickly in some part of the system. If a gas must be maintained at a constant temperature, it should be passed through a long coil of copper tubing immersed in a constant-temperature bath. One hundred feet of $\frac{1}{4}$-in. copper tubing is adequate for flow rates up to about 5 L min^{-1}.

Needle Valves. For control of gas flow at ordinary pressures, needle valves give much better control than stopcocks. The hard-steel tapered needle, at the end of a screw-threaded shaft, seats in a cylindrical hole so that the area of open space for gas flow is gradually increased or decreased on rotating the shaft. These usually do *not* provide a reliable shut-off and are used for flow control only. Persons whose acquaintance with valves is limited to water faucets often damage needle valves by needlessly overtightening them when shutting off the flow. This results in a decrease in the sensitivity of control of the gas flow. *It is important not to exert any more force than necessary.*

Hoses. Gases for open systems may be carried by ordinary $\frac{1}{4}$- or $\frac{5}{16}$-in. gum-rubber tubing. Closed systems may require heavy-wall rubber or plastic pressure tubing, which can safely be used with pressures up to several atmospheres. **Warning:** Do not subject