

19-25. (a) We use $\epsilon = L_V/N$, where L_V is the heat of vaporization and N is the number of molecules per gram. The molar mass of atomic hydrogen is 1 g/mol and the molar mass of atomic oxygen is 16 g/mol so the molar mass of H_2O is 1 + 1 + 16 = 18 g/mol. There are $N_A = 6.02 \times 10^{23}$ molecules in a mole so the number of molecules in a gram of water is $(6.02 \times 10^{23} \text{ mol}^{-1})/(18 \text{ g/mol}) = 3.34 \times 10^{22}$ molecules/g. Thus $\epsilon = (539 \text{ cal/g})/(3.34 \times 10^{22}/\text{g}) = 1.61 \times 10^{-20} \text{ cal}$. This is $(1.61 \times 10^{-20} \text{ cal})(4.186 \text{ J/cal}) = 6.76 \times 10^{-20} \text{ J}$.

(b) The average translational kinetic energy is

$$K_{\text{avg}} = \frac{3}{2}kT = \frac{3}{2}(1.38 \times 10^{-23} \text{ J/K}) [(32.0 + 273.15) \text{ K}] = 6.32 \times 10^{-21} \text{ J} .$$

The ratio ϵ/K_{avg} is $(6.76 \times 10^{-20} \text{ J})/(6.32 \times 10^{-21} \text{ J}) = 10.7$.

19-29. (a) We use the ideal gas law $pV = nRT = NkT$, where p is the pressure, V is the volume, T is the temperature, n is the number of moles, and N is the number of molecules. The substitutions $N = nN_A$ and $k = R/N_A$ were made. Since 1 cm of mercury = 1333 Pa, the pressure is $p = (10^{-7})(1333) = 1.333 \times 10^{-4} \text{ Pa}$. Thus,

$$\begin{aligned} \frac{N}{V} &= \frac{p}{kT} = \frac{1.333 \times 10^{-4} \text{ Pa}}{(1.38 \times 10^{-23} \text{ J/K})(295 \text{ K})} \\ &= 3.27 \times 10^{16} \text{ molecules/m}^3 = 3.27 \times 10^{10} \text{ molecules/cm}^3 . \end{aligned}$$

(b) The molecular diameter is $d = 2.00 \times 10^{-10} \text{ m}$, so, according to Eq. 19-25, the mean free path is

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V} = \frac{1}{\sqrt{2}\pi(2.00 \times 10^{-10} \text{ m})^2(3.27 \times 10^{16} \text{ m}^{-3})} = 172 \text{ m} .$$

19-46. Two formulas (other than the first law of thermodynamics) will be of use to us. It is straightforward to show, from Eq. 19-11, that for any process that is depicted as a *straight line* on the pV diagram — the work is

$$W_{\text{straight}} = \left(\frac{p_i + p_f}{2} \right) \Delta V$$

which includes, as special cases, $W = p\Delta V$ for constant-pressure processes and $W = 0$ for constant-volume processes. Further, Eq. 19-44 with Eq. 19-51 gives

$$E_{\text{int}} = n \left(\frac{f}{2} \right) RT = \left(\frac{f}{2} \right) pV$$

where we have used the ideal gas law in the last step. We emphasize that, in order to obtain work and energy in Joules, pressure should be in Pascals (N/m^2) and volume should be in cubic meters. The degrees of freedom for a diatomic gas is $f = 5$.

(a) The internal energy change is

$$\begin{aligned} E_{\text{int } c} - E_{\text{int } a} &= \frac{5}{2}(p_c V_c - p_a V_a) \\ &= \frac{5}{2}((2000 \text{ Pa})(4.0 \text{ m}^3) - (5000 \text{ Pa})(2.0 \text{ m}^3)) \\ &= -5000 \text{ J} . \end{aligned}$$

(b) The work done during the process represented by the diagonal path is

$$W_{\text{diag}} = \left(\frac{p_a + p_c}{2} \right) (V_c - V_a) = (3500 \text{ Pa})(2.0 \text{ m}^3)$$

which yields $W_{\text{diag}} = 7000 \text{ J}$. Consequently, the first law of thermodynamics gives

$$Q_{\text{diag}} = \Delta E_{\text{int}} + W_{\text{diag}} = -5000 + 7000 = 2000 \text{ J} .$$

- (c) The fact that ΔE_{int} only depends on the initial and final states, and not on the details of the “path” between them, means we can write

$$\Delta E_{\text{int}} = E_{\text{int } c} - E_{\text{int } a} = -5000 \text{ J}$$

for the indirect path, too. In this case, the work done consists of that done during the constant pressure part (the horizontal line in the graph) plus that done during the constant volume part (the vertical line):

$$W_{\text{indirect}} = (5000 \text{ Pa})(2.0 \text{ m}^3) + 0 = 10000 \text{ J} .$$

Now, the first law of thermodynamics leads to

$$Q_{\text{indirect}} = \Delta E_{\text{int}} + W_{\text{indirect}} = -5000 + 10000 = 5000 \text{ J} .$$

- 19-54. (a) We use Eq. 19-54 with $V_f/V_i = \frac{1}{2}$ for the gas (assumed to obey the ideal gas law).

$$p_i V_i^\gamma = p_f V_f^\gamma \implies \frac{p_f}{p_i} = \left(\frac{V_i}{V_f} \right)^\gamma = 2^{1.3}$$

which yields $p_f = (2.46)(1.0 \text{ atm}) = 2.46 \text{ atm}$.

- (b) Similarly, Eq. 19-56 leads to

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{\gamma-1} = (273 \text{ K})(1.23) = 336 \text{ K} .$$

- (c) We use the gas law in ratio form (see Sample Problem 19-1) and note that when $p_1 = p_2$ then the ratio of volumes is equal to the ratio of (absolute) temperatures. Consequently, with the subscript 1 referring to the situation (of small volume, high pressure, and high temperature) the system is in at the end of part (a), we obtain

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} = \frac{273 \text{ K}}{336 \text{ K}} = 0.813 .$$

The volume V_1 is half the original volume of one liter, so

$$V_2 = 0.813(0.50 \text{ L}) = 0.406 \text{ L} .$$

- 19-59. In the following $C_V = \frac{3}{2}R$ is the molar specific heat at constant volume, $C_p = \frac{5}{2}R$ is the molar specific heat at constant pressure, ΔT is the temperature change, and n is the number of moles.

- (a) The process 1 \rightarrow 2 takes place at constant volume. The heat added is

$$\begin{aligned} Q &= nC_V \Delta T = \frac{3}{2}nR \Delta T \\ &= \frac{3}{2}(1.00 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})(600 \text{ K} - 300 \text{ K}) = 3.740 \times 10^3 \text{ J} . \end{aligned}$$

Since the process takes place at constant volume the work W done by the gas is zero, and the first law of thermodynamics tells us that the change in the internal energy is

$$\Delta E_{\text{int}} = Q = 3.740 \times 10^3 \text{ J} .$$

- (d) The process 2 \rightarrow 3 is adiabatic. The heat added is zero. The change in the internal energy is

$$\begin{aligned} \Delta E_{\text{int}} &= nC_V \Delta T = \frac{3}{2}nR \Delta T \\ &= \frac{3}{2}(1.00 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})(455 \text{ K} - 600 \text{ K}) = -1.807 \times 10^3 \text{ J} . \end{aligned}$$

According to the first law of thermodynamics the work done by the gas is

$$W = Q - \Delta E_{\text{int}} = +1.807 \times 10^3 \text{ J} .$$

(g) The process $3 \rightarrow 1$ takes place at constant pressure. The heat added is

$$\begin{aligned} Q &= nC_p \Delta T = \frac{5}{2}nR \Delta T \\ &= \frac{5}{2}(1.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K} - 455 \text{ K}) = -3.220 \times 10^3 \text{ J} . \end{aligned}$$

The change in the internal energy is

$$\begin{aligned} \Delta E_{\text{int}} &= nC_V \Delta T = \frac{3}{2}nR \Delta T \\ &= \frac{3}{2}(1.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K} - 455 \text{ K}) = -1.932 \times 10^3 \text{ J} . \end{aligned}$$

According to the first law of thermodynamics the work done by the gas is

$$W = Q - \Delta E_{\text{int}} = -3.22 \times 10^3 \text{ J} + 1.93 \times 10^3 \text{ J} = -1.288 \times 10^3 \text{ J} .$$

(j) For the entire process the heat added is

$$Q = 3.74 \times 10^3 \text{ J} + 0 - 3.22 \times 10^3 \text{ J} = 519 \text{ J} ,$$

the change in the internal energy is

$$\Delta E_{\text{int}} = 3.74 \times 10^3 \text{ J} - 1.81 \times 10^3 \text{ J} - 1.93 \times 10^3 \text{ J} = 0 ,$$

and the work done by the gas is

$$W = 0 + 1.81 \times 10^3 \text{ J} - 1.29 \times 10^3 \text{ J} = 519 \text{ J} .$$

(m) We first find the initial volume. Use the ideal gas law $p_1 V_1 = nRT_1$ to obtain

$$V_1 = \frac{nRT_1}{p_1} = \frac{(1.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{(1.013 \times 10^5 \text{ Pa})} = 2.46 \times 10^{-2} \text{ m}^3 .$$

Since $1 \rightarrow 2$ is a constant volume process $V_2 = V_1 = 2.46 \times 10^{-2} \text{ m}^3$. The pressure for state 2 is

$$p_2 = \frac{nRT_2}{V_2} = \frac{(1.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(600 \text{ K})}{2.46 \times 10^{-2} \text{ m}^3} = 2.02 \times 10^5 \text{ Pa} .$$

This is equivalent to 1.99 atm.

(o) Since $3 \rightarrow 1$ is a constant pressure process, the pressure for state 3 is the same as the pressure for state 1: $p_3 = p_1 = 1.013 \times 10^5 \text{ Pa}$ (1.00 atm). The volume for state 3 is

$$V_3 = \frac{nRT_3}{p_3} = \frac{(1.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(455 \text{ K})}{1.013 \times 10^5 \text{ Pa}} = 3.73 \times 10^{-2} \text{ m}^3 .$$

MB.Vx2.dat

MB.speed2.dat

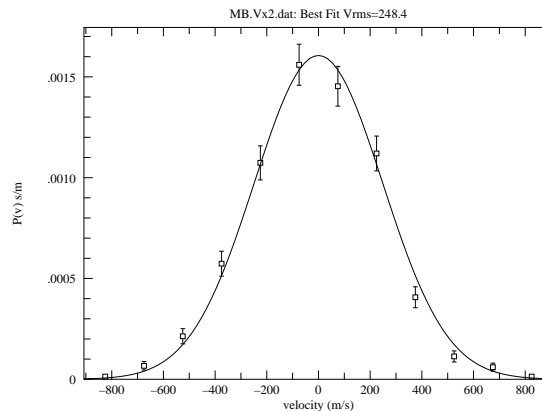
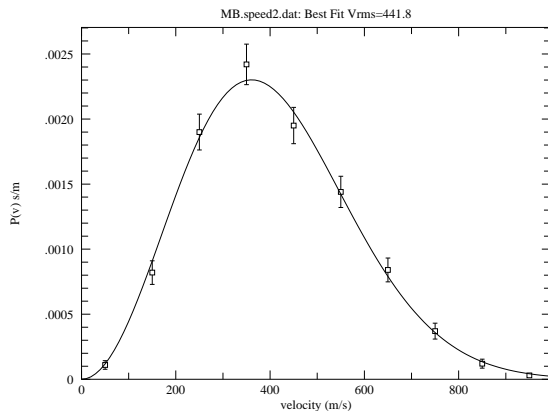
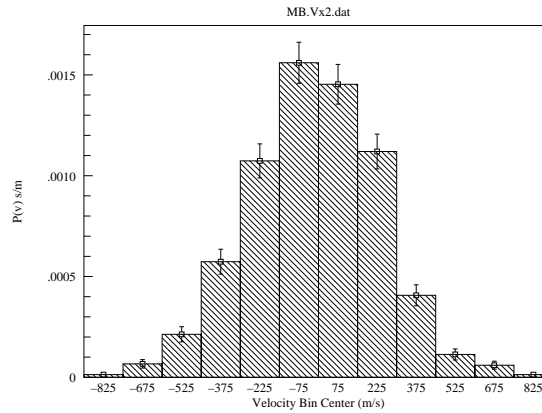
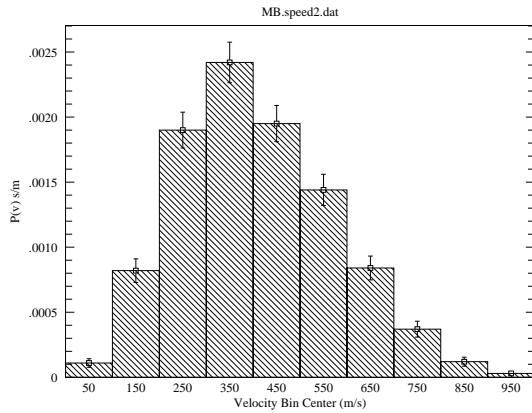
bin center	count N	error \sqrt{N}	$P(v)$ $(\text{m/s})^{-1}$	$\delta P(v)$ $(\text{m/s})^{-1}$
50	11	3.3	0.00011	0.00003
150	82	9.1	0.00082	0.00009
250	190	14.	0.00190	0.00014
350	242	16.	0.00242	0.00016
450	195	14.	0.00195	0.00014
550	144	12.	0.00144	0.00012
650	84	9.2	0.00084	0.00009
750	37	6.1	0.00037	0.00006
850	12	3.5	0.00012	0.00003
950	3	1.7	0.00003	0.00002

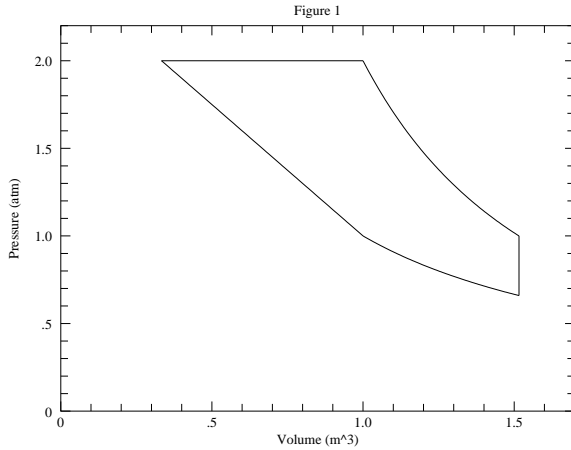
bin center	count N	error \sqrt{N}	$P(v)$ $(\text{m/s})^{-1}$	$\delta P(v)$ $(\text{m/s})^{-1}$
-825	2	1.4	0.00001	0.00001
-675	10	3.2	0.00007	0.00002
-525	32	5.7	0.00021	0.00004
-375	86	9.3	0.00057	0.00006
-225	161	13.	0.00107	0.00008
-75	234	15.	0.00156	0.00010
75	218	15.	0.00145	0.00010
225	168	13.	0.00112	0.00009
375	61	7.8	0.00041	0.00005
525	17	4.1	0.00011	0.00003
675	9	3.0	0.00006	0.00002
825	2	1.4	0.00001	0.00001

MB.speed2.dat: $V(P) = 350$, $V(rms) = 439.2$, $V(mean) = 406.6$
 $V(P)/V(rms) = .797$ vs $.816$, $V(mean)/V(rms) = .926$ vs $.921$

MB.Vx2.dat: $V(P) = -75$, $V(mean) = -16.9$, (both nearly zero)
 $V(rms) = 252.2$, $V(rms) \Rightarrow T = 306$ K,

$$\frac{1}{3} 439.2^2 = 64296.45 \approx 63609.03 = 252.2^2$$





path:	a	b	c	d	e
ΔT	-	+	-	-	0
ΔE_{int}	-	+	-	-	0
Q	-	+	0	-	-
W	-	+	+	0	-

Most signs can be determined simply from the nature of the isothermal hyperbolas: cool is near the origin and hot is large, positive p and V . I've plotted below the isotherms for temperatures of 300 K (starting temperature), 200 K (temperature at the end of step a), and 455 K (temperature at the end of step c). Again, this plot of isotherms was *not* required to answer this question, but a knowledge of the general shape of isotherms makes finding many signs automatic. The sign of ΔT gives many answers: the sign of ΔE_{int} always, and the sign of Q when there is a specific heat (C_V and C_p)— and of course $Q = 0$ for step (c). For isothermal process remember that $Q = W$. The sign of ΔT is not obvious in step (a): use $pV \propto T$ to see that $\Delta T < 0$. The temperature at the end of step (c) is not obvious, but V needs to be calculated to make the sketch (use $pV^\gamma = \text{constant}$), and the pV product shows that the temperature is greater than 300 K. Thus $\Delta T < 0$ for step (d). The sign of W should be clear, as it is the area under the curve. For future reference, note that the sign of Q gives the sign of ΔS .

