2

Heat, Work, Internal Energy, Enthalpy, and the First Law of Thermodynamics

Problem numbers in italics indicate that the solution is included in the *Student Solutions Manual.*

Conceptual Problems

Q2.1 Electrical current is passed through a resistor immersed in a liquid in an adiabatic container. The temperature of the liquid is varied by 1°C. The system consists solely of the liquid. Does heat or work flow across the boundary between the system and surroundings? Justify your answer.

Although work is done on the resistor, this work is done in the surroundings. Heat flows across the boundary between the surroundings and the system because of the temperature difference between them.

Q2.2 Two ideal gas systems undergo reversible expansion under different conditions starting from the same P and V. At the end of the expansion, the two systems have the same volume. The pressure in the system that has undergone adiabatic expansion is lower than in the system that has undergone isothermal expansion. Explain this result without using equations.

In the system undergoing adiabatic expansion, all the work done must come through the lowering of ΔU, and therefore of the temperature. By contrast, some of the work done in the isothermal expansion can come at the expense of the heat that has flowed across the boundary between the system and surroundings.

Q2.3 You have a liquid and its gaseous form in equilibrium in a piston and cylinder assembly in a constant temperature bath. Give an example of a reversible process.

Water drips onto the piston, increasing the conversion of gas to liquid. This process is essentially reversible if the rate of evaporation of the water is nearly equal to the rate of water deposition.

Q2.4 Describe how reversible and irreversible expansions differ by discussing the degree to which equilibrium is maintained between the system and the surroundings.

In a reversible expansion, the system and surroundings are always in equilibrium with one another. In an irreversible expansion, they are not in equilibrium with one another.

Q2.5 For a constant pressure process, $\Delta H = q_p$. Does it follow that q_p is a state function? Explain.

Heat is never a state function, even if the heat transferred in a process has a unique value because a system at equilibrium does not possess heat.

Q2.6 A cup of water at 278 K (the system) is placed in a microwave oven and the oven is turned on for 1 minute during which it begins to boil. State whether each of q, w, and ΔU is positive, negative, or zero?

The heat q is positive because heat flows across the system-surrounding boundary into the system. The work w is negative because the vaporizing water does work on the surroundings. ΔU is positive because the temperature increases and some of the liquid is vaporized.

Q2.7 In the experiment shown in Figure 2.4a and 2.4b, $\Delta U_{\text{surroundings}} < 0$, but $\Delta T_{\text{surroundings}} > 0$. Explain how this is possible.

This is only possible if a process, such as a chemical reaction in this case, occurs to change the composition of the system.

Q2.8 What is wrong with the following statement? *Burns caused by steam at 100°C can be more severe than those caused by water at 100°C because steam contains more heat than water*. Rewrite the sentence to convey the same information in a correct way.

Heat is not a substance that can be stored. When steam is in contact with your skin, it condenses to the liquid phase. In doing so, energy is released that is absorbed by the skin. Hot water does not release as much energy in the same situation, because no phase change occurs.

Q2.9 Why is it incorrect to speak of the heat or work associated with a system?

Heat and work are transients that exist only in the transition between equilibrium states. Therefore, a state at equilibrium is not associated with values of heat or work.

Q2.10 You have a liquid and its gaseous form in equilibrium in a piston and cylinder assembly in a constant temperature bath. Give an example of an irreversible process.

A large mass is placed on the piston, leading to complete conversion of gaseous to liquid water.

Q2.11 What is wrong with the following statement? *Because the well-insulated house stored a lot of heat, the temperature didn't fall much when the furnace failed.* Rewrite the sentence to convey the same information in a correct way.

Heat can't be stored because it exists only as a transient. A possible rephrasing follows. Because the house was well insulated, the walls were nearly adiabatic. Therefore, the temperature of the house did not fall as rapidly when in contact with the surroundings at a lower temperature as would have been the case if the walls were diathermal.

Q2.12 Explain how a mass of water in the surroundings can be used to determine q for a process. Calculate q if the temperature of a 1.00 kg water bath in the surroundings increases by 1.25°C. Assume that the surroundings are at a constant pressure.

If heat flows across the boundary between the system and the surroundings, it will lead to a temperature change in the surroundings given by $\Delta T = \dfrac{q}{C_P}$. For the case of interest,

$$q = -q_{surroundings} = -mC_P\Delta T = -1000\text{ g} \times 4.19\text{ J g}^{-1}\text{ K}^{-1} \times 1.25\text{ K} = -5.24 \times 10^3\text{ J}$$

Q2.13 A chemical reaction occurs in a constant volume enclosure separated from the surroundings by diathermal walls. Can you say whether the temperature of the surroundings increases, decreases, or remains the same in this process? Explain.

No, because any of these possibilities could occur, depending on the potential energy stored in the bonds of the reactants and those of the products.

The temperature will increase if the reaction is exothermic, decrease if the reaction is endothermic, and not change if no energy is evolved in the reaction.

Q2.14 Explain the relationship between the terms *exact differential* and *state function.*

In order for a function $f(x,y)$ to be a state function, it must be possible to write the total differential df in the form $df = \left(\dfrac{\partial f}{\partial x}\right)_y dx + \left(\dfrac{\partial f}{\partial y}\right)_x dy$. If the form df as written exists, it is an exact differential.

Q2.15 In the experiment shown in Figure 2.4b, the weight drops in a very short time. How will the temperature of the water change with time?

Initially, there will not be a unique value of the temperature for the whole system, because diffusion is too slow to ensure equilibrium. At a location far from the filament, the temperature will be observed to rise and asympotically approach its equilibrium value.

Q2.16 Discuss the following statement: If the temperature of the system increased, heat must have been added to it.

The statement is incorrect. The temperature of the system will increase either if work is done on it or heat flows into it. The energy of the system can also increase if $q < 0$ as long as w is positive and its magnitude is greater than that of q.

Q2.17 Discuss the following statement: Heating an object causes its temperature to increase.

The statement is incorrect. It is correct only if $w \geq 0$. If $w < 0$ and larger in magnitude than q, the temperature can fall even though $q > 0$.

Q2.18 An ideal gas is expanded reversibly and adiabatically. Decide which of q, w, ΔU, and ΔH is positive, negative, or zero.

Because the process is adiabatic, $q = 0$. Because the system expands, $w < 0$. Therefore $\Delta U = q + w < 0$. Because $\Delta U < 0, \Delta T < 0$ and $\Delta H = \Delta U + nR\Delta T < 0$.

Q2.19 An ideal gas is expanded reversibly and isothermally. Decide which of q, w, ΔU, and ΔH is positive, negative, or zero.

Because $\Delta T = 0$, $\Delta U = \Delta H = 0$. Because $\Delta V > 0, w < 0$. Because $q = \Delta U - w$, $q > 0$.

Q2.20 An ideal gas is expanded adiabatically into a vacuum. Decide which of q, w, ΔU and ΔH is positive, negative, or zero.

Because the process is adiabatic, $q = 0$. Because $P_{external} = 0$, $w = 0$. Because $\Delta U = q + w$, $\Delta U = 0$. Because $\Delta U = 0$, $\Delta T = 0$. Because $\Delta T = 0$, $\Delta H = \Delta U + nR\Delta T = 0$.

Q2.21 A bowling ball (a) rolls across a table and (b) falls on the floor. Is the work associated with each part of this process positive, negative, or zero?

If the rolling is viewed as friction free, $w = 0$. If not, the motion of the ball is opposed by a frictional force and therefore $w < 0$. In falling, the force and displacement are in the same direction, so $w > 0$.

Q2.22 A perfectly insulating box is partially filled with water in which an electrical resistor is immersed. An external electrical generator converts the change in potential energy of a mass m which falls by a vertical distance h into electrical energy which is dissipated in the resistor. What value do q, w, and ΔU have if the system is defined as the resistor and the water? Everything else is in the surroundings.

Because the resistor is in the system, $w > 0$. Because no energy flows in or out of the system due to a temperature difference, $q = 0$. $\Delta U = w + q > 0$.

Q2.23 A student gets up from her chair and pushes a stack of books across the table. They fall to the floor. Is the work associated with each part of this process positive, negative, or zero?

In each case, the system and the surroundings need to be defined to answer the question. We define the student to be the system in the first two actions. As the student gets up, she is opposing the gravitational force and $w > 0$ because work is done on her. In pushing the books across the floor, the student does work against a frictional force and $w < 0$. In the third action, we consider the books to be the system. As the books fall to the floor, the force and displacement are in the same direction and $w > 0$.

Q2.24 Explain why ethene has a higher value for $C_{V,m}$ at 800. K than CO.

Ethene has more vibrational modes that are at least partially excited at 800. K than CO, which has only one vibrational mode. Therefore, ethene has a higher value for $C_{V,m}$ at 800. K than CO.

Q2.25 Explain why $C_{P,m}$ is a function of temperature for ethane, but not for argon in a temperature range in which electronic excitations do not occur.

The translational modes for both Ar and ethane are fully excited at very low temperature. Ar has no internal modes that can take up energy, whereas ethane has both rotational and vibrational modes. The vibrational modes are only fully excited at higher temperatures, so $C_{P,m}$ is a function of temperature for ethane.

Q2.26 What is the difference between a quasi-static process and a reversible process?

In a quasi-static process, the system is always in internal equilibrium. In a reversible process, the system is additionally in equilibrium with the surroundings.

Numerical Problems

P2.1 A 3.75 mole sample of an ideal gas with $C_{V,m} = 3/2\ R$ initially at a temperature $T_i = 298$ K and $P_i = 1.00$ bar is enclosed in an adiabatic piston and cylinder assembly. The gas is compressed by placing a 725 kg mass on the piston of diameter 25.4 cm. Calculate the work done in this process and the distance that the piston travels. Assume that the mass of the piston is negligible.

We first calculate the external pressure and the initial volume.

$$P_{external} = P_{atm} + \frac{F}{A} = 10^5\ \text{Pa} + \frac{mg}{\pi r^2} = 10^5\ \text{Pa} + \frac{725\ \text{kg} \times 9.81\ \text{m s}^{-2}}{\pi \times (\frac{1}{2} \times 0.254\ \text{m})^2} = 2.40 \times 10^5\ \text{Pa}$$

$$V_i = \frac{nRT}{P_i} = \frac{3.75\ \text{mol} \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 298\ \text{K}}{10^5\ \text{Pa}} = 0.0929\ \text{m}^3 = 92.9\ \text{L}$$

Following Example Problem 2.6,

$$T_f = T_i\left(\frac{C_{V,m} + \dfrac{RP_{external}}{P_i}}{C_{V,m} + \dfrac{RP_{external}}{P_f}}\right) = 298\ \text{K} \times \left(\frac{12.47\ \text{J mol}^{-1}\text{K}^{-1} + \dfrac{8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 2.40 \times 10^5\ \text{Pa}}{1.00 \times 10^5\ \text{Pa}}}{12.47\ \text{J mol}^{-1}\text{K}^{-1} + \dfrac{8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 2.40 \times 10^5\ \text{Pa}}{2.40 \times 10^5\ \text{Pa}}}\right) = 465\ \text{K}$$

$$V_f = \frac{nRT}{P_f} = \frac{3.75\ \text{mol} \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 465\ \text{K}}{2.40 \times 10^5\ \text{Pa}} = 6.04 \times 10^{-2}\ \text{m}^3$$

$$w = -P_{external}(V_f - V_i) = -2.40 \times 10^5\ \text{Pa} \times (6.04 \times 10^{-2}\ \text{m}^3 - 9.29 \times 10^{-2}\ \text{m}^3) = 7.82 \times 10^3\ \text{J}$$

$$h = -\frac{V_f - V_i}{\pi r^2} = \frac{3.26 \times 10^{-2}\ \text{m}^3}{5.07 \times 10^{-2}\ \text{m}^2} = 0.642\ \text{m}$$

P2.2 The temperature of 1.75 moles of an ideal gas increases from 10.2°C to 48.6°C as the gas is compressed adiabatically. Calculate q, w, ΔU, and ΔH for this process assuming that $C_{V,m} = 3/2\ R$.

$q = 0$ because the process is adiabatic.

$$w = \Delta U = nC_{V,m}\Delta T = 1.75\ \text{mol} \times \frac{3 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1}}{2} \times (48.6°\text{C} - 10.2°\text{C}) = 838\ \text{J}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta T = 8.38 \times 10^2\ \text{J} + 1.75\ \text{mol} \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times (48.6°\text{C} - 10.2°\text{C})$$

$$\Delta H = 1.40 \times 10^3\ \text{J}$$

P2.3 A 2.50 mole sample of an ideal gas, for which $C_{V,m} = 3/2\ R$, is subjected to two successive changes in state: (1) From 25.0°C and $125. \times 10^3$ Pa, the gas is expanded isothermally against a constant pressure of 15.2×10^3 Pa to twice the initial volume. (2) At the end of the previous process, the gas is cooled at constant volume from 25.0°C to –29.0°C. Calculate q, w, ΔU, and ΔH for each of the stages. Also calculate q, w, ΔU, and ΔH for the complete process.

a. $$V_i = \frac{nRT}{P_i} = \frac{2.50\ \text{mol} \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 298\ \text{K}}{125 \times 10^3\ \text{Pa}} = 4.96 \times 10^{-2}\ \text{m}^3$$

$$V_f = 2V_i = 9.92 \times 10^{-2}\ \text{m}^3$$

$$w = -P_{ext}(V_f - V_i) = -15.2 \times 10^3\ \text{Pa} \times (9.92 \times 10^{-2}\text{m}^3 - 4.96 \times 10^{-2}\text{m}^3) = -754\ \text{J}$$

ΔU and $\Delta H = 0$ because $\Delta T = 0$

$q = -w = 754$ J

b. $\Delta U = nC_{V,m}(T_f - T_i) = 2.50\text{ mol} \times 1.5 \times 8.314\text{ J mol}^{-1}\text{K}^{-1} \times (244\text{ K} - 298\text{ K}) = -1.68 \times 10^3\text{ J}$

$w = 0$ because $\Delta V = 0$

$q = \Delta U = -1.68 \times 10^3\text{ J}$

$$\begin{aligned}\Delta H &= nC_{P,m}(T_f - T_i) = n(C_{V,m} + R)(T_f - T_i)\\ &= 2.50\text{ mol} \times 2.5 \times 8.314\text{ J mol}^{-1}\text{K}^{-1} \times (244\text{ K} - 298\text{ K})\\ &= -2.81 \times 10^3\text{ J}\end{aligned}$$

$\Delta U_{total} = 0 - 1.684 \times 10^3\text{ J} = -1.68 \times 10^3\text{ J}$

$w_{total} = 0 - 754\text{ J} = -754\text{ J}$

$q_{total} = 754\text{ J} - 1.684 \times 10^3\text{ J} = -930.\text{ J}$

$\Delta H_{total} = 0 - 2.81 \times 10^3\text{ J} = -2.81 \times 10^3\text{ J}$

P2.4 A hiker caught in a thunderstorm loses heat when her clothing becomes wet. She is packing emergency rations which if completely metabolized will release 35 kJ of heat per gram of rations consumed. How much rations must the hiker consume to avoid a reduction in body temperature of 2.5 K as a result of heat loss? Assume the heat capacity of the body equals that of water and that the hiker weighs 51 kg. State any additional assumptions.

$$q = \frac{m_{hiker}C_P\Delta T}{M_{H_2O}} = \frac{51 \times 10^3\text{ g} \times 75.3\text{ J K}^{-1}\text{ mol}^{-1} \times 2.5\text{ K}}{18.02\text{ g mol}^{-1}} = 533\text{ kJ}$$

$$m_{rations} = \frac{q}{q_{rations}} = \frac{533\text{ kJ}}{35\text{ kJ g}^{-1}} = 15\text{ g}$$

P2.5 Count Rumford observed that using cannon boring machinery a single horse could heat 11.6 kg of ice water $(T = 273\text{ K})$ to $T = 355\text{ K}$ in 2.5 hours. Assuming the same rate of work, how high could a horse raise a 225 kg weight in 2.5 minutes? Assume the heat capacity of water is $4.18\text{ J K}^{-1}\text{ g}^{-1}$.

$$Rate = \frac{C_P m_{water}\Delta T}{time_1} = \frac{4.18\text{ J K}^{-1}\text{ g}^{-1} \times 11.6 \times 10^3\text{ g} \times (355 - 273)\text{ K}}{2.5\text{ hr} \times 3600\text{ s hr}^{-1}} = 442\text{ J s}^{-1}$$

$$h = \frac{Rate \times time_2}{m_{weight}g} = \frac{442\text{ J s}^{-1} \times 150\text{ s}}{225\text{ kg} \times 9.81\text{ m s}^{-2}} = 30.\text{ m}$$

P2.6 A 1.50 mole sample of an ideal gas at 28.5°C expands isothermally from an initial volume of 22.5 dm^3 to a final volume of 75.5 dm^3. Calculate w for this process (a) for expansion against a constant external pressure of 0.498×10^5 Pa and (b) for a reversible expansion.

a. $w = -P_{external}\Delta V = -0.498 \times 10^5\text{ Pa} \times (75.5 - 22.5) \times 10^{-3}\text{ m}^3 = -2.64 \times 10^3\text{ J}$

b. $$w_{reversible} = -nRT\ \ln\frac{V_f}{V_i} = -1.50\text{ mol} \times 8.314\text{ J mol}^{-1}\text{K}^{-1} \times (273.15 + 28.5)\text{ K} \times \ln\frac{75.5\text{ dm}^3}{22.5\text{ dm}^3}$$

$$= -4.55 \times 10^3\text{ J}$$

P2.7 Calculate q, w, ΔU, and ΔH if 2.25 mol of an ideal gas with $C_{v,m} = 3/2\,R$ undergoes a reversible adiabatic expansion from an initial volume $V_i = 5.50\text{ m}^3$ to a final volume $V_f = 25.0\text{ m}^3$. The initial temperature is 275 K.

$q = 0$ because the process is adiabatic.

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma}$$

$$T_f = \left(\frac{25.0\ \text{m}^3}{5.50\ \text{m}^3}\right)^{1-\frac{5}{3}} \times T_i = 100.\ \text{K}$$

$$\Delta U = w = nC_{V,n}\Delta T = 2.25\ \text{mol} \times \frac{3 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1}}{2} \times (100.\ \text{K} - 300\ \text{K}) = -4.90 \times 10^3\ \text{J}$$

$$\Delta H = \Delta U + nR\Delta T = -4.904 \times 10^3\ \text{J} + 2.25\ \text{mol} \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times (100.\ \text{K} - 300\ \text{K})$$

$$\Delta H = -8.17 \times 10^3\ \text{J}$$

P2.8 Calculate w for the adiabatic expansion of 2.50 mol of an ideal gas at an initial pressure of 2.25 bar from an initial temperature of 450. K to a final temperature of 300. K. Write an expression for the work done in the isothermal reversible expansion of the gas at 300. K from an initial pressure of 2.25 bar. What value of the final pressure would give the same value of w as the first part of this problem? Assume that $C_{P,m} = 5/2R$.

$$w_{ad} = \Delta U = n(C_{P,m} - R)\,\Delta T = -2.50\ \text{mol} \times \frac{3}{2} \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times (450. - 300.)\ \text{K} = -4.68 \times 10^3\ \text{J}$$

$$w_{reversible} = -nRT\ln\frac{P_i}{P_f}; \qquad \ln\frac{P_i}{P_f} = \frac{-w_{reversible}}{nRT}$$

$$\ln\frac{P_i}{P_f} = -\frac{w_{reversible}}{nRT} = -\frac{-4.68 \times 10^3\ \text{J}}{2.50\ \text{mol} \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 300.\ \text{K}} = -0.750$$

$$P_f/P_i = 0.472 \qquad P_f = 1.06\ \text{bar}$$

P2.9 At 298 K and 1 bar pressure, the density of water is $0.9970\ \text{g cm}^{-3}$, and $C_{P,m} = 75.3\ \text{J K}^{-1}\ \text{mol}^{-1}$. The change in volume with temperature is given by $\Delta V = V_i\beta\Delta T$, where β, the coefficient of thermal expansion, is $2.07 \times 10^{-4}\ \text{K}^{-1}$. If the temperature of 325 g of water is increased by 25.5 K, calculate w, q, ΔH, and ΔU.

$$V_i = \frac{m}{\rho} = \frac{0.325\ \text{kg}}{997\ \text{kg m}^{-3}} = 3.26 \times 10^{-4}\ \text{m}^3$$

$$\Delta V = V_i\beta\Delta T = 3.26 \times 10^{-4}\ \text{m}^3 \times 2.07 \times 10^{-4}\ \text{K}^{-1} \times 25.5\ \text{K} = 1.72 \times 10^{-6}\ \text{m}^3$$

$$w = -P_{ext}\Delta V = -10^5\ \text{Pa} \times 1.72 \times 10^{-6}\ \text{m}^3 = -0.172\ \text{J}$$

$$\Delta H = q = nC_{P,m}\Delta T = \frac{325\ \text{g}}{18.02\ \text{g mol}^{-1}} \times 75.3\ \text{J K}^{-1}\ \text{mol}^{-1} \times 25.5\ \text{K} = 34.6 \times 10^3\ \text{J}$$

$$\Delta U = q + w = 34.6 \times 10^3\ \text{J}$$

P2.10 A muscle fiber contracts by 3.5 cm and in doing so lifts a weight. Calculate the work performed by the fiber. Assume the muscle fiber obeys Hooke's law $F = -k\,x$ with a force constant, k, of $750.\ \text{N m}^{-1}$.

$$w = \frac{1}{2}kx^2 = \frac{1}{2} \times 750.\ \text{N m}^{-1} \times (3.5 \times 10^{-2}\ \text{m})^2 = 0.46\ \text{J}$$

This is the work done on the weight by the fiber. It is positive because the weight is higher than its initial position and has therefore gained energy. The work done on the fiber by the weight has the opposite sign.

P2.11 A cylindrical vessel with rigid adiabatic walls is separated into two parts by a frictionless adiabatic piston. Each part contains 45.0 L of an ideal monatomic gas with $C_{V,m} = 3/2R$. Initially, $T_i = 300$ K and $P_i = 1.75 \times 10^5$ Pa in each part. Heat is slowly introduced into the left part using an electrical heater until the piston has moved sufficiently to the right to result in a final pressure $P_f = 4.00$ bar in the right part. Consider the compression of the gas in the right part to be a reversible process.

a. Calculate the work done on the right part in this process and the final temperature in the right part.

b. Calculate the final temperature in the left part and the amount of heat that flowed into this part.

The number of moles of gas in each part is given by

$$n = \frac{P_i V_i}{RT_i} = \frac{1.75\times10^5\ \text{Pa}\times 45.0\times10^{-3}\ \text{m}^3}{8.314\ \text{Pa m}^3\ \text{mol}^{-1}\text{K}^{-1}\times 300.\ \text{K}} = 3.16\ \text{mol}$$

(a) We first calculate the final temperature in the right side.

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma} = \left(\frac{T_f}{T_i}\right)^{1-\gamma}\left(\frac{P_i}{P_f}\right)^{1-\gamma};= \left(\frac{T_f}{T_i}\right)^{\gamma} = \left(\frac{P_i}{P_f}\right)^{1-\gamma};\ \frac{T_f}{T_i} = \left(\frac{P_i}{P_f}\right)^{\frac{1-\gamma}{\gamma}}$$

$$T_f = \left(\frac{1.74\times10^5\ \text{Pa}}{4.00\times10^5\ \text{Pa}}\right)^{\frac{1-\frac{5}{3}}{\frac{5}{3}}}\times 325\ \text{K} = 418\ \text{K}$$

$$\Delta U = w = nC_{V,m}\Delta T = 3.16\ \text{mol}\times\frac{3\times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}}{2}\times(418\ \text{K} - 300.\ \text{K}) = 4.63\times10^3\ \text{J}$$

(b) We first calculate the final volume of the right part.

$$V_{rf} = \frac{nRT_{rf}}{P_{rf}} = \frac{3.16\ \text{mol}\times 8.314\times10^{-2}\ \text{L bar mol}^{-1}\ \text{K}^{-1}\times 418\ \text{K}}{4.00\ \text{bar}} = 27.4\ \text{L}$$

Therefore, $V_{lf} = 90.0\ \text{L} - 27.4\ \text{L} = 62.6\ \text{L}$.

$$T_{lf} = \frac{P_{lf}V_{lf}}{nR} = \frac{4.00\ \text{bar}\times 62.6\ \text{L}}{3.16\ \text{mol}\times 8.314\times10^{-2}\ \text{L bar mol}^{-1}\text{K}^{-1}} = 954\ \text{K}$$

$$\Delta U = nC_{V,m}\Delta T = 3.16\ \text{mol}\times 3/2\times 8.314\ \text{J mol}^{-1}\text{K}^{-1}\times(954\ \text{K} - 300.\ \text{K}) = 25.7\times10^3\ \text{J}$$

From part (a), $w = 4.63\times10^3$ J.

$$q = \Delta U - w = 25.7\times10^3\ \text{J} + 4.63\times10^3\ \text{J} = 30.4\times10^3\ \text{J}$$

P2.12 In the reversible adiabatic expansion of 1.75 mol of an ideal gas from an initial temperature of 27.0°C, the work done on the surroundings is 1300. J. If $C_{V,m} = 3/2R$, calculate q, w, ΔU, and ΔH.

$$\begin{aligned}
q &= 0 \text{ because the process is adiabatic}\\
\Delta U &= w = -1300.\ \text{J}\\
\Delta U &= nC_{V,m}(T_f - T_i)\\
T_f &= \frac{\Delta U + nC_{V,m}T_i}{nC_{V,m}}\\
&= \frac{-1300.\ \text{J} + 1.75\ \text{mol}\times 1.5\times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\times 300.\ \text{K}}{1.75\ \text{mol}\times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}}\\
&= 241\ \text{K}
\end{aligned}$$

$$\begin{aligned}
\Delta H &= nC_{P,m}(T_f - T_i) = n(C_{V,m} + R)(T_f - T_i)\\
&= 1.75\ \text{mol}\times 2.5\times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}(241\ \text{K} - 300\ \text{K})\\
&= -2.17\times10^3\ \text{J}
\end{aligned}$$

P2.13 A system consisting of 82.5 g of liquid water at 300. K is heated using an immersion heater at a constant pressure of 1.00 bar. If a current of 1.75 A passes through the 25.0 ohm resistor for 100. s, what is the final temperature of the water?

$$q = I^2Rt = nC_{P,m}(T_f - T_i); \qquad T_f = \frac{I^2Rt + nC_{P,m}T_i}{nC_{P,m}}$$

$$T_f = \frac{(1.75\text{ A})^2 \times 25.0\text{ Ohm} \times 100.\text{ s} + \dfrac{82.5\text{ g}}{18.02\text{ g mol}^{-1}} \times 75.3\text{ J mol}^{-1}\text{ K}^{-1} \times 300.\text{ K}}{\dfrac{82.5\text{ g}}{18.02\text{ g mol}^{-1}} \times 75.3\text{ J mol}^{-1}\text{ K}^{-1}} = 322\text{ K}$$

P2.14 A 1.25 mole sample of an ideal gas is expanded from 320. K and an initial pressure of 3.10 bar to a final pressure of 1.00 bar, and $C_{P,m} = 5/2R$. Calculate w for the following two cases:

a. The expansion is isothermal and reversible.

b. The expansion is adiabatic and reversible.

Without resorting to equations, explain why the result to part (b) is greater than or less than the result to part (a).

(a) $$w = -nRT\ln\frac{V_f}{V_i} = -nRT\ln\frac{P_i}{P_f}$$

$$= -1.25\text{ mol} \times 8.314\text{ J mol}^{-1}\text{ K}^{-1} \times 320.\text{ K} \times \ln\frac{3.10\text{ bar}}{1.00\text{ bar}} = -3.76 \times 10^3\text{ J}$$

(b) Because $q = 0$, $w = \Delta U$. In order to calculate ΔU, we first calculate T_f.

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma} = \left(\frac{T_f}{T_i}\right)^{1-\gamma}\left(\frac{P_i}{P_f}\right)^{1-\gamma}; \quad \left(\frac{T_f}{T_i}\right)^{\gamma} = \left(\frac{P_i}{P_f}\right)^{1-\gamma}; \quad \frac{T_f}{T_i} = \left(\frac{P_i}{P_f}\right)^{\frac{1-\gamma}{\gamma}}$$

$$T_f = T_i \times \left(\frac{3.10\text{ bar}}{1.00\text{ bar}}\right)^{\frac{1-\frac{5}{3}}{\frac{5}{3}}} = 204\text{ K}$$

$$w = \Delta U = nC_{V,m}\Delta T = 1.25\text{ mol} \times \frac{3 \times 8.314\text{ J mol}^{-1}\text{ K}^{-1}}{2} \times (204\text{ K} - 320.\text{ K}) = -1.82 \times 10^3\text{ J}$$

Less work is done on the surroundings in part (b) because in the adiabatic expansion, the temperature falls and therefore the final volume is less than that in part (a).

P2.15 A bottle at 325 K contains an ideal gas at a pressure of 162.5×10^3 Pa. The rubber stopper closing the bottle is removed. The gas expands adiabatically against $P_{external} = 120.0 \times 10^3$ Pa, and some gas is expelled from the bottle in the process. When $P = P_{external}$, the stopper is quickly replaced. The gas remaining in the bottle slowly warms up to 325 K. What is the final pressure in the bottle for a monatomic gas, for which $C_{V,m} = 3/2R$, and a diatomic gas, for which $C_{V,m} = 5/2R$?

In this adiabatic expansion, $\Delta U = w$.

$$nC_{V,m}(T_f - T_i) = -P_{ext}(V_f - V_i)$$

$$nC_{V,m}(T_1 - T_i) = -P_{ext}\left(\frac{nRT_1}{V_f} - \frac{nRT_i}{V_i}\right)$$

$$\left(C_{V,m} + \frac{RP_{ext}}{P_f}\right)T_1 = \left(C_{V,m} + \frac{RP_{ext}}{P_i}\right)T_i$$

$$\frac{T_1}{T_i} = \frac{C_{V,m} + \dfrac{RP_{ext}}{P_i}}{C_{V,m} + \dfrac{RP_{ext}}{P_f}}$$

$$T_1 = \frac{1.5 \times 8.314 \text{ J mol}^{-1}\text{ K}^{-1} + \dfrac{8.314 \text{ J mol}^{-1}\text{ K}^{-1} \times 120.0 \times 10^3 \text{ Pa}}{162.5 \times 10^3 \text{ Pa}}}{1.5 \times 8.314 \text{ J mol}^{-1}\text{ K}^{-1} + 8.314 \text{ J mol}^{-1}\text{ K}^{-1}} \times 325 \text{ K} = 291 \text{ K}$$

Once the stopper is put in place, the gas makes a transformation from

$$T_i = 291 \text{ K}, P_i = 120.0 \times 10^3 \text{ Pa to } T_f = 325 \text{ K and } P_f$$

$$\frac{P_iV_i}{T_i} = \frac{P_fV_f}{T_f}, \text{ but } V_i = V_f$$

$$P_f = \frac{T_f}{T_i}P_i = \frac{325 \text{ K}}{291 \text{ K}} \times 120.0 \times 10^3 \text{ Pa} = 134.0 \times 10^3 \text{ Pa}$$

The same calculation carried out for $C_{V,m} = \frac{5}{2}R$ gives

$$T_f = 301 \text{ K}$$

$$P_f = 129.7 \times 10^3 \text{ Pa}$$

P2.16 A 2.25 mole sample of an ideal gas with $C_{V,m} = 3/2R$ initially at 310. K and 1.25×10^5 Pa undergoes a reversible adiabatic compression. At the end of the process, the pressure is 3.10×10^6 Pa. Calculate the final temperature of the gas. Calculate q, w, ΔU, and ΔH for this process.

$q = 0$ because the process is adiabatic.

$$T_f = T_i\left(\frac{P_i}{P_f}\right)^{\frac{1-C_P/C_V}{C_P/C_V}} = 325 \text{ K} \times \left(\frac{1.25 \times 10^5 \text{ Pa}}{3.10 \times 10^5 \text{ Pa}}\right)^{\frac{1-5/3}{5/3}} = 1.12 \times 10^3 \text{ K}$$

$$w = \Delta U = nC_{V,m}\Delta T = 2.25 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (1120 \text{ K} - 310. \text{ K}) = 22.7 \times 10^3 \text{ J}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta T$$

$$= 22.78 \times 10^3 \text{ J} + 2.25 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (1120 \text{ K} - 310. \text{ K})$$

$$\Delta H = 37.9 \times 10^3 \text{ J}$$

P2.17 A vessel containing 1.50 mol of an ideal gas with $P_i = 1.00$ bar and $C_{P,m} = 5/2R$ is in thermal contact with a water bath. Treat the vessel, gas, and water bath as being in thermal equilibrium, initially at 298 K, and as separated by adiabatic walls from the rest of the universe. The vessel, gas, and water bath have an average heat capacity of $C_P = 2450.$ J K^{-1}. The gas is compressed reversibly to $P_f = 20.5$ bar. What is the temperature of the system after thermal equilibrium has been established?

Assume initially that the temperature rise is so small that the reversible compression can be thought of as an isothermal reversible process. If the answer substantiates this assumption, it is valid.

$$w = -nRT_1 \ln\frac{V_f}{V_i} = -nRT_1 \ln\frac{P_i}{P_f}$$

$$= -1.50 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 312 \text{ K} \times \ln\frac{1.00 \text{ bar}}{20.5 \text{ bar}} = 11.2 \times 10^3 \text{ J}$$

$$\Delta U_{combined\ system} = C_P \Delta T$$

$$\Delta T = \frac{\Delta U_{combined\ system}}{C_P} = \frac{11.2\times 10^3\ \text{J}}{2450\ \text{J K}^{-1}} = 3.05\ \text{K}$$

$$T_f = 301\ \text{K}$$

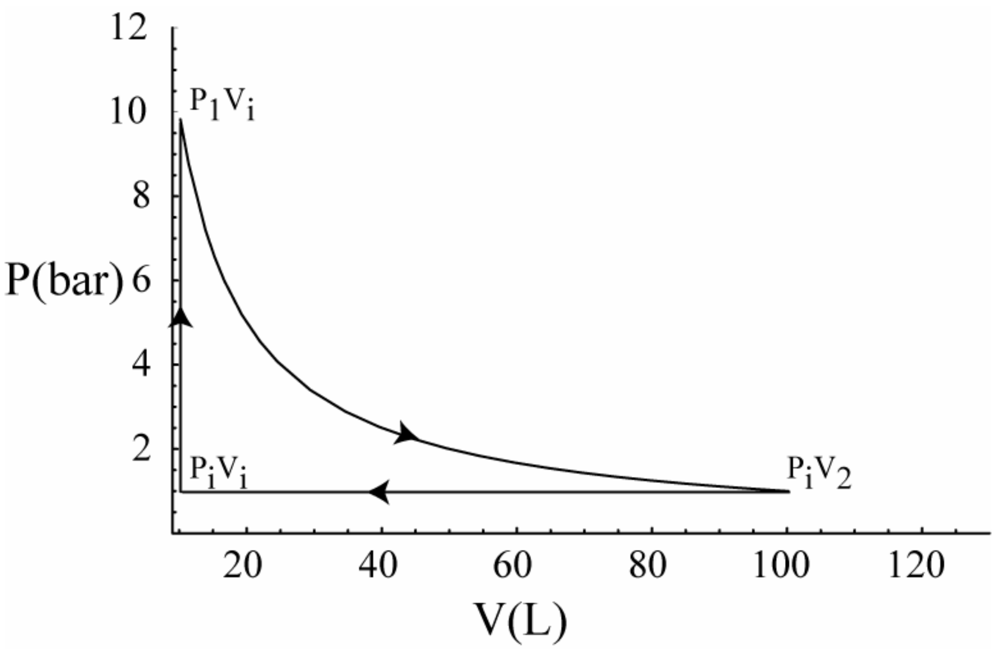
The result justifies the assumption.

P2.18 An ideal gas undergoes an expansion from the initial state described by P_i, V_i, T to a final state described by P_f, V_f, T in (a) a process at the constant external pressure P_f and (b) in a reversible process. Derive expressions for the largest mass that can be lifted through a height *h* in the surroundings in these processes.

a. $w = mgh = -P_f(V_f - V_i);\quad m = \left|-\frac{P_f(V_f - V_i)}{gh}\right|$

b. $w = mgh = -nRT\ln\frac{V_f}{V_i};\quad m = \left|-\frac{nRT}{gh}\ln\frac{V_f}{V_i}\right|$

P2.19 An ideal gas described by $T_i = 275\ \text{K}, P_i = 1.10$ bar, and $V_i = 10.0\ \text{L}$ is heated at constant volume until $P = 10.0$ bar. It then undergoes a reversible isothermal expansion until $P = 1.10$ bar. It is then restored to its original state by the extraction of heat at constant pressure. Depict this closed-cycle process in a *P*–*V* diagram. Calculate *w* for each step and for the total process. What values for *w* would you calculate if the cycle were traversed in the opposite direction?



$$n = \frac{P_iV_i}{RT_i} = \frac{1.10\ \text{bar}\times 10.0\ \text{L}}{8.3145\times 10^{-2}\ \text{L bar mol}^{-1}\ \text{K}^{-1}\times 275\ \text{K}} = 0.481\ \text{mol}$$

The process can be described by

step 1: $P_i, V_i, T_i \rightarrow P_1 = 10.0\ \text{bar}, V_\text{i}, T_1$

step 2: $P_1, V_i, T_1 \rightarrow P_i, V_2, T_1$

step 3: $P_i, V_2, T_1 \rightarrow P_i, V_i, T_i$.

In step 1, $P_i,V_i,T_i \rightarrow P_1,V_i,T_1, w = 0$ because V is constant.

In step 2, $P_1,V_i,T_1 \rightarrow P_i,V_2,T_1$.

Before calculating the work in step 2, we first calculate T_1.

$$T_1 = T_i\frac{P_1}{P_i} = 275\text{ K} \times \frac{10.0\text{ bar}}{1.10\text{ bar}} = 2500\text{ K}$$

$$w = -nRT_1\ln\frac{V_f}{V_i} = -nRT_1\ln\frac{P_i}{P_f}$$

$$= -0.481\text{ mol} \times 8.314\text{ J mol}^{-1}\text{ K}^{-1} \times 2500\text{ K} \times \ln\frac{10.0\text{ bar}}{1.10\text{ bar}} = -22.0 \times 10^3\text{ J}$$

In step 3,

$$P_1V_i = P_iV_2;\quad V_2 = \frac{P_1V_i}{P_i} = \frac{9.80\text{ bar}}{1.10\text{ bar}}V_i = 90.9\text{ L}$$

$$w = -P_{external}\Delta V = -1.10\text{ bar} \times \frac{10^5\text{ Pa}}{\text{bar}} \times (10.00\text{ L} - 90.9\text{ L}) \times \frac{10^{-3}\text{ m}^3}{\text{L}} = 8.90 \times 10^3\text{ J}$$

$$w_{cycle} = 0 - 22.0 \times 10^3\text{ J} + 8.90 \times 10^3\text{ J} = -13.1 \times 10^3\text{ J}$$

If the cycle were traversed in the opposite direction, the magnitude of each work term would be unchanged, but all signs would change.

P2.20 In an adiabatic compression of one mol of an ideal gas with $C_{V,m} = 5/2$ R, the temperature rises from 278 K to 450. K. Calculate q, w, ΔH, and ΔU.

$q = 0$ because the process is adiabatic.

$$\Delta U = nC_{V,m}\Delta T$$

$$= 1\text{ mol} \times 2.5 \times 8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 172\text{ K}$$

$$\Delta U = w = 3.58 \times 10^3\text{ J}$$

$$\Delta H = n(C_{V,m} + R)\Delta T = 5.00 \times 10^3\text{ J}$$

P2.21 The heat capacity of solid lead oxide is given by

$$C_{P,m} = 44.35 + 1.47 \times 10^{-3}\frac{T}{\text{K}}\text{ in units of J K}^{-1}\text{ mol}^{-1}$$

Calculate the change in enthalpy of 1.75 mol of PbO(s) if it is cooled from 825 to 375 K at constant pressure.

$$\Delta H = n\int_{T_i}^{T_f} C_{p,m}dT$$

$$= 1.75\text{ mol} \times \int_{825}^{375}\left(44.35 + 1.47 \times 10^{-3}\frac{T}{\text{K}}\right)d\left(\frac{T}{\text{K}}\right)$$

$$= 1.75\text{ mol} \times \left(\begin{array}{l} 44.35 \times (375\text{ K} - 825\text{ K}) \\ \quad + \left[\dfrac{1.47 \times 10^{-3}}{2}\left(\dfrac{T}{\text{K}}\right)^2\right]_{825\text{ K}}^{375\text{ K}} \end{array}\right)$$

$$= -34.9 \times 10^3\text{ J} - 695\text{ J}$$

$$= -35.6 \times 10^3\text{ J}$$

P2.22 A 2.25 mole sample of carbon dioxide, for which $C_{P,m} = 37.1\text{ J K}^{-1}\text{ mol}^{-1}$ at 298 K, is expanded reversibly and adiabatically from a volume of 4.50 L and a temperature of 298 K to a final volume of 32.5 L. Calculate the final temperature, q, w, ΔH, and ΔU. Assume that $C_{P,m}$ is constant over the temperature interval.

$q = 0$ because the process is adiabatic.

$$T_f = T_i\left(\frac{V_f}{V_i}\right)^{1-C_P/C_V} = 300\text{ K}\times\left(\frac{32.5\text{ L}}{4.50\text{ L}}\right)^{1-[37.1/(37.1-8.314)]} = 168\text{ K}$$

$$\Delta U = C_V(T_f - T_i) = (37.1 - 8.314)\text{J K}^{-1}\text{ mol}^{-1}\times(168\text{ K} - 298\text{ K})$$

$$\Delta U = w = -8.40\times10^3\text{ J mol}^{-1}$$

$$\Delta H = (C_V + R)(T_f - T_i) = -10.8\times10^3\text{ J mol}^{-1}$$

P2.23 A 1.75 mole sample of an ideal gas for which $P = 2.50\text{ bar}$ and $T = 335\text{ K}$ is expanded adiabatically against an external pressure of 0.225 bar until the final pressure is 0.225 bar. Calculate the final temperature, q, w, ΔH, and ΔU for (a) $C_{V,m} = 3/2\text{ R}$ and (b) $C_{V,m} = 5/2\text{ R}$.

a. for $C_{V,m} = 3/2\text{ R}$

$$nC_{V,m}(T_f - T_i) = -nRP_{external}\left(\frac{T_f}{P_f} - \frac{T_i}{P_i}\right)$$

$$T_f\left(nC_{V,m} + \frac{nRP_{external}}{P_f}\right) = T_i\left(nC_{V,m} + \frac{nRP_{external}}{P_i}\right)$$

$$T_f = T_i\left(\frac{C_{V,m} + \dfrac{RP_{external}}{P_i}}{C_{V,m} + \dfrac{RP_{external}}{P_f}}\right) = 335\text{ K}\times\left(\frac{1.5\times8.314\text{ J mol}^{-1}\text{K}^{-1} + \dfrac{8.314\text{ J mol}^{-1}\text{K}^{-1}\times0.225\text{ bar}}{2.50\text{ bar}}}{1.5\times8.314\text{ J mol}^{-1}\text{K}^{-1} + \dfrac{8.314\text{ J mol}^{-1}\text{K}^{-1}\times2.50\text{ bar}}{2.50\text{ bar}}}\right)$$

$$T_f = 213\text{ K}$$

$$\Delta U = w = C_V\Delta T = 1.75\text{ mol}\times8.314\text{ J K}^{-1}\text{ mol}^{-1}(213 - 335)\text{K} = -2.66\times10^3\text{ J}$$

$$\Delta H = (C_V + R)\Delta T = -4.44\times10^3\text{ J}$$

b. for $C_{V,m} = 5/2\text{ R}$

$$T_f = T_i\left(\frac{C_{V,m} + \dfrac{RP_{external}}{P_i}}{C_{V,m} + \dfrac{RP_{external}}{P_f}}\right) = 300.\text{ K}\times\left(\frac{2.5\times8.314\text{ J mol}^{-1}\text{K}^{-1} + \dfrac{8.314\text{ J mol}^{-1}\text{K}^{-1}\times0.225\text{ bar}}{2.50\text{ bar}}}{2.5\times8.314\text{ J mol}^{-1}\text{K}^{-1} + \dfrac{8.314\text{ J mol}^{-1}\text{K}^{-1}\times2.50\text{ bar}}{2.50\text{ bar}}}\right)$$

$$T_f = 248\text{ K}$$

$$\Delta U = w = C_V\Delta T = 2.5\times8.314\text{ J K}^{-1}\text{ mol}^{-1}(248 - 335)\text{ K}$$

$$= -3.17\times10^3\text{ J}$$

$$\Delta H = (C_V + R)\Delta T = -4.44\times10^3\text{ J}$$

P2.24 A 3.50 mole sample of N_2 in a state defined by $T_i = 250.\text{ K}$ and $V_i = 3.25\text{ L}$ undergoes an isothermal reversible expansion until $V_f = 35.5\text{ L}$. Calculate w assuming (a) that the gas is described by the ideal gas law and (b) that the gas is described by the van der Waals equation of state. What is the percent error in using the ideal gas law instead of the van der Waals equation? The van der Waals parameters for N_2 are listed in Table 7.4.

a. for the ideal gas

$$w_{reversible} = -nRT\ln\frac{V_f}{V_i} = -3.50\text{ mol}\times 8.314\text{ J mol}^{-1}\text{K}^{-1}\times 250.\text{ K}\times\ln\frac{35.5\text{ L}}{3.25\text{ L}}$$
$$= -17.393\times 10^{3}\text{ J}$$

for the van der Waals gas

$$w = -\int_{V_i}^{V_f} P_{external}\,dV = -\int_{V_i}^{V_f}\left(\frac{nRT}{V-nb}-\frac{n^2a}{V^2}\right)dV$$
$$= -\int_{V_i}^{V_f}\left(\frac{RT}{V_m-b}\right)dV + \int_{V_i}^{V_f}\left(\frac{a}{V_m^2}\right)dV$$

The first integral is solved by making the substitution $y = V - nb$.

$$-\int_{V_i}^{V_f}\left(\frac{nRT}{V-nb}\right)dV = -n\int_{y_i}^{y_f}\left(\frac{RT}{y}\right)dy = -nRT\left[\ln(V_f-nb)-\ln(V_i-nb)\right]$$

Therefore, the work is given by

$$w = -nRT\ln\frac{(V_f-nb)}{(V_i-nb)} - n^2a\left(\frac{1}{V_i}-\frac{1}{V_f}\right)$$
$$= -3.50\text{ mol}\times 8.314\text{ J mol}^{-1}\text{K}^{-1}\times 250.\text{ K}\times\ln\frac{35.5\text{ L}-3.5\text{ mol}\times 0.0387\text{ L mol}^{-1}}{3.25\text{ L}-3.5\text{ mol}\times 0.0387\text{ L mol}^{-1}}$$
$$+\,1.370\text{ L}^2\text{ mol}^{-2}\text{ bar}\times(3.5\text{ mol})^2\times\left(\frac{1}{3.25\text{ L}}-\frac{1}{35.5\text{ L}}\right)$$
$$w = -17.670\times 10^{3}\text{ J} + 4.68\text{ J} = -17.675\times 10^{3}\text{ J}$$

$$\text{Percent error} = 100\times\frac{-17.675\times 10^{3}\text{ J}+17.393\times 10^{3}\text{ J}}{-17.675\times 10^{3}\text{ J}} = 1.57\%$$

P2.25 A major league pitcher throws a baseball with a speed of 162 kilometers per hour. If the baseball weighs 235 grams and its heat capacity is 1.7 J $\text{g}^{-1}\text{ K}^{-1}$, calculate the temperature rise of the ball when it is stopped by the catcher's mitt. Assume no heat is transferred to the catcher's mitt and that the catcher's arm does not recoil when he or she catches the ball.

$$\text{v} = 162\times 10^{3}\text{ m hr}^{-1}\times\frac{\text{hr}}{3600\text{ s}} = 45.0\text{ m s}^{-1}$$
$$q_P = C_P\Delta T = \tfrac{1}{2}m\text{v}^2$$
$$\Delta T = \frac{\tfrac{1}{2}m\text{v}^2}{C_P m} = \frac{0.5\times 0.235\text{ kg}\times(45.0\text{ m s}^{-1})^2}{1700\text{ J kg}^{-1}\text{ K}^{-1}} = 0.60\text{ K}$$

P2.26 A 2.50 mol sample of an ideal gas for which $C_{V,m} = 3/2\text{R}$ undergoes the following two-step process: (1) From an initial state of the gas described by $T = 13.1^{\circ}\text{C}$ and $P = 1.75\times 10^{5}$ Pa, the gas undergoes an isothermal expansion against a constant external pressure of 3.75×10^{4} Pa until the volume has doubled. (2) Subsequently, the gas is cooled at constant volume. The temperature falls to −23.6°C. Calculate q, w, ΔU, and ΔH for each step and for the overall process.

a. For the first step, $\Delta U = \Delta H = 0$ because the process is isothermal.

$$V_i = \frac{nRT_i}{P_i}$$

$$= \frac{2.50\text{ mol} \times 8.314\text{ J mol}^{-1}\text{K}^{-1} \times (273.15 + 13.1)\text{ K}}{1.75 \times 10^4\text{ Pa}} = 0.0340\text{ m}^3$$

$$w = -q = -P_{external}\Delta V = -3.75 \times 10^4\text{ Pa} \times 2 \times 0.0340\text{ m}^3$$

$$= -1.27 \times 10^3\text{ J}$$

b. For the second step, $w = 0$ because $\Delta V = 0$.

$$q = \Delta U = nC_V\Delta T = 2.50\text{ mol} \times \frac{3 \times 8.314\text{ J mol}^{-1}\text{K}^{-1}}{2} \times (-23.6^{\text{o}}\text{C} - 13.1^{\text{o}}\text{C}) = -1.14 \times 10^3\text{ J}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta T = -1.14 \times 10^3\text{ J}$$
$$+2.50\text{ mol} \times 8.314\text{ J mol}^{-1}\text{K}^{-1} \times (-23.6^{\text{o}}\text{C} - 13.1^{\text{o}}\text{C})$$

$$\Delta H = -1.91 \times 10^3\text{ J}$$

For the overall process,

$$w = -1.27 \times 10^3\text{ J}, q = 130\text{ J}$$
$$\Delta U = -1.14 \times 10^3\text{ J, and }\Delta H = -1.91 \times 10^3\text{ J}$$

P2.27 A 2.35 mole sample of an ideal gas, for which $C_{V,m} = 3/2R$, initially at 27.0°C and 1.75×10^6 Pa undergoes a two-stage transformation. For each of the stages described in the following list, calculate the final pressure, as well as q, w, ΔU, and ΔH. Also calculate q, w, ΔU, and ΔH for the complete process.

a. The gas is expanded isothermally and reversibly until the volume triples.

b. Beginning at the end of the first stage, the temperature is raised to 105°C at constant volume.

(a) $$P_1 = \frac{P_0V_1}{V_2} = \frac{P_0}{3} = 5.83 \times 10^5\text{ Pa}$$

$$w = -nRT\ \ln\frac{V_2}{V_1} = -2.35\text{ mol} \times 8.314\text{ J mol}^{-1}\text{K}^{-1} \times 300.\text{ K} \times \ln 3 = -6.44 \times 10^3\text{ J}$$

$$\Delta U = 0 \text{ and } \Delta H = 0 \text{ because } \Delta T = 0$$

$$q = -w = 6.44 \times 10^3\text{ J}$$

(b) $$\frac{T_1}{P_1} = \frac{T_2}{P_2};\ P_2 = \frac{T_2P_1}{T_1} = \frac{378\text{ K} \times 1.75 \times 10^6\text{ Pa}}{300.\text{ K}} = 7.35 \times 10^5\text{ Pa}$$

$$\Delta U = nC_{V,m}\Delta T = 2.35\text{ mol} \times 1.5 \times 8.314\text{ J mol}^{-1}\text{K}^{-1} \times (378\text{ K} - 300.\text{ K}) = 2.29 \times 10^3\text{ J}$$

$$w = 0 \quad \text{because} \quad \Delta V = 0$$

$$q = \Delta U = 2.29 \times 10^3\text{ J}$$

$$\Delta H = nC_{P,m}\Delta T = n(C_{V,m} + R)\Delta T = 2.35\text{ mol} \times \frac{5}{2} \times 8.314\text{ J mol}^{-1}\text{K}^{-1} \times (378\text{ K} - 300.\text{ K}) = 3.81 \times 10^3\text{ J}$$

For the overall process,

$$q = 6.44 \times 10^3\text{ J} + 2.29 \times 10^3\text{ J} = 8.73 \times 10^3\text{ J}$$
$$w = -6.44 \times 10^3\text{ J} + 0 = -6.44 \times 10^3\text{ J}$$
$$\Delta U = 0 + 2.29 \times 10^3\text{ J} = 2.29 \times 10^3\text{ J}$$
$$\Delta H = 0 + 3.81 \times 10^3\text{ J} = 3.81 \times 10^3\text{ J}$$

P2.28 A 3.50 mole sample of an ideal gas with $C_{V,m} = 3/2R$ is expanded adiabatically against a constant external pressure of 1.45 bar. The initial temperature and pressure are $T_i = 310.\text{ K}$ and $P_i = 15.2$ bar. The final pressure is $P_f = 1.45$ bar. Calculate q, w, ΔU, and ΔH for the process.

$$\Delta U = nC_{V,m}(T_f - T_i) = -P_{external}(V_f - V_i) = w$$

$q = 0$ because the process is adiabatic.

$$nC_{V,m}(T_f - T_i) = -nRP_{external}\left(\frac{T_f}{P_f} - \frac{T_i}{P_i}\right)$$

$$T_f\left(nC_{V,m} + \frac{nRP_{external}}{P_f}\right) = T_i\left(nC_{V,m} + \frac{nRP_{external}}{P_i}\right)$$

$$T_f = T_i\left(\frac{C_{V,m} + \dfrac{RP_{external}}{P_i}}{C_{V,m} + \dfrac{RP_{external}}{P_f}}\right) = 310.\text{ K} \times \left(\frac{1.5 \times 8.314\text{ J mol}^{-1}\text{K}^{-1} + \dfrac{8.314\text{ J mol}^{-1}\text{K}^{-1} \times 1.45\text{ bar}}{15.2\text{ bar}}}{1.5 \times 8.314\text{ J mol}^{-1}\text{K}^{-1} + \dfrac{8.314\text{ J mol}^{-1}\text{K}^{-1} \times 1.45\text{ bar}}{1.45\text{ bar}}}\right)$$

$$T_f = 198\text{ K}$$

$$\Delta U = w = nC_{V,n}\Delta T = 3.50\text{ mol} \times \frac{3 \times 8.314\text{ J mol}^{-1}\text{K}^{-1}}{2} \times (197\text{ K} - 310.\text{ K}) = -4.90 \times 10^3\text{ J}$$

$$\Delta H = \Delta U + nR\Delta T = -4.90 \times 10^3\text{ J} + 3.50\text{ mol} \times 8.314\text{ J mol}^{-1}\text{K}^{-1} \times (197\text{ K} - 310.\text{ K})$$

$$\Delta H = -8.16 \times 10^3\text{ J}$$

P2.29 A nearly flat bicycle tire becomes noticeably warmer after it has been pumped up. Approximate this process as a reversible adiabatic compression. Assume the initial pressure and temperature of the air before it is put in the tire to be $P_i = 1.00$ bar and $T_i = 280.\text{ K}$. The final pressure in the tire is $P_f = 3.75$ bar. Calculate the final temperature of the air in the tire. Assume that $C_{V,m} = 5/2R$.

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma} = \left(\frac{T_f}{T_i}\right)^{1-\gamma}\left(\frac{P_i}{P_f}\right)^{1-\gamma}; = \left(\frac{T_f}{T_i}\right)^{\gamma} = \left(\frac{P_i}{P_f}\right)^{1-\gamma}; \frac{T_f}{T_i} = \left(\frac{P_i}{P_f}\right)^{\frac{1-\gamma}{\gamma}}$$

$$T_f = \left(\frac{1.00\text{ bar}}{3.75\text{ bar}}\right)^{\frac{1-\frac{7}{5}}{\frac{7}{5}}} \times 280.\text{ K} = 408\text{ K}$$

P2.30 For 1.25 mol of an ideal gas, $P_{external} = P = 350. \times 10^3$ Pa. The temperature is changed from 135°C to 21.2°C, and $C_{V,m} = 3/2R$. Calculate q, w, ΔU, and ΔH.

$$\Delta U = nC_{V,m}\Delta T = 1.25\text{ mol} \times \frac{3}{2} \times 8.314\text{ J mol}^{-1}\text{K}^{-1} \times (408\text{ K} - 294\text{ K}) = -1.77 \times 10^3\text{ J}$$

$$\begin{aligned}\Delta H = nC_{P,m}\Delta T &= n(C_{V,m} + R)\Delta T \\ &= 1.25\text{ mol} \times \frac{5}{2} \times 8.314\text{ J mol}^{-1}\text{K}^{-1} \times (408\text{ K} - 294\text{ K}) \\ &= -2.96 \times 10^3\text{ J} \\ &= q_P\end{aligned}$$

$$w = \Delta U - q_P = -1.77 \times 10^3 + 2.96 \times 10^3\text{ J} = 1.18 \times 10^3$$

P2.31 Suppose an adult is encased in a thermally insulating barrier so that all the heat evolved by metabolism of foodstuffs is retained by the body. What is her temperature increase after 2.5 hours? Assume the heat capacity of the body is 4.18 J $g^{-1}K^{-1}$ and that the heat produced by metabolism is 9.4 kJ kg^{-1} hr^{-1}.

$$\Delta T = \frac{q}{C_p} = \frac{9.4\times10^3 \text{ J kg}^{-1}\text{ hr}^{-1}\times 2.5\text{ h}}{4.18\times10^3\text{ J kg}^{-1}} = 5.6\text{ K}$$

P2.32 Consider the isothermal expansion of 2.35 mol of an ideal gas at 415 K from an initial pressure of 18.0 bar to a final pressure of 1.75 bar. Describe the process that will result in the greatest amount of work being done by the system with $P_{external} \geq 1.75$ bar, and calculate w. Describe the process that will result in the least amount of work being done by the system with $P_{external} \geq 1.75$ bar and calculate w. What is the least amount of work done without restrictions on the external pressure?

The greatest amount of work is done in a reversible expansion. The work is given by

$$w_{reversible} = -nRT\ln\frac{V_f}{V_i} = -nRT\ln\frac{P_i}{P_f} = -2.35\text{ mol}\times 8.314\text{ J mol}^{-1}\text{K}^{-1}\times 415\text{ K}\times\ln\frac{18.0\text{ bar}}{1.75\text{ bar}} = -18.9\times10^3\text{ J}$$

The work done by the system is 18.9×10^3 J.

The least amount of work is done in a single stage expansion at constant pressure with the external pressure equal to the final pressure. The work is given by

$$\begin{aligned} w &= -P_{external}(V_f - V_i) = -nRTP_{external}\left(\frac{1}{P_f} - \frac{1}{P_i}\right) \\ &= -2.35\text{ mol}\times 8.314\text{ J mol}^{-1}\text{K}^{-1}\times 415\text{ K}\times 1.75\text{ bar}\times\left(\frac{1}{1.75\text{ bar}} - \frac{1}{18.0\text{ bar}}\right) \\ &= -7.30\times10^3\text{ J} \end{aligned}$$

The work done by the system is 7.30×10^3 J.

The least amount of work done without restrictions on the pressure is zero, which occurs when $P_{external} = 0$.

P2.33 An automobile tire contains air at $225.\times10^3$ Pa at 25.0°C. The stem valve is removed and the air is allowed to expand adiabatically against the constant external pressure of one bar until $P = P_{external}$. For air, $C_{V,m} = 5/2R$. Calculate the final temperature. Assume ideal gas behavior.

Because $q = 0$, $\Delta U = w$.

$$nC_{V,m}(T_f - T_i) = -P_{ext}(V_f - V_i)$$

$$nC_{V,m}(T_f - T_i) = -P_{ext}\left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}\right)$$

The factor n cancels out. Rearranging the equation,

$$\left(C_{V,m} + \frac{RP_{ext}}{P_f}\right)T_f = \left(C_{V,m} + \frac{RP_{ext}}{P_i}\right)T_i$$

$$T_f = \frac{C_{V,m} + \dfrac{RP_{ext}}{P_i}}{C_{V,m} + \dfrac{RP_{ext}}{P_f}} \times T_i$$

$$= \left(\frac{2.5 \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} + \dfrac{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 10^5\ \text{Pa}}{2.25 \times 10^5\ \text{Pa}}}{2.5 \times 8.314\ \ \text{J mol}^{-1}\ \text{K}^{-1} + \dfrac{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 10^5\ \text{Pa}}{10^5\ \text{Pa}}}\right) \times 298\ \text{K}$$

$$T_f = 251\ \text{K}$$

P2.34 One mole of an ideal gas is subjected to the following changes. Calculate the change in temperature for each case if $C_{V,m} = 3/2R$.

a. $q = -425$ J, $w = 185$ J

b. $q = 315.$ J, $w = -315$ J

c. $q = 0$, $w = 225$ J

(a) $\Delta U = q + w = -240.$ J

$C_{V,m} = 1.5\,R = 12.47\ \text{J K}^{-1}\ \text{mol}^{-1}$

$$\Delta T = \frac{\Delta U}{C_{V,m}} = \frac{-240.\ \text{J mol}^{-1}}{12.47\ \text{J K}^{-1}\ \text{mol}^{-1}} = -19.2\ \text{K}$$

(b) $\Delta U = q + w = 0$

$$\Delta T = \frac{\Delta U}{C_{V,m}} = \frac{0}{12.47\ \text{J K}^{-1}\ \text{mol}^{-1}} = 0$$

(c) $\Delta U = q + w = 225$ J

$$\Delta T = \frac{\Delta U}{C_{V,m}} = \frac{225\ \text{J mol}^{-1}}{12.47\ \text{J K}^{-1}\ \text{mol}^{-1}} = 18.0\ \text{K}$$

P2.35 Consider the adiabatic expansion of 0.500 mol of an ideal monatomic gas with $C_{V,m} = 3/2R$. The initial state is described by $P = 6.25$ bar and $T = 300.$ K.

a. Calculate the final temperature if the gas undergoes a reversible adiabatic expansion to a final pressure of $P = 1.25$ bar.

b. Calculate the final temperature if the same gas undergoes an adiabatic expansion against an external pressure of $P = 1.25$ bar to a final pressure $P = 1.25$ bar.

Explain the difference in your results for parts (a) and (b).

(a) $$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma} = \left(\frac{T_f}{T_i}\right)^{1-\gamma}\left(\frac{P_i}{P_f}\right)^{1-\gamma}; = \left(\frac{T_f}{T_i}\right)^{\gamma} = \left(\frac{P_i}{P_f}\right)^{1-\gamma}; \frac{T_f}{T_i} = \left(\frac{P_i}{P_f}\right)^{\frac{1-\gamma}{\gamma}}$$

$$T_f = \left(\frac{6.25\text{ bar}}{1.25\text{ bar}}\right)^{\frac{1-\frac{5}{3}}{\frac{5}{3}}} \times 300.\text{ K} = 158\text{ K}$$

(b) $$\Delta U = nC_{V,m}(T_f - T_i) = -P_{external}(V_f - V_i)$$

$$nC_{V,m}(T_f - T_i) = -nRP_{external}\left(\frac{T_f}{P_f} - \frac{T_i}{P_i}\right)$$

$$T_f\left(nC_{V,m} + \frac{nRP_{external}}{P_f}\right) = T_i\left(nC_{V,m} + \frac{nRP_{external}}{P_i}\right)$$

$$T_f = T_i\left(\frac{C_{V,m} + \frac{RP_{external}}{P_i}}{C_{V,m} + \frac{RP_{external}}{P_f}}\right) = 300.\text{ K} \times \left(\frac{1.5 \times 8.314\text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314\text{ J mol}^{-1}\text{K}^{-1} \times 1.25\text{ bar}}{6.25\text{ bar}}}{1.5 \times 8.314\text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314\text{ J mol}^{-1}\text{K}^{-1} \times 1.25\text{ bar}}{1.25\text{ bar}}}\right)$$

$$T_f = 204\text{ K}$$

More work is done on the surroundings in the reversible expansion, and therefore ΔU and the temperature decrease more than for the irreversible expansion.

P2.36 A pellet of Zn of mass 31.2 g is dropped into a flask containing dilute H_2SO_4 at a pressure of $P = 1.00$ bar and temperature of $T = 300.$ K. What is the reaction that occurs? Calculate w for the process.

$$\text{Zn}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{SO}_4{}^{2-}(aq) + \text{H}_2(g)$$

The volume of H_2 produced is given by

$$V = \frac{31.2\ g}{65.39\ g(\text{mol Zn})^{-1}} \times \frac{1\text{ mol H}_2}{1\text{ mol Zn}} \times \frac{8.314\text{ J mol}^{-1}\text{ K}^{-1} \times 300.\text{ K}}{1 \times 10^5\text{ Pa}} = 11.9 \times 10^{-3}\text{ m}^3$$

$$w = -P_{external}\ \Delta V$$

$\Delta V \approx$ volume of H_2 produced.

$$w = -1 \times 10^5\text{ Pa} \times 11.9 \times 10^{-3}\text{ m}^3 = -1190\text{ J}$$

P2.37 Calculate ΔH and ΔU for the transformation of 2.50 mol of an ideal gas from 19.0°C and 1.00 atm to 550.°C and 19.5 atm if

$C_{P,m} = 20.9 + 0.042\frac{T}{\text{K}}$ in units of J K^{-1} mol^{-1}.

$$\begin{aligned}\Delta H &= n\int_{T_i}^{T_f} C_{P,m}\, dT \\ &= \int_{292\ K}^{823\ K}\left(20.9 + 0.042\frac{T'}{\text{K}}\right)dT' \\ &= 20.9 \times (695\text{ K} - 308\text{ K})\text{J} + \left[0.021\,T^2\right]_{292\text{ K}}^{823\text{ K}}\text{ J} \\ &= 2.774 \times 10^4\text{ J} + 3.109 \times 10^4\text{ J} \\ &= 5.88 \times 10^4\text{ J}\end{aligned}$$

$$\begin{aligned}\Delta U &= \Delta H - \Delta(PV) = \Delta H - nR\Delta T\\ &= 5.88\times10^{4}\text{ J} - 8.314\text{ J K}^{-1}\text{mol}^{-1}\times(823-292)\text{ K}\\ &= 4.78\times10^{4}\text{ J}\end{aligned}$$

P2.38 A 1.75 mole sample of an ideal gas for which $C_{V,m} = 20.8\text{ J K}^{-1}\text{ mol}^{-1}$ is heated from an initial temperature of 21.2°C to a final temperature of 380.°C at constant volume. Calculate q, w, ΔU, and ΔH for this process.

$w = 0$ because $\Delta V = 0$.

$$\Delta U = q = nC_V\Delta T = 1.75\text{ mol}\times20.8\text{ J mol}^{-1}\text{ K}^{-1}\times358.8\text{ K} = 13.1\times10^{3}\text{ J}$$

$$\begin{aligned}\Delta H &= \Delta U + \Delta(PV) = \Delta U + nR\Delta T = 13.1\times10^{3}\text{ J} + 1.75\text{ mol}\times8.314\text{ J mol}^{-1}\text{ K}^{-1}\times358.8\text{ K}\\ &= 18.3\times10^{3}\text{ J}\end{aligned}$$

P2.39 An ideal gas undergoes a single-stage expansion against a constant external pressure $P_{external} = P_f$ at constant temperature from T, P_i, V_i, to T, P_f, V_f.

a. What is the largest mass m that can be lifted through the height h in this expansion?

b. The system is restored to its initial state in a single-state compression. What is the smallest mass m' that must fall through the height h to restore the system to its initial state?

c. If $h = 15.5\text{ cm}$, $P_i = 1.75\times10^{6}\text{ Pa}$, $P_f = 1.25\times10^{6}\text{ Pa}$, $T = 280.\text{ K}$, and $n = 2.25\text{ mol}$, calculate the values of the masses in parts (a) and (b).

Consider the expansion

(a) $w = mgh = -P_{ext}(V_f - V_i)$

$$m = \left|\frac{-P_{ext}(V_f - V_i)}{gh}\right|$$

For the final volume to be V_f, the external pressure can be no bigger than P_f

$$m_{\max} = \left|\frac{-P_f(V_f - V_i)}{gh}\right|$$

(b) Consider the compression

$$m' = \left|\frac{-P_{ext}(V_i - V_f)}{gh}\right|$$

For the final volume to be V_i, the pressure can be no smaller than P_i

$$m'_{\min} = \left|\frac{-P_i(V_i - V_f)}{gh}\right|$$

(c) $V_i = \dfrac{nRT}{P_i} = \dfrac{1.50\text{ mol}\times8.314\text{ J mol}^{-1}\text{K}^{-1}\times300.\text{ K}}{2.50\times10^{6}\text{ Pa}} = 2.99\times10^{-3}\text{ m}^3$

$P_fV_f = P_iV_i$

$V_f = \dfrac{P_iV_i}{P_f} = \dfrac{2.50\times10^{6}\text{ Pa}\times1.50\times10^{-3}\text{ m}^3}{0.750\times10^{6}\text{ Pa}} = 4.19\times10^{-3}\text{ m}^3$

$$m_{\max} = \left|\frac{-1.25\times10^{6}\text{ Pa}\times(4.19\times10^{-3}\text{ m}^3 - 2.99\times10^{-3}\text{ m}^3)}{9.81\text{ m s}^{-2}\times0.155\text{ m}}\right| = 984\text{ kg}$$

$$m'_{\min} = \left|\frac{-1.75\times10^{6}\text{ Pa}\times(2.99\times10^{-3}\text{ m}^3 - 4.19\times10^{3}\text{ m}^3)}{9.81\text{ m s}^{-2}\times0.155\text{ m}}\right| = 1.38\times10^{3}\text{ kg}$$

P2.40 The formalism of the Young's modulus is sometimes used to calculate the reversible work involved in extending or compressing an elastic material. Assume a force F is applied to an elastic rod of cross-sectional area A_0 and length L_0. As a result of this force, the rod changes in length by ΔL. The Young's modulus E is defined as

$$E = \frac{\text{tensile stress}}{\text{tensile strain}} = \frac{F/A_0}{\Delta L/L_0} = \frac{FL_0}{A_0 \Delta L}$$

a. Relate k in Hooke's Law to the Young's modulus expression just given.

b. Using your result in part (a), show that the magnitude of the reversible work involved in changing the length L_0 of an elastic cylinder of cross-sectional area A_0 by ΔL is $w = \frac{1}{2}\left(\frac{\Delta L}{L_0}\right)^2 EA_0L_0$.

$$E = \frac{FL_0}{A_0\Delta L} \quad F = \frac{EA_0\Delta L}{L_0} = k'\Delta L$$

$$w_{twist} = \int_0^{\Delta L} Fdx = k'\Delta L d\Delta L = \frac{1}{2}k'\Delta L^2 = \frac{1}{2}EA_0L_0\left(\frac{\Delta L}{L_0}\right)^2$$

P2.41 The Young's modulus (see P2.40) of muscle fiber is approximately 2.80×10^7 Pa. A muscle fiber 3.25 cm in length and 0.125 cm in diameter is suspended with a mass M hanging at its end. Calculate the mass required to extend the length of the fiber by 10%.

$$F = \frac{EA_0\Delta L}{L_0} = k'\Delta L = gm$$

$$m = \frac{EA_0\Delta L}{L_0 g} = \frac{2.80 \times 10^7 \text{ Pa} \times 0.10 \times 0.0325 \text{ m} \times \pi \times \left(\frac{0.00125 \text{ m}}{2}\right)^2}{0.0325 \text{ m} \times 9.81 \text{ m s}^{-2}} = 0.35 \text{ kg}$$

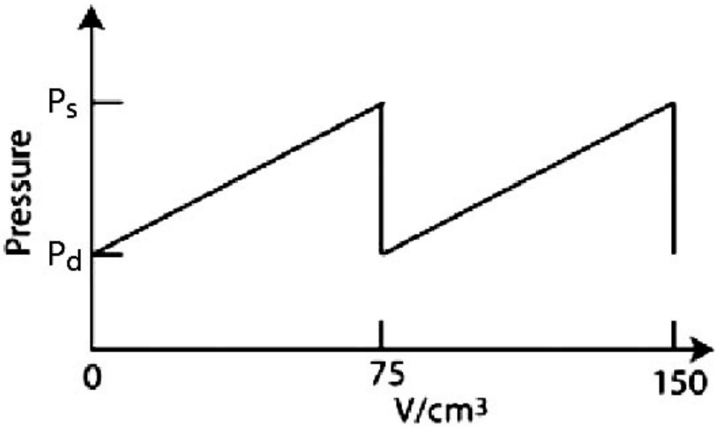
P2.42 DNA can be modeled as an elastic rod which can be twisted or bent. Suppose a DNA molecule of length L is bent such that it lies on the arc of a circle of radius R_c. The reversible work involved in bending DNA without twisting is $w_{bend} = \frac{BL}{2R_c^2}$ where B is the bending force constant. The DNA in a nucleosome particle is about 680. Å in length. Nucleosomal DNA is bent around a protein complex called the histone octamer into a circle of radius 55 Å. Calculate the reversible work involved in bending the DNA around the histone octamer if the force constant $B = 2.00 \times 10^{-28}$ J m^{-1}.

$$w_{bend} = \frac{BL}{2R_c^2} = \frac{2.00 \times 10^{-28} \text{ J m} \times 680. \times 10^{-10} \text{ m}}{2 \times (55 \times 10^{-10} \text{ m})^2} = 2.2 \times 10^{-19} \text{ J}$$

P2.43 A 1.75 mole sample of an ideal gas is compressed isothermally from 62.0 L to 19.0 L using a constant external pressure of 2.80 atm. Calculate q, w, ΔU, and ΔH.

$$\begin{aligned} w &= -P_{external}\Delta V \\ &= -2.80 \times 1.013 \times 10^5 \text{ Pa} \times (19.0 \times 10^{-3} \text{ L} - 62.0 \times 10^{-3} \text{ L}) = 1.22 \times 10^4 \text{ J} \\ \Delta U &= 0 \text{ and } \Delta H = 0 \text{ because } \Delta T = 0 \\ q &= -w = -1.22 \times 10^4 \text{ J} \end{aligned}$$

P2.44 Assume the following simplified dependence of the pressure in a ventricle of the human heart as a function of the volume of blood pumped.



P_s, the systolic pressure, is 120. mm Hg, corresponding to 0.158 atm. P_d, the diastolic pressure, is 80.0 mm Hg, corresponding to 0.105 atm. If the volume of blood pumped in one heartbeat is $75.0\ \text{cm}^3$, calculate the work done in a heartbeat.

$$
\begin{aligned}
w &= -\int_{V_i}^{V_f} P_{external}\,dV \\
&= -\int_{0}^{75\times10^{-6}\ \text{m}^3} \left(P_d + \frac{V}{75\times10^{-6}\ \text{m}^3}(P_s - P_d) \right) dV \\
&= 0.79\ \text{J} + 0.20\ \text{J} = 0.99\ \text{J}
\end{aligned}
$$