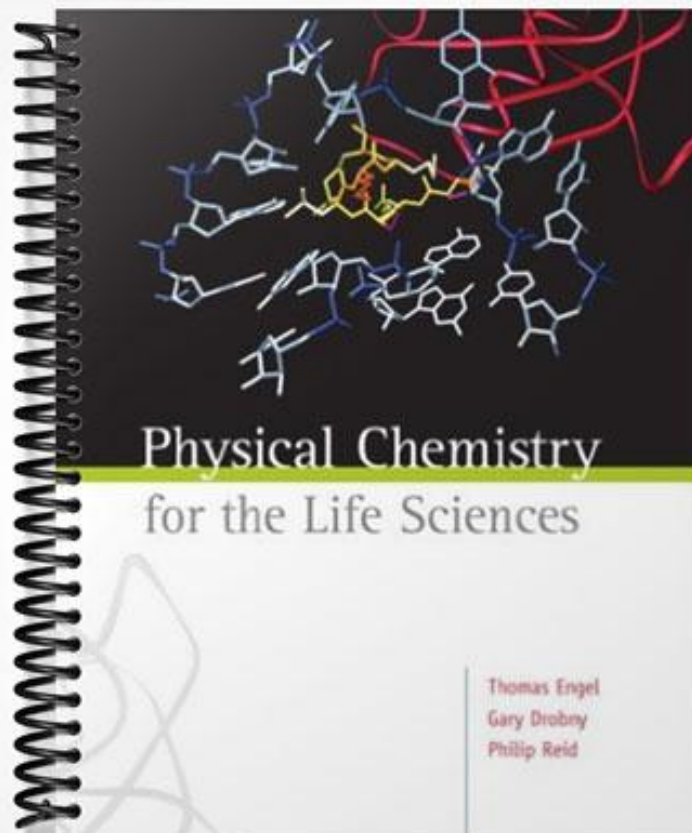


SOLUTIONS MANUAL



Physical Chemistry for the Life Sciences

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Chapter 2: Heat, Work, Internal Energy, Enthalpy, and the First Law of Thermodynamics

Questions on Concepts

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.

The work on the resistor is done by the surroundings. Heat flows across the boundary between the surroundings and the system because of the temperature difference between them.

Q2.2) 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 surroundings, it will lead to a temperature change in the surroundings given by $\Delta T = \frac{q}{C_p}$. For the case of interest, we obtain:

$$q = q_{\text{surroundings}} = -m C_p \Delta T = (1000 \text{ g}) \times (4.19 \text{ J g}^{-1} \text{ K}^{-1}) \times (1.15 \text{ K}) = \underline{\underline{-5.24 \times 10^3 \text{ J}}}$$

Q2.3) Explain the relationship between the terms *exact differential* and *state function*.

In order for a function to be a state function $f(x,y)$, it must be possible to express the function as a total differential df as:

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$$

If that form exists, it is called the exact differential.

Q2.4) Why is it incorrect to speak of the heat or work associated with a system?

Heat and work exist only during the transitions of a given system between states. At system in a particular state is not associated with heat or work.

Q2.5) Two ideal gas systems undergo reversible expansion 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 an adiabatic expansion, all work that is done comes from lowering of ΔU , and therefore of the temperature. On the other hand, some of the work that is done in an isothermal expansion can come at the expense of the heat that has flown across the boundary between the system and surroundings.

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. Which of q , w , and ΔU are positive, negative, or zero?

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

Q2.7) 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 not be stored since it only exists in transitions. The sentence should be rephrased to:

Since the house is well insulated, the walls are nearly adiabatic. Therefore, the temperature of the house did not fall rapidly when in contact with the surroundings at lower temperature, as it would have if the walls would be more or less diathermal.

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 gets into 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 heat in the same situation since it does not undergo a phase transition.

Q2.9) 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 at equilibrium with one another. In an irreversible expansion, they are not at equilibrium with one another.

Q2.10) 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, the temperature will increase if the reaction is exothermic, decrease if the reaction is endothermic, and not change if no energy evolution or consumption takes place in the reaction.

Problems

Problem numbers in **RED** indicate that the solution to the problem is given in the *Student Solutions Manual*.

P2.1) 3.00 moles of an ideal gas at 27.0°C expand isothermally from an initial volume of 20.0 dm³ to a final volume of 60.0 dm³. Calculate w for this process (a) for expansion against a constant external pressure of 1.00×10^5 Pa and (b) for a reversible expansion.

a) w for an expansion against a constant pressure is:

$$w = -p_{\text{ext}} \times (V_{\text{final}} - V_{\text{initial}}) = (1.00 \times 10^5 \text{ Pa}) \times (0.06 \text{ m}^3 - 0.02 \text{ m}^3) = \underline{4.00 \times 10^3 \text{ J}}$$

b) w for a reversible expansion is:

$$w = -n R T \frac{V_{\text{final}}}{V_{\text{initial}}} = -(3.00 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \times \ln \left(\frac{0.06 \text{ m}^3}{0.02 \text{ m}^3} \right) = \underline{-8.22 \times 10^3 \text{ J}}$$

P2.2) A major league pitcher throws a baseball at a speed of 150. km/h. If the baseball weighs 220. g and its heat capacity is $2.0 \text{ J g}^{-1} \text{ K}^{-1}$, 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. Assume also that the catcher's arm does not recoil when he or she catches the ball.

The kinetic energy, $E_{\text{kin}} = \frac{1}{2} m v^2$, of the ball is transferred into heat, $q_p = C_p \Delta T$, in the mitt:

$$E_{\text{kin}} = \frac{1}{2} m v^2 = q_p = C_p \Delta T$$

Solving for ΔT yields:

$$\Delta T = \frac{\frac{1}{2} m v^2}{C_p} = \frac{\frac{1}{2} (0.22 \text{ kg}) \times (41.667^2 \text{ m}^2 \text{ s}^{-2})}{(2.0 \text{ J g}^{-1} \text{ K}^{-1}) \times (220.0 \text{ g})} = \underline{0.43 \text{ K}}$$

P2.3) 3.00 moles of an ideal gas are compressed isothermally from 60.0 to 20.0 L using a constant external pressure of 5.00 atm. Calculate q , w , ΔU , and ΔH .

The work against a constant pressure:

$$w = -p_{\text{external}} \Delta V = -(5 \times 101325 \text{ Pa}) \times (60 \times 10^{-3} \text{ m}^3 - 20 \times 10^{-3} \text{ m}^3) = \underline{-2.03 \times 10^4 \text{ J}}$$

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

$$q = -w = \underline{2.03 \times 10^4 \text{ J}}$$

P2.4) A system consisting of 57.5 g of liquid water at 298 K is heated using an immersion heater at a constant pressure of 1.00 bar. If a current of 1.50 A passes through the 10.0-ohm resistor for 150 s, what is the final temperature of the water? The heat capacity for water can be found in Appendix B.

The heat produced by the resistor is:

$$q = I^2 R t = n C_{p,m} R (T_f - T_i)$$

Solving for T_f yields:

$$T_f = \frac{(I^2 R t + n C_{p,m} T_i)}{n C_{p,m}}$$

$$= \frac{\left((1.5 \text{ A})^2 \times (10 \text{ Ohm}) \times (150 \text{ s}) + \left(\frac{57.5 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \times (75.291 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K}) \right)}{\left(\frac{57.5 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \times (75.291 \text{ J mol}^{-1} \text{ K}^{-1})} = \underline{312 \text{ K}}$$

P2.5) Using the results from Problem P1.4, determine the average heat evolved by the oxidation of foodstuffs in an average adult per hour per kilogram of body weight. Assume the weight of an average adult is 70. kg. State any assumptions you make. Assume 420. kJ of heat are evolved per mole of oxygen consumed as a result of the oxidation of foodstuffs.

From P1.4 we know that the number of moles of O_2 inhaled are:

$$n_{O_2} = 0.01966 \text{ mol min}^{-1} = 1.1796 \text{ mol h}^{-1}$$

The average heat evolved by the oxidation of foodstuffs is then:

$$q_{\text{avg}} = \frac{q_{\text{O}_2} n_{\text{O}_2}}{m} = \frac{(1.1796 \text{ mol h}^{-1}) \times (420 \times 10^3 \text{ J mol}^{-1})}{(70 \text{ kg})} = \underline{7.08 \text{ kJ h}^{-1} \text{ kg}^{-1}}$$

We assumed that all the oxygen that is inhaled is used in the oxidation of foodstuffs.

P2.6) Suppose an adult body were encased in a thermally insulating barrier. If as a result of this barrier all the heat evolved by metabolism of foodstuffs were retained by the body, what would the temperature of the body reach after 3 hours? Assume the heat capacity of the body is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$. Use the results of Problem P2.5 in your solution.

From P2.5 we know that the heat produced after 3 h would be:

$$q(3 \text{ h}) = (7.08 \text{ kJ h}^{-1} \text{ kg}^{-1}) \times (3 \text{ h}) = 21.24 \text{ kJ kg}^{-1}$$

Then using $q = C_p \Delta T$, we obtain:

$$q = C_p \Delta T = \frac{q(3 \text{ h})}{C_p} = \frac{(2.124 \times 10^4 \text{ J kg}^{-1})}{(4.18 \text{ J K}^{-1} \text{ g}^{-1}) \times (1000 \text{ g kg}^{-1})} = \underline{5.08 \text{ K}}$$

P2.7) For 1.00 mol of an ideal gas, $P_{\text{external}} = P = 200.0 \times 10^3 \text{ Pa}$. The temperature is changed from 100.0°C to 25.0°C , and $C_{V,m} = 3/2R$. Calculate q , w , ΔU , and ΔH .

$$\Delta U = n C_{V,m} \Delta T = \frac{3}{2} \times (1.0 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K} - 373 \text{ K}) = \underline{-935 \text{ J}}$$

$$\Delta H = n C_{p,m} \Delta T = (n C_{V,m} + R) \Delta T = \frac{5}{2} \times (1.0 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K} - 373 \text{ K}) = \underline{-1560 \text{ J}}$$

$$\underline{\Delta H = q_p}$$

$$w \Delta U - q_p = (-935 \text{ J}) - (-1560 \text{ J}) = \underline{625 \text{ J}}$$

P2.8) Consider the isothermal expansion of 5.25 mol of an ideal gas at 450. K from an initial

pressure of 15.0 bar to a final pressure of 3.50 bar. Describe the process that will result in the greatest amount of work being done by the system with $P_{\text{external}} \geq 3.50$ bar and calculate w . Describe the process that will result in the least amount of work being done by the system with $P_{\text{external}} \geq 3.50$ bar and calculate w . What is the least amount of work done without restrictions on the external pressure?

The most work is performed in a reversible process:

$$\begin{aligned} w_{\text{reversible}} &= -n R T \ln\left(\frac{V_f}{V_i}\right) = -n R T \ln\left(\frac{p_f}{p_i}\right) \\ &= -(5.25 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K}) \times \ln\left(\frac{15.0 \text{ bar}}{3.50 \text{ bar}}\right) = \underline{-28.6 \times 10^3 \text{ J}} \end{aligned}$$

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

$$\begin{aligned} w &= -P_{\text{external}} (V_f - V_i) = -n R T P_{\text{external}} \left(\frac{1}{p_f} - \frac{1}{p_i}\right) \\ &= -(5.25 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K}) \times (3.50 \text{ bar}) \times \ln\left(\frac{1}{15.0 \text{ bar}} - \frac{1}{3.50 \text{ bar}}\right) = \underline{-15.1 \times 10^3 \text{ J}} \end{aligned}$$

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

P2.9) A hiker caught in a thunderstorm loses heat when her clothing becomes wet. She is packing emergency rations that, if completely metabolized, will release 30. kJ of heat per gram of rations consumed. How much rations must the hiker consume to avoid a reduction in body temperature of 4.0 K as a result of heat loss? Assume the heat capacity of the body equals that of water. Assume the hiker weighs 55 kg. State any additional assumptions.

We start by calculating the heat that corresponds to a temperature decrease of 4 K. Using

$q = C_p \Delta T$, we obtain:

$$q_{4K} = C_p \Delta T = (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times (4.0 \text{ K}) \times \frac{1}{(18.02 \times 10^{-3} \text{ kg mol}^{-1})} = 17000 \text{ J kg}^{-1}$$

We then determine the heat lost for a 55 kg person as:

$$q_{\text{person}} = q_{4K} m = (17000 \text{ J kg}^{-1}) \times (55 \text{ kg}) = 9.2 \times 10^5 \text{ J}$$

And finally the mass of rations that needs to be consumed is given by:

$$m_{\text{rations}} = \frac{q_{\text{person}}}{q_{\text{rations}}} = \frac{(9.2 \times 10^5 \text{ J})}{(3.0 \times 10^4 \text{ J g}^{-1})} = 31.0 \text{ g}$$

P2.10) A muscle fiber contracts by 2.0 cm and in doing so lifts a weight. Calculate the work performed by the fiber and the weight lifted. Assume the muscle fiber obeys Hooke's law with a constant of 800. N m⁻¹.

The work is given by:

$$w = \frac{1}{2} k d^2 = \frac{1}{2} (800.0 \text{ N m}^{-1}) \times (0.02 \text{ m})^2 = \underline{0.16 \text{ J}}$$

P2.11) Calculate ΔH and ΔU for the transformation of 1.00 mol of an ideal gas from 27.0°C and 1.00 atm to 327°C and 17.0 atm if

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

For an ideal gas, ΔH is given by:

$$\Delta H = n \int_{T_i}^{T_f} C_{p,m} dT = n \int_{300 \text{ K}}^{600 \text{ K}} \left(20.9 + 0.042 \frac{T}{\text{K}} \right) dT'$$

$$\begin{aligned} \Delta H &= 20.9 \times (600 \text{ K} - 300 \text{ K}) \text{ J} + \left[0.21 T^2 \right]_{300 \text{ K}}^{600 \text{ K}} \text{ J} \\ &= (6.27 \times 10^3 \text{ J}) + (56.7 \times 10^3 \text{ J}) = \underline{63.0 \times 10^3 \text{ J}} \end{aligned}$$

$$\begin{aligned}\Delta U &= \Delta H - \Delta(pV) = \Delta H - n R \Delta T \\ &= (63.0 \times 10^3 \text{ J}) - (1 \text{ mol}) \times (8.314472 \text{ J mol}^{-1} \text{ K}^{-1}) \times (300 \text{ K}) = \underline{60.5 \times 10^3 \text{ J}}\end{aligned}$$

P2.12) Calculate w for the adiabatic expansion of 1.00 mol of an ideal gas at an initial pressure of 2.00 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 2.00 bar. What value of the final pressure would give the same value of w as the first part of this problem? Assume that $C_{P,m} = 5/2R$.

$$w_{\text{ad}} = \Delta U = n (C_{p,m} - R) \Delta T = \left(-\frac{3}{2} \text{ mol} \right) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (150 \text{ K}) = \underline{-1.87 \times 10^3 \text{ J}}$$

$$w_{\text{reversible}} = -n R T \ln \left(\frac{p_i}{p_f} \right) \quad \text{and} \quad \ln \left(\frac{p_i}{p_f} \right) = \frac{-w_{\text{reversible}}}{n R T}$$

$$\ln \left(\frac{p_i}{p_f} \right) = \frac{-w_{\text{reversible}}}{n R T} = \frac{(1.87 \times 10^3 \text{ J})}{(1 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})} = 0.7497$$

$$\frac{p_i}{p_f} = 2.12$$

$$p_f = \frac{p_i}{2.12} = \underline{0.944}$$

P2.13) In the adiabatic expansion of 1.00 mol of an ideal gas from an initial temperature of 25.0°C, the work done on the surroundings is 1200. J. If $C_{V,m} = 3/2R$, calculate q , w , ΔU , and ΔH .

For an adiabatic expansion of an ideal gas:

$$q = \underline{0}$$

$$w = \Delta U = C_{V,m} \times (T_{\text{final}} - T_{\text{initial}}) = \underline{-1200 \text{ J}}$$

$$\Delta H = C_{P,m} \times (T_{\text{final}} - T_{\text{initial}}) = (C_{V,m} + R) \times \left(\frac{\Delta U}{C_{V,m}} \right) = \left(\frac{3}{2} R + R \right) \times \left(\frac{\Delta U}{\frac{3}{2} R} \right) = \frac{5}{2} \times \Delta U = \underline{-2000 \text{ J}}$$

P2.14) According to a story told by Lord Kelvin, one day when walking down from Chamonix to commence a tour of Mt. Blanc, “whom should I meet walking up (the trail) but (James) Joule, with a long thermometer in his hand, and a carriage with a lady in it not far off. He told me he had been married since we parted from Oxford, and he was going to try for (the measurement of the) elevation of temperature in waterfalls.” Suppose Joule encountered a waterfall 30. m in height. Calculate the temperature difference between the top and bottom of this waterfall.

The decrease in potential energy ($m \times g \times h$) must equal the heat evolved as the water falls.

($m \times C_{p,m} \times \Delta T$). Note that the mass cancels. Heat is evolved so T increases, translating into a negative sign in front of heat term:

$$m g h = -m C_{p,m} \Delta T$$

$$\Delta T = -\frac{g h}{C_{p,m}} = \frac{(9.81 \text{ m s}^{-2}) \times (30.0 \text{ m})}{(75.3 \text{ J m}^{-1} \text{ K}^{-1})} \times (18.02 \times 10^{-3} \text{ kg mol}^{-1}) = \underline{-0.0704 \text{ K}}$$

P2.15) 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.

$$w = m g h = -p_f (V_f - V_i) \qquad m = \left| -\frac{p_f (V_f - V_i)}{g h} \right|$$

$$w = m g h = -n R T \ln\left(\frac{V_f}{V_i}\right) \qquad m = \left| -\frac{n R T}{g h} \ln\left(\frac{V_f}{V_i}\right) \right|$$

P2.16) An automobile tire contains air at $320. \times 10^3 \text{ Pa}$ at 20.0°C . The stem valve is removed and the air is allowed to expand adiabatically against the constant external pressure of $100. \times 10^3$

Pa until $P = P_{\text{external}}$. For air, $C_{V,m} = 5/2R$. Calculate the final temperature. Assume ideal gas behavior.

Since $q = 0$, we have $\Delta U = w$

$$n C_{V,m} (T_f - T_i) = -P_{\text{ext}} (V_f - V_i)$$

$$n C_{V,m} (T_f - T_i) = -P_{\text{ext}} \left(\frac{n R T_f}{P_f} - \frac{n R T_i}{P_i} \right)$$

The factors n cancel out. Rearranging the equation gives:

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

$$\frac{T_f}{T_i} = \frac{\left(C_{V,m} + \frac{R P_{\text{ext}}}{P_i} \right)}{\left(C_{V,m} + \frac{R P_{\text{ext}}}{P_f} \right)} = \frac{\left((2.5 \times 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) + \frac{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (10^5 \text{ Pa})}{(3.20 \times 10^5 \text{ Pa})} \right)}{\left((2.5 \times 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) + \frac{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (10^5 \text{ Pa})}{(10^5 \text{ Pa})} \right)}$$

$$T_f = 0.804 T_i = \underline{235 \text{ K}}$$

P2.17) Count Rumford observed that using cannon-boring machinery, a single horse could heat 11.6 kg of 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 150.-kg weight in 1 minute? Assume the heat capacity of water is $4.18 \text{ kJ K}^{-1} \text{ kg}^{-1}$.

The rate of work, L , for warming the water sample can be calculated as the ratio of work and time:

$$L = \frac{w}{t} = \frac{C m \Delta T}{t} = \frac{(4.18 \text{ kJ K}^{-1} \text{ kg}^{-1}) \times (11.6 \text{ kg}) \times (82 \text{ K})}{(9000 \text{ s})} = 0.442 \text{ kJ s}^{-1} = 442 \text{ J s}^{-1}$$

The rate of work for lifting the weight depends on the potential energy:

$L = \frac{w}{t} = \frac{m g h}{t}$, where m , g , and h are mass, gravitational acceleration, and height, respectively.

Solving for h yields:

$$h = \frac{L t}{m g} = \frac{(442 \text{ J s}^{-1}) \times (60 \text{ s})}{(150.0 \text{ kg}) \times (9.80665 \text{ m s}^{-2})} = \underline{18.03 \text{ m}}$$

P2.18) Count Rumford also observed that nine burning candles generate heat at the same rate that a single horse-driven cannon-boring piece of equipment generates heat. James Watt observed that a single horse can raise a 330.-lb. weight 100. feet in 1 minute. Using the observations of Watt and Rumford, determine the rate at which a candle generates heat. (*Note:* 1.00 m = 3.281 ft.)

First we convert the units:

$$m = 330.0 \text{ lb} = 149.685 \text{ kg}$$

$$h = 100 \text{ ft} = 30.479 \text{ m}$$

Then using $q = w$, we obtain for the heat that horse generates:

$$q_{9 \text{ candles}} = w = \frac{m g h}{t} = \frac{(149.685 \text{ kg}) \times (9.80665 \text{ m s}^{-2}) \times (30.479 \text{ m})}{(1 \text{ min})} = 44754.948 \text{ J min}^{-1}$$

Since this heat is equivalent to the heat that nine candles generate, the heat evolved by one candle is:

$$q_{1 \text{ candle}} = \frac{q_{9 \text{ candles}}}{\text{number of candles}} = \frac{(44754.948 \text{ J min}^{-1})}{9} = \underline{4972.8 \text{ J min}^{-1}}$$

P2.19) 3.50 moles of an ideal gas are expanded from 450. K and an initial pressure of 5.00 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 for part (b) is greater than or less than the result for part (a).

a) Calculating the initial and final volumina:

$$V_i = \frac{n R T}{p_i} = \frac{(3.50 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K})}{(5.00 \times 10^5 \text{ Pa})} = 0.0262 \text{ m}^3$$

$$V_f = \frac{n R T}{p_f} = \frac{(3.50 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K})}{(1.00 \times 10^5 \text{ Pa})} = 0.1310 \text{ m}^3$$

w for an isothermal, reversible process is then given by:

$$w = -n R T \ln\left(\frac{V_{\text{final}}}{V_{\text{initial}}}\right) = -(3.50 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K}) \times \ln\left(\frac{0.1310 \text{ m}^3}{0.0262 \text{ m}^3}\right)$$

$$w = -21076 \text{ J} = \underline{-21.1 \text{ kJ}}$$

b) For an adiabatic, reversible process:

$$\ln\left(\frac{T_{\text{final}}}{T_{\text{initial}}}\right) = -(\gamma - 1) \ln\left(\frac{V_{\text{final}}}{V_{\text{initial}}}\right), \text{ where } \gamma = C_{P,m}/C_{V,m}$$

$$\ln\left(\frac{T_{\text{final}}}{T_{\text{initial}}}\right) = -(\gamma - 1) \ln\left(\frac{T_{\text{final}} p_{\text{initial}}}{T_{\text{initial}} p_{\text{final}}}\right) = -\frac{(\gamma - 1)}{\gamma} \ln\left(\frac{p_{\text{initial}}}{p_{\text{final}}}\right)$$

Therefore:

$$T_{\text{final}} = \text{Exp}\left[-\frac{(\gamma - 1)}{\gamma} \ln\left(\frac{p_{\text{initial}}}{p_{\text{final}}}\right) + \ln(T_{\text{initial}})\right]$$

With $C_{P,m} = \frac{5}{2} R$, and $C_{V,m} = \frac{3}{2} R$, the final temperature is:

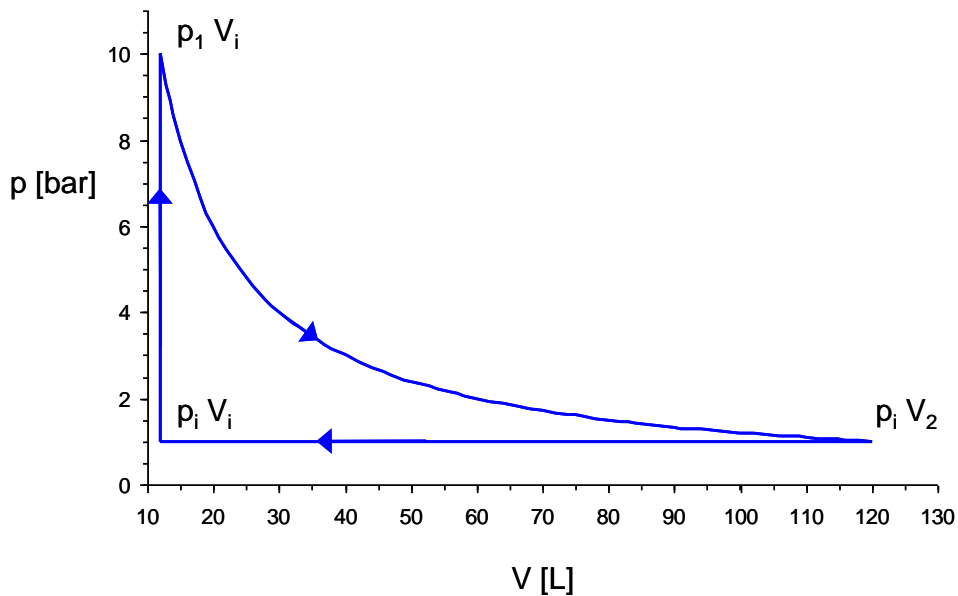
$$T_{\text{final}} = \text{Exp}\left[\left(-0.4 \times \ln\left(\frac{5 \text{ bar}}{1 \text{ bar}}\right)\right) + \ln(450 \text{ K})\right] = 236 \text{ K}$$

And finally w for an adiabatic process and for 3.5 moles of gas:

$$w = C_V \Delta T = \frac{3}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K} - 236 \text{ K}) \times (3.5 \text{ mol}) = \underline{-9340.85 \text{ J} = -9.34 \text{ kJ}}$$

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).

P2.20) An ideal gas described by $T_i = 300. \text{ K}$, $P_i = 1.00 \text{ bar}$, and $V_i = 10.0 \text{ L}$ is heated at constant volume until $P = 10.0 \text{ bar}$. It then undergoes a reversible isothermal expansion until $P = 1.00 \text{ bar}$. 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?



First we calculate the number of moles:

$$n = \frac{p_i V_i}{R T_i} = \frac{(1.00 \text{ bar}) \times (10.0 \text{ L})}{(8.314472 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})} = 0.401 \text{ mol}$$

The process in the diagram above is described by the steps:

- step 1: $p_i, V_i, T_i \rightarrow p_1, V_i, T_i$
- step 2: $p_1, V_i, T_1 \rightarrow p_i, V_2, T_1$
- step 3: $p_i, V_2, T_1 \rightarrow p_1, V_i, T_i$

In step 1 ($p_i, V_i, T_i \rightarrow p_1, V_i, T_i$) $w_1 = 0$ since V stays constant

In step 2 ($p_i, V_i, T_1 \rightarrow p_i, V_2, T_1$) we first calculate T_1 :

$$T_1 = T_i \frac{p_1}{p_i} = (300 \text{ K}) \times \frac{(10.0 \text{ bar})}{(1.00 \text{ bar})} = 3000 \text{ K}$$

Then the work is:

$$\begin{aligned} w_2 &= -n R T \ln\left(\frac{V_f}{V_i}\right) = -n R T \ln\left(\frac{p_f}{p_i}\right) \\ &= -(0.401 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (3000 \text{ K}) \times \ln\left(\frac{10.0 \text{ bar}}{1.00 \text{ bar}}\right) = \underline{-23.0 \times 10^3 \text{ J}} \end{aligned}$$

In step 3 ($p_i, V_2, T_1 \rightarrow p_1, V_i, T_1$) we first calculate V_2 :

$$p_1 V_i = p_i V_2 \text{ and } V_2 = \frac{p_1 V_i}{p_i} = 10V_i = 100 \text{ L}$$

And the work:

$$w_3 = -p_{\text{external}} \Delta V = -(1.00 \text{ bar}) \times \frac{(10^5 \text{ Pa})}{(1 \text{ bar})} \times (10 \text{ L} - 100 \text{ L}) \times \frac{(10^{-3} \text{ m}^3)}{(1 \text{ L})} = 9.00 \times 10^3 \text{ J}$$

And for the entire circle:

$$w_{\text{cycle}} = w_1 + w_2 + w_3 = 0 \text{ J} - 23.0 \times 10^3 \text{ J} + 9.00 \times 10^3 \text{ J} = \underline{-14.0 \times 10^3 \text{ J}}$$

P2.21) 3.00 mols of an ideal gas with $C_{V,m}=3/2R$ initially at a temperature $T_i = 298 \text{ K}$ and $P_i = 1.00 \text{ bar}$ are enclosed in an adiabatic piston and cylinder assembly. The gas is compressed by placing a 625-kg mass on the piston of diameter 20.0 cm. Calculate the work done in this process and the distance that the piston travels. Assume that the mass of the piston is negligible.

The constant pressure during compression p_{const} , which is also the final pressure, p_f , can be calculated using the gravitational acceleration. Pressure is force divided by area:

$$p_f = p_{\text{const}} = \frac{F}{A} = \frac{m g}{A} = \frac{m g}{\left(\frac{\pi}{4} d^2\right)} = \frac{(625 \text{ kg}) \times (9.80667 \text{ m s}^{-2})}{\frac{\pi}{4} (0.2 \text{ m})^2} = 195084.2 \text{ Pa}$$

For a adiabatic, non-reversible compression:

$$nC_{v,m}(T_f - T_i) = -p_{\text{const}}(V_f - V_i) = -p_{\text{const}}\left(\frac{nR T_f}{p_f} - \frac{nR T_i}{p_i}\right)$$

Solving for T_f and using $C_{v,m} = \frac{3}{2}R$ yields:

$$T_f = \frac{2}{5} \times \left(\frac{p_{\text{const}} T_i}{p_i} + \frac{3}{2} T_i \right) = \frac{2 \times (195084.2 \text{ Pa}) \times (298 \text{ K})}{5 \times (1 \times 10^5 \text{ Pa})} + \frac{3}{5} (298 \text{ K}) = 411.34 \text{ K}$$

The work performed by the gas is:

$$w = n C_{v,m} (T_f - T_i) = (3.0 \text{ mol}) \times \frac{3}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (411.34 \text{ K} - 298 \text{ K}) = \underline{4.24 \times 10^3 \text{ J}}$$

calculate the distance the cylinder moved, we need the final volume of the piston:

$$V_f = \frac{nR T_f}{p_f} = \frac{(3.0 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (411.34 \text{ K})}{(195084.2 \text{ Pa})} = 0.05259 \text{ m}^3$$

The height of the cylinder that the gas filled initially is then:

$$h_i = \frac{V_i}{A} = \frac{(0.07433 \text{ m}^3)}{(0.0314 \text{ m}^2)} = 2.367 \text{ m}$$

The reduced height of the cylinder filled with gas after compression is:

$$h_f = \frac{h_i V_f}{V_i} = \frac{(2.367 \text{ m}) \times (0.0526 \text{ m}^3)}{(0.07433 \text{ m}^3)} = 1.675 \text{ m}$$

That means the piston moved the difference in height:

$$\Delta h = h_i - h_f = 2.367 \text{ m} - 1.675 \text{ m} = \underline{0.69 \text{ m}}$$

P2.22) A bottle at 21.0°C contains an ideal gas at a pressure of $126.4 \times 10^3 \text{ Pa}$. The rubber stopper closing the bottle is removed. The gas expands adiabatically against $P_{\text{external}} = 101.9 \times 10^3 \text{ Pa}$, and some gas is expelled from the bottle in the process. When $P = P_{\text{external}}$, the stopper is quickly replaced. The gas remaining in the bottle slowly warms up to 21.0°C . 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 an adiabatic expansion $\Delta U = w$:

$$n C_{V,m} (T_f - T_i) = -p_{\text{ext}} (V_f - V_i)$$

$$n C_{V,m} (T_f - T_i) = -p_{\text{ext}} \left(\frac{n R T_f}{p_f} - \frac{n R T_i}{p_i} \right)$$

The factors n cancel out. Rearranging the equation gives:

$$\left(C_{V,m} + \frac{R p_{\text{ext}}}{p_f} \right) T_f = \left(C_{V,m} + \frac{R p_{\text{ext}}}{p_i} \right) T_i$$

$$\frac{T_f}{T_i} = \frac{\left(C_{V,m} + \frac{R p_{\text{ext}}}{p_i} \right)}{\left(C_{V,m} + \frac{R p_{\text{ext}}}{p_f} \right)} = \frac{\left((1.5 \times 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) + \frac{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (101.9 \times 10^3 \text{ Pa})}{(126.4 \times 10^3 \text{ Pa})} \right)}{\left((1.5 \times 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) + \frac{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (101.9 \times 10^3 \text{ Pa})}{(101.9 \times 10^3 \text{ Pa})} \right)}$$

$$T_f = 0.923 T_i = 271 \text{ K}$$

Once the stopper is in place, the gas makes a transformation:

$$T_i = 214 \text{ K}, p_i = 101.9 \times 10^3 \text{ Pa} \text{ to } T_f = 294 \text{ K} \text{ and } p_f.$$

$$\frac{p_i V_i}{T_i} = \frac{p_f V_f}{T_f}$$

With $V_i = V_f$:

$$p_f = \frac{T_f}{T_i} p_i = \frac{(294 \text{ K})}{(271 \text{ K})} \times (101.9 \times 10^3 \text{ Pa}) = 110.5 \times 10^3 \text{ Pa}$$

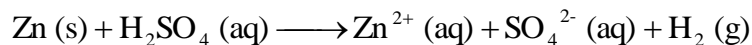
The same calculation carried out for $C_{V,m} = \frac{5}{2} R$ gives:

$$\frac{T_f}{T_i} = 0.945, T_f = 278 \text{ K}$$

$$p_f = \underline{107.8 \times 10^3 \text{ Pa}}$$

P2.23) A pellet of Zn of mass 10.0 g is dropped into a flask containing dilute H₂SO₄ at a pressure of $P = 1.00$ bar and temperature of $T = 298$ K. What is the reaction that occurs? Calculate w for the process.

The chemical equation for the process is:



First we calculate the volume of H₂ that is produced:

$$V_{\text{H}_2} = \frac{(10 \text{ g})}{(65.39 \text{ g mol}^{-1})} \times \frac{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{(1 \times 10^5 \text{ Pa})} = 3.79 \times 10^{-4} \text{ m}^3$$

Assuming that $(V_f - V_i) \approx V_{\text{H}_2}$, the work is:

$$w = -p_{\text{ext}}(V_f - V_i) = -(1 \times 10^5 \text{ Pa}) \times (3.79 \times 10^{-3} \text{ m}^3) = \underline{379 \text{ J}}$$

P2.24) One mole 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 0.00°C to a final temperature of 275°C at constant volume. Calculate q , w , ΔU , and ΔH for this process.

For a process with $V = \text{constant}$:

$$w = 0$$

$$q = \Delta U = C_v \Delta T = (20.8 \text{ J K}^{-1} \text{ mol}^{-1}) \times (275 \text{ K}) \times (1.0 \text{ mol}) = \underline{5720.0 \text{ J} = 5.72 \text{ kJ}}$$

$$\Delta H = C_p \Delta T = (nR + C_v) \Delta T =$$

$$\left((8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1.0 \text{ mol}) + (20.8 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1.0 \text{ mol}) \right) \times (273 \text{ K}) = \underline{8006.0 \text{ J} = 8.0 \text{ kJ}}$$

P2.25) One mole of an ideal gas, for which $C_{V,m} = 3/2R$, initially at 20.0°C and 1.00×10^6 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 doubles.

b. Beginning at the end of the first stage, the temperature is raised to 80.0°C at constant volume.

$$\text{a) } p_2 = \frac{p_1 V_1}{V_2} = \frac{p_1}{2} = 0.500 \times 10^6 \text{ Pa}$$

$$w = -n R T \ln\left(\frac{V_f}{V_i}\right) = -(1.0 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293.15 \text{ K}) \times \ln(2) = \underline{-1.69 \times 10^3 \text{ J}}$$

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

$$q = -w = \underline{1.69 \times 10^3 \text{ J}}$$

$$\text{b) } \frac{T_1}{p_1} = \frac{T_2}{p_2}, \text{ and therefore } p_2 = \frac{T_2 p_1}{T_1} = \frac{(0.500 \times 10^6 \text{ Pa}) \times (353 \text{ K})}{(293 \text{ K})} = 6.02 \times 10^5 \text{ Pa}$$

$$\Delta U = n C_{p,m} \Delta T = (1.0 \text{ mol}) \times \frac{3}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (353 \text{ K} - 293 \text{ K}) = \underline{748 \text{ J}}$$

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

$$\underline{q = \Delta U = 748 \text{ J}}$$

$$\Delta H = n C_{p,m} \Delta T = n (C_{v,m} + R) \Delta T = (1.0 \text{ mol}) \times \frac{5}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (353 \text{ K} - 293 \text{ K}) = \underline{1.25 \times 10^3 \text{ J}}$$

For the overall process:

$$q = (1.69 \times 10^3 \text{ J}) + (748 \text{ J}) = \underline{2.44 \times 10^3 \text{ J}}$$

$$w = (-1.69 \times 10^3 \text{ J}) + (0 \text{ J}) = \underline{-1.69 \times 10^3 \text{ J}}$$

$$\Delta U = (748 \text{ J}) + (0 \text{ J}) = \underline{748 \text{ J}}$$

$$\Delta H = (1.25 \times 10^3 \text{ J}) + (0 \text{ J}) = \underline{1.25 \times 10^3 \text{ J}}$$

P2.26) One mole of an ideal gas, for which $C_{V,m} = 3/2R$, initially at 298 K and $1.00 \times 10^5 \text{ Pa}$ undergoes a reversible adiabatic compression. At the end of the process, the pressure is $1.00 \times 10^6 \text{ Pa}$. Calculate the final temperature of the gas. Calculate q , w , ΔU , and ΔH for this process.

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

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

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

$$\left(\frac{T_f}{T_i}\right) = \left(\frac{(1.00 \times 10^5 \text{ Pa})}{(1.00 \times 10^6 \text{ Pa})}\right)^{\frac{(1-\frac{5}{3})}{\frac{5}{3}}} = (0.100)^{-0.4} = 2.51$$

$$T_f = (2.51) \times (298 \text{ K}) = 749 \text{ K}$$

$q = 0$ for an adiabatic process.

$$w = \Delta U = n C_{p,m} \Delta T = (1.0 \text{ mol}) \times \frac{3}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (749 \text{ K} - 298 \text{ K}) = \underline{5.62 \times 10^3 \text{ J}}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + R \Delta T = (5.62 \times 10^3 \text{ J}) + (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (749 \text{ K} - 298 \text{ K}) = \underline{9.37 \times 10^3 \text{ J}}$$

P2.27) The temperature of 1 mol of an ideal gas increases from 18.0° to 55.1°C as the gas is compressed adiabatically. Calculate q , w , ΔU , and ΔH for this process assuming that $C_{V,m} = 3/2R$. $q = 0$ for an adiabatic process.

$$w = \Delta U = n C_{p,m} \Delta T = (1.0 \text{ mol}) \times \frac{3}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (55.1^\circ \text{C} - 18.0^\circ \text{C}) = \underline{463 \text{ J}}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + R \Delta T = (463 \text{ J}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (55.1^\circ \text{C} - 18.0^\circ \text{C}) = \underline{771 \text{ J}}$$

P2.28) A 1.00-mol sample of an ideal gas for which $C_{V,m} = 3/2R$ undergoes the following two-step process: (1) From an initial state of the gas described by $T = 28.0^\circ\text{C}$ and $P = 2.00 \times 10^4 \text{ Pa}$, the gas undergoes an isothermal expansion against a constant external pressure of $1.00 \times 10^4 \text{ Pa}$ until the volume has doubled. (2) Subsequently, the gas is cooled at constant volume. The temperature falls to -40.5°C . Calculate q , w , ΔU , and ΔH for each step and for the overall process.

1) For an isothermal process:

$$q = w = -p_{\text{ext}} (V_f - V_i) = -p_{\text{ext}} (2V_i - V_i) = -p_{\text{ext}} V_i$$

The initial volume is:

$$V = \frac{nRT}{p} = \frac{(1 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (301.15 \text{ K})}{(2.00 \times 10^4 \text{ Pa})} = 0.1251 \text{ m}^3$$

And:

$$q = w = -(0.1251 \text{ m}^3) \times (1.00 \times 10^4 \text{ Pa}) = \underline{-1251 \text{ J}}$$

$$\Delta H = \Delta U = 0$$

2) For a process with $V = \text{constant}$:

$$\underline{w = 0}$$

$$q = \Delta U = n C_{V,m} \Delta T = \frac{3}{2} (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (68.5 \text{ K}) \times (1.0 \text{ mol}) = \underline{854.3 \text{ J}}$$

$$\Delta H = n C_{p,m} \Delta T = (nR + \frac{3}{2} nR) \Delta T = \frac{5}{2} nR = \frac{5}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1.0 \text{ mol}) \times (68.5 \text{ K}) = \underline{1423.9 \text{ J}}$$

For the overall process:

$$w_{\text{tot}} = w_1 + w_2 = \underline{-1251\text{J}}$$

$$q_{\text{tot}} = q_1 + q_2 = 1251\text{J} + 854.3\text{J} = \underline{-2.1 \times 10^3 \text{J}}$$

$$\Delta U_{\text{tot}} = \Delta U_1 + \Delta U_2 = \underline{854.3\text{J}}$$

$$\Delta H_{\text{tot}} = \Delta H_1 + \Delta H_2 = \underline{1423.9\text{J}}$$

P2.29) A cylindrical vessel with rigid adiabatic walls is separated into two parts by a frictionless adiabatic piston. Each part contains 50.0 L of an ideal monatomic gas with $C_{V,m} = 3/2R$. Initially, $T_i = 298 \text{ K}$ and $P_i = 1.00 \text{ bar}$ 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 $P_f = 7.50 \text{ bar}$ 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 in each part is given by:

$$n = \frac{p_i V_i}{R T_i} = \frac{(1.00 \text{ bar}) \times (50.0 \text{ L})}{(8.314472 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = 2.02 \text{ mol}$$

a) We first calculate the final temperature in the right side:

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

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

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

$$\left(\frac{T_f}{T_i}\right) = \left(\frac{(1.00 \text{ bar})}{(7.50 \text{ bar})}\right)^{\frac{(1-\frac{5}{3})}{\frac{5}{3}}} = 2.24$$

$$T_f = (2.24) \times (298 \text{ K}) = 667 \text{ K}$$

$$w = \Delta U = n C_v \Delta T = (2.02 \text{ mol}) \times \frac{3}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (667 \text{ K} - 298 \text{ K}) = \underline{9.30 \times 10^3 \text{ J}}$$

b) First we calculate the volume of the right part:

$$V_{rf} = \frac{n R T_{rf}}{P_{rf}} = \frac{(2.02 \text{ mol}) \times (8.314472 \times 10^{-2} \text{ bar L K}^{-1} \text{ mol}^{-1}) \times (667 \text{ K})}{(7.50 \text{ bar})} = 14.9 \text{ L}$$

Therefore $V_{if} = (1000 \text{ L}) - (14.9 \text{ L}) = 85.1 \text{ L}$, and

$$T_{if} = \frac{P_{if} V_{if}}{n R} = \frac{(7.50 \text{ bar}) \times (85.1 \text{ L})}{(2.02 \text{ mol}) \times (8.314472 \times 10^{-2} \text{ bar L K}^{-1} \text{ mol}^{-1})} = 3800 \text{ K}$$

$$\Delta U = n C_v \Delta T = (2.02 \text{ mol}) \times \frac{3}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (3800 \text{ K} - 298 \text{ K}) = \underline{88.2 \times 10^3 \text{ J}}$$

From part a) $w = 9.30 \times 10^3 \text{ J}$

$$q = \Delta U - w = 88.2 \times 10^3 \text{ J} + 9.30 \times 10^3 \text{ J} = \underline{97.5 \times 10^3 \text{ J}}$$

P2.30) A vessel containing 1.00 mol of an ideal gas with $P_i = 1.00 \text{ bar}$ 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 equi-

librium, 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 $C_P = 7500. \text{ J K}^{-1}$. The gas is compressed reversibly to $P_f = 10.5 \text{ bar}$. What is the temperature of the system after thermal equilibrium has been established?

From P2.19 for a reversible, adiabatic process:

$$T_{\text{final}} = \text{Exp} \left[-\frac{(\gamma - 1)}{\gamma} \ln \left(\frac{P_{\text{initial}}}{P_{\text{final}}} \right) + \ln(T_{\text{initial}}) \right]$$

$$T_{\text{final}} = \text{Exp} \left[-0.4 \times \ln \left(\frac{1 \text{ bar}}{10.5 \text{ bar}} \right) + \ln(298 \text{ K}) \right] = 763.29 \text{ K}$$

The heat transferred to the bath in the adiabatic process is:

$$q = C_{v,m}(\text{gas}) \Delta T = \frac{5}{2} (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (763.3 \text{ K} - 298 \text{ K}) \times (1.0 \text{ mol}) = 9671.6 \text{ J}$$

The temperature of the bath increases to:

$$T_f = \frac{q}{C_P(\text{system})} + T_i = \frac{(9671.6 \text{ J})}{(7500 \text{ J K}^{-1})} + (298 \text{ K}) = \underline{299.3 \text{ K}}$$

P2.31) DNA can be modeled as an elastic rod that 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

$$w_{\text{bend}} = \frac{BL}{2R_c^2} \text{ where } B \text{ is the bending force constant. The DNA}$$

in a nucleosome particle is about 680 \AA in length. Nucleosomal DNA is bent around a protein complex called the histone octamer into a circle of radius 55 \AA . Calculate the reversible work involved in bending the DNA around the histone octamer if the force constant $B = 2.00 \times 10^{-28} \text{ J m}^{-1}$.

The bending work is given by:

$$W_{\text{bend}} = \frac{B L}{2 R_c^2} = \frac{(2.00 \times 10^{-28} \text{ J m}^{-1}) \times (680 \times 10^{-10} \text{ m})}{2 \times (55 \times 10^{-10} \text{ m})^2} = \underline{2.25 \times 10^{-19} \text{ J m}^{-2}}$$

P2.32) Compare the energy of DNA bending calculated in Problem 2.31 to the thermal energy $k_B T$, where k_B is Boltzmann's constant. Assume $T = 310$. K. Propose a source for the excess energy required to bend the DNA in Problem 2.31.

The thermal energy at 310 K is:

$$E_{\text{thermal}} = k_B T = (1.38 \times 10^{-23} \text{ J K}^{-1}) \times (310 \text{ K}) = \underline{4.278 \times 10^{-21} \text{ J}}$$

The ratio between the energy from P2.31 and the thermal energy is:

$$\frac{E_{\text{bend}}}{E_{\text{thermal}}} = \frac{(2.25 \times 10^{-19} \text{ J})}{(4.278 \times 10^{-21} \text{ J})} = \underline{52.6}$$

The energy source could be the formation of intermolecular interactions.

P2.33) The reversible work involved in twisting a short DNA molecule depends quadratically on ϕ/L , the angle of twist per unit length, where the twist angle is expressed in units of radians. The expression for the reversible work is:

$$w_{\text{twist}} = \frac{CL}{2} \left(\frac{\phi}{L} \right)^2. \text{ A DNA oligomer 20 base pairs in length}$$

undergoes a twisting deformation of 36 degrees in order to bind to a protein. Calculate the reversible work involved in this twisting deformation. Assume $C = 2.5 \times 10^{-28} \text{ J m}$. Assume also that each base pair is 3.4 Å in length ($1 \text{ Å} = 10^{-10} \text{ m}$).

$$w_{\text{twist}} = \frac{CL}{2} \left(\frac{\phi}{L} \right)^2 = \frac{(2.5 \times 10^{-28} \text{ J m}) \times (20) \times (3.4 \times 10^{-10} \text{ m})}{2} \left(\frac{\left(\frac{36^\circ \times \text{Pi rad}}{180^\circ} \right)}{(20) \times (3.4 \times 10^{-10} \text{ m})} \right)^2 = \underline{7.26 \times 10^{-21} \text{ J}}$$

P2.34) The formalism of 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 . 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. Derive Hooke's law from the Young's modulus expression just given.
- b. Using your result from part (a), show that the reversible work involved in changing by ΔL the length L_0 of an elastic cylinder of cross-sectional area A_0

$$\text{is } w = \frac{1}{2} \left(\frac{\Delta L}{L_0} \right)^2 EA_0 L_0.$$

a) Hooke's law says that the force with which a mass on a spring opposes displacement is directly proportional to the displacement:

$$F = k d$$

Young's modulus shows the same dependency of the force:

$$E = \frac{FL_0}{A_0 \Delta L}$$

$$F = \frac{E \Delta L A_0}{L_0} = k' \Delta L,$$

where k is a constant given by:

$$k' = \frac{E A_0}{L_0}$$

b) The work is given by the integral:

$$w_{\text{twist}} = \int_0^{\Delta L} F ds = k' \int_0^{\Delta L} \Delta L ds = \frac{1}{2} k' \Delta L^2 = \frac{1}{2} \frac{E A_0}{L_0} \Delta L^2 = \frac{1}{2} E A_0 L_0 \left(\frac{\Delta L}{L_0} \right)^2$$

P2.35) The heat capacity of solid lead oxide is given by

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

Calculate the change in enthalpy of 1 mol of $\text{PbO}(s)$ if it is cooled from 500 to 300 K at constant pressure.

$$\Delta H = n C_p \Delta T = (44.35 + 1.47 \times 10^{-3} \times 300 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1.0 \text{ mol}) \times (300 \text{ K} - 500 \text{ K}) = \underline{-8.96 \times 10^3 \text{ J}}$$

P2.36) 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 $P = 3.25$ bar and $T = 300$. K.

- Calculate the final temperature if the gas undergoes a reversible adiabatic expansion to a final pressure of $P = 1.00$ bar.
- Calculate the final temperature if the same gas undergoes an adiabatic expansion against an external pressure of $P = 1.00$ bar to a final pressure of $P = 1.00$ bar.
- Explain the difference in your results for parts (a) and (b).

a) The final temperature for the reversible adiabatic expansion is:

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

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

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

$$\left(\frac{T_f}{T_i}\right) = \left(\frac{(3.25 \text{ bar})}{(1.00 \text{ bar})}\right)^{\frac{(1-\frac{5}{3})}{\frac{5}{3}}} = 0.626$$

$$T_f = (0.626) \times (300 \text{ K}) = \underline{188 \text{ K}}$$

b) The final temperature for the expansion against an external pressure can be obtained by using the fact that in an adiabatic expansion $\Delta U = w$:

$$n C_{v,m} (T_f - T_i) = -p_{\text{ext}} (V_f - V_i)$$

$$n C_{v,m} (T_f - T_i) = -p_{\text{ext}} \left(\frac{n R T_f}{p_f} - \frac{n R T_i}{p_i} \right)$$

The factors n cancel out. Rearranging the equation gives:

$$\left(C_{v,m} + \frac{R p_{\text{ext}}}{p_f} \right) T_f = \left(C_{v,m} + \frac{R p_{\text{ext}}}{p_i} \right) T_i$$

$$\frac{T_f}{T_i} = \frac{\left(C_{v,m} + \frac{R p_{\text{ext}}}{p_i} \right)}{\left(C_{v,m} + \frac{R p_{\text{ext}}}{p_f} \right)} = \frac{\left((1.5 \times 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) + \frac{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1.00 \text{ bar})}{(3.25 \text{ bar})} \right)}{\left((1.5 \times 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) + \frac{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1.00 \text{ bar})}{(1.00 \text{ bar})} \right)}$$

$$T_f = 0.723 T_i = \underline{217 \text{ K}}$$

P2.37) The relationship between Young's modulus and the bending force constant for a deformable cylinder is $B = EI$, where, $I = \pi R^4/4$ and R is the radius of the cylinder.

a. Calculate the Young's modulus associated with a DNA of radius $10. \text{ \AA}$ ($1 \text{ \AA} = 10^{-10} \text{ m}$).

Assume the value of B given in Problem 2.31.

b. Suppose a DNA molecule 100 base pairs in length is extended by $10. \text{ \AA}$. Calculate the reversible work assuming the DNA can be treated as a deformable rod.

c. Compare this work to the thermal energy. Assume $T = 310. \text{ K}$.

a) Young's modulus is given by:

$$E = \frac{B}{I} = \frac{4B}{\pi R^4} = \frac{4 \times (2.00 \times 10^{-28} \text{ J m}^1)}{\pi \times (10 \times 10^{-10} \text{ m})^4} = \underline{2.55 \times 10^8 \text{ J m}^{-3}}$$

b) Assuming $3 \times 10^{-10} \text{ m}$ per base pair for the DNA, the work is given by:

$$w = \frac{E A_0 \Delta L^2}{2 L_0} = \frac{\pi \times (10 \times 10^{-10} \text{ m})^2 \times (2.55 \times 10^8 \text{ J m}^{-3}) \times (10 \times 10^{-10} \text{ m})^2}{2 \times (300 \times 10^{-10} \text{ m})} = \underline{4.45 \times 10^{-22} \text{ J}}$$

c) The thermal energy at 310 K is:

$$E_{\text{thermal}} = k T = (1.38 \times 10^{-23} \text{ J K}^{-1}) \times (310 \text{ K}) = \underline{4.28 \times 10^{-21} \text{ J}}$$

P2.38) The Young's modulus of muscle fiber is approximately $3.12 \times 10^7 \text{ Pa}$. If a muscle fiber 2.00 cm in length and 0.100 cm in diameter is suspended with a weight M hanging at its end, calculate the weight M required to extend the length of the fiber by 10%.

We use the result from P2.34 a):

$$F = \frac{E \Delta L A_0}{L_0} = k' \Delta L,$$

We set this force equal to the force exerted by the weight in the earth's gravitational field

$F = g m$, and solve for the mass, m :

$$\frac{E \Delta L A_0}{L_0} = g m$$

$$m = \frac{E \Delta L A_0}{L_0 g} = \frac{E \Delta L \pi r^2}{L_0 g} = \frac{E \Delta L \pi \left(\frac{d}{2}\right)^2}{L_0 g} = \frac{(3.12 \times 10^7 \text{ Pa}) \times (0.1 \times 0.02 \text{ m}) \times \pi \times \left(\frac{0.001 \text{ m}}{2}\right)^2}{(0.02 \text{ m}) \times (9.81 \text{ m s}^{-2})} = \underline{0.25 \text{ kg}}$$

P2.39) An ideal gas undergoes a single-stage expansion against a constant external pressure P_{ex} .

ernal at constant temperature from T, P_i, V_i to T, P_f, V_f .

- What is the largest mass m that can be lifted through the height h in this expansion?
- The system is restored to its initial state in a single-stage compression. What is the smallest mass m that must fall through the height h to restore the system to its initial state?
- If $h = 10.0 \text{ cm}$, $P_i = 1.00 \times 10^6 \text{ Pa}$, $P_f = 0.500 \times 10^6 \text{ Pa}$, $T = 300. \text{ K}$, and $n = 1.00 \text{ mol}$, calculate the values of the masses in parts (a) and (b).

a) For the expansion:

$$w = m g h = -P_{\text{ext}} (V_f - V_i)$$

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

For a final volume of V_f , the external pressure can not be larger than p_f :

$$m_{\max} = \left| \frac{-p_f (V_f - V_i)}{g h} \right|$$

b) For the compression:

$$w = m g h = -p_{\text{ext}} (V_i - V_f)$$

$$m = \left| \frac{-p_{\text{ext}} (V_i - V_f)}{g h} \right|$$

For a final volume of V_i , the external pressure can not be larger than p_i :

$$m_{\min} = \left| \frac{-p_i (V_i - V_f)}{g h} \right|$$

$$c) V_i = \frac{n R T_i}{p_i} = \frac{(1.0 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{(1.00 \times 10^6 \text{ Pa})} = 2.49 \times 10^{-3} \text{ m}^3$$

$$p_i V_i = p_f V_f$$

$$V_f = \frac{p_i V_i}{p_f} = \frac{(1.00 \times 10^6 \text{ Pa}) \times (2.49 \times 10^{-3} \text{ m}^3)}{(0.500 \times 10^6 \text{ Pa})} = 4.98 \times 10^{-3} \text{ m}^3$$

$$m_{\max} = \left| \frac{-p_f (V_f - V_i)}{g h} \right| = \left| \frac{-(0.500 \times 10^6 \text{ Pa}) \times \{(4.98 \times 10^{-3} \text{ m}^3) - (2.49 \times 10^{-3} \text{ m}^3)\}}{(9.81 \text{ m s}^{-2}) \times (0.100 \text{ m})} \right| = \underline{1.27 \times 10^3 \text{ kg}}$$

$$m_{\min} = \left| \frac{-p_i (V_f - V_i)}{g h} \right| = \left| \frac{-(1.00 \times 10^6 \text{ Pa}) \times \{(4.98 \times 10^{-3} \text{ m}^3) - (2.49 \times 10^{-3} \text{ m}^3)\}}{(9.81 \text{ m s}^{-2}) \times (0.100 \text{ m})} \right| = \underline{2.54 \times 10^3 \text{ kg}}$$

P2.40) Calculate q , w , ΔU , and ΔH if 1.00 mol of an ideal gas with $C_{V,m} = 3/2R$ undergoes a reversible adiabatic expansion from an initial volume $V_i = 5.25 \text{ m}^3$ to a final volume $V_f = 25.5 \text{ m}^3$.

The initial temperature is 300. K.

For an adiabatic process:

$$q=0$$

From P2.19 for a reversible, adiabatic process:

$$T_{\text{final}} = \text{Exp} \left[-(\gamma - 1) \ln \left(\frac{V_{\text{final}}}{V_{\text{initial}}} \right) + \ln(T_{\text{initial}}) \right], \quad \gamma = \frac{C_{p,m}}{C_{v,m}} = \frac{(nR + C_{v,m})}{C_{v,m}} = \frac{(nR + \frac{3}{2}R)}{\frac{3}{2}R} = \frac{5}{3}$$

$$T_{\text{final}} = \text{Exp} \left[-\left(\frac{5}{3} - 1\right) \times \ln \left(\frac{25.5 \text{ m}^3}{5.25 \text{ m}^3} \right) + \ln(300 \text{ K}) \right] = 104.6 \text{ K}$$

$$w = \Delta U = C_{v,m} \Delta T = \frac{3}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K} - 104.6 \text{ K}) \times (1.0 \text{ mol}) = \underline{2437.0 \text{ J} = 2.44 \text{ kJ}}$$

$$\Delta H = C_{p,m} \Delta T = \frac{5}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K} - 104.6 \text{ K}) \times (1.0 \text{ mol}) = \underline{4061.6 \text{ J} = 4.06 \text{ kJ}}$$

P2.41) 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 $P_i = 1.00 \text{ bar}$ and $T_i = 298 \text{ K}$, respectively. The final volume of the air in the tire is $V_f = 1.00 \text{ L}$ and the final pressure is $P_f = 5.00 \text{ bar}$. Calculate the final temperature of the air in the tire. Assume that $C_{v,m} = 5/2R$

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

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

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

$$\left(\frac{T_f}{T_i} \right) = \left(\frac{(1.00 \text{ bar})}{(5.00 \text{ bar})} \right)^{\frac{\left(\frac{1-\frac{7}{5}}{\frac{7}{5}}\right)}{\frac{7}{5}}} = 1.58$$

$$T_f = (1.58) \times (298 \text{ K}) = \underline{472 \text{ K}}$$

P2.42) One mole of an ideal gas with $C_{V,m} = 3/2R$ is expanded adiabatically against a constant external pressure of 1.00 bar. The initial temperature and pressure are $T_i = 300.$ K and $P_i = 25.0$ bar, respectively. The final pressure is $P_f = 1.00$ bar. Calculate q , w , ΔU , and ΔH for the process.

For an adiabatic, irreversible process:

$$q = 0$$

However, $dw = -pdV$, where p is the pressure of the system. Rather we have $dw = -p_f dV$, where p_f is the constant, external pressure that is producing the work. Since we are still assuming an ideal gas in this case, we again have $dU = nC_{V,m}dT$. Equating these expressions for dw and dU , we obtain:

$$nC_{V,m} dT = -p_f dV$$

Integrating on both sides yields:

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

$$C_{V,m} (T_f - T_i) = -\frac{R T_f}{V_f} (V_f - V_i) = R T_f \left(\frac{V_i}{V_f} - 1 \right)$$

Solving for T_f results in:

$$T_f = \frac{R T_i p_f}{p_i (C_{V,m} + R)} + \frac{C_{V,m} T_i}{(C_{V,m} + R)} = \frac{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \times (1 \times 10^5 \text{ Pa})}{(25 \times 10^5 \text{ Pa}) \left(\frac{5}{2} \times 8.314472 \text{ J K}^{-1} \text{ mol}^{-1} \right)} + \frac{3}{5} \times (300 \text{ K}) = 184.8 \text{ K}$$

For an adiabatic process:

$$w = \Delta U = C_{V,m} \Delta T = \frac{3}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K} - 184.8 \text{ K}) \times (1.0 \text{ mol}) = \underline{1436.7 \text{ J}} = \underline{1.44 \text{ kJ}}$$

$$\Delta H = C_{p,m} \Delta T = \frac{5}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K} - 184.8 \text{ K}) \times (1.0 \text{ mol}) = \underline{2394.6 \text{ J}} = \underline{2.39 \text{ kJ}}$$

P2.43) One mole of N_2 in a state defined by $T_i = 300.$ K and $V_i = 2.50$ L undergoes an isothermal reversible expansion until $V_f = 23.0$ 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 1.3.

a) For an ideal gas:

$$w_{\text{reversible}} = -n R T \ln\left(\frac{V_f}{V_i}\right) = -(1.0 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \times \ln\left(\frac{23.0 \text{ L}}{2.50 \text{ L}}\right) = \underline{-5.54 \times 10^3 \text{ J}}$$

b) For a van der Waals gas:

$$w = -\int_{V_i}^{V_f} p_{\text{external}} dV = -\int_{V_i}^{V_f} \left(\frac{R T}{V_m - b} - \frac{a}{V_m^2} \right) dV = -\int_{V_i}^{V_f} \left(\frac{R T}{V_m - b} \right) dV + \int_{V_i}^{V_f} \left(-\frac{a}{V_m^2} \right) dV$$

The first integral can be solved by substituting $y = V_m - b$:

$$-\int_{V_i}^{V_f} \left(\frac{R T}{V_m - b} \right) dV = -\int_{y_i}^{y_f} \left(\frac{R T}{y} \right) dy = -R T [\ln(V_f + b) - \ln(V_i + b)]$$

Therefore, the work is given by:

$$\begin{aligned} w_{\text{reversible}} &= -n R T \ln\left(\frac{(V_f - b)}{(V_i - b)}\right) + a \left(\frac{1}{V_i} - \frac{1}{V_f} \right) \\ &= -(1.0 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \times \ln\left(\frac{(23.0 \text{ L} - 0.0380 \text{ L})}{(2.50 \text{ L} - 0.0380 \text{ L})}\right) \\ &\quad + (1.366 \text{ L}^2 \text{ bar}) \times \frac{(10^5 \text{ Pa})}{(1 \text{ bar})} \times (10^{-6} \text{ m}^6 \text{ L}^2) \times \left(\frac{1}{(2.50 \times 10^{-3} \text{ m}^3)} - \frac{1}{(23.0 \times 10^{-3} \text{ m}^3)} \right) = \underline{-5.52 \times 10^3 \text{ J}} \end{aligned}$$

And the percent error is:

$$\text{percent error} = 100 \times \frac{\{(-5.52 \times 10^3 \text{ J}) - (-5.54 \times 10^3 \text{ J})\}}{(-5.52 \times 10^3 \text{ J})} = \underline{-0.4\%}$$

P2.44) One mole of an ideal gas, for which $C_{V,m} = 3/2R$, is subjected to two successive changes in state: (1) From 25.0°C and $100. \times 10^3 \text{ Pa}$, the gas is expanded isothermally against a constant pressure of $20.0 \times 10^3 \text{ Pa}$ to twice the initial volume. (2) At the end of the previous process, the gas is cooled at constant volume from 25.0° to -25.0°C . Calculate q , w , ΔU , and ΔH for each of the stages. Also calculate q , w , ΔU , and ΔH for the complete process.

1) For an isothermic expansion against a constant pressure:

$$w = -p_{\text{ext}} \times (V_{\text{final}} - V_{\text{initial}}) = -p_{\text{ext}} \frac{n R T}{p_i}$$

$$w = -(100 \times 10^3 \text{ Pa}) \times \frac{(1.0 \text{ mol}) \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{(100 \times 10^3 \text{ Pa})} = \underline{-495.8 \text{ J}}$$

$\Delta H = \Delta U = 0$, since process is isothermal

$$q = -w = 495.8 \text{ J}$$

2) For cooling at constant volume:

$w = 0$, since $V = \text{constant}$

$$q = \Delta U = C_v \Delta T = \frac{3}{2} (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (50.0 \text{ K}) \times (1.0 \text{ mol}) = \underline{-623.6 \text{ J}}$$

$$\Delta H = -C_p \Delta T = -(n R + \frac{3}{2} n R) \Delta T = \frac{5}{2} n R = \frac{5}{2} \times (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1.0 \text{ mol}) \times (50.0 \text{ K}) = \underline{-1039.3 \text{ J}}$$

For the overall process:

$$w_{\text{tot}} = w_1 + w_2 = \underline{-495.8 \text{ J}}$$

$$q_{\text{tot}} = q_1 + q_2 = 495.8 \text{ J} - 623.6 \text{ J} = \underline{-127.8 \text{ J}}$$

$$\Delta U_{\text{tot}} = \Delta U_1 + \Delta U_2 = \underline{623.6 \text{ J}}$$

$$\Delta H_{\text{tot}} = \Delta H_1 + \Delta H_2 = \underline{-1039.3 \text{ J}}$$

P2.45) The adhesion of leukocytes (white blood cells) to target cells is a crucial aspect of the body's immune system. The force required to detach leukocytes from a substrate can be measured with an atomic force microscope (AFM). The work of de-adhesion is proportional to the cell-substrate contact area A_c , which in turn is related to Young's modulus, the force F applied to

the cell by the AFM, and the radius R of the cell by $A_c = \pi \times \left(\frac{RF}{E} \right)^{2/3}$. Assuming $R = 5.00 \times$

10^{-6} m and $F = 2.00 \times 10^{-7} \text{ N}$, calculate the change in contact area when Young's modulus is re-

duced from 1.40 to 0.30 kPa. By what amount does the work of de-adhesion change when

Young's modulus is changed from 1.40 to 0.30 kPa? Explain this effect.

The difference in contact area is:

$$\Delta A_c = \left| \pi \left(\frac{R F}{E_1} \right)^{\frac{2}{3}} - \pi \left(\frac{R F}{E_2} \right)^{\frac{2}{3}} \right| = \left| \pi \left(\frac{(5.00 \times 10^{-6} \text{ m}) \times (2.00 \times 10^{-7} \text{ N})}{(1400 \text{ Pa})} \right)^{\frac{2}{3}} - \pi \left(\frac{(5.00 \times 10^{-6} \text{ m}) \times (2.00 \times 10^{-7} \text{ N})}{(300 \text{ Pa})} \right)^{\frac{2}{3}} \right|$$

$$= \left| (2.51 \times 10^{-10} \text{ m}^2) - (7.01 \times 10^{-10} \text{ m}^2) \right| = \underline{4.50 \times 10^{-10} \text{ m}^2}$$

Since the work is proportional the cell-substrate area, the work ratio is the ratio of the two areas:

$$\frac{F_2}{F_1} = \frac{(7.01 \times 10^{-10} \text{ m}^2)}{(2.51 \times 10^{-10} \text{ m}^2)} = \underline{2.78}$$