

Answers to HW 5#

- 12.4** For a parcel of falling water of mass m under the stated assumptions

$$-mg\Delta h = c_s m \Delta T$$

The m cancels out. Express c_s in $\text{J K}^{-1}\text{kg}^{-1}$ so that the units will work out correctly:

$$-(9.81 \text{ m s}^{-2})(-100 \text{ m}) = (4180 \text{ J K}^{-1}\text{kg}^{-1}) \Delta T \quad \text{from which} \quad \Delta T = +0.235 \text{ K}$$

- 12.12** Assume that the water and zinc are thermally isolated from the rest of the world. Then,

$$q_{\text{water}} + q_{\text{zinc}} = 0$$

$$(c_{s,\text{water}} m_{\text{water}} \Delta t_{\text{water}}) + (c_{s,\text{zinc}} m_{\text{zinc}} \Delta t_{\text{zinc}}) = 0$$

The Δt of the zinc is $(t_f - 20.0)^\circ\text{C}$ and the Δt of the water is $(t_f - 100.0)^\circ\text{C}$. Substitute the given specific heat capacities,¹ the masses, and the temperature changes into this equation

$$(4.22 \text{ J } (^\circ\text{C})^{-1} \text{ g}^{-1})(200.0 \text{ g})(t_f - 100.0^\circ\text{C}) + (0.389 \text{ J } (^\circ\text{C})^{-1} \text{ g}^{-1})(60.0 \text{ g})(t_f - 20.0^\circ\text{C}) = 0$$

Solving gives $t_f = 97.8^\circ\text{C}$.

- 12.19** a) The statement of the problem gives the initial amount (2.00 mol), pressure (3.00 atm), and temperature (350 K) of the ideal monatomic gas. The initial volume of the gas is $V = nRT/P = 19.15 \text{ L}$. The final volume is *twice* this original volume or **38.3 L**. The change in volume ΔV is $38.30 - 19.15 = 19.15 \text{ L}$.

b) The adiabatic expansion occurs against a *constant* pressure of 1.00 atm. Under that circumstance, the work done on the gas is

$$w = -P\Delta V = -1.00(19.15) \text{ L atm} \times \left(\frac{101.325 \text{ J}}{1 \text{ L atm}} \right) = \boxed{-1.94 \times 10^3 \text{ J}}$$

The expansion is adiabatic so **$q = 0$** by definition, and

$$\Delta U = q + w = 0 - 1.94 \times 10^3 \text{ J} = \boxed{-1.94 \times 10^3 \text{ J}}$$

c) Any change in the internal energy of an ideal gas causes a change in temperature in direct proportion

$$\Delta U = nc_v \Delta T$$

Solve for ΔT and substitute the various values

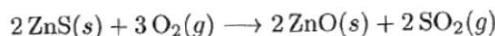
$$\Delta T = \frac{\Delta U}{nc_v} = \frac{-1.94 \times 10^3 \text{ J}}{2.00 \text{ mol} (3/2) 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} = -77.8 \text{ K}$$

Thus, T_2 , the final temperature, is $T_1 + \Delta T = 350 + (-77.8) = \boxed{272 \text{ K}}$.

12.26 (a) $\Delta H = n C_p \Delta T = 5.08 \text{ kJ}$

(b) $\Delta H = n C_p \Delta T = 0.662 \text{ kJ}$

12.41 a) As in problem 12.39



$$\Delta H^\circ = 2 \underbrace{(-348.28)}_{\text{ZnO}(s)} + 2 \underbrace{(-296.83)}_{\text{SO}_2(g)} - 2 \underbrace{(-205.98)}_{\text{ZnS}(s)} - 3 \underbrace{(0)}_{\text{O}_2(g)} = \boxed{-878.26 \text{ kJ}}$$

b) Compute the chemical amount of ZnS (in moles) and multiply it by the molar ΔH° to get the amount of heat absorbed in the roasting of the 3.00 metric tons of ZnS. It is known that 2 mol of ZnS(s) has a ΔH° of -878.26 kJ . Hence

$$q_p = \Delta H^\circ = 3.00 \text{ ton ZnS} \times \left(\frac{10^6 \text{ g}}{\text{ton}} \right) \left(\frac{1 \text{ mol}}{97.456 \text{ g}} \right) \left(\frac{-878.26 \text{ kJ}}{2 \text{ mol ZnS}} \right) = \boxed{-1.35 \times 10^7 \text{ kJ}}$$

12.57 During any adiabatic process $q = 0$. During this *reversible* adiabatic expansion of an ideal gas

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

where γ is c_p/c_v and the subscripts refer to the initial and final states of the gas. In this problem, V_1 is 20.0 L, V_2 is 60.0 L, γ is 5/3, and T_1 is 300 K. Solving for T_2 and substituting gives

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = (300 \text{ K}) \left(\frac{20.0 \text{ L}}{60.0 \text{ L}} \right)^{5/3-3/3} = 300 \left(\frac{20.0 \text{ L}}{60.0 \text{ L}} \right)^{2/3} \text{ K} = 144.22 \text{ K} = \boxed{144 \text{ K}}$$

Meanwhile, the ΔU of an ideal gas in any process depends solely on the change in its temperature

$$\Delta U = n c_v \Delta T = (2.00 \text{ mol}) \left(\frac{3}{2} 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \right) (-155.78 \text{ K}) = \boxed{-3.89 \text{ kJ}}$$

This number also equals w , the work done on the gas, because $\Delta U = q + w$ and q is zero in this adiabatic process. Finally, ΔH of an ideal gas also depends entirely on ΔT

$$\Delta H = n c_p \Delta T = (2.00 \text{ mol}) \left(\frac{5}{2} 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \right) (-155.78 \text{ K}) = \boxed{-6.48 \text{ kJ}}$$

12.67 a) The system is the 2.00 mol of argon gas. The work done *on* the system is $-P\Delta V$. Since the gas is ideal and P is constant, $P\Delta V = nR\Delta T$ for the system. In this case ΔT is given as -100 K . Then

$$w = -nR\Delta T = -(2.00 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(-100 \text{ K}) = \boxed{+1.66 \times 10^3 \text{ J}}$$

b) The process goes on at constant pressure so the heat absorbed is q_p

$$q_p = n c_p \Delta T = (2.00 \text{ mol}) \left(\frac{5}{2} 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \right) (-100 \text{ K}) = \boxed{-4.16 \times 10^3 \text{ J}}$$

c) Use the first law of thermodynamics: $\Delta U = q + w = -4157 + 1663 = -2494 \text{ J}$. This rounds off to $\boxed{-2.49 \text{ kJ}}$. Note the use of un-rounded answers from parts a) and b) in the addition.

d) The ΔH of a system during a change always equals q_p . Hence, ΔH is $\boxed{-4.16 \text{ kJ}}$.

- 12.81 a) The gases trapped inside the cylinder of the “one-lung” engine have volume V_1 when the piston is fully withdrawn but a smaller volume V_2 when the piston is thrust home. The compression ratio is 8 : 1 so $V_1 = 8V_2$. The area of the base of the engine’s cylinder is πr^2 , where r is the radius of the base. The volume of a cylinder is the area of its base times its height h

$$V_1 = Ah \quad \text{and} \quad V_2 = A(h - 12.00 \text{ cm})$$

which employs the (given) fact that full compression shortens h by 12.00 cm. Because r is 5.00 cm, the area A is 78.54 cm². Substituting for V_1 and V_2 in terms of A and h gives

$$Ah = 8A(h - 12.00 \text{ cm})$$

The A ’s cancel, allowing solution for h . The result is 13.714 cm. Once h is known, it is easy to compute V_1 and V_2 , which equal 1.077 L and 0.1347 L respectively.

The temperature and pressure of the air-fuel mixture are 353 K (80°C) and 1.00 atm when the mixture enters the cylinder with fully withdrawn piston (V_1). Assuming the air-fuel mixture is an ideal gas

$$n_{\text{mixture}} = \frac{(1.00 \text{ atm})(1.077 \text{ L})}{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(353 \text{ K})} = 0.0372 \text{ mol}$$

The molar ratio of air to fuel (C_8H_{18}) is 62.5 to 1, so $n_{\text{air}} = 62.5 n_{\text{fuel}}$. and it follows that at the start the cylinder contains 0.0366 mol of air and 5.86×10^{-4} mol of octane fuel.

During the compression stroke, the system undergoes an irreversible adiabatic compression to one-eighth of its initial volume. None of the relationships that govern *reversible* adiabatic processes applies. Assume however, as advised in the problem, that the compression is near to reversible. If it is, and if the mixture of gases in the cylinder is approximately ideal, then

$$T_1 V_1^{\gamma-1} \approx T_2 V_2^{\gamma-1} \quad \text{where } \gamma = \frac{c_p}{c_v} = \frac{c_p}{c_p - R} = \frac{35 \text{ J K}^{-1}\text{mol}^{-1}}{(35 - 8.315) \text{ J K}^{-1}\text{mol}^{-1}} = 1.31$$

The temperature after the compression stroke is

$$T_2 \approx T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = (353 \text{ K}) \left(\frac{1.077 \text{ L}}{0.1347 \text{ L}} \right)^{0.31} = (353 \text{ K})(8)^{0.31} = \boxed{673 \text{ K}}$$

- b) The compressed gases occupy a volume of $\boxed{0.135 \text{ L}}$ just before they are ignited, as calculated above.

- c) The pressure of the compressed air-fuel mixture just before ignition is P_2 . Compute it by applying the ideal-gas equation to the system with $T_2 = 673 \text{ K}$, $V_2 = 0.1347 \text{ L}$, and $n = 0.0372 \text{ mol}$.

$$P_2 \approx \frac{nRT_2}{V_2} = \frac{0.0372 \text{ mol}(0.082057 \text{ L atm mol}^{-1}\text{K}^{-1})(673 \text{ K})}{0.1347 \text{ L}} = \boxed{15.3 \text{ atm}}$$

Alternatively, estimate P_2 using the formula for a reversible adiabatic change

$$P_2 \approx P_1 \left(\frac{V_1}{V_2} \right)^{\gamma} = 1.00 \text{ atm} \left(\frac{1.077}{0.1347} \right)^{1.31} = \boxed{15.3 \text{ atm}}$$

(d)

According to the problem, the system does not change its volume during the actual combustion of the fuel, so w is zero. Furthermore, q is zero (the combustion happens so fast that there is no time for heat to be lost or gained). Since w and q both equal zero, ΔU of the system equals zero, by the first law of thermodynamics. Imagine the combustion to occur in two stages: a : the reaction goes at a constant temperature of 600 K; b : the product gases heat up at constant volume. The sum of these two changes is the overall change within the cylinder during combustion. Therefore

$$\Delta U_{\text{sys}} = 0 = \Delta U_a + \Delta U_b \quad \text{which means} \quad \Delta U_a = -\Delta U_b$$

The problem offers data pertaining to enthalpy changes, not energy changes, in the two steps. Deal with this by substituting for the ΔU_a and ΔU_b in terms of ΔH 's:

$$\Delta H_a - \Delta(PV)_a = -(\Delta H_b - \Delta(PV)_b)$$

Step a involves ideal gases, takes place at a constant temperature, and involves change in the chemical amount of gas. Therefore $\Delta(PV)_a$ equals $\Delta n_g RT$, where Δn_g is the change in the chemical amount of gases during the combustion reaction (step a). Step b is the quick after-the-reaction heating of the ideal gases inside the cylinder that goes on, according to the story of the problem, before any expansion or loss of heat by conduction to the outside. The term $\Delta(PV)_b$ therefore equals $n_{\text{after}} R \Delta T$ where " n_{after} " specifies the chemical amount of gases present after the reaction. Finally, for the change in temperature that comprises step b , ΔH_b is equal to $n_{\text{after}} c_p \Delta T$, just as in text equation 12.11, as long as the molar heat capacity c_p is independent of temperature, which it is under the assumption of ideality. Inserting these three relations into the preceding equation gives

$$\Delta H_a - \Delta n_g RT = -(n_{\text{after}} c_p \Delta T - n_{\text{after}} R \Delta T)$$

The octane burns according to



$$\underbrace{\Delta H_{600}^\circ}_{\text{(combustion)}} = 9 \underbrace{(-241.8)}_{\text{H}_2\text{O}(g)} + 8 \underbrace{(-393.5)}_{\text{CO}_2(g)} - 1 \underbrace{(-57.4)}_{\text{octane}(g)} - 12.5 \underbrace{(0.00)}_{\text{O}_2(g)} = -5266.8 \text{ kJ mol}^{-1}$$

$$\Delta H_a = \left(\frac{-5266.8 \text{ kJ}}{1 \text{ mol}} \right) \times (5.86 \times 10^{-4} \text{ mol}) = -3.09 \text{ kJ}$$

$$\Delta T = \frac{\Delta H_a - \Delta n_g RT}{nR - n c_p}$$

$$\Delta T = \frac{-3090 \text{ J} - (0.002051 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(673 \text{ K})}{(0.0393 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) - (0.0393 \text{ mol})(35 \text{ J K}^{-1} \text{ mol}^{-1})} = 2960 \text{ K}$$

The temperature inside the cylinder rises by 2960 K to a maximum of 3630 K.

e) Assume that the expansion stroke is not only adiabatic but reversible. Then the formula

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

applies. In this case, T_1 is 3630 K. The ratio V_1/V_2 is 1 to 8 because now the initial state is the *small* volume state just before the expansion stroke of the piston. The exponent $\gamma - 1$ is still 0.31, as previously established. Substituting gives

$$T_2 = (3\,630\text{ K}) \left(\frac{1}{8} \right)^{0.31} = \boxed{1\,900\text{ K}}$$

This is the temperature of the exhaust gases.