Chapter 19, example problems:

- (19.06) A gas undergoes two processes. First: constant volume @ 0.200 m^3 , isochoric. Pressure increases from 2.00×10^5 Pa to 5.00×10^5 Pa. Second: Constant pressure @ 5.00×10^5 Pa, isobaric. Volume compressed from 0.200 m^3 to 0.120 m^3 .
 - $(10^5 \, \text{Pa})$ (a) Show both processes in a pV diagram: (b) $W_{a \rightarrow b} = 0$, 5.00 b $W_{\rm b\to c} = p \,\Delta V$ (for isobaric processes) = $5.00 \times 10^5 \text{ N/m}^2 \times (0.120 \text{ m}^3 - 0.200 \text{ m}^3)$, $= -4.00 \times 10^4$ J. а 2.00 $\therefore W_{\text{total}} = W_{a \rightarrow b} + W_{b \rightarrow c}$ $= -4.00 \times 10^4$ J. $V(m^3)$ 0.120 0.200 (Note: $\Delta V = V_{\text{final}} - V_{\text{initial}}$)
- (19.08) Bicycle tire pump. Nozzle closed off. Slowly depress plunger until $V \rightarrow V/2$. Assume air is an ideal gas. Temperature T = constant.
 - (a) Work positive or negative? Volume reduced while pressure increased (at constant *T*). $W = \int p \, dV$ is <u>negative</u>. That is, to compress the gas isothermally, work must be done to the gas.
 - (b) Heat flow positive or negative? $Q = \Delta U + W$. Here $\Delta U = 0$ since *T* is not changed. So Q = W is also <u>negative</u>. That is, for isothermal compression, <u>heat</u> <u>must flow out of the system</u> (into a thermal reservoir, which is so large that it can absorb quite an amount of heat without raising its temperature appreciably). If heat is not allowed to flow out (by using some thermal insulation), then it is called an adiabatic compression. ΔU must then be positive, so that *Q* can be zero. The temperature of the system must therefore go up. The pressure of the system must also rise more than that of the corresponding isothermal compression by the same ΔV .
 - (c) Relative magnitudes of the heat flow and the work: They are equal, because $\Delta U = 0$ when T does not change. (For an ideal gas, U depends on T only).
- (19.12) A gas in a cylinder. Held @ constant pressure 2.30×10^5 N/m². Cooled and Compressed from 1.70 m³ to 1.20 m³. Internal energy decreases by 1.40×10^5 J.
 - (a) Work done $W = 2.30 \times 10^5 \text{ N/m}^2 \times (1.20 \text{ m}^3 1.70 \text{ m}^3) = -1.15 \times 10^5 \text{ J}.$
 - (b) $Q = \Delta U + W = (-1.40 \times 10^5 \text{ J}) + (-1.15 \times 10^5 \text{ J}) = -2.55 \times 10^5 \text{ J}.$ That is, $2.55 \times 10^5 \text{ J}$ of heat must flow <u>out of the system</u> to the environment. [Note: For *Q*, flowing in is positive. For *W*, coming out (doing work to the environment) is positive.]
 - (c) The gas does not have to be ideal, since the ideal gas law has not been used, and we also did not use the fact that U is a function of T alone.

- (19.22) Cylinder contains 0.0100 mol of helium at T = 27.0 °C.
 - (a) To raise the temperature to 67.0 °C, keeping the volume constant, the heat needed is $Q = nC_V\Delta T$. $C_V = (3/2)R$ for monatomic helium gas. Therefore $Q = 0.0100 \text{ mol} \times (3/2) \times 8.314 \text{ J/mol} \cdot \text{K} \times 40 \text{ K} = 4.988 \text{ J}.$ [Note: ΔT in K is the same as ΔT in °C.]
 - (b) To raise the temperature to 67.0 °C, keeping the pressure constant, the heat needed is $Q = nC_p\Delta T$. $C_p = (5/2)R$ for monatomic helium gas. Therefore $Q = 0.0100 \text{ mol} \times (5/2) \times 8.314 \text{ J/mol} \cdot \text{K} \times 40 \text{ K} = \underline{8.314 \text{ J}}.$



- (c) The difference 8.314 J 4.988 J = 3.326 J is due to $W = p \Delta V$ (for isobaric processes) = $p(V_{\text{final}} V_{\text{initial}}) = nR(T_{\text{final}} T_{\text{initial}})$ = 0.0100 mol × 8.314 J/mol·K × 40 K = <u>3.326 J</u>. <u>More heat is required in the case when the pressure is kept constant</u>, since then the volume will increase as the temperature is raised, and therefore the system will do work to the environment.
- (d) The gas is ideal. The change in U is the same as the Q at constant volume, and is equal to 4.988 J, because W = 0 in this case. Because ΔU is path (process) independent, so the same change of U also happens in the case when the pressure is kept constant. This is because $\Delta U = U_{\text{final}} U_{\text{initial}}$ depends only on the initial and final temperatures. (For an ideal gas, U depends only on T.) If you calculate ΔU using the formula $\Delta U = Q W$ for the isobaric process, you get the same answer, namely 8.314 J 3.326 J = 4.988 J. You can also use the formula U = (3/2)RT to calculate ΔU for a monatomic gas, and get the same answer.
- (19.38) Cylinder containing 0.100 mol of an ideal monatomic gas. Initially, $p = 1.00 \times 10^5$ Pa, and $V = 2.50 \times 10^{-3}$ m³.
 - (a) Initial absolute temperature T = pV/nR= 1.00 × 10⁵ N/m² × 2.50 × 10⁻³ m³/ 0.100 mol × 8.314 J/mol·K = <u>300.7 K</u>.
 - (b) $V \rightarrow 2V$.
 - (i) Isothermal. $T_{\text{final}} = T_{\text{initial}} = \underline{300.7 \text{ K}}. \ p_{\text{final}} = p_{\text{initial}} / 2 = \underline{0.50 \times 10^5 \text{ Pa.}}$
 - (ii) Isobaric. $T_{\text{final}} = 2T_{\text{initial}} = \underline{601.4 \text{ K}}$. $p_{\text{final}} = p_{\text{initial}} = \underline{1.00 \times 10^5 \text{ Pa}}$.
 - (iii) Adiabatic. $p_{\text{initial}} V_{\text{initial}} \gamma = p_{\text{final}} V_{\text{final}} \gamma$. $\gamma = 5/3$ for a monatomic gas. $\therefore p_{\text{final}} = p_{\text{initial}} (V_{\text{initial}} / V_{\text{final}})^{\gamma} = 1.00 \times 10^5 \text{ Pa} \times (1/2)^{5/3} = 0.315 \times 10^5 \text{ Pa}.$ $T_{\text{final}} = pV/nR$ $= 0.315 \times 10^5 \text{ Pa} \times 5.00 \times 10^{-3} \text{ m}^3 / 0.100 \text{ mol} \times 8.314 \text{ J/mol} \cdot \text{K} = 189.4 \text{ K}.$ (You can also calculate T_{final} using the formula $T_{\text{initial}} V_{\text{initial}} \gamma^{-1} = T_{\text{final}} V_{\text{final}} \gamma^{-1}$, and obtain $T_{\text{final}} = T_{\text{initial}} (V_{\text{initial}} / V_{\text{final}})^{\gamma-1} = 300.7 \text{ K} \times (1/2)^{2/3} = 189.4 \text{ K}.$)



(b) $w_{\text{total}} = w_{a \to b} + w_{b \to c} = 3.0 \times 10^{-10} \text{ N/m}^2 \times 0.001 \text{ m}^3 + 2.0 \times 10^5 \text{ N/m}^2 \times 0.001 \text{ m}^3$ = <u>500 J.</u> (c) $T_{\text{initial}} = T_a = 4.0 \times 10^5 \text{ N/m}^2 \times 0.002 \text{ m}^3/$



 $0.5 \text{ mol} \times 8.314 \text{ J/mol} \cdot \text{K} = 192.4 \text{ K}.$

Thus $\Delta U = 0$ between the state *a* and the state *c*, and therefore Q = W = 500 J for this composite process. This heat *Q* is positive, and is therefore flowing into the system.

(Note that we can not calculate $Q_{a\to b}$ or $Q_{b\to c}$ here, since we do not know what type of ideal gas is involved here (monatomic, or diatomic, or polyatomic), and the process ab is not any of the known process. But we do know that $Q_{a\to b\to c} = Q_{a\to b} + Q_{b\to c}$. If we were given that the ideal gas is monatomic or diatomic, we would be able to calculate $Q_{b\to c}$. Then $Q_{a\to b}$ would follow from $Q_{a\to b\to c} - Q_{b\to c}$. But we still cannot calculate $Q_{a\to b}$ directly.)



(Another way to do $W_{c\to b}$ is to use the formulas $pV^{\gamma} = p_c V_c^{\gamma} = p_b V_b^{\gamma}$ for an adiabatic process, and obtain

$$W = \int_{V_c} {}^{V_b} p dV = p_c V_c^{\gamma} \int_{V_c} {}^{V_b} dV / V^{\gamma} = p_c V_c^{\gamma} (V_b^{-\gamma+1} - V_c^{-\gamma+1}) / (-\gamma+1)$$

= $(p_c V_c - p_b V_b) / (\gamma - 1) = nR (T_c - T_b) / (\gamma - 1)$
= $3 \text{ mol} \times 8.314 \text{ J/mol} \cdot \text{K} \times (492 \text{ K} - 600 \text{ K}) / (1.40 - 1.00)$
= -6734 J . (That we did not get -6735 J as above is because the given C_p =

29.1 J/mol·K does not have four-significant-digits accuracy. Since this second approach does not need C_p it is actually more accurate if *n* and the temperatures given are exact.)

[Note that we have used $\gamma = C_p / C_V = C_p / (C_p - R)$.]

- (19.54) Thermodynamic process in a solid. Cu cube, 2.00 cm on a side. Suspended by a string. (data on Table 14.1, 17.2, 17.3) Heated from 20.0 °C to 90.0 °C. $p = 1 \text{ atm} = 1.01 \times 10^5 \text{ N/m}^2$.
 - (a) $\Delta V = ? \beta = 5.10 \times 10^{-5} (^{\circ}\text{C})^{-1}.$ $\Delta V = \beta \Delta T V_0 = 5.10 \times 10^{-5} (^{\circ}\text{C})^{-1} \times (90.0 \ ^{\circ}\text{C} - 20.0 \ ^{\circ}\text{C}) \times (0.02 \ \text{m})^3$ $= 2.856 \times 10^{-8} \ \text{m}^3.$
 - (b) $W = p \Delta V$ (for isobaric processes) = $1.01 \times 10^5 \text{ N/m}^2 \times 2.856 \times 10^{-8} \text{ m}^3$ = $2.88 \times 10^{-3} \text{ J}$. $Q = mc \Delta T = (\rho V_0) c \Delta T$ = $[8.90 \times 10^3 \text{ kg/m}^3 \times (0.02 \text{ m})^3] \times 390 \text{ J/kg} \cdot ^{\circ}\text{C} \times 70 \text{ }^{\circ}\text{C} = 1943.8 \text{ J}$.
 - (c) $\Delta U = Q W \cong 1943.8 \text{ J}$
 - (d) This result shows that c_p and c_V are practically the same for a solid because the volume change under constant pressure as temperature is changed is too small to be important (because β is in general very small). Thus isochoric and isobaric processes practically involve the same Q if the temperature change is the same. This is very different from the behavior of a gas, for which $C_p = C_V + R$ is true, which is equivalent to $c_p = c_V + R/M$. Note that in this respect the behaviors of liquid and solid are similar.
- (19.62) System with piston containing 0.250 mol of $O_2 @ 2.40 \times 10^5 \text{ N/m}^2$ and 355 K. Treat O_2 as ideal gas. First expands isobarically to $2V_0$ (from V_0). It is then compressed isothermally back to V_0 . Finally it is cooled isochorically back to p_0 .
 - (a) Show all processes in a *pV* diagram: Isobaric expansion: $a \rightarrow b$ Volume increased from V_0 to $2V_0$, Temperature increased. $T_b > T_a$ (= 355 K). Isothermal compression: $b \rightarrow c$ Volume reduced from $2V_0$ back to V_0 , Temperature stays constant. $T_c = T_b > T_a$. Isochoric cooling: $c \rightarrow a$ Temperature drops back to $T_a = 355$ K.
 - (b) $\underline{T_b} = 2 T_a = \underline{710 \text{ K}}. \ \underline{T_c} = T_b = \underline{710 \text{ K}}.$
 - (c) $p_{\text{max}} = p_c = 2 p_a = \frac{4.80 \times 10^5 \text{ N/m}^2}{4.80 \times 10^5 \text{ Pa}}.$



(d) $W_{\text{cycle}} = W_{a \to b} + W_{b \to c}$ $(W_{c \to a} = 0.)$ $W_{a \to b} = p_0 \times (2V_0 - V_0) = p_a \times V_a = nRT_a = 0.250 \text{ mol} \times 8.314 \text{ J/mol} \cdot \text{K} \times 355 \text{ K}$ = 737.9 J $W_{construction} = \int_{-\infty}^{-V_c} p(V_c) dV = nRT_c \int_{-\infty}^{-V_c} (1/V_c) dV = nRT_c \ln (V_c / V_c)$

$$W_{b \to c} = \int_{V_b} V_b p(V) \, dV = nRT_b J_{V_b} (1/V) \, dV = nRT_b \ln (V_c / V_b)$$

= 0.250 mol × 8.314 J/mol·K × 710 K ln (1/2) = -1022.9 J
$$W_{cycle} = 737.9 \text{ J} - 1022.9 \text{ J} = -285.0 \text{ J}.$$

- (19.64) System with piston containing 0.150 mol of N₂ @ 1.80×10^5 N/m² and 300 K. Treat N₂ as ideal gas. First compressed isobarically to (1/2) V₀ (from V₀). It then expands adiabatically to V₀. Finally, it is heated isochorically to original pressure p_0 .
 - (a) Show all processes in a *pV* diagram: Isobaric compression: *a* → *b* Volume dropped from *V*₀ to (1/2)*V*₀, Temperature dropped. Adiabatic expansion: *b* → *c* Volume expanded from (1/2)*V*₀ to *V*₀, <u>Temperature dropped further</u>, Isochoric heating: *c* → *a* Temperature raised back to *T_a* = 300 K.
 - (b) $V \propto T$ @ constant $p. \therefore \underline{T_b} = \underline{150 \text{ K}}.$ $T_b V_b^{\gamma - 1} = T_c V_c^{\gamma - 1}. \quad \gamma = 7/5 \text{ for diatomic}$ gases. $\therefore \underline{T_c} = T_b (V_b / V_c)^{\gamma - 1}$ $= 150 \text{ K} (1/2)^{0.4} = \underline{113.7 \text{ K}}.$



(c)
$$p_{\min} = p_c$$
. But $p_b V_b^{\gamma} = p_c V_c^{\gamma}$. $\therefore \underline{p_c} = p_b (V_b/V_c)^{\gamma} = 1.80 \times 10^5 \text{ N/m}^2 \times (1/2)^{7/5}$
= $6.82 \times 10^5 \text{ N/m}^2$ or $6.821 \times 10^5 \text{ Pa}$.

Note: p_c can also be computed by using $p_c V_c = nRT_c$, or

 $p_c/T_c = nR/V_c = nR/V_a = p_a/T_a = 1.80 \times 10^5 \text{ N/m}^2 / 300 \text{ K}.$

 $\therefore \underline{p_c} = 113.7 \text{ K} \times (1.80 \times 10^5 \text{ N/m}^2 / 300 \text{ K}) = \underline{6.822 \times 10^5 \text{ N/m}^2}.$

The slight difference in the fourth significant digit is because T_c is more accurately_113.68 K. The error is one part in about 6800! This occurs in the fifth significant digit in T_c . Which answer is more accurate? The first one which used $p_b V_b^{\gamma} = p_c V_c^{\gamma}$, so it did not use the calculated T_c . Of course, if one uses the measured value for γ , instead of the theoretical value 7/5, it would be even more accurate.