

Additional Practice Problems: THERMODYNAMICS

9. A system is comprised of 10 g of Ar gas at 0°C and $P = 1\text{atm}$. When 3400 J of heat are added to the system at constant pressure, the resultant reversible expansion causes the system to perform 900 J of work. Calculate (a) the initial state (P,V,T), (b) the final state (P,V,T), and (c) ΔU for the process, if the gas is assumed ideal.

The number of moles of gas is:

$$n = \frac{10\text{g}}{39.95\text{ g mol}^{-1}} = \frac{1}{4}\text{ moles} \quad (1)$$

- (a) Initially, the pressure and temperature are given: $P = 1\text{ atm}$ and $T = 0^\circ\text{C} = 273\text{ K}$. The initial volume is determined from the ideal gas law:

$$V_{\text{initial}} = \frac{nRT}{P} = \frac{(\frac{1}{4}\text{ mol})(0.082057\text{ L atm K}^{-1}\text{ mol}^{-1})(273\text{ K})}{1\text{ atm}} = 5.60\text{ L} \quad (2)$$

- (b) In the final state, the volume and temperature have attained new values,

$$dw = -PdV \quad (3)$$

$$w = -\int PdV = -P \int_{V_{\text{initial}}}^{V_{\text{final}}} dV = -P(V_{\text{final}} - V_{\text{initial}}) \quad (4)$$

$$V_{\text{final}} = \frac{w}{-P} + V_{\text{initial}} = \frac{900\text{ J}}{1\text{ atm}} \frac{0.082057\text{ L atm}}{8.3144\text{ J}} + 5.60\text{ L} \quad (5)$$

$$V_{\text{final}} = 14.5\text{ L} \quad (6)$$

$$(7)$$

Note that the work is negative since the gas did work on the surroundings (the internal energy must be lowered by this process!) Given this change in volume, the temperature is now,

$$T_{\text{final}} = \frac{PV_{\text{final}}}{nR} = \frac{(1\text{ atm})(14.5\text{ L})}{(\frac{1}{4}\text{ mol})(0.082057\text{ L atm K}^{-1}\text{ mol}^{-1})} = 707\text{ K} \quad (8)$$

- (c) To determine the change in internal energy, the first law is applied:

$$dU = dq + dw \quad (9)$$

$$\Delta U = 3400 - 900 = 2500\text{ J} \quad (10)$$

10. Determine the total internal energy change and net heat transferred to one mole of an ideal gas undergoing the 4-step process shown schematically below, in terms of T_1 , T_2 , V_1 , and V_2 .

We know that the internal energy is a state function. This means that its value only depends on its current state and not on the path taken to get to that state. Since we know the starting and end states (they are the same state), we can directly determine the change in internal energy:

$$\Delta U = \int_{initial\,state}^{final\,state} dU = U_{final} - U_{initial} = 0 \quad (11)$$

This is a general result for *any* state function: The change in the value of a state function in a cyclic process (one which begins and ends in the same state) is zero.// Because we know that the change in internal energy for the cycle, we can determine the total heat transfer for the cycle (the cycle is the four-step process). Applying the first law:

$$\Delta U = 0 = q_1 + w_1 + q_2 + q_3 + w_3 + q_4 = 0 \quad (12)$$

$$q_{total} = q_1 + q_2 + q_3 + q_4 = -w_1 - w_3 \quad (13)$$

we have applied the first law to the cycle, and the work in steps 2 and 4 is zero due to constant volume. (Note also that $q_2 = \int c_v dT = c_v(T_2 - T_1) = -q_4$. This information is interesting but not necessary to solve the problem....Here, $c_v = \frac{3}{2}$ is independent of temperature.)

$$w_1 = - \int_{V_1}^{V_2} PdV = - \int_{V_1}^{V_2} \frac{nRT_1}{V} dV = nRT_1 \ln \frac{V_1}{V_2} \quad (14)$$

$$w_3 = - \int_{V_2}^{V_1} PdV = - \int_{V_2}^{V_1} \frac{nRT_2}{V} dV = nRT_2 \ln \frac{V_2}{V_1} \quad (15)$$

$$q_{total} = -(w_1 + w_3) = nR(T_1 - T_2) \ln \frac{V_2}{V_1} = R(T_1 - T_2) \ln \frac{V_2}{V_1} \quad (16)$$

11. Many gases do not obey the ideal gas law, but are better described by another equation of state, known as the Van der Waals equation of state:

$$P + \frac{an^2}{V^2}(V - nb) = nRT$$

Carbon dioxide is described by the Van der Waals equation of state, with parameters $a = 0.3640 (Pa\ m^5\ mol^{-2})$ and $b = 4.267 \times 10^{-5} (m^3\ mol^{-1})$. Compare the work needed to reversibly compress 1 mole of carbon dioxide from 6 L to 2 L at a constant temperature of 298 K using the ideal gas

model vs. the Van der Waals equation of state.

First, if we treat CO₂ as an ideal gas, we have:

$$w = - \int_{V_i}^{V_f} P dV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV = -RT \ln \frac{V_f}{V_i} = RT \ln \frac{V_i}{V_f} = 2721 \text{ J} \quad (17)$$

For the Van der Waals gas, first we re-arrange the equation of state to obtain an expression for the pressure P :

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \quad (18)$$

Then the work can be calculated as:

$$w = - \int_{V_i}^{V_f} P dV = - \int_{V_i}^{V_f} \left(\frac{RT}{V - b} - \frac{a}{V^2} \right) dV = -RT \ln \frac{V_f - b}{V_i - b} + \frac{a}{V_f} - \frac{a}{V_i} = 2636 \text{ J} \quad (19)$$

We see that the Van der Waals equation of state predicts a lower amount of work performed to compress the gas—this arises due to the second term in the pressure: the constant a accounts for Van der Waals attractions (induced dipole-induced dipole) between molecules within the gas, which reduce the pressure relative to that of the ideal gas. Thus, the ideal gas law *overestimates* the amount of work required to compress a gas with weak self-attractive interactions. The constant b in this equation of state accounts for the finite volume of real molecules.