Chemistry 431 Exam Number 1 Fall 2023 Solutions  $R = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$  $R = .08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$  $k = 1.381 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$  $h = 6.626 \times 10^{-34} \text{ Js}$  $N_A = 6.022 \times 10^{23} \text{ molecules mol}^{-1}$ 1 kg = 1000. g $1 \text{ L} = 10^3 \text{ cm}^3$  $10^2 \text{ cm} = 1 \text{ m}$ T = t + 273.15 $0.001 \text{ m}^3 \text{ L}^{-1}$ 

1. Consider the one-dimensional collision between an oxygen atom and a carbon monoxide molecule to form a carbon dioxide molecule in the reaction

$$O_{(g)} + CO_{(g)} \longrightarrow OCO_{(g)}.$$

For the one-dimensional collision where the oxygen atom collides directly with the carbon atom of the diatomic molecule, when the initial velocity of the CO molecule is 0, the change in the vibrational energy of the system from the collision is found to be  $7.521 \times 10^{-21}$  J. Calculate the initial velocity of the oxygen atom. Answer:

$$m_O v_{i,O} = m_{CO_2} v_f$$
  

$$\Delta KE = 7.521 \times 10^{-21} J = \frac{1}{2} m_O v_{i,O}^2 - \frac{1}{2} m_{CO_2} v_f^2$$
  

$$7.521 \times 10^{-21} J = \frac{1}{2} m_O v_{i,O}^2 - \frac{1}{2} m_{CO_2} \left(\frac{m_O v_{O,i}}{m_{CO_2}}\right)^2$$
  

$$= \frac{1}{2} m_O v_{i,O}^2 - \frac{1}{2} \frac{m_{O,i}^2}{m_{CO_2}} v_{O,i}^2$$
  

$$= \frac{1}{2} \left(\frac{10.18 \text{ kg}}{6.022 \times 10^{26}}\right) v_{O,i}^2 \qquad v_{O,i} = 943.2 \text{ m s}^{-1}$$

2. In a two-step process, 2.50 mol of an ideal diatomic gas are initially placed in a cylinder fitted with a frictionless piston where the initial temperature is 298 K and the initial pressure is 2.00 bar. In the first step of the process, the gas is heated at constant pressure until q = 600 J. In the second step, the gas is compressed reversibly and isothermally until the final volume is half the system volume at the end of the first step. Calculate  $q, w, \Delta U$  and  $\Delta H$  for the overall, two-step process.

Answer:

$$\begin{aligned} 600 \ \mathrm{J} &= C_P(T_f - T_i) \\ &= \frac{7}{2} (2.50 \ \mathrm{mol}) (8.3144 \ \mathrm{J} \ \mathrm{mol}^{-1} \mathrm{K}^{-1}) (T_1 - 298 \ \mathrm{K}) \quad T_1 = 306.2 \ \mathrm{K} \\ q_2 &= nRT_1 \ln \frac{1}{2} = (2.50 \ \mathrm{mol}) (8.3144 \ \mathrm{J} \ \mathrm{mol}^{-1} \mathrm{K}^{-1}) (306.2 \ \mathrm{K}) \ln \frac{1}{2} = -4412 \ \mathrm{J} \\ q &= q_1 + q_2 = 600 \ \mathrm{J} - 4412 \ \mathrm{J} = -3812 \ \mathrm{J} \\ \Delta U &= C_V \Delta T = \frac{5}{2} (2.50 \ \mathrm{mol}) (8.3144 \ \mathrm{J} \ \mathrm{mol}^{-1} \mathrm{K}^{-1}) (306.2 \ \mathrm{K} - 298 \ \mathrm{K}) = 426 \ \mathrm{J} \\ \Delta H &= \frac{7}{5} \Delta U = 597 \ \mathrm{J} \\ w &= \Delta U - q = 4238 \ \mathrm{J} \end{aligned}$$

3. Each of two distinct samples of 1.50 moles ideal monatomic gas both at T = 298 K and a pressure of 3.25 bar are labeled samples A and B. Samples A and B are placed in separate cylinders fitted with frictionless pistons. Sample A is allowed to expand adiabatically against a constant external pressure of 1.25 bar until equilibrium is reached. Sample B expands reversibly and adiabatically until its final volume is identical to the final volume of sample A. Calculate  $w_A$  and  $w_B$ , the work done respectively for samples A and B. **Answer**:

Sample A:

$$-P_{ext}\left(\frac{nRT_f}{P_{ext}} - \frac{nRT_i}{P}\right) = C_V(T_f - T_i)$$
  
$$-T_f + \frac{1.25}{3.25}(298 \text{ K}) = \frac{3}{2}(T_f - 298 \text{ K}) \quad T_f = 225 \text{ K}$$
  
$$w_A = \Delta U = C_V \Delta T = \frac{3}{2}(1.50 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(225 \text{ K} - 298 \text{ K}) = -1366 \text{ J}$$

Sample B:

$$V_{f} = \frac{nRT_{f}}{P_{ext}} = \frac{(1.50 \text{ mol})(0.083144 \text{ L bar mol}^{-1}\text{K}^{-1})(225 \text{ K})}{1.25 \text{ bar}} = 22.45 \text{ L}$$

$$V_{i} = \frac{nRT_{i}}{P_{i}} = \frac{(1.50 \text{ mol})(0.083144 \text{ L bar mol}^{-1}\text{K}^{-1})(298 \text{ K})}{3.25 \text{ bar}} = 11.43 \text{ L}$$

$$T_{i}V_{i}^{\gamma-1} = T_{f}V_{f}^{\gamma-1}$$

$$(298 \text{ K})(11.43)^{2/3} = T_{f}(22.45)^{2/3} \quad T_{f} = 190 \text{ K}$$

$$w_{B} = \Delta U = C_{V}\Delta T = \frac{3}{2}(1.50 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(190 \text{ K} - 298 \text{ K}) = -2020 \text{ J}$$



Figure 1: High = 100, Median = 56, Mean = 55