

Chemistry 431
Problem Set 2
Fall 2022
Solutions

1. Two moles of an ideal monatomic gas occupy a cylinder fitted with a piston at 25. °C and 1.0 bar pressure. These initial conditions apply to each of the four problems given below.

- (a) Calculate the work done on the gas if it is compressed isothermally against a constant external pressure of 2.0 bar until equilibrium is reached.

Answer:

$$V_i = \frac{nRT}{P} = \frac{(2 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(298 \text{ K})}{1 \text{ bar}} = 49.55 \text{ L}$$

$$V_f = \frac{nRT}{P} = \frac{(2 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(298 \text{ K})}{2 \text{ bar}} = 24.78 \text{ L}$$

$$w = -P_{ext}\Delta V = -(2 \text{ bar})(24.78 \text{ L} - 49.55 \text{ L}) = 49.55 \text{ L bar}$$

- (b) Calculate q , w , ΔU and ΔH , if the gas temperature is raised to 100.°C at a constant pressure of 1.0 bar.

Answer:

$$q = C_p\Delta T = \frac{5}{2}nR\Delta T$$

$$= \frac{5}{2}(2. \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(100\text{K} - 25\text{K}) = 31.18 \text{ L bar}$$

$$V_f = \frac{nRT}{P} = \frac{(2 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K})(373 \text{ K})}{1 \text{ bar}} = 62.02 \text{ L}$$

$$w = -(1 \text{ bar})(62.02 \text{ L} - 49.55 \text{ L}) = -12.47 \text{ L bar}$$

$$\Delta U = q + w = (31.18 - 12.47) \text{ L bar} = 18.71 \text{ L bar}$$

$$\Delta H = \Delta U + \Delta(pV)$$

$$= 18.71 \text{ L bar} + [1 \text{ bar}(62.02 \text{ L}) - 1 \text{ bar}(49.55 \text{ L})] = 31.18 \text{ L bar}$$

Note $q = \Delta H$ because P is constant.

- (c) Calculate $q, w, \Delta U$ and ΔH if the gas temperature is raised to $100.^\circ\text{C}$ at constant volume.

Answer:

$$\begin{aligned}
 w &= 0 \\
 \Delta U &= q = C_V \Delta T = \frac{3}{2} n R \Delta T \\
 &= \frac{3}{2} (2 \text{ mol}) (0.08314 \text{ L bar mol}^{-1} \text{K}^{-1}) (75 \text{ K}) = 18.71 \text{ L bar} \\
 P_f &= \frac{nRT}{V} = \frac{(2 \text{ mol}) (0.08314 \text{ L bar mol}^{-1} \text{K}^{-1}) (373 \text{ K})}{49.55 \text{ L}} = 1.25 \text{ bar} \\
 \Delta H &= \Delta U + \Delta(PV) \\
 &= 18.71 \text{ L bar} + [(1.25 \text{ bar}) (49.55 \text{ L}) - (1 \text{ bar}) (49.55 \text{ L})] = 31.10 \text{ L bar}
 \end{aligned}$$

- (d) Calculate the work if the gas is expanded isothermally and reversibly to double its volume.

Answer:

$$\begin{aligned}
 w &= - \int P dV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV \\
 &= -nRT \ln \frac{V_f}{V_i} = -nRT \ln 2 \\
 &= -(2 \text{ mol}) (0.08314 \text{ L bar mol}^{-1} \text{K}^{-1}) (298 \text{ K}) \ln 2 = -34.34 \text{ L bar}
 \end{aligned}$$

2. When 2.0 moles of an ideal diatomic gas at 25.0°C are placed in a cylinder fitted with a frictionless piston, the initial volume is found to be 10.0 L. The gas is then expanded at constant pressure until 500.0 J of heat are absorbed from the surroundings. Calculate $w, \Delta U$ and ΔH for the process.

Answer:

$$\begin{aligned}
 q &= \Delta H = C_P \Delta T \\
 \Delta H &= 500.0 \text{ J} = \frac{7}{2} (2.0 \text{ mol}) (8.3144 \text{ J mol}^{-1} \text{K}^{-1}) (T_f - 298 \text{ K}) \\
 T_f &= 307 \text{ K} \\
 \Delta U &= C_V \Delta T = \frac{5}{2} (2.0 \text{ mol}) (8.3144 \text{ J mol}^{-1} \text{K}^{-1}) (307 \text{ K} - 298 \text{ K}) = 374 \text{ J} \\
 w &= \Delta U - q = -126 \text{ J}
 \end{aligned}$$

3. A certain gas obeys the Berthelot equation of state

$$P = \frac{nRT}{V - nb} - \frac{an^2}{TV^2}$$

where a and b are constants. Determine expressions for the work done on the gas if one mole of the gas is expanded

- (a) against a constant external pressure, P_{ext} , from an initial volume V_1 to a final volume V_2 ;

Answer:

$$\begin{aligned} w &= - \int_{V_1}^{V_2} P_{ext} dV \\ &= -P_{ext}(V_2 - V_1) \end{aligned}$$

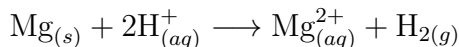
- (b) reversibly and isothermally from a volume V_1 to a volume V_2 .

Answer:

$$\begin{aligned} w &= - \int_{V_1}^{V_2} P dV \\ &= - \int_{V_1}^{V_2} \left[\frac{nRT}{V - nb} - \frac{an^2}{TV^2} \right] dV \\ &= -nRT \ln \left[\frac{V_2 - nb}{V_1 - nb} \right] - \frac{an^2}{T} \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \end{aligned}$$

4. Calculate the work done on the surroundings when 5.0 g of magnesium metal are dissolved in excess hydrochloric acid. Assume the atmospheric pressure is 1.0 bar and the temperature is 25.°C.

Answer:



$$(5.0 \text{ g}) \left(\frac{\text{mol}}{24.32 \text{ g}} \right) = 0.21 \text{ mol}$$

$$w_{surr} = P_{ext} \Delta V$$

$$\Delta V = \frac{RT}{P} \Delta n = \frac{(0.21 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(298\text{K})}{1.0 \text{ bar}} = 5.20 \text{ L}$$

$$w_{surr} = (1 \text{ bar})(5.20 \text{ L}) = 5.20 \text{ L bar}$$

5. One mole of an ideal diatomic gas at 25.°C and 3.0 bar pressure is heated against a constant external pressure of 3.0 bar until 1000. J of work are done on the surroundings. Find the final temperature and calculate q , w , ΔU and ΔH for the process.

Answer:

$$\begin{aligned} w_{surr} &= P \Delta V \\ &= P \left(\frac{nRT_f}{P} - \frac{nRT_i}{P} \right) \\ &= nR(T_f - T_i) \end{aligned}$$

$$1000 \text{ J} = (1 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(T_f - 298 \text{ K})$$

$$T_f = 418 \text{ K}$$

$$q = C_p \Delta T = \frac{7}{2} (1 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(418 \text{ K} - 298 \text{ K}) = 3492 \text{ J}$$

$$\Delta U = q + w = 3492 \text{ J} - 1000 \text{ J} = 2492 \text{ J}$$

$$\Delta H = q = 3492 \text{ J} \quad (\text{Constant pressure process})$$

6. Two moles of an ideal diatomic gas occupy a cylinder at 1.0 bar pressure and have a temperature of 25.°C. If the gas is compressed reversibly and isothermally to 100. bar pressure, calculate $q, w, \Delta U$ and ΔH for the process.

Answer:

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

$$w = - \int_{P_1}^{P_2} P dV$$

$$V = \frac{nRT}{P} \quad dV = -\frac{nRT}{P^2} dP$$

$$w = \int_{P_1}^{P_2} \frac{nRT}{P} dP = nRT \ln \frac{P_2}{P_1}$$

$$= (2 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K}) \ln \frac{100}{1} = 22820 \text{ J}$$

$$q = -w = -22820 \text{ J}$$

7. Two moles of an ideal diatomic gas occupy a cylinder with the same initial conditions as in problem 6. If the gas is compressed isothermally against a constant external pressure of 100. bar until equilibrium is reached, calculate $q, w, \Delta U$ and ΔH for the process. Is $q = \Delta H$? Why or why not?

Answer:

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

$$V_1 = \frac{nRT}{P} = \frac{(2 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(298 \text{ K})}{1 \text{ bar}} = 49.55 \text{ L}$$

$$V_2 = 49.55 \text{ L} \frac{1}{100} = 0.4955 \text{ L}$$

$$w = -P_{ext}\Delta V = -100 \text{ bar}(0.4955 - 49.55) \text{ L} = 4905 \text{ L bar}$$

$$q = -w = -4905 \text{ L bar}$$

Note that $q \neq \Delta H$ because this is not a constant pressure process (only P_{ext} is constant).

8. Two moles of an ideal diatomic gas occupy a cylinder with the same initial conditions as in problem 6. If the gas is heated at constant volume until the final pressure is 2.0 bar, calculate $q, w, \Delta U$ and ΔH for the process.

Answer:

$$T_f = \frac{pV}{nR} = \frac{(2 \text{ bar})(49.55 \text{ L})}{(2 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})} = 596 \text{ K}$$

$$q = \Delta U = C_V\Delta T = \frac{5}{2}(2 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(596\text{K} - 298\text{K}) = 12388 \text{ J}$$

$$w = 0$$

$$\Delta H = C_p \Delta T = \frac{7}{5} \Delta U = 17344 \text{ J}$$

9. Two moles of an ideal diatomic gas occupy a cylinder with the same initial conditions as in problem 6. If the gas is heated to 100°C at constant pressure, calculate q , w , ΔU and ΔH for the process.

Answer:

$$\Delta H = q = C_p \Delta T = \frac{7}{2} (2 \text{ mol})(8.3144 \text{ J mol}^{-1} \text{K}^{-1})(373 \text{ K} - 298 \text{ K}) = 4365 \text{ J}$$

$$\Delta U = C_V \Delta T = \frac{5}{7} \Delta H = 3118 \text{ J}$$

$$w = \Delta U - q = -1247 \text{ J}$$

Note that $q = \Delta H$ because this is a constant pressure process.

10. The initial state of an ideal monatomic gas is defined by a pressure of 3.0 bar, a temperature of 25.0°C and a volume of 16.5 L. Starting from this initial state, the gas is taken through the two step process:

- a constant volume heating to 200.°C
- a constant pressure cooling to 35.0°C.

Calculate q , w , ΔU and ΔH for the overall process.

Answer: *Method 1*

$$w_a = 0 \text{ J}$$

$$q_a = C_V \Delta T = \frac{3}{2} n R \Delta T$$

$$n = \frac{PV}{RT} = \frac{(3 \text{ bar})(16.5 \text{ L})}{(0.08314 \text{ L bar mol}^{-1} \text{K}^{-1})(298 \text{ K})} = 2 \text{ mol}$$

$$q_a = \frac{3}{2} (2 \text{ mol})(8.3144 \text{ J mol}^{-1} \text{K}^{-1})(175 \text{ K}) = 4365 \text{ J}$$

$$q_b = C_P \Delta T = \frac{5}{2} n R \Delta T = \frac{5}{2} (2 \text{ mol})(8.3144 \text{ J mol}^{-1} \text{K}^{-1})(-165 \text{ K}) = -6859 \text{ J}$$

$$w_b = -P \Delta V = -P \left(\frac{nRT_f}{P} - \frac{nRT_i}{P} \right) = -nR \Delta T$$

$$= -(2 \text{ mol})(8.3144 \text{ J mol}^{-1} \text{K}^{-1})(-165 \text{ K}) = 2744 \text{ J}$$

$$q = q_a + q_b = -2494 \text{ J} \quad w = w_a + w_b = 2744 \text{ J}$$

$$\Delta U = q + w = 250 \text{ J}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR \Delta T = 250 \text{ J} + (2 \text{ mol})(8.3144 \text{ J mol}^{-1} \text{K}^{-1})(10 \text{ K}) = 416 \text{ J}$$

Method 2

$$\Delta U = C_V \Delta T = \frac{3}{2} n R \Delta T$$

Using the value of n from Method 1

$$\Delta U = \frac{3}{2} (2 \text{ mol})(8.3144 \text{ J mol}^{-1} \text{K}^{-1})(10 \text{ K}) = 250 \text{ J}$$

$$\Delta H = C_P \Delta T = \frac{5}{2} n R \Delta T = \frac{5}{3} \Delta U = 416 \text{ J}$$

$$w_a = 0$$

$$w_b = w = -P \Delta V = -P \left(\frac{nRT_f}{P} - \frac{nRT_i}{P} \right) = -nR \Delta T$$

$$= -(2 \text{ mol})(8.3144 \text{ J mol}^{-1} \text{K}^{-1})(-165 \text{ K}) = 2744 \text{ J}$$

$$q = \Delta U - w = 250 \text{ J} - 2744 \text{ J} = -2494 \text{ J}$$

11. Two moles of an ideal diatomic gas at an initial pressure of 2.0 bar and a temperature of 25.0°C are compressed isothermally against a constant external pressure of 10.0 bar until equilibrium is reached, followed by a reversible isothermal expansion until the pressure matches the starting pressure of 2.0 bar. Calculate q , w , ΔU and ΔH for the process.

Answer:

The starting state of the system is identical to the final state of the system. Because U and H are state functions

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

$$w_1 = -P_{ext} \Delta V = -P_{ext} \left(\frac{nRT}{P_f} - \frac{nRT}{P_i} \right)$$

$$= -nRT(10 \text{ bar}) \left(\frac{1}{10 \text{ bar}} - \frac{1}{2 \text{ bar}} \right) = 4nRT = 4(2 \text{ mol})(8.3144 \text{ J mol}^{-1} \text{K}^{-1})(298 \text{ K}) = 19822 \text{ J}$$

$$w_2 = nRT \ln \frac{P_2}{P_1} = (2 \text{ mol})(8.3144 \text{ J mol}^{-1} \text{K}^{-1})(298 \text{ K}) \ln \frac{2}{10} = -7975 \text{ J}$$

$$w_{tot} = w_1 + w_2 = 11847 \text{ J}$$

$$q + w = \Delta U = 0$$

$$q = -w = -11847 \text{ J}$$

12. Initially 2.00 moles of an ideal diatomic gas occupy a 30.0 L container at a pressure of 2.05 bar. The gas is first heated at constant pressure to a temperature that is exactly twice the initial temperature. The gas is then compressed isothermally against a constant external pressure of 5.00 bar until the final volume is 28.0 L. Calculate

$q, w, \Delta U$ and ΔH for the overall process.

Answer:

$$T_i = \frac{P_i V_i}{nR} = \frac{(2.05 \text{ bar})(30.0 \text{ L})}{(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(2.00 \text{ mol})} = 370. \text{ K}$$

$$T_2 = 2 \times T_i = 740. \text{ K}$$

$$\Delta U = C_V \Delta T = \frac{5}{2} nR \Delta T = \frac{5}{2} (2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(370. \text{ K}) = 15400 \text{ J}$$

$$\Delta H = \frac{7}{5} \Delta U = 21500 \text{ J}$$

$$\begin{aligned} w_1 = -P \Delta V &= -P \left(\frac{nRT_2}{P} - \frac{nRT_i}{P} \right) = -nR \Delta T = -(2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(370. \text{ K}) \\ &= -6150 \text{ J} \end{aligned}$$

$$V_2 = \frac{nRT_f}{P} = \frac{(2.00 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(740. \text{ K})}{2.05 \text{ bar}} = 60.0 \text{ L}$$

$$w_2 = -P_{ext} \Delta V = -5.00 \text{ bar}(28.0 \text{ L} - 60.0 \text{ L}) \left(\frac{8.3144 \text{ J}}{0.08314 \text{ L bar}} \right) = 16000 \text{ J}$$

$$w = w_1 + w_2 = 9850 \text{ J}$$

$$q = \Delta U - w = 5550 \text{ J}$$

13. When 2.00 moles of an ideal monatomic gas at an initial temperature of 50.0°C are heated at a constant pressure of 10.0 bar, the heat is measured to be $q = 1000. \text{ J}$. Calculate the final temperature of the gas and $w, \Delta U$ and ΔH for the process.

Answer:

$$q = C_P(T_f - T_i)$$

$$1000. \text{ J} = \frac{5}{2} (2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(T_f - 323. \text{ K})$$

$$T_f = 347. \text{ K}$$

$$\begin{aligned} w &= -P(V_f - V_i) = -P \left(\frac{nRT_f}{P} - \frac{nRT_i}{P} \right) = -nR(T_f - T_i) \\ &= -(2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(347. \text{ K} - 323 \text{ K}) = -400. \text{ J} \end{aligned}$$

$$\Delta U = q + w = 600. \text{ J}$$

$$\begin{aligned} \Delta H &= \Delta U + \Delta(PV) = \Delta U + nR \Delta T = 600. \text{ J} + 2(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(347. \text{ K} - 323. \text{ K}) \\ &= 1000. \text{ J} = q \end{aligned}$$

14. The initial state of 3.0 moles of an ideal diatomic gas in a cylinder fitted with a frictionless piston is defined by $T = 298\text{K}$ and $P = 5.0\text{ bar}$. The external pressure is released to 1.0 bar and the gas expands isothermally until equilibrium is reached. The gas is then heated at constant volume until the pressure increases from 1.0 bar to the original pressure of 5.0 bar. Calculate $q, w, \Delta U$ and ΔH for the overall process.

Answer:

$$w_1 = -P_{ext}(V_f - V_i) = -P_{ext} \left(\frac{nRT}{P_f} - \frac{nRT}{P_i} \right)$$

$$= -(1.0\text{ bar})(3.0\text{ mol})(0.08314\text{ L bar mol}^{-1}\text{K}^{-1})(298\text{ K}) \left(\frac{1}{1.0\text{ bar}} - \frac{1}{5.0\text{ bar}} \right) = -59.5\text{ L bar}$$

$$\Delta H_1 = \Delta U_1 = 0 \quad q_1 = -w_1 = 59.5\text{ L bar}$$

$$V_f = \frac{nRT}{P} = \frac{(3.0\text{ mol})(0.08314\text{ L bar mol}^{-1}\text{K}^{-1})(298\text{ K})}{1.0\text{ bar}} = 74.3\text{ L}$$

$$T_f = \frac{P_f V_f}{nR} = \frac{(5.0\text{ bar})(74.3\text{ L})}{(3.0\text{ mol})(0.08314\text{ L bar mol}^{-1}\text{K}^{-1})} = 1489.\text{ K}$$

$$w_2 = 0$$

$$q_2 = C_V \Delta T = \frac{5}{2}(3.0\text{ mol})(0.08314\text{ L bar mol}^{-1}\text{K}^{-1})(1489.\text{ K} - 298.\text{ K}) = 743.\text{ L bar}$$

$$w = w_1 + w_2 = -59.5\text{ L bar} \quad q = q_1 + q_2 = 802\text{ L bar}$$

$$\Delta U = q + w = 743\text{ L bar}$$

$$\Delta H = \Delta U + \Delta PV = \Delta U + nR\Delta T = 743.\text{ L bar}$$

$$+ (3.0\text{ mol})(0.08314\text{ L bar mol}^{-1}\text{K}^{-1})(1489.\text{ K} - 298.\text{ K})$$

$$= 1040.\text{ J}$$

Alternative Solution:

$$w_1 = -P_{ext}(V_f - V_i) = -P_{ext} \left(\frac{nRT}{P_f} - \frac{nRT}{P_i} \right)$$

$$= -(1.0\text{ bar})(3.0\text{ mol})(0.08314\text{ L bar mol}^{-1}\text{K}^{-1})(298\text{ K}) \left(\frac{1}{1.0\text{ bar}} - \frac{1}{5.0\text{ bar}} \right) = -59.5\text{ L bar}$$

$$w_2 = 0 \quad w = -59.5\text{ L bar}$$

$$V_f = \frac{nRT}{P} = \frac{(3.0\text{ mol})(0.08314\text{ L bar mol}^{-1}\text{K}^{-1})(298\text{ K})}{1.0\text{ bar}} = 74.3\text{ L}$$

$$T_f = \frac{P_f V_f}{nR} = \frac{(5.0\text{ bar})(74.3\text{ L})}{(3.0\text{ mol})(0.08314\text{ L bar mol}^{-1}\text{K}^{-1})} = 1489.\text{ K}$$

$$\Delta U = C_V \Delta T = \frac{5}{2}nR\Delta T = \frac{5}{2}(3.0\text{ mol})(0.08314\text{ L bar mol}^{-1}\text{K}^{-1})(1489.\text{ K} - 298.\text{ K}) = 743.\text{ L bar}$$

$$\Delta H = C_P \Delta T = \frac{7}{5}\Delta U = 1040.\text{ L bar}$$

$$q = \Delta U - w = 802\text{ L bar}$$

15. 2.00 moles of an ideal monatomic gas at 25.0° C and a total pressure of 3.50 bar are placed in a cylinder fitted with a frictionless piston, and the gas then expands isothermally against a constant external pressure of 1.00 bar until equilibrium is reached. In a second step the gas is then compressed reversibly and isothermally until the work done on the gas is equal in magnitude and opposite in sign to the work for the gas in the first step. Calculate the final volume after the second step is completed, and calculate ΔU , ΔH , q and w for the overall two-step process.

Answer:

Isothermal, so

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

$$w_1 = -w_2 \quad \text{so that} \quad w_{tot} = 0$$

$$q + w = 0 \quad \text{so that} \quad q = 0$$

$$\begin{aligned} w_1 &= -P_{ext}(V_f - V_i) = -P_{ext} \left(\frac{nRT}{P_{ext}} - \frac{nRT}{P_i} \right) \\ &= -nRT \left(\frac{1}{1.00 \text{ bar}} - \frac{1}{3.50 \text{ bar}} \right) \\ &= -(1.00 \text{ bar})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(298. \text{ K}) \\ &\quad \times \left(\frac{1}{1.00 \text{ bar}} - \frac{1}{3.50 \text{ bar}} \right) \\ &= -35.4 \text{ L bar} \\ 35.4 \text{ L bar} &= -nRT \ln \frac{V_f}{V_i} = -nRT \ln \frac{P_i V_f}{nRT} \\ &= -(2.00 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1}) \\ &\quad \times (298. \text{ K}) \ln \frac{V_f(1.00 \text{ bar})}{(2.00 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(298. \text{ K})} \\ V_f &= 24.2 \text{ L} \end{aligned}$$

16. One mole of an ideal gas is heated at constant pressure of 2.0 bar from 0.°C to 75.°C.

- (a) Calculate the amount of work in the process.

Answer:

$$\begin{aligned} V_i &= \frac{nRT}{P_i} = \frac{(1 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(273 \text{ K})}{2 \text{ bar}} = 11.34 \text{ L} \\ V_f &= \frac{(1 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(348 \text{ K})}{2 \text{ bar}} = 14.47 \text{ L} \\ w &= -P_{ext}\Delta V = -2 \text{ bar}(14.47 \text{ L} - 11.34 \text{ L}) = -6.26 \text{ L bar} \end{aligned}$$

- (b) If the gas were expanded isothermally and reversibly from 2.0 bar to some other pressure, P , at $0.^{\circ}\text{C}$, what must P be if the isothermal reversible work is equal to the work found in part “a?”

Answer:

$$w_{rev} = - \int_{P_i}^P P dV = nRT \int_{P_i}^P \frac{dP}{P} = nRT \ln \frac{P}{P_i}$$

$$\ln \frac{P}{2} = - \frac{6.26 \text{ L bar}}{(1 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(273 \text{ K})} = -0.27$$

$$p = (2 \text{ bar}) \exp(-0.27) = 1.52 \text{ bar}$$

17. A cylinder fitted with a frictionless piston contains 2.00 moles of an ideal diatomic gas at an initial pressure of 3.00 bar and an initial temperature of 298 K. The gas is first compressed reversibly and isothermally until 1000. J of work are done on the system. In a second step the gas is then heated at constant pressure until the final temperature is 398 K. Calculate $q, w, \Delta U$ and ΔH for the two-step process.

Answer:

$$w_1 = 1000. \text{ J} \quad \Delta U_1 = C_V \Delta T = 0 \quad q_1 = -1000. \text{ J}$$

$$q_2 = C_P \Delta T = \frac{7}{2} nR \Delta T = \frac{7}{2} (2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(398 \text{ K} - 298 \text{ K}) = 5820 \text{ J}$$

$$q = q_1 + q_2 = 4820 \text{ J}$$

For the overall process

$$\Delta U = C_V \Delta T = \frac{5}{2} nR \Delta T = \frac{5}{2} (2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(398 \text{ K} - 298 \text{ K}) = 4157 \text{ J}$$

$$w = \Delta U - q = -663. \text{ J}$$

$$\Delta H = C_P \Delta T = 5820 \text{ J}$$

18. A cylinder fitted with a frictionless piston contains 5.00 moles of an ideal diatomic gas at an initial pressure of 2.00 bar and an initial temperature of 298 K. The gas is first compressed isothermally and reversibly until 13610. J of work are done on the system. The gas then expands isothermally against a constant external pressure of 0.500 bar until equilibrium is reached. Calculate $\Delta U, \Delta H, q$ and w for the overall two-step process.

Answer:

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

$$w_1 = nRT \ln \frac{P_1}{P_i} = 13610. \text{ J} = (5.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K}) \ln \frac{P_1}{2.00 \text{ bar}}$$

$$P_1 = 6.00 \text{ bar}$$

$$w_2 = -P_{ext} \left(\frac{nRT}{P_{ext}} - \frac{nRT}{6.00 \text{ bar}} \right) = -0.500 \text{ bar} \left(\frac{nRT}{0.500 \text{ bar}} - \frac{nRT}{6.00 \text{ bar}} \right)$$

$$\begin{aligned}
&= -nRT \left(1 - \frac{1}{12}\right) = -(5.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})(298 \text{ K}) \left(\frac{11}{12}\right) \\
&= -11356 \text{ J} \\
w_{tot} &= w_1 + w_2 = 2254 \text{ J} \\
q_{tot} + w_{tot} &= \Delta U = 0 \quad q_{tot} = -2254 \text{ J}
\end{aligned}$$

19. A sample of an ideal diatomic gas consists of $n = 2.00$ moles at an initial temperature and pressure of $t = 50.^\circ\text{C}$ and $P = 2.00$ bar. The gas is first reversibly and isothermally compressed to a final pressure of 4.00 bar followed by a heating at constant pressure until the work done on the system in the second step is -1200 J. Calculate $q, w, \Delta U$ and ΔH for the two-step process.

Answer:

$$\begin{aligned}
w_1 &= - \int_{P_i}^{P_f} P dV = \int_{P_i}^{P_f} \frac{nRT}{P} dP = nRT \ln \frac{P_f}{P_i} \\
&= (2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(323. \text{ K}) \ln \frac{4.00}{2.00} = 3723 \text{ J} \\
w_2 &= -1200. \text{ J} \quad w = w_1 + w_2 = 2523 \text{ J} \\
w_2 &= -P_{ext}(V_f - V_i) = -P_{ext} \left(\frac{nRT_f}{P_{ext}} - \frac{nRT_i}{P_{ext}} \right) = -nR(T_f - T_i) \\
-1200 \text{ J} &= -(2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(T_f - 323. \text{ K}) \quad T_f = 395. \text{ K} \\
\Delta U &= C_V \Delta T = \frac{5}{2}(2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(395. \text{ K} - 323. \text{ K}) = 2993. \text{ J} \\
q &= \Delta U - w = 470. \text{ J} \\
\Delta H &= C_P \Delta T = \frac{7}{5} \Delta U = 4190. \text{ J}
\end{aligned}$$