Homework Problem Set 4 Solutions

1. One mole of an ideal gas at 25°C is expanded reversibly at constant pressure from 2.0 L to 5.0 L. Determine the amount of work done in Joules.

We start with the basic definition of work,

\[ w = -\int P_{\text{ext}} \, dV. \]

For a reversible process, the external pressure equals the pressure of the gas, \( P_{\text{ext}} = P \), so the expression for the work becomes

\[ w = -\int P \, dV. \]

Since the pressure is constant, we can pull it out of the integral and integrate from \( V_1 \) to \( V_2 \),

\[ w = -P \int_{V_1}^{V_2} dV = -P(V_2 - V_1). \]

In order to evaluate the work done, the pressure must be calculated. We can use the ideal gas equation, along with the initial values of the temperature and volume to determine the pressure,

\[
P = \frac{nRT_1}{V_1} = \frac{(1 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(298.15 \text{ K})}{(2.0 \text{ L})} = 12.394 \text{ bar}.
\]

The work done is then given by

\[ w = -P(V_2 - V_1) = -(12.394 \text{ bar})(5.0 \text{ L} - 2.0 \text{ L}) = -37.18 \text{ L bar}. \]

The units of L-bar may then be converted to Joules,

\[ w = (-37.18 \text{ L bar}) \left( \frac{100 \text{ J}}{1 \text{ L bar}} \right) = -3718 \text{ J}. \]
2. Two moles of $O_2$ gas, initially at 300 K, are expanded at constant volume from 1 atm to 0.02 atm. Determine the volume of the system and the work done in Joules assuming ideal behavior.

The ideal gas equation may be employed to determine the volume of the system,

$$V = \frac{nRT_1}{P_1}$$

$$= \frac{(2 \text{ mol})(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(300 \text{ K})}{(1.0 \text{ atm})}$$

$$V = 49.24 \text{ L}.$$ 

The work is defined as

$$dw = -P_{ext}dV.$$ 

Since the process takes place at constant volume, and therefore $dV = 0$, there is no work done, $w = 0$. 

3. (a) One mole of an ideal gas at 298 K is expanded reversibly and isothermally from 1.0 L to 10 L. Determine the amount of work in Joules.

We start with the basic definition of work,

\[ w = - \int P_{\text{ext}} \, dV. \]

Since the process is reversible, \( P_{\text{ext}} = P \), which gives

\[ w = - \int P \, dV. \]

Substituting the ideal gas equation for \( P \) leads to

\[ w = - \int \frac{nRT}{V} \, dV. \]

Since the process is isothermal, \( T \) can be pulled out of the integral (along with \( n \) and \( R \)) to yield

\[ w = - nRT \int_{V_1}^{V_2} \frac{1}{V} \, dV \]

\[ w = - nRT \ln \left( \frac{V_2}{V_1} \right). \]

Now, we are given the initial and final volumes along with the temperature. Substituting,

\[ w = - nRT \ln \left( \frac{10 \text{ L}}{1.0 \text{ L}} \right) \]

\[ w = - 5704 \text{ J}. \]

Notice that the work is negative, indicating work done by the system on the surroundings during the expansion.

(b) One mole of an ideal gas is expanded irreversibly from 1.0 L to 10.0 L against a constant external pressure of 1.0 atm. Determine the amount of work in Joules.

Again, using the definition of work, we have

\[ w = - \int P_{\text{ext}} \, dV. \]

In this case, the external pressure is constant, so it can be pulled out of the integral,

\[ w = - P_{\text{ext}} \int_{V_1}^{V_2} dV \]

\[ w = - P_{\text{ext}} (V_2 - V_1). \]
3 (b). Continued

Substituting,

\[ w = - P_{\text{eff}} (V_2 - V_1) \]
\[ = - (1 \text{ atm})(10 \text{ L} - 1.0 \text{ L}) \]
\[ w = - 9.0 \text{ L atm}. \]

Since the result is requested in units of Joules, we must convert units of L atm to Joules.

\[ w = (-9.0 \text{ L atm}) \left( \frac{101.3 \text{ J}}{1 \text{ L atm}} \right) \]
\[ w = -912 \text{ J}. \]

Note that work done in this irreversible process is lower in magnitude (even though the initial and final volumes are the same) compared to the work done in part (a) for a reversible process. The reversible process always yields the maximum amount of work.
4. (a) One mole of nitrogen gas initially at 25°C and 1 bar is expanded reversibly and isothermally to a final pressure of 0.132 bar. Determine the amount of work done in Joules, assuming ideal behavior.

We start with the basic definition of work,

\[ w = - \int P_{\text{ext}} \, dV. \]

We saw in problem 3(a) for a reversible isothermal expansion that the work is given by

\[ w = -nRT \ln \left( \frac{V_2}{V_1} \right). \]

Now, we are given the initial and final pressures rather than the initial and final volumes, so the equation above is not directly applicable. However, since \( T \) is constant, for the initial state we have (from the ideal gas equation)

\[ T = \frac{P_1 V_1}{nR}. \]

After the expansion, we have for the final state

\[ T = \frac{P_2 V_2}{nR}. \]

Since the temperatures are equal, we can equate the two relations to give

\[ P_1 V_1 = P_2 V_2, \]

or

\[ \frac{V_2}{V_1} = \frac{P_1}{P_2}. \]

Substituting this relation into the expression for the work in a reversible isothermal expansion,

\[ w = -nRT \ln \left( \frac{V_2}{V_1} \right) \]

or

\[ w = -nRT \ln \left( \frac{P_1}{P_2} \right). \]

Substituting the numerical values yields,

\[ w = -nRT \ln \left( \frac{P_1}{P_2} \right) \]

\[ = (1 \text{ mol}) \left( \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{298.15 \text{ K}} \right) \ln \left( \frac{1.0 \text{ bar}}{0.132 \text{ bar}} \right) \]

\[ w = -5020 \text{ J}. \]

The work is negative, indicating work done by the system on the surroundings during the expansion.
4. (b) One mole of nitrogen gas initially at 25°C and 1 bar is expanded isothermally against a constant external pressure of 0.132 bar. Determine the amount of work done in Joules, assuming ideal behavior.

This time, the expansion is not reversible, but it is still isothermal. The equation for the work is

\[ w = -\int P_{\text{ext}} \, dV. \]

Since the external pressure is constant, it can be pulled outside the integral as in problem 3(b) and we get

\[ w = -P_{\text{ext}} \int_{V_1}^{V_2} dV = -P_{\text{ext}} (V_2 - V_1). \]

The external pressure is given in the problem (0.132 bar), but the initial and final volumes are not given. The initial volume can be calculated from the ideal gas equation,

\[ V_1 = \frac{nRT}{P_1} = \frac{(1 \text{ mol})(0.08314 \text{ L bar mol}^{-1} \text{K}^{-1})(298.15 \text{ K})}{(1 \text{ bar})} = 24.79 \text{ L}. \]

The final volume can be calculated from the ideal gas equation assuming that the expansion begins with the gas at 1 bar pressure and continues until the pressure of the gas equals the opposing (or external) pressure (since this is the equilibrium state).

Thus, we assume that \( P_2 = P_{\text{ext}} \) and calculate,

\[ V_2 = \frac{nRT}{P_2} = \frac{(1 \text{ mol})(0.08314 \text{ L bar mol}^{-1} \text{K}^{-1})(298.15 \text{ K})}{(0.132 \text{ bar})} = 187.8 \text{ L}. \]

Finally, the work can be determined as

\[ w = -P_{\text{ext}} (V_2 - V_1) = -(0.132 \text{ bar})(187.8 \text{ L} - 24.8 \text{ L}) = -21.5 \text{ L bar}. \]

The units of L bar are converted to Joules,

\[ w = (-21.5 \text{ L bar}) \left( \frac{100 \text{ J}}{1 \text{ L bar}} \right) = -2150 \text{ J}. \]
5. A quantity of 4.50 g of CaC$_2$ is reacted at 300 K with excess water in a closed container fitted with a piston,

$$\text{CaC}_2 (s) + 2 \text{H}_2\text{O} (\ell) \rightarrow \text{Ca(OH)}_2 (\text{aq}) + \text{C}_2\text{H}_2 (g) .$$

Calculate the work done by the production of C$_2$H$_2$ gas against an external pressure of 1 bar. Assume that the reaction proceeds until the pressure of the gas produced equals the opposing (or external) pressure.

The way to start this calculation is to realize that the reaction starts initially with no gas produced; therefore, $V_1 = 0$.

To get the final volume, we assume that $P_2 = P_{\text{ext}}$ and use the ideal gas equation,

$$V_2 = \frac{nRT}{P_2} .$$

In order to determine the final volume using the equation above, we need to know how many moles of C$_2$H$_2$ are produced. Since we started with 4.50 g CaC$_2$, we have

$$\frac{4.50 \text{ g CaC}_2}{64.10 \text{ g CaC}_2} \left(\frac{1 \text{ mol C}_2\text{H}_2}{1 \text{ mol CaC}_2}\right) = 0.0702 \text{ mol C}_2\text{H}_2.$$

Then, the final volume can be calculated using

$$V_2 = \frac{nRT}{P_2} = \frac{(0.0702 \text{ mol})(0.08314 \text{ L bar} \text{ mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{(1 \text{ bar})} = 1.75 \text{ L} .$$

The work for an expansion against constant external pressure can be calculated as

$$w = -P_{\text{ext}}(V_2 - V_1) = -(1 \text{ bar})(1.75 \text{ L} - 0 \text{ L}) = -1.75 \text{ L bar} \left(\frac{100 \text{ J}}{1 \text{ L bar}}\right) = -175 \text{ J} .$$
6. Derive an expression for the work done in a reversible isothermal expansion from \( V_1 \) to \( V_2 \) for a gas that obeys the equation of state given by

\[
P(V_m - b) = RT,
\]

where \( b \) is a constant.

Starting from the definition of work, we have

\[
w = - \int P_{ext} \, dV.
\]

Since the process is reversible, \( P_{ext} = P \), which leads to

\[
w = - \int P \, dV.
\]

In order to evaluate the integral, we need to express \( P \) in terms of \( V \). Solving the equation of state for \( P \) leads to

\[
P = \frac{RT}{V_m - b},
\]

or in terms of \( V \) rather than \( V_m \), the pressure is

\[
P = \frac{nRT}{V - nb}.
\]

Substituting this relation into the equation for work yields

\[
w = - \int_{V_1}^{V_2} \frac{nRT}{V - nb} \, dV.
\]

Since the process is isothermal, \( T \) can be pulled out of the integral along with the other constants to give

\[
w = -nRT \int_{V_1}^{V_2} \frac{1}{V - nb} \, dV.
\]

Integrating leads to the result

\[
w = - nRT \ln \left( \frac{V_2 - nb}{V_1 - nb} \right).
\]
7. (a) Derive an expression for the work done in a reversible isothermal expansion of a van der Waals gas from $V_1$ to $V_2$.

This problem is very similar to Problem 6. We can start from the definition of work,

$$w = - \int P_{\text{ext}} dV.$$ 

Since the process is reversible, $P_{\text{ext}} = P$, and so we have

$$w = - \int P dV.$$ 

An expression for $P$ is required – this comes from the van der Waals equation. Solving the van der Waals equation for $P$ leads to

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

Substituting this relation into the equation for work yields

$$w = - \int_{V_1}^{V_2} \left( \frac{nRT}{V - nb} - \frac{an^2}{V^2} \right) dV$$

$$w = - \int_{V_1}^{V_2} \frac{nRT}{V - nb} dV + \int_{V_1}^{V_2} \frac{an^2}{V^2} dV.$$ 

Since the process is isothermal, $T$ can be pulled out of the integral along with the other constants to give

$$w = - nRT \int_{V_1}^{V_2} \frac{1}{V - nb} dV + an^2 \int_{V_1}^{V_2} \frac{1}{V^2} dV.$$ 

Integrating leads to the result

$$w = - nRT \ln \left( \frac{V_2 - nb}{V_1 - nb} \right) - an^2 \left( \frac{1}{V_2} - \frac{1}{V_1} \right).$$
7. Continued

(b) One mole of methane expands reversibly from 1 to 50 L at 25°C. Calculate the work done assuming (1) the gas behaves ideally, and (2) the gas obeys the van der Waals equation.

Part 1: Ideal gas behavior

In this case, we can use the result from problem 3(a) for a reversible isothermal expansion of an ideal gas, and substitute the numerical values to obtain the result,

\[ w = -nRT \ln \left( \frac{V_2}{V_1} \right) \]
\[ = -1 \text{ mol} \left( 8.314 \text{ J mol}^{-1} \text{K}^{-1} \right) \ln \left( \frac{50 \text{ L}}{1 \text{ L}} \right) \]
\[ w = -9700 \text{ J} . \]

Part 2: van der Waals gas behavior

For a reversible isothermal expansion of a van der Waals gas, we can use the result developed in part (a) of this question, along with the van der Waals constants for methane (from the textbook) to calculate the work.

\[ w = -nRT \ln \left( \frac{V_2 - nb}{V_1 - nb} \right) - an^2 \left( \frac{1}{V_2} - \frac{1}{V_1} \right) \]
\[ = -1 \text{ mol} \left( 0.08205 \text{ L atm mol}^{-1} \text{K}^{-1} \right) \ln \left[ \frac{50 \text{ L} - 1 \text{ mol} \left( 0.0428 \text{ L mol}^{-1} \right)}{1 \text{ L} - 1 \text{ mol} \left( 0.0428 \text{ L mol}^{-1} \right)} \right] \]
\[ = -2.253 \text{ L}^2 \text{ atm} \text{ mol}^{-2} \left( 1 \text{ mol} \right)^2 \left( \frac{1}{50 \text{ L}} - \frac{1}{1 \text{ L}} \right) \]
\[ = -96.75 \text{ L atm} + 2.21 \text{ L atm} \]
\[ = (-94.54 \text{ L atm}) \left( \frac{101.325 \text{ J}}{1 \text{ L atm}} \right) \]
\[ w = -9580 \text{ J} . \]

Note that the work for the expansion of the van der Waals gas is slightly smaller in magnitude than that for the ideal gas. The van der Waals gas does less work because some energy is required to overcome the intermolecular interactions in a real gas.