Chemistry 360  
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Problem Set 3 Solutions

1.  (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,

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

\[ = - (1 \text{ mol})(8.314 \text{ Jmol}^{-1}\text{K}^{-1})(298 \text{ K}) \ln \left( \frac{10 \text{ L}}{1.0 \text{ L}} \right) \]

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

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

(b) Determine the work done in Joules when one mole of an ideal gas is expanded irreversibly from 1.0 L to 10 L against a constant external pressure of 1.0 atm.

Again, using the definition of work,

\[ w = - \int P_{\text{ext}} \, dV. \]
1. (b) Continued

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

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

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

Substituting,

\[ w = -P_{\text{ext}} (V_2 - V_1) \]

\[ = -(1 \text{ atm})(10 \text{ L} - 1.0 \text{ L}) \]

\[ w = -9.0 \text{ L atm}. \]

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.

2. 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 \( V_2 \),

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

\[ w = -P(V_2 - V_1). \]
2. Continued

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,

\[ P = \frac{nRT_1}{V_1} \]

\[ = \left(1 \text{ mol}\right) \left(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1}\right) \left(298.15 \text{ K}\right) \left(2.0 \text{ L}\right) \]

\[ P = 12.394 \text{ bar}. \]

The work done is then given by

\[ w = -P(V_2 - V_1) \]

\[ = -(12.394 \text{ bar})(5.0 \text{ L} - 2.0 \text{ L}) \]

\[ w = -37.18 \text{ L bar}. \]

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

\[ w = \left(-37.18 \text{ L bar}\right) \left(100 \text{ J} \right) \left(1 \text{ L bar}\right) \]

\[ w = -3718 \text{ J}. \]

3. (a) One mole of nitrogen gas at 25°C and 1 bar is expanded reversibly and isothermally to a 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 1(a) for a reversible isothermal expansion that the work is

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

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)

\[ T = \frac{P_1V_1}{nR}. \]

After the expansion, we have for the final state

\[ T = \frac{P_2V_2}{nR}. \]

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

\[ P_1V_1 = P_2V_2, \]
3 (a) Continued

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

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,

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

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

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

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

(b) Determine the work done when one mole of nitrogen gas at 25°C and 1 bar is expanded isothermally against a constant external pressure of 0.132 bar 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 1b and we get

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

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

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,

\[ V_1 = \frac{nRT}{P_1} \]

\[ = \left( 1 \text{ mol} \right) \left[ 0.08314 \text{ L bar mol}^{-1}\text{K}^{-1} \right] \left( 298.15 \text{ K} \right) \]

\[ V_1 = 24.79 \text{ L}. \]

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).
3. (b) Continued

Thus, we assume that $P_2 = P_{ext}$ and calculate,

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

$$V_2 = 187.8 \text{ L}.$$

Finally, the work can be determined as

$$w = -P_{ext}(V_2 - V_1) = -(0.132 \text{ bar})(187.8 \text{ L} - 24.8 \text{ L})$$

$$w = -21.5 \text{ L bar}.$$

The units of L bar are converted to Joules,

$$w = (-21.5 \text{ L bar})\left(\frac{100 \text{ J}}{1 \text{ L bar}}\right) = -2150 \text{ J}.$$

4. 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,

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

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, assume that the reaction proceeds until the pressure of the gas equals the external pressure. Thus, we assume that $P_2 = P_{ext}$ 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

$$4.50 \text{ g CaC}_2 \left(\frac{\text{mol}}{64.10 \text{ g CaC}_2}\right) \left(\frac{1 \text{ molC}_2\text{H}_2}{1 \text{ molCaC}_2}\right) = 0.0702 \text{ molC}_2\text{H}_2.$$
4. **Continued**

Then, the final volume can be calculated using

\[ V_2 = \frac{nRT}{P_2} \]

\[ = \frac{(0.0702 \text{ mol})(0.08314 \text{ L bar}^{-1} \text{ K}^{-1})(300 \text{ K})}{(1 \text{ bar})} \]

\[ V_2 = 1.75 \text{ L}. \]

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

\[ w = -P_{\text{ext}}(V_2 - V_1) \]

\[ = -(1 \text{ bar})(1.75 \text{ L} - 0 \text{ L}) \]

\[ = -1.75 \text{ L bar} \left( \frac{100 \text{ J}}{1 \text{ L bar}} \right) \]

\[ w = -175 \text{ J}. \]

5. **Two moles of O}_2\text{ 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.**

Under the conditions given, the O}_2\text{ gas would be expected to behave ideally (i.e., moderate temperature and low pressures). The ideal gas equation may thus be employed to determine the volume of the system.

\[ V = \frac{nRT_1}{P_1} \]

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

\[ V = 49.24 \text{ L}. \]

The work done is defined as

\[ w = -P_{\text{ext}} \Delta V. \]

Since the process takes place at constant volume, and therefore \( \Delta V = 0 \), there is no work done; \( w = 0 \).

6. **(a) Derive an expression for the work done in a reversible isothermal expansion of a van der Waals gas from \( V_1 \) to \( V_2 \).**

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
6. (a) Continued

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

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

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

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

(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 1 for a reversible isothermal expansion of an ideal gas,

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

$$= -\left(1 \text{ mol} \right) \left( 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \right) \left( 298.15 \text{ K} \right) \ln \left( \frac{50 \text{ L}}{1 \text{ L}} \right)$$

$$w = -9700 \text{ J}.$$
6. (b) Continued

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.

\[ w = -nRT \ln \left( \frac{V_2 - nb}{V_1 - nb} \right) - a \ln \left( \frac{1}{V_2 - V_1} \right) \]

\[ = -(1 \text{ mol}) [0.08205 \text{ L atm mol}^{-1} \text{K}^{-1}] (298.15 \text{ K}) \]

\[ \times \ln \left[ \frac{50 \text{ L} - (1 \text{ mol}) [0.0428 \text{ L mol}^{-1}]}{1 \text{ L} - (1 \text{ mol}) [0.0428 \text{ L mol}^{-1}] \right] \]

\[ = (2.303 \text{ L atm mol}^{-2})(1 \text{ mol})^2 \left( \frac{1}{50 \text{ L}} - \frac{1}{1 \text{ L}} \right) \]

\[ = -96.75 \text{ L atm} + 2.26 \text{ L atm} \]

\[ = (-94.49 \text{ L atm}) \left( \frac{101.3251}{1 \text{ L atm}} \right) \]

\[ w = -9574 \text{ J}. \]

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.

7. Derive an expression for the reversible isothermal work from \( V_1 \) to \( V_2 \) done by a gas that obeys the equation of state given by

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

where \( b \) is a constant.

This problem is very similar to Problem 6(a). Starting from the definition of work, we have

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

Since the process is reversible, \( P_{\text{ext}} = P \), 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
\[ P = \frac{nRT}{V - nb}. \]

7. **Continued**

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

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

8. **Determine whether or not the following differentials are exact.**

(a) \( df = xy^2 \, dx - x^2 \, y \, dy \)

An exact differential has the form

\[ df = A(x,y) \, dx + B(x,y) \, dy, \]

where

\[ A(x,y) = \left( \frac{\partial f}{\partial x} \right)_y \quad \text{and} \quad B(x,y) = \left( \frac{\partial f}{\partial y} \right)_x. \]

Since the mixed second partial derivatives are equal, the test for exactness is

\[ \left( \frac{\partial A}{\partial y} \right)_x = \left( \frac{\partial B}{\partial x} \right)_y. \]

For the differential given above, we have

\[ A(x,y) = xy^2 \quad \text{and} \quad B(x,y) = -x^2y. \]

Taking the partial derivatives leads to

\[ \left( \frac{\partial A}{\partial y} \right)_x = 2xy \quad \text{and} \quad \left( \frac{\partial B}{\partial x} \right)_y = -2xy. \]

Since the partial derivatives are not equal, this differential is NOT EXACT.
8. **Continued**

(b) \( df = \frac{1}{y} \, dx - \frac{x}{y^2} \, dy \)

For this differential, we have

\[
A(x,y) = \frac{1}{y} \quad \text{and} \quad B(x,y) = -\frac{x}{y^2}.
\]

Taking the partial derivatives leads to

\[
\left( \frac{\partial A}{\partial y} \right)_x = -\frac{1}{y^2} \quad \text{and} \quad \left( \frac{\partial B}{\partial x} \right)_y = -\frac{1}{y^2}.
\]

Since the partial derivatives are equal, in this case the differential is EXACT.

9. **Determine whether or not the following differentials are exact.**

(a) \( dq = C_v \, dT + \frac{RT}{V} \, dV \) (assume that \( C_v \) and \( R \) are constant)

In this problem, the differential has the form

\[
dq = A(T,V) \, dT + B(T,V) \, dV.
\]

The criterion for exactness is

\[
\left( \frac{\partial A}{\partial V} \right)_T = \left( \frac{\partial B}{\partial T} \right)_V.
\]

For the differential given above, we have

\[
A(T,V) = C_v \quad \text{and} \quad B(T,V) = \frac{RT}{V}.
\]

Taking the partial derivatives leads to

\[
\left( \frac{\partial A}{\partial V} \right)_T = 0 \quad \text{and} \quad \left( \frac{\partial B}{\partial T} \right)_V = \frac{R}{V}.
\]

Since the partial derivatives are not equal, \( dq \) is NOT EXACT.
9. Continued

(b) \[ dS = \frac{C_v}{T} \ dT + \frac{R}{V} \ dV \]  \( S \) is another thermodynamic function called entropy

In this problem, the differential has the form

\[ dS = A(T,V) \ dT + B(T,V) \ dV . \]

The criterion for exactness is

\[ \left( \frac{\partial A}{\partial V} \right)_T = \left( \frac{\partial B}{\partial T} \right)_V. \]

For the differential given above, we have

\[ A(T,V) = \frac{C_v}{T} \quad \text{and} \quad B(T,V) = \frac{R}{V}. \]

Taking the partial derivatives leads to

\[ \left( \frac{\partial A}{\partial V} \right)_T = 0 \quad \text{and} \quad \left( \frac{\partial B}{\partial T} \right)_V = 0. \]

Since the partial derivatives are equal, the differential \( dS \) is EXACT.

10. Many compressed gases come in large metal cylinders. An 80.0 L tank of nitrogen gas pressurized to 172 atm is left in the sun and heats from its normal temperature of 20.0 °C to 140.0 °C. Determine (a) the final pressure inside the tank and (b) the work, heat, and \( \Delta U \) of the process. Assume that the nitrogen gas behaves ideally and that the constant volume heat capacity of diatomic nitrogen is 21.0 J/mol-K.

Part (a)
To get the final pressure, the ideal gas equation may be employed,

\[ P_2 = \frac{nRT}{V_2}. \]

Everything is known on the right side of this equation except for the number of moles. The number of moles can be determined from the initial conditions and the ideal gas equation,

\[ n = \frac{P_1 V_1}{RT} = \frac{(172 \text{ atm})(80.0 \text{ L})}{(0.08205 \text{ L atm/molK})(293.15 \text{ K})} = 572.1 \text{ mol}. \]
Now the final pressure may be determined,

\[ P_2 = \frac{nRT}{V_2} = \frac{(572.1 \text{ mol})(0.08205 \text{ L atm/mol K})(413.15 \text{ K})}{(80.0 \text{ L})} \]

\[ P_2 = 242 \text{ atm}. \]

**Part (b)**
The work is defined as

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

Since there is no change in volume in the process, \( dV = 0 \) and therefore \( w = 0 \).

Assuming that the gas behaves ideally, the differential of internal energy \( dU \) is defined as

\[ dU = C_v \, dT. \]

If \( C_v \) is constant, we can integrate both sides,

\[ \Delta U = C_v \int dT, \]

or \( \Delta U = C_v \Delta T \).

The molar constant volume heat capacity of nitrogen, \( C_{v,m} \), is given in the problem as 21.0 J/molK. To convert this to heat capacity, \( C_v \), it must be multiplied by the number of moles,

\[ C_v = n \, C_{v,m} = (572.1 \text{ mol})(21.0 \text{ J/mol K}) \]

\[ C_v = 12014 \text{ J/K}. \]

Substituting,

\[ \Delta U = C_v \Delta T = (12014 \text{ J/K})(413.15 \text{ K} - 293.15 \text{ K}) \]

\[ \Delta U = 1441690 \text{ J} \quad \text{or} \quad 1442 \text{ kJ}. \]

Now, since \( w \) and \( \Delta U \) are known, the heat \( q \) may be calculated from the first law,

\[ \Delta U = q + w. \]

We know that \( w = 0 \), so this yields

\[ \Delta U = q. \]

Therefore, the heat \( q \) is the same as the internal energy change,
\[ q = \Delta U = 1442\text{kJ}. \]