Problem Set 4. Due Feb. 13 in class.

Chapter 3 Numerical

6. One can store energy by compressing air, and then later use it to power a turbine to create energy when needed. However, you have to heat the room temperature compressed air to make this effective. You can avoid this if you initially compress the air under adiabatic conditions, so the gas is already hot when you need it to generate electricity. This is called adiabatic compressed air energy storage (CAES). Inside a typical power plant, $5.8 \times 10^6$ kg of N$_2$ gas is at 25 °C is compressed from atmospheric to pressure into a volume of 300,000 m$^3$ (they use abandoned salt mines). The process is done reversibly and adiabatically. What is $\Delta q$, $n$, $V_i$, $P_f$, $\Delta T$, $\Delta U$, $\Delta w$, and $\Delta H$ and for this process? ($C_{p,m} = 29.12$ J/K/mol and $C_{v,m} = 20.80$ J/K/mol for N$_2$). Assume perfect gas behavior.

Answer. First, the change in heat $\Delta q$ is 0 J, it’s adiabatic afterall. Next, you need to calculate the work by knowing the change in U which is calculated by you will need the number of moles of gas which happens to be $5.8 \times 10^6$ kg × 1000 g/kg / 28 g/mol = $2.07 \times 10^8$ mol. This also gives us the real heat capacity which is $C_v = n \cdot C_{v,m} = 2.07 \times 10^8$ mol × 20.8 J/K/mol = $4.31 \times 10^9$ J/K. Next, we need to know the change in temperature given the change in volume. I gave the final volume but not the initial one, which is:

$101,325 \text{ Pa} \times ?\text{m}^3 = 2.07 \times 10^8 \text{ mol} \times 8.314 \text{ J/K/mol} \times 298.15 \text{ K}$

giving me an initial volume of $5.07 \times 10^6$ m$^3$. As this is adiabatic and reversible, we will use (from the handout I have on the web):

\[
\left(\frac{T_f}{T_i}\right)^{\frac{nR}{C_v}} = \frac{V_i}{V_f}
\]

which rearranges to:

\[
T_f = 298.15 \text{ K} \cdot \left(\frac{5.07 \times 10^6 \text{ m}^3}{3.00 \times 10^5 \text{ m}^3}\right)^{\frac{2.07 \times 10^8 \text{ mol} \times 8.314 \text{ J/K/mol}}{4.31 \times 10^7 \text{ J/K}}},
\]

which makes the final temperature 922 K and thus $\Delta T = 624$ K.

Also the final pressure is:

$?\text{Pa} \times 300,000 \text{ m}^3 = 2.07 \times 10^8 \text{ mol} \times 8.314 \text{ J/K/mol} \times 923 \text{ K} \rightarrow P_f = 5.3 \text{ MPa}$.

This gives us the change in U and work:

$\Delta U = \Delta w = C_v \times \Delta T = 4.31 \times 10^9 \text{ J/K} \cdot 624 \text{ K} = 2.7 \times 10^{12}$ J.

Last: $\Delta H = \Delta U + \Delta(P \cdot V) = \Delta U + nR \Delta T = 2.7 \times 10^{12}$ J + $2.07 \times 10^8 \text{ mol} \times 8.314 \text{ J/K/mol} \times 624 \text{ K} = 3.76 \times 10^{12}$ J.

You could have solved it via:
\[ \Delta H = C_p \times \Delta T = 2.07 \times 10^8 \text{ mol} \times 29.12 \text{ J/K/mol} \times 624 \text{ K} = 3.76 \times 10^{12} \text{ J}. \]

8. A four-cylinder 1.2 L car engine has individual cylinders (pistons) that hold a total of 0.3 L of fuel + air gas mixture. When the fuel + air gas mixture enters the piston at 1 atm pressure at a standard engine temperature of \(\sim 90 \, ^\circ\text{C}\) (again 0.3 L volume), it is compressed adiabatically and irreversibly by a constant external pressure of 608 kPa. Assuming the \(C_{v,m}\) of the fuel + air gas mixture is \(C_{v,m} = 20.8 \text{ J/K/mol}\), what is \(\Delta q, \Delta n, P_f, T_f, \Delta U, \Delta w, \Delta H\)? Assume perfect gas behavior.

**Answer:** First, recognize that this is an adiabatic irreversible transition, thus \(\Delta q = 0 \text{ J}\). The initial temperature is \((273.15 + 90) \text{ K} = 363.15 \text{ K}\). We have to know the number of moles, which is \(101.325 \text{ kPa} \times 0.3 \text{ L} = ? \text{ mol} \times 8.314 \text{ J/K/mol} \times 363.15 \text{ K}\), making \(n = 0.0101 \text{ mol}\). Next, the piston will contract until the interior pressure is 608 kPa; with this we have to figure out the change in temperature and volume. To do so, we will use the fact that:

\[ \partial U = \partial w = C_v \times \partial T = -P_{\text{ext}} \times \partial V. \]

Next we integrate over limits, making:

\[ \Delta U = C_v \times (T_f - T_i) = -P_{\text{ext}} \times (V_f - V_i). \]

Fill in the blanks on what you know:

\[ 0.0101 \text{ mol} \times 20.8 \text{ J/K/mol} \times (T_f - 363.15 \text{ K}) = -608 \text{ kPa} \times (V_f - 0.3 \text{ L}) \]

Now we have one equation with two unknowns (\(V_f\) and \(T_f\)); but, we can relate the two together as shown here - this is the final volume as a function of the final temperature:

\[ V_f = \frac{0.0101 \text{ mol} \times 8.314 \text{ J/K/mol} \times T_f}{608 \text{ kPa}}. \]

If you insert that into the above you get:

\[ 0.0101 \text{ mol} \times 20.8 \text{ J/K/mol} \times (T_f - 363.1 \text{ K}) = -608 \text{ kPa} \times \left(0.0101 \text{ mol} \times 8.314 \text{ J/K/mol} \times T_f \right) \left(\frac{1}{608 \text{ kPa}} - 0.3 \text{ L}\right) \]

While it will take a while, you can solve for \(T_f\), which is 882 K making \(\Delta T = 519 \text{ K}\). This also makes the final volume 0.1214 L. Adiabatic work is always:

\[ n \times C_{v,m} \times \Delta T = 0.0101 \text{ mol} \times 20.8 \text{ J/K/mol} \times (882 \text{ K} - 363.15 \text{ K}) = 109 \text{ J} \]

This is the same as \(\Delta U\) since \(\Delta q = 0 \text{ J}\). Last, the change in enthalpy:

\[ \Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta(T) = 109 \text{ J} + 0.0101 \text{ mol} \times 8.314 \text{ J/K/mol} \times (882 \text{ K} - 363.15 \text{ K}) = 152 \text{ J}. \]
9. Say 0.0101 moles of gas in a car engine cylinder under a pressure of 608 kPa at 882 K expands adiabatically and irreversibly against 1 atm pressure. The $C_{v,m}$ of the gas is 20.8 J/K/mol while $C_{p,m} = 29.12$ J/K/mol, so what is $\Delta q$, $V_i$, $T_f$, $P_f$, $\Delta U$, $\Delta w$, and $\Delta H$? (7 pts)

**Answer:** First, recognize that this is an adiabatic irreversible transition, thus $\Delta q=0$ J. As usual, we need to find the final temperature. To do so, we will use as before:

$$\Delta U = C_v \times (T_f - T_i) = -P_{ext} \times (V_f - V_i).$$

So I need to know $V_i$, which is:

$$608 \text{ kPa} \times ? \text{L} = 0.0101 \text{ mol} \times 8.314 \text{ J/K/mol} \times 882 \text{ K}$$

giving me an initial volume of 0.1214 L.

Next, fill in the blanks on what you know:

0.0101 mol $\times$ 20.8 J/K/mol $\times$ (T_f $-$ 882 K) = $-101.325$ kPa $\times$ (V_f $-$ 0.1214 L)

Now we have one equation with two unknowns ($V_f$ and $T_f$); but, we can relate the two together as shown here- this is the final volume as a function of the final temperature:

$$V_f = \frac{0.0101 \text{ mol} \times 8.314 \text{ J/K/mol} \times T_f}{101.325 \text{ kPa}}.$$ If you insert that into the above you get:

$$0.0101 \text{ mol} \times 20.8 \text{ J/K/mol} \times (T_f - 882 \text{ K}) = -101.325 \text{ kPa} \times \left( \frac{0.0101 \text{ mol} \times 8.314 \text{ J/K/mol} \times T_f}{101.325 \text{ kPa}} - 0.1214 \text{ L} \right)$$

Now while it will take a while, you can solve for $T_f$, which is 672 K making $\Delta T = -210$ K. This also makes the final volume 0.555 L. Adiabatic work is always:

$$n \times C_{v,m} \times \Delta T = 0.0101 \text{ mol} \times 20.8 \text{ J/K/mol} \times (672 \text{ K} - 882 \text{ K}) = -44 \text{ J}$$

This is the same as $\Delta U$ since $\Delta q = 0$ J. Last, the change in enthalpy:

$$\Delta H = \Delta U + \Delta (PV) = \Delta U + nR\Delta(T) =$$

-44 J $+$ 0.0101 mol $\times$ 8.314 J/K/mol $\times$ (672 K $-$ 882 K) = -61.5 J.

10. Say 0.0101 moles of gas in a car engine cylinder at atmospheric pressure at 90 °C contracts adiabatically and reversibly until it is at 608 kPa pressure. The $C_{v,m}$ of the gas is 20.8 J/K/mol while $C_{p,m} = 29.12$ J/K/mol, so what is $\Delta q$, $T_i$, $P_f$, $\Delta U$, $\Delta w$, and $\Delta H$? (10 pts)

**Hint:** $P_i \over P_f = \left( \frac{T_f}{T_i} \right)^{C_v+nR \over nR}$

**Answer:** First, recognize that this is an adiabatic reversible transition, thus $\Delta q = 0$ J. Next, the piston will expand until $P_f = 608$ kPa; with this we have to figure out the change in temperature
and volume. To do so, we will use this adiabatic equation of state: \( \frac{P_i}{P_f} = \left( \frac{T_i}{T_f} \right)^{\frac{C_v+nR}{nR}} \); plugging in values gives: \( \frac{608 \text{ kPa}}{101.325 \text{ kPa}} = \left( \frac{606 \text{ K}}{T_f} \right)^{\frac{C_v+nR}{nR}} \). Rearranging the equation as so makes calculating \( T_f \) easy: \( \frac{608 \text{ kPa}}{101.325 \text{ kPa}} \times 0.0101 \text{ mol} \times 20.8 \text{ J/K/mol} \times 0.0101 \times 8.314 \frac{\text{J}}{\text{K/mol}} = \frac{606 \text{ K}}{T_f} \); therefore \( T_f = 606 \text{ K} \).

Adiabatic work is always:
\[ n \times C_{v,m} \times \Delta T = 0.0101 \text{ mol} \times 20.8 \frac{\text{J}}{\text{K/mol}} \times (606 - 363.15) \text{ K} = 50.8 \text{ J} \]
This is the same as \( \Delta U \) since \( \Delta q = 0 \text{ J} \). Last, the change in enthalpy:
\[ \Delta H = \Delta U + \Delta (PV) = \Delta U + n \times R \times \Delta T = 50.8 \text{ J} + 0.0101 \text{ mol} \times 8.314 \frac{\text{J}}{\text{K/mol}} \times (606 - 363.15) \text{ K} = 71.1 \text{ kJ} \]

11. Say 0.0101 moles of gas in a car engine cylinder under a pressure of 608 kPa at 606 K expands adiabatically and reversibly until it is at 1 atm pressure. The \( C_{v,m} \) of the gas is 20.8 J/K/mol while \( C_{p,m} = 29.12 \frac{\text{J}}{\text{K/mol}} \), so what is \( \Delta q, T_f, \Delta U, \Delta w, V_f, \) and \( \Delta H \)? (10 pts)

**Hint:** \( \frac{P_i}{P_f} = \left( \frac{T_i}{T_f} \right)^{\frac{C_v+nR}{nR}} \)

**Answer:** First, recognize that this is an adiabatic reversible transition, thus \( \Delta q = 0 \text{ J} \). Next, the piston will expand until \( P_f = 1 \text{ atm} \); with this we have to figure out the change in temperature and volume. To do so, we will use this adiabatic equation of state: \( \frac{P_i}{P_f} = \left( \frac{T_i}{T_f} \right)^{\frac{C_v+nR}{nR}} \); plugging in values gives:
\[ \frac{608 \text{ kPa}}{101.325 \text{ kPa}} = \left( \frac{606 \text{ K}}{T_f} \right)^{\frac{C_v+nR}{nR}} \]
Rearranging the equation as so makes calculating \( T_f \) easy:
\[ \frac{608 \text{ kPa}}{101.325 \text{ kPa}} \times 0.0101 \text{ mol} \times 20.8 \text{ J/K/mol} \times 0.0101 \times 8.314 \frac{\text{J}}{\text{K/mol}} = \frac{606 \text{ K}}{T_f} \]; therefore \( T_f = 363 \text{ K} \).

Adiabatic work is always:
\[ n \times C_{v,m} \times \Delta T = 0.0101 \text{ mol} \times 20.8 \frac{\text{J}}{\text{K/mol}} \times (363 - 606) \text{ K} = -50.8 \text{ J} \]
This is the same as \( \Delta U \) since \( \Delta q = 0 \text{ J} \). Last, the change in enthalpy:
\[ \Delta H = \Delta U + \Delta (PV) = \Delta U + n \times R \times \Delta T = -50.8 \text{ J} + 0.0101 \text{ mol} \times 8.314 \frac{\text{J}}{\text{K/mol}} \times (363 - 606) \text{ K} = -71.1 \text{ J} \]
The final volume is from:

\[101.325 \text{ kPa} \times 0.0101 \text{ mol} \times 8.314 \text{ J/K/mol} \times 363 \text{ K} \]

\[V_f = 0.3 \text{ L}, \text{ same as } V_i \text{ in question } 10.\]

Chapter 3 Theoretical

1. In questions 10 and 11 of the previous section, you may have noticed that the starting state in #11 was the end state in #10. Also the end state in #11 was the starting state in #10. Note that all the work, \(\Delta U\) and \(\Delta H\) were equal but opposite of eachother. Now I can also tell you that in questions 9 and 8, you may have noticed that the starting state in #9 was the end state in #8. However, the end state in #9 was not the starting state in #8. Also, while the thermodynamic variables were of opposite sign, they were not equal in magnitude. Why is that happening?

(2 pts)

**Answer.** Now you see what reversible and irreversible really mean. Questions 8 and 9 were done under irreversible conditions, so I couldn’t return to my starting point whereas I could in questions 10 and 11. You may have also stated that total entropy was increasing in 8 and 9, but not in 10 and 11.

2. According to the adiabatic equation of state:

\[
\left( \frac{T_f}{T_i} \right) = \frac{V_i}{V_f}
\]

expanding a gas will result in it getting cold. However, in the adiabatic Joule experiment, expanding a gas like hydrogen or helium will cause those gases to get hot (unlike all other gases). What gives?

(4 pts)

**Answer.** The Joule experiment was performed under conditions of constant internal energy, but when you just expand a gas in a piston wrapped in glass wool, \(U\) is not constant. Different conditions give different results.

7. The text shows that:

\[
\frac{\partial U}{\partial T} = \frac{\partial U}{\partial T_p}
\]

Can you show that:

\[
\frac{\partial H}{\partial T} = \frac{\partial H}{\partial T_p}
\]

Hint, starting with:

\[
\partial H = \frac{\partial H}{\partial T} \partial T + \cdots
\]

(5 pts)

**Answer.** First write out the change in \(H\) as so:

\[
\partial H = \frac{\partial H}{\partial T} \partial T + \frac{\partial H}{\partial P} \partial P.
\]

Next, divide by the change in \(T\) at constant \(V\) gives:

\[
\frac{\partial H}{\partial T} = \frac{\partial H}{\partial T} \frac{\partial T}{\partial T} + \frac{\partial H}{\partial P} \frac{\partial P}{\partial T}.
\]

Note that \(\frac{\partial H}{\partial P} \bigg|_T = 0 \text{ J/Pa} \) due to the constant temperature and \(\frac{\partial T}{\partial V} = 1\). Thus,

\[
\frac{\partial H}{\partial T} = \frac{\partial H}{\partial T}.
\]
10. Starting with $\left( \frac{\partial H}{\partial P} \right)_T = \left( \frac{\partial (U + PV)}{\partial P} \right)_T$, can you show that $\left( \frac{\partial U}{\partial P} \right)_T$ and $\left( \frac{\partial H}{\partial P} \right)_T$ are in fact equal? Hint: you will need to use the perfect gas law. (7 pts)

**Answer:** Starting with $\left( \frac{\partial H}{\partial P} \right)_T = \left( \frac{\partial (U + PV)}{\partial P} \right)_T$, use the product rule:

$$\left( \frac{\partial H}{\partial P} \right)_T = \left( \frac{\partial U}{\partial P} \right)_T + \left( \frac{P \partial V}{\partial P} \right)_T + V. \quad \text{Next, derive the middle term:} \quad \left( \frac{P \partial V}{\partial P} \right)_T = P \frac{-nRT}{P} = -\frac{nRT}{P} = -V. \quad \text{Thus you are left with} \quad \left( \frac{\partial H}{\partial P} \right)_T = \left( \frac{\partial U}{\partial P} \right)_T. $$

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**Chapter 4 Numerical**

2. In my dreams I’m a Roman Centurion! I need to heat my iron anvil (mass of 1000 g, $C_{p,m} = 25.1 \text{ J/K/mol}$) from room temperature (25 °C) to 800 °C to do some metal work.

**a.** How much entropy is created by this? (Assume the volume of the anvil is constant) (3 pts)

**b.** Is entropy created by keeping the anvil at 800 °C? (hint, how do you keep the anvil hot?) (2 pts)

**Answer: a.** Without a change in volume, the formula is: $\Delta S = n \cdot C_{p,m} \cdot \ln \left( \frac{T_f}{T_i} \right)$. Note that this is different than the usual formula with $C_V$, because the anvil is not in a cylinder or piston and you cannot prevent it from expanding etc. when heated.

Given: 1000g / 55.85 g/mol = 17.91 mol and the data above, the answer is: $\Delta S = 17.91 \text{ mol} \cdot 25.1 \text{ J/K/mol} \cdot \ln \left( \frac{1073.15K}{298.15K} \right) = 575.6 \text{ J/K}.$

**b.** If the anvil stays at 800 °C on its own, there is no need to create more entropy. But in reality the anvil will need to be constantly heated as otherwise it will cool, so practically heat has to be added and entropy must be created in the process.

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