COHEM 452B – Homework 2 (B)

1) Consider work on (or by) an ideal gas in a cylinder with a piston of area A. As with the spring the energy in the gas (the system) is proportional to PV and PV = Fh, where F is the force the gas exerts on the walls and h is the height of the gas. The gas is not doing work by maintaining the piston at height, h. The force balance occurs when the Mass, M, (due to gravity) exerts a force (pushing downward) that is balanced by the force of the gas (pushing upward). The external force is F = Mg or Fh = Mg h and the internal force, times length is: Fh = PV. At equilibrium the pressure in the gas (PV = nRT) must balance (or equal) the pressure from the mass P_{ext} = Mg/A and at equilibrium P = P_{ext}.

In the following problem please try to express your answers in terms of the parameter, P, V, n, and T, and h at the start of the process (and other constants like R and A as needed). If you find that too challenging then assume we have one mole of a gas (ideal monotonic) at STP, (i.e. 273K and 1 Atm) in a container that must have a volume of 22.4 liters. Assume the cylinder has a height of 2 meters, so the area of the piston is 0.01123 m^2 or the radius is ~0.06 m (around 2+ inches). You will learn more doing the algebra than working with numbers.

A) Isothermal Compression:

So T1 = T0, DT = 0, no temperature change.

a) The system in state 1: n moles of a gas are in a cylinder at temperature, T0, and pressure, P0, at volume V0 = Ah0, initially at equilibrium with a mass M0 on the top of the piston. (Neglect air pressure.) An additional mass, m is added to the top of the piston. To make life simple assume the new added mass is the same as the old, so the new total mass is 2M0. Assume the compression is isothermal. What is the new pressure?

New pressure \( P_{ext} = P_1 = \frac{F}{A} = \frac{(M_0 + m) g}{A} = \frac{M_0 g}{A} \left(1 + \frac{m}{M_0}\right) = P_0 \left(1 + \frac{m}{M_0}\right) = 2P_0 \)

b) What is the new height?

\( P_0 V_0 = P_1 V_1 \) or \( P_0 h_0 = P_1 h_1 \) or \( h_1 = \frac{P_0}{P_1} h_0 = \frac{1}{2} h_0 \)

c) Compute the work done by the masses (in the environment)

\( w = -P_{ext} \Delta V = -P_0 \left(V_1 - V_0\right) \) from before \( V_1 = \frac{1}{2} V_0 \)

\( w = -P_1 \left(V_1 - V_0\right) = -2P_0 V_0 \left(\frac{1}{2} - 1\right) = P_0 V_0 \)

d) Compute the increase in internal energy. (It is a somewhat “trick question”.)

\( \Delta U = C_v \Delta T = 0 \)

e) Explain, qualitatively, what the energy flow is in this process.

The gas is compressed, so work is lost in the environment (work is positive) the lost work is converted to heat (after a sojourn in the gas) that is expelled from the system that goes into the environment.

B) Adiabatic Compression: No heat is allowed in or out, q = 0.

a) Same system as part a above, but now the gas is compressed adiabatically. What is the new pressure

The new pressure is the same as the problem above:
\[ P_{ext} = P_i = P_o \left(1 + \frac{m}{M_o}\right) = 2P_o \]

b) What is the new height?

Getting the new volume is very hard because the Temperature is changing.

\[ \frac{V_i}{V_o} = \frac{h_i}{h_o} \text{ or } h_i = 0.7h_o \text{ (see below)} \]

c) Compute the work done by the masses (in the environment)

\[ q = 0: \]

\[ \Delta U = C_V \Delta T = w = -P_i \Delta V = -2P_o \left(0.7V_o - V_o\right) = +0.6 \cdot P_o V_o \]

See below for state 1 values.

Now use the two equations to solve for the new T and the new V (which are connected)

\[ q = 0: \]

\[ \Delta U = C_V \Delta T = w = -P_i \Delta V \]

\[ nRT_o \left(\frac{T_i}{T_o} - 1\right) = -\frac{P_i}{P_o} P_o V_o \left(\frac{V_i}{V_o} - 1\right) \]

\[ 3\left(\frac{T_i}{T_o} - 1\right) = -\frac{P_i}{P_o} \left(\frac{V_i}{V_o} - 1\right) = -\left(\frac{T_i}{T_o} - \frac{P_i}{P_o}\right) \]

\[ \frac{5}{2} \frac{T_i}{T_o} = \left(\frac{3 + \frac{P_i}{P_o}}{2}\right) \text{ and } \frac{P_i}{P_o} \frac{V_i}{V_o} = \frac{T_i}{T_o} \]

\[ \frac{T_i}{T_o} = \frac{7}{5} = 1.4 \text{ and } \frac{2}{5} \frac{V_i}{V_o} = \frac{7}{5} \therefore \frac{V_i}{V_o} = 0.7 \]

d) Compute the increase in internal energy. Done in c as it equals the work.

e) Explain, qualitatively, what the energy flow is in this process.

Now the work in the environment must go into increasing the energy of the gas, so this means the temperature must rise. Therefore the new volume must be larger than that of the isothermal case.

f) Compare the energy flow for adiabatic compression (and contrast it with the isothermal compression case, done above).

In the isothermal case, the energy just flowed through the system, work was converted to heat. Now with an adiabatic process heat is not allowed out, so the work must increase the temperature of the system and all is trapped internally. The work done (on the gas) was 60% of that done isothermally, because the hotter gas would not let the mass fall as far.

2) Reversible Work: General principle of reversible vs irreversible work

(a) Calculate the work done by the system (in Joules) when 1 mole of ideal gas at 2.0 bar pressure and 300 K is expanded isothermally to a pressure of 1.5 bar, with the external pressure held constant at 1.5 bar. (Ans: -623 J)

One step work isothermal work: (see above)
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\[ P_0 = 2\text{bar} \quad \text{and} \quad P_1 = 1.5\text{bar} \]
\[ P_0V_0 = P_1V_1 = RT \]
\[ w = -P_e \Delta V = -P_1(V_1 - V_0) = -P_1V_1 \left(1 - \frac{V_0}{V_1}\right) = -RT \left(1 - \frac{P_1}{P_0}\right) \]
\[ w = -2.5(1 - 1.5 / 2)kJ = -625J \]

(b) Calculate the work done (on the system) when 1 mole of an ideal gas at 1.5 bars pressure and 300K is compressed isothermally to a pressure of 2.0 bar, with the external pressure held constant at 2.0 bar.

\[ P_0 = 1.5\text{bar} \quad \text{and} \quad P_1 = 2\text{bar} \]
\[ P_0V_0 = P_1V_1 = RT \]
\[ w = -RT \left(1 - \frac{P_1}{P_0}\right) \]
\[ w = -2.5(1 - 2 / 1.5)kJ = +833J \]

(c) Calculate the work done if the same gas is expanded isothermally and reversibly to the same final volume and pressure. (Ans: -717 J). And the work done if the gas is compressed reversibly between the same two points as part b).

Reversible Work
\[ P_0 = 2\text{bar} \quad \text{and} \quad P_1 = 1.5\text{bar} \]
\[ P_0V_0 = P_1V_1 = RT \]
\[ w = -P_e \Delta V = -\int PdV = -nRT \ln \left(\frac{V_1}{V_0}\right) = +RT \ln \left(\frac{P_1}{P_0}\right) \]
\[ w = 2.5 \ln \left(1.5 / 2\right)kJ = 720J \]

(d) Compare the values of the work determined for the three different processes (a-c) and order the work, showing that the reversible work is always “greater” than the irreversible work. Show the same inequality holds for both expansion and compression. Comment on the meaning of the word “greater”. Comment on equations 2.24 and 2.25 and suggest a way to write a single expression that is correct for both expansion and compression.

For compression the rev work < 1step work because 720 < 833, but for the expansion rev work < 1 step because -720 < -625, another way of writing is that -w_{i-step} < -w_{reversible}, and this shows that when the work is coming from (out of) the system the reversible work is the maximum work you will get from the system.

3) QA) (adapted from problem P2.5) The chemical reaction: \( \text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \) is the fundamental reaction in the body burning sugars or carbohydrates. This reaction produces about 400 kJ of (heat) energy per mole of oxygen consumed. The consumption of oxygen (as given in problem P1.4 in EDR) is 0.02 moles of oxygen per minute in an adult. How much heat does an adult generate per hour?
\[ q = \Delta U \cdot \text{rate} = 400 \frac{kJ}{\text{rxn}} \cdot \frac{1}{O_2} \cdot 0.02 \frac{\text{moles}}{\text{min}} \cdot 60 \frac{\text{min}}{\text{hr}} = 480 \frac{kJ}{\text{hr}} \]

QB) How many hours will it take an adult to burn off the contents of a cup of yogurt, which delivers about 100 Cal (C = big calories or kilocalories). Use the rate of burn from question QA).

\[
\frac{100\text{Cal} \times 4.18kJ}{480kJ/hr} \sim 1\text{hr}
\]

QC) How many calories then, given this burn rate, does an adult need in a day? (How does this square with nutritional guides?)

\[
480 \times 24 = 11MJ = 2,800\frac{Cal}{\text{day}}
\]

Most nutritional guides give about 2000-2500Cal, depending on age, sex and height, or only a bit less than this amount; probably just rounding.

QD) Given the heat production from part QA), if the body were wrapped for one hour so that the heat remained in the body, what would the temperature rise by. Assume the heat capacity of a body is the same as that of water (a good assumption) and that the average person weighs 70 kg. (Actually the average weight in US is about 80 kg, but then 75% are overweight.)

\[
q = 480 \frac{kJ}{hr} \cdot 1\text{hr} = \Delta U = C_v \Delta T = 70\text{kg} \cdot 4.18 \frac{kJ}{kg \cdot K} \Delta T
\]

\[
\Delta T = \frac{480 kJ}{70 \cdot 4.18} = 1.6K
\]

The body temperature would rise by 1.6C or 3.1F, which would cause severe distress.

Extra problems, as applications of principles to biological systems (just study; don’t fill out an answer unless you want to):

Ex1) In class we did not have time to derive the atmospheric distribution of air. But we can do it here. Imagine that you are at some altitude \( z \) and at that altitude there is some air mass above you pushing down (by gravity) causing pressure. If you consider a small increase in altitude \( h \) or \( dh \) the pressure will drop by a small amount. In that thin slice of air from \( z \) to \( z+h \) is air of mass \( m \) (a small amount of mass). The air due to that slice provides a pressure in addition to all the other mass above it. The additional pressure then is \( dP = \frac{mg}{A} \). Where \( A \) is some arbitrary area at altitude \( z \). The local density is \( d = \frac{m}{V} = \frac{m}{A \cdot h} \). You can combine these expressions to obtain an expression for the pressure as a function of the altitude, \( z \). Use the relation that \( dP(h) = -dP(z) \) (because the extra pressure is added to the lower value of \( z \), so as \( z \) increases the pressure must drop so the change in pressure must be negative) to obtain a relation between the pressure of the gas at altitude \( z \) and the local density \( d \).
Use the ideal gas equation, $P = CRT$ and $M \cdot P = \rho \cdot RT$, to obtain an expression for $dP$ as a function of $P(z)$. [The temperature is a function of the height as well, but for now assume it is constant, 15°C] You can then solve for the expression that the Pressure is a function of the height, assuming that the pressure of each species is the partial pressure at the surface of the earth. Dry air contains roughly (by volume) 78.09% nitrogen, 20.95% oxygen, 0.93% argon, 0.039% carbon dioxide, and small amounts of other gases. Air also contains a variable amount of water vapor, on average around 1%. http://en.wikipedia.org/wiki/Atmosphere_of_Earth. Carbon dioxide is in the air in very small amount (about 0.046% by mass or 0.039% by volume).

Integrate from the surface of the earth where $P=Po$ and $z=0$ up to any height $z$ assume the temperature is a constant (this is actually a poor assumption, but that can be fixed later).

As an example for how to handle equations of this sort:

Given the composition at the surface of the earth, what is the composition of the atmosphere 5 miles up and why is it not the same as on earth? (You may consider only the N2 and O2.)
For each species need to calculate \( \frac{RT}{Mg} \) this quantity has units of meter.

\[
\frac{RT}{Mg} = \begin{bmatrix} 8.7 & 7.7 & 6.1 \end{bmatrix} \text{km}
\]

So the concentrations that used to be at 5m = 8 km

\[
\begin{bmatrix} 0.78 & 0.21 & 0.01 \end{bmatrix}
\]

becomes

\[
\begin{bmatrix} 0.31 & 0.07 & 0.003 \end{bmatrix}
\]

So the percent composition is 80% 19% and 0.7%, so the N2 which is the lightest is slightly enriched, by 2% and the Ar drops from 1 to 0.7%.

What is the total pressure 5 miles up (Airplanes fly between 5 and 6 miles up). From the values above the pressure is 0.38 Atm

How far up do you have to go to contain \( \frac{1}{2} \) the N\(_2\) between the earth and that point?

\[
\int P(z) \, dz
\]

The answer is the fraction is: \( f(z) = \frac{1}{2} - e^{-z/L} \) for \( f=1/2 \), then \( z=L\ln(2) \), which is 6 km for N2 and 4.2 km for Ar and even slightly less for CO2, at 3.8kM.

How far up do you have to go to contain \( \frac{1}{2} \) the CO\(_2\) between the earth and that point? Comment on the potential advantage of the relative hieghts of CO\(_2\) and N\(_2\) for trees.

Ex2) Chapter 2, Problem P2.33 from the EDR Text.

The reversible work involved in twisting a short DNA molecule depends quadratically on \( \phi/L \), the angle of twist per unit length, where the twist angle is expressed in units of radians. The expression for the reversible work is:

\[
w_{\text{twist}} = \frac{CL}{2} \left( \frac{\phi}{L} \right)^2
\]

A DNA oligomer 20 base pairs in length undergoes a twisting deformation of 36 degrees in order to bind to a protein. Calculate the reversible work involved in this twisting deformation. Assume \( C = 2.5 \times 10^{-28} \) J m. Assume also that each base pair is 3.4 Å in length (1 Å = 10\(^{-10}\) m).

\[
w_{\text{twist}} = \frac{CL}{2} \left( \frac{\phi}{L} \right)^2 = \frac{1.2 \times 10^{-28}}{20 \times 3.4 \times 10^{-10} \left( \frac{2 \cdot \pi}{10} \right)^2} = 7 \times 10^{-21} J = 4.2 kJ / mol
\]