PHY7A Practice Solutions

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Before using these solutions, make sure you have first made a solid attempt at solving them yourself. Asking a friend or reaching out to me for a hint will lead to more effective learning, even if it takes longer. **For direct preparation for the final, consider reviewing the DLs, and working through the past finals available on Canvas first.**

A lot of the questions are intended to give an extra challenge, and push just beyond the course. Here is an outline that roughly describes the concepts and skills:

- **1.1 'Glasswork'** Thermal and bond energy, deducing equilibrium state, working with numbers
- **1.2 'Substance $\mathcal{A}$ in water'** Deducing heats, thermal equilibrium, sketching a three-phase plot
- **2.1 'On the slopes'** Kinetic and potential energy, calculating work, converting to heat
- **2.2 'Orbiting the sun'** Reading a potential, formulas and derivatives, sketching a potential
- **3.1 'Frozen modes'** Relating atomic structure to modes, particle model of thermal energy
- **3.2 'Bond energy in a cube'** Finding neighbors, particle model of bond energy
- **4.1 'Cycle of constants'** Work & Heat, heat capacities, sketching PV diagram, calculating entropy
- **4.2 'Fridge'** Work & Heat, sketching PV and TS diagrams, thinking of entropy

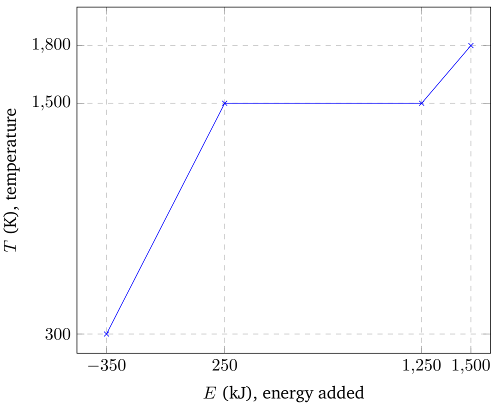
1 Applying Models to Thermal Phenomena

Question 1.1 ‘Glasswork’

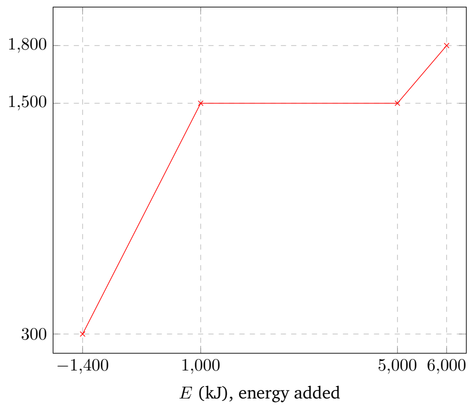
1. *Make new two-phase plots for the* 0.5 *kg of blue glass and the* 2.0 *kg of red glass, labeling the numbers on the axes.*

   Since the only change from the plot given is the mass of glass, one only needs to modify the labels on the x-axis for the energy. For the blue glass, we have half the mass, and so half the energy change; for the red glass, we have double the mass, and so double the energy change.

   Two-phase diagram of 0.5 kg of blue glass

   Two-phase diagram of 2 kg of red glass

2. *How much energy is added to the blue glass in step (i)? How much energy is added to the red glass?*

   The values can be read from the graph by looking at differences between points on the x-axis. For the blue glass, it takes 600 kJ to heat to 1500 K from 300 K. For the red glass, the values are four times larger, and we need to heat further, so one finds 7400 kJ.

3. *What is the temperature and phase of the glass once it reaches thermal equilibrium after mixing? What type(s) of energy does each glass gain/lose in step (ii)?*

   The blue and red glass will exchange energy with each other until they reach the same temperature. The blue glass is about to gain bond energy (until it may fully melt), and the red glass is about to lose thermal energy (until it may reach the melting point).

   $$\Delta E_{\text{bond,blue}} = 1000 \text{ kJ}, \quad \Delta E_{\text{thermal,red}} = -1000 \text{ kJ}.$$

   Since the magnitude of the energies is the same, they actually finish their processes together. Both glasses end up fully melted, but exactly at the melting point 1500 K.

   The blue glass gained bond energy, and the red glass lost thermal energy.

4. *How long does she need to wait for the glass to cool back down to room temperature in step (iii)?*

   The total energy gained by the glass is 8000 kJ (600 from blue and 7400 from red), and this is the energy it has to lose to return to room temperature. Since the glass cools by 1 kJ every second, it will then take 8000 seconds for this energy to leave the glass, or about 2 hours and 13 minutes.

5. *Repeat parts (2-4) for* 0.25 *kg of blue glass and for* 1.0 *kg of blue glass.*

   When there are 0.25 kg of blue glass, it only takes 300 kJ to heat it to 1500 K. The total energy gained is then 7700 kJ, so it will take 7700 seconds to cool, or about 2 hours and 8 minutes.

   Then, when the glass is mixed, we find $\Delta E_{\text{bond,blue}} = 500 \text{ kJ} < |\Delta E_{\text{thermal,red}}| = 1000 \text{ kJ}$, so the blue glass finished melting before the red glass finishes cooling. Thus, the blue glass will continue to heat up until they reach the same temperature

$$\Delta E_{\text{blue}} = \Delta E_{\text{bond,blue}} + \Delta E_{\text{thermal,blue}} = -\Delta E_{\text{thermal,red}}.$$

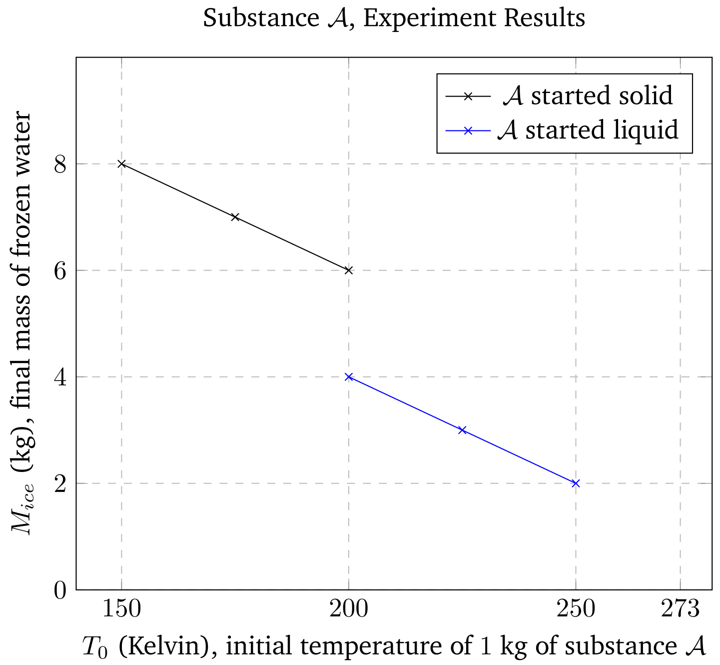
The specific heat capacity of both types of glass can be found from the plot for 1 kg: $c_{\text{glass}} = \frac{5}{3}$ kJ/(kg K). Then, we can plug this into the equation to find

$$\begin{aligned}
500 + m_{\text{blue}} c_{\text{glass}}(T - 1500) &= -m_{\text{red}} c_{\text{glass}}(T - 1800) \\
\implies 500 + \frac{5}{12}(T - 1500) &= \frac{10}{3}(1800 - T) \\
\implies \left(\frac{5}{12} + \frac{10}{3}\right) T &= \frac{5}{12} \cdot 1500 + \frac{10}{3} \cdot 1800 - 500 \\
\implies T &= 1633.33 \text{ K}
\end{aligned}$$

When there is 1 kg of blue glass, it takes 1200 kJ to heat it to 1500 K. The total energy gained is then 8600 kJ, so it will take 8600 seconds to cool, or about 2 hours and 23 minutes.

Then, when the glass is mixed, we find $\Delta E_{\text{bond,blue}} = 2000$ kJ $> |\Delta E_{\text{thermal,red}}| = 1000$ kJ, so the red glass is finished cooling to the melting point before the blue glass is done melting. At that point, they will both be at 1500 K, so they have reached a thermal equilibrium, and end up in a mixed solid-liquid phase.

Question 1.2 ‘Substance $\mathcal{A}$ in water’



The key to this question is recognizing that, since the system is isolated, the amount of energy gained by the substance $\mathcal{A}$ is directly related to the energy lost by the water:

$$\Delta E_{tot} = 0 \implies \Delta E_{\mathcal{A}} + \Delta E_{H_2O} = 0 \implies \Delta E_{\mathcal{A}} = -\Delta E_{H_2O} = |\Delta H_{H_2O} \Delta m_{H_2O}|.$$

We can use this to calculate all the energy differences, and the corresponding heat capacity or heat of melting.

(a) *What is the specific heat of solid $\mathcal{A}$?*

$$\begin{aligned} \Delta E_{\text{solid } \mathcal{A}} &= |\Delta H_{H_2O} \Delta m_{H_2O}| \\ &\implies m_{\mathcal{A}} c_{\text{solid } \mathcal{A}} \Delta T = |\Delta H_{H_2O} \Delta m_{H_2O}| \\ &\implies c_{\text{solid } \mathcal{A}} = \frac{|\Delta H_{H_2O} \Delta m_{H_2O}|}{m_{\mathcal{A}} \Delta T} = \frac{333.5 \cdot 2}{50 \cdot 1} \text{ kJ/K} = 13.34 \text{ kJ/(kg K)} \end{aligned}$$

(b) *What is the heat of melting of $\mathcal{A}$?*

$$\begin{aligned} \Delta E_{\text{melting } \mathcal{A}} &= |\Delta H_{H_2O} \Delta m_{H_2O}| \\ &\implies |\Delta m_{\mathcal{A}} \Delta H_{\text{melting } \mathcal{A}}| = |\Delta H_{H_2O} \Delta m_{H_2O}| \\ &\implies \Delta H_{\text{melting } \mathcal{A}} = \frac{|\Delta H_{H_2O} \Delta m_{H_2O}|}{\Delta m_{\mathcal{A}}} = \frac{333.5 \cdot 2}{1} \text{ kJ/K} = 667 \text{ kJ/kg} \end{aligned}$$

(c) *What is the specific heat of liquid $\mathcal{A}$?*

$$\begin{aligned} \Delta E_{\text{liquid } \mathcal{A}} &= |\Delta H_{H_2O} \Delta m_{H_2O}| \\ &\implies m_{\mathcal{A}} c_{\text{liquid } \mathcal{A}} \Delta T = |\Delta H_{H_2O} \Delta m_{H_2O}| \\ &\implies c_{\text{liquid } \mathcal{A}} = \frac{|\Delta H_{H_2O} \Delta m_{H_2O}|}{m_{\mathcal{A}} \Delta T} = \frac{333.5 \cdot 2}{50 \cdot 1} \text{ kJ/K} = 13.34 \text{ kJ/(kg K)} \end{aligned}$$

(d) *How much energy does $\mathcal{A}$ absorb if it started as a liquid at $T_0 = 250$ K?*

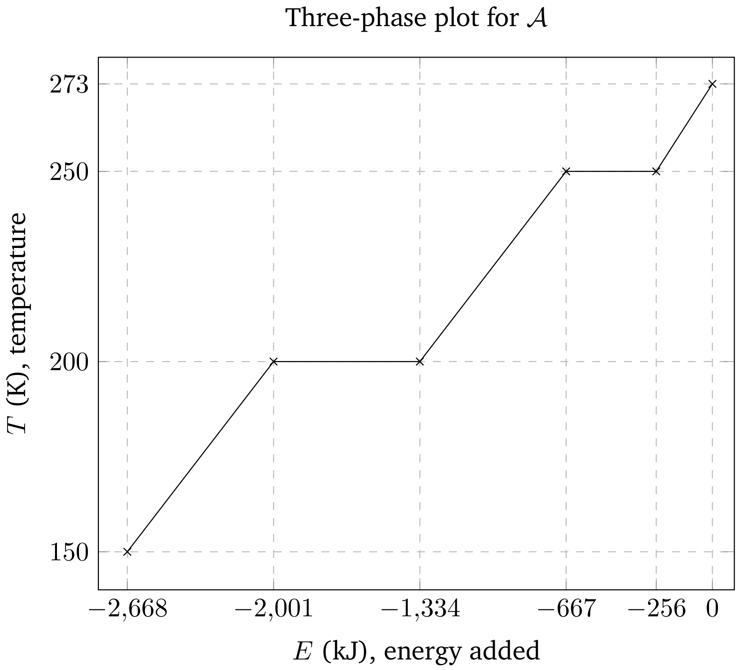
$$\Delta E_{\text{from 250 K}} = |\Delta H_{H_2O} \Delta m_{H_2O}| = 333.5 \cdot 2 \text{ kJ} = 667 \text{ kJ}$$

(e) *Given that gaseous $\mathcal{A}$ has a (constant volume) specific heat of* 11.12 *kJ/(kg K), what is the heat of vaporization?*

For this part, we need to use the result from (d) and recognize that this energy accounts for both the phase and temperature change.

$$\Delta E_{\text{from 250 K}} = \Delta E_{bond} + \Delta E_{th} = |\Delta H_{\text{vaporizing } \mathcal{A}} \Delta m_{\mathcal{A}}| + m_{\mathcal{A}} c_{\mathcal{A}} \Delta T$$
$$\implies \Delta H_{\text{vaporizing } \mathcal{A}} = \frac{\Delta E_{\text{from 250 K}} - m_{\mathcal{A}} c_{\mathcal{A}} \Delta T}{|\Delta m_{\mathcal{A}}|} = \frac{667 - 1 \cdot 11.12 \cdot 23}{1} \text{ kJ/kg} = 411.24 \text{ kJ/kg}$$

With all the calculations we have done, including appropriate calculations for intermediate energies, the three-phase plot for $\mathcal{A}$ should be



(f) *Based on the ratio between the specific heat of solid $\mathcal{A}$ and gaseous $\mathcal{A}$, what can you say about the number of active modes that gaseous $\mathcal{A}$ has at 250 K?*

Recall that the molar heat capacity of a substance is related to the number of modes as

$$c_{\text{molar}} = \frac{(\text{\# of modes})}{2} R.$$

The relationship between specific heat and molar heat capacity is determined by the molar mass. Since the solid and gas are both made of $\mathcal{A}$, they have the same molar mass, and so we find

$$\frac{c_{\text{specific,gas}}}{c_{\text{specific,solid}}} = \frac{c_{\text{molar,gas}}}{c_{\text{molar,solid}}} = \frac{(\text{\# of modes in gas } \mathcal{A})}{(\text{\# of modes in solid } \mathcal{A})}.$$

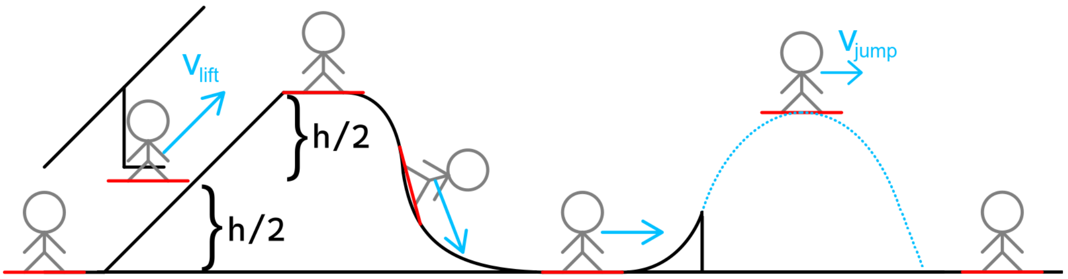
Recalling that solids have 6 modes (3 kinetic and 3 potential modes), one finds

$$(\text{\# of modes in gas } \mathcal{A}) = (\text{\# of modes in solid } \mathcal{A}) \frac{c_{\text{specific,gas}}}{c_{\text{specific,solid}}} = 6 \cdot \frac{11.12}{13.34} = 5.00,$$

so the gas has 5 active modes.

2 Applying Models to Mechanical Phenomena

Question 2.1 ‘On the slopes’



A picture corresponding to the question. The velocity of the snowboarder is indicated by the light blue arrow. Not to scale.

(a) *How much work does the lift do by the time the snowboarder is at a height $h/2$? How much more work does it take to get the snowboarder to h?*

We can calculate the total energy at the three points by considering the kinetic and potential energies:

$$
\begin{aligned}
E_{\text{bottom}} &= Mg(0) + \frac{1}{2}M(0)^2 = 0,\\
E_{\text{middle}} &= Mg(h/2) + \frac{1}{2}M(v_{\text{lift}})^2,\\
E_{\text{top}} &= Mg(h) + \frac{1}{2}M(0)^2 = Mgh.
\end{aligned}
$$

Since there is no heat involved with the lift, we have $\Delta E = W$, so we find

$$
\begin{aligned}
W_{\text{from bottom to middle}} &= E_{\text{middle}} - E_{\text{bottom}} = Mg(h/2) + \frac{1}{2}M(v_{\text{lift}})^2,\\
W_{\text{from middle to top}} &= E_{\text{top}} - E_{\text{middle}} = Mg(h/2) - \frac{1}{2}M(v_{\text{lift}})^2.
\end{aligned}
$$

Notice that in the amount of work done in the first half is larger than in the second half, since the snowboarder acquires kinetic energy at the start and loses kinetic energy at the end.

(b) *How much energy to the snowboarder have before he goes down the slope? At the bottom of the slope? At the peak of his jump?*

Since the slope (and flying through the air) is frictionless, the energy will be the same at each of the three points. We already calculated E_{top} in the first part as Mgh.

(c) *Calculate the speed when the snowboarder is moving fastest.*

The snowboarder has the highest speed when they have the highest kinetic energy. By conservation of energy, this must be when they have the lowest potential energy. This occurs at the bottom of the hill, with $PE = 0$. Then,

$$
E_{\text{bottom}} = Mgh = \frac{1}{2}Mv^2 \implies v = \sqrt{2gh}.
$$

(d) *Calculate the height of the snowboarder’s jump.*

At the peak of the snowboarder’s jump, they are not moving vertically. As a result, the kinetic energy is simply

$$
KE_{\text{peak}} = \cancelto{0}{\frac{1}{2}Mv_y^2} + \frac{1}{2}Mv_x^2 = \frac{1}{2}Mv_{\text{jump}}^2.
$$

Then,

$$E_{\text{jump}} = Mgh = PE + KE = Mgh_{\text{jump}} + \frac{1}{2}Mv_{\text{jump}}^2 \implies h_{\text{jump}} = h - \frac{1}{2g}v_{\text{jump}}^2.$$

(e) *How much snow does the snowboarder melt as he comes to a stop after his jump?*
Assume the snow is at $0\ {}^\circ C$*, and has a heat of melting of* ΔH_{melt}*, and that no energy is lost elsewhere.*

Since all the energy went into melting the snow, we have

$$\Delta E_{\text{snowboard}} + \Delta E_{\text{snow}} = 0 \implies \Delta E_{\text{snow}} = -\Delta E_{\text{snowboard}}.$$

Plugging in the formulas we know

$$\Delta m_{\text{melted snow}} \Delta H_{\text{melt}} = -(0 - Mgh) \implies \Delta m_{\text{melted snow}} = \frac{Mgh}{\Delta H_{\text{melt}}}$$

Question 2.2 'Orbiting the sun'

(a) *Which term corresponds to the gravitational force?*

We know that the gravitational force should be attractive, i.e. it pulls towards smaller values of r. Since the force goes in the direction of decreasing potential energy, we need to analyze which of the terms decreases as one goes towards smaller values of r.

Notice that the magnitude of each term increases for smaller radii

$$r_{\text{small}} < r_{\text{large}} \implies \left|\frac{A}{(r_{\text{small}})^2}\right| > \left|\frac{A}{(r_{\text{large}})^2}\right|, \quad \left|\frac{B}{r_{\text{small}}}\right| > \left|\frac{B}{r_{\text{large}}}\right|.$$

Then, the term that decreases for smaller r is the one with a minus sign:

$$-\frac{B}{r_{\text{small}}} < -\frac{B}{r_{\text{large}}},$$

so this is the term corresponding to gravity.

(b) *What are the units of A and B?*

The units of each term in an equation should be the same. In the equation

$$PE(r) = \frac{A}{r^2} - \frac{B}{r},$$

the left hand side (LHS) has units of energy, so the right hand side (RHS) should too.

So, using square brackets $[\cdots]$ to denote the units of some quantity, we have

$$\left[\frac{A}{r^2}\right] = \text{Energy} \implies [A] = \text{Energy} \cdot \text{Length}^2 \text{ (e.g. J} \cdot \text{m}^2\text{)}$$

$$\left[\frac{B}{r}\right] = \text{Energy} \implies [B] = \text{Energy} \cdot \text{Length (e.g. J} \cdot \text{m)}$$

(c) *For what radius is the potential energy zero?*

Setting the potential energy equal to zero, we can solve for the radius

$$PE(r) = 0 \implies \frac{A}{r^2} - \frac{B}{r} = 0 \implies A - Br = 0 \implies r = \frac{A}{B}.$$

(d) *What value does the potential energy approach for very, very large radii?*

For very large radii, the magnitudes of both of the terms A/r^2 and B/r become small. Phrased more rigorously

$$\lim_{r\to\infty} PE(r) = \lim_{r\to\infty}\left(\frac{A}{r^2} - \frac{B}{r}\right) = 0.$$

(e) *What value does the potential energy approach for very, very small radii?*

For very small radii, the magnitudes of both of the terms A/r^2 and $-B/r$ become very large, approaching infinity. However, A/r^2 grows much more quickly than $-B/r$, so the end result is positive.

$$\lim_{r\to 0^+} PE(r) = \lim_{r\to 0^+}\left(\frac{A}{r^2} - \frac{B}{r}\right) = \lim_{r\to 0^+}\left(\frac{A - Br}{r^2}\right) = +\infty.$$

(f) For what radius is the force zero?

The force due to a potential is $F(r) = -dPE(r)/dr$. Applying this to the potential given

$$F(r) = -\frac{dPE(r)}{dr} = -\left(-2\frac{A}{r^3} + \frac{B}{r^2}\right) = 2\frac{A}{r^3} - \frac{B}{r^2}.$$

We find as expected that the term corresponding to the gravitational force is negative for an attractive force.

Solving for when the force is zero, we find

$$F(r) = 0 \implies 2\frac{A}{r^3} - \frac{B}{r^2} = 0 \implies 2A - Br = 0 \implies r = \frac{2A}{B}.$$

Note that the force also approaches zero for very large radii.

(g) *What is the potential energy when the force is zero?*

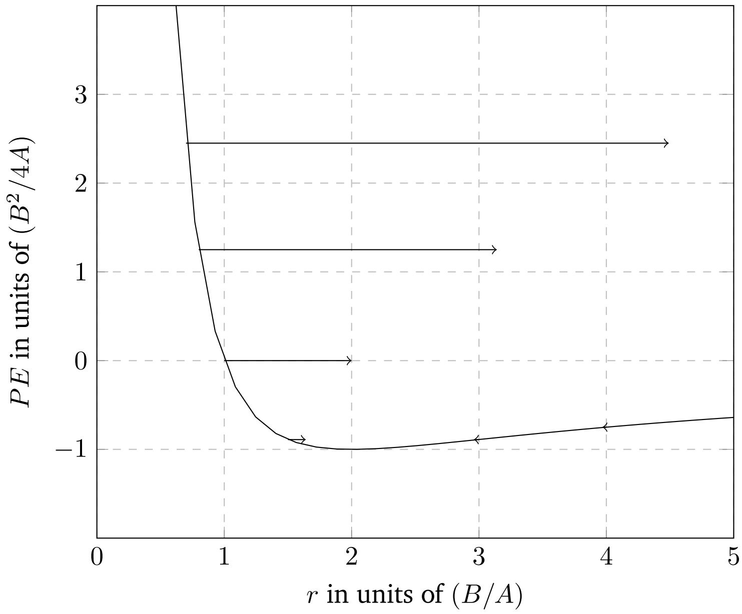
Simply plugging in the value we got from the previous part,

$$PE(2A/B) = \frac{A}{(2A/B)^2} - \frac{B}{(2A/B)} = \frac{B^2}{4A} - \frac{B^2}{2A} = -\frac{B^2}{4A}.$$

(h) *Sketch the potential, and draw arrows corresponding to the force.*

In order to make drawing it easier, we can choose values of A and B where the x-intercept and well-depth are both equal to 1; this would be similar to choose $\sigma = \varepsilon = 1$ for the Lennard-Jones potential.

The x-intercept is at A/B and the well-depth is $B^2/4A$, so we can choose $A = B = 4$, and sketch something like



Note that in the image the behavior for large r is not obvious since it takes very large values to come close to $PE \simeq 0$. Gravity acts at much longer ranges than the force caused by the Lennard-Jones potential.

3 Applying Particle Models to Matter

Question 3.1 ‘Frozen modes’

(a) *Assuming none of the modes are frozen at $T = 2000$ K, how many atoms does each gas have?*

Recall that a monatomic gas has 3 modes (all translational kinetic), so Gas 1 is monatomic.

A linear gas has 3 translational modes and 2 rotational modes, leaving $3(\#\text{ of atoms}) - 5$ vibrational kinetic modes, which are each paired with a vibrational potential mode. This gives a total for $6(\#\text{ of atoms}) - 5$ modes for a linear gas, which accounts for both Gas 2 (with 2 atoms) and Gas 3 (with 3 atoms).

For completeness, for a non-linear gas one would use the same reasoning with 3 rotational modes to find $6(\#\text{ of atoms}) - 6$ modes.

(b) *In one mole of particles of gas 2 at 900K, how many have 5 active modes?*

At 900 K, gas 2 has 6 active modes per particle on average. Since the kinetic and potential vibrational modes activate together, it is only possible for the gas to be at either 5 or 7 modes.

In order to reach an average of 6, half must have 5 active modes.

(c) *At what temperature does every particle in gas 3 have 2 active vibrational modes?*

Since gas 3 is linear triatomic, it has 3 translational and 2 rotational kinetic modes. When 2 vibrational modes are active, there are 7 active modes total, which we see is at 300 K from the graph.

(d) *How much thermal energy per mole does each gas have at 2000 K? 500 K?*

Using the formula for E_{th}, we have

$$\begin{aligned}
E_{th,1,\text{molar}}(2000\text{ K}) &= \frac{R}{2}(3)(2000\text{ K}) = 24.942\text{ kJ/mol},\\
E_{th,2,\text{molar}}(2000\text{ K}) &= \frac{R}{2}(7)(2000\text{ K}) = 58.198\text{ kJ/mol},\\
E_{th,3,\text{molar}}(2000\text{ K}) &= \frac{R}{2}(13)(2000\text{ K}) = 108.082\text{ kJ/mol}.
\end{aligned}$$

For temperatures between 300 K and 1500 K, we can calculate the number of modes for gas 2 and 3 to be precise:

$$\begin{aligned}
f_2(T) &= 5 + \frac{2}{1200}(T - 300),\\
f_3(T) &= 7 + \frac{6}{1200}(T - 300).
\end{aligned}$$

So, at 500 K, the 3 gases have: 3 modes, $16/3$ modes, and 8 modes.

$$\begin{aligned}
E_{th,1,\text{molar}}(500\text{ K}) &= \frac{R}{2}(3)(500\text{ K}) = 6.236\text{ kJ/mol},\\
E_{th,2,\text{molar}}(500\text{ K}) &= \frac{R}{2}\left(\frac{16}{3}\right)(500\text{ K}) = 11.085\text{ kJ/mol},\\
E_{th,3,\text{molar}}(500\text{ K}) &= \frac{R}{2}(8)(500\text{ K}) = 16.628\text{ kJ/mol}.
\end{aligned}$$

(e) *Suppose 1 mole of gas 1 at 1500 K is mixed with a very large amount of gas 3 at 500 K. How much heat is exchanged between the two gases as they reach thermal equilibrium?*

Since there is a very large amount of gas 3 at 500 K, that is the temperature at which thermal equilibrium will be reached. So, we need to calculate the change in thermal energy for one mole of gas 1 from 1500 K to 500 K:

$$|Q| = |\Delta E_{th}| = \frac{R}{2}|\Delta(fT)| = \frac{3R}{2}|(1500 - 500)| = 12.471 \text{ kJ}.$$

This energy is transfered from the hotter gas to the colder gas.

(f) *Suppose 1 mole of gas 3 at* 1500 *K is mixed with a very large amount of gas 1 at* 500 *K. How much heat is exchanged between the two gases as they reach thermal equilibrium?*

Since there is a very large amount of gas 1 at 500 K, that is the temperature at which thermal equilibrium will be reached. So, we need to calculate the change in thermal energy for one mole of gas 3 from 1500 K to 500 K. Note that this difference will involve using different numbers of modes:

$$|Q| = |\Delta E_{th}| = \frac{R}{2}|\Delta(fT)| = \frac{R}{2}|(13 \cdot 1500 - 8 \cdot 500)| = 64.433 \text{ kJ}.$$

This energy is transfered from the hotter gas to the colder gas.

(g) *Suppose 1 mole of gas 3 at* 500 *K is mixed with 1 mole of gas 2 at* 1500 *K. What temperature do they reach for thermal equilibrium?*

Assuming a closed system, we need to have $\Delta E_{th,2} + \Delta E_{th,3} = 0$. Calculating each independently first:

$$\begin{aligned} \Delta E_{th,2} &= \frac{R}{2}(f_2(T) \cdot T - 7 \cdot 1500), \\ \Delta E_{th,3} &= \frac{R}{2}(f_3(T) \cdot T - 8 \cdot 500). \end{aligned}$$

Then, we turn this into an equation

$$\begin{aligned} &\Delta E_{th,2} + \Delta E_{th,3} = 0 \\ \Longrightarrow\ &(f_2(T) \cdot T - 7 \cdot 1500) + (f_3(T) \cdot T - 8 \cdot 500) = 0 \\ \Longrightarrow\ &T(f_2(T) + f_3(T)) - 14500 = 0 \\ \Longrightarrow\ &T(12 + \frac{1}{150}(T - 300)) - 14500 = 0 \\ \Longrightarrow\ &\frac{1}{150}T^2 + 10T - 14500 = 0 \\ \Longrightarrow\ &T = \frac{-10 + \sqrt{100 + 386.67}}{\frac{2}{150}} = 905 \text{ K}, \end{aligned}$$

where one takes the positive solution to the quadratic since the negative solution gives a negative temperature (unphysical).

Question 3.2 ‘Bond energy in a cube’

(a) *How many atoms are there in a cube of size $L = 2$? Size $L = 3$? Arbitrary L?*

The number of atoms in a cube of size L is simply L^3. So, for $L = 2$ there are 8 atoms, and for $L = 3$ there are 27 atoms.

(b) *What value of L do you need to get approximately N_A atoms?*

Solving $L^3 = N_A$, we find $L = \sqrt[3]{N_A} = 8.4 \cdot 10^7$.

(c) *How many nearest neighbor pairs are there in a cube of size $L = 2$? Size $L = 3$? Arbitrary L?*

If you take a single row of the cube, there are L atoms in a row, with $L - 1$ atoms between them.

Lets take only the rows that go in one direction, e.g. all the bonds that go along the x-axis. There are L^2 such rows.

Now, since there are 3 directions, with L^2 rows in each direction, with $L - 1$ bonds in each such row, there are $3L^2(L - 1)$ bonds in the entire cube.

(d) *What is the number of nearest neighbor bonds per atom? What does this value approach for very large L? Justify this value using the nearest neighbor approximation.*

The number of nearest neighbors per atom is

$$\frac{(\text{\# number of nearest neighbors})}{(\text{\# number of atoms})} = \frac{3L^2(L-1)}{L^3}$$

where for very large values of L, we find

$$\lim_{L\to\infty} \frac{3L^2(L-1)}{L^3} = 3.$$

Since most of the atoms are inside of the cube, they have 6 nearest neighbors. Since each bond is shared between two atoms, there are 3 nearest neighbor bonds per atom.

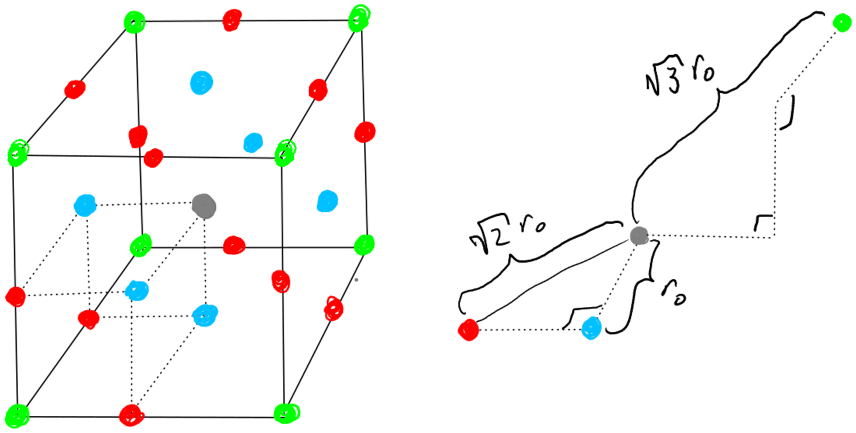
The reason we don’t have exactly 3 nearest neighbor bonds per atom is because some of the atoms on the surface of the cube have fewer bonds.

(e) *What is the approximate bond energy in a cube of size L? What is the molar heat of vaporizing such a cube?*

Each bond contributes $-\varepsilon$ to the bond energy. (Remember that the bond energy is negative, so one would need to add heat to break bonds!) So, with approximately $3L^3$ bonds, we have

$$E_{\text{bond}} = (-\varepsilon)3L^3.$$

When we have N_A atoms, we have $L^3 = N_A$, so the molar heat of vaporizing this cube is $\Delta H_{\text{molar}} = 3\varepsilon N_A$.



My best attempt at drawing a cubic lattice with labeling neighbors of some atom. Consider the atom marked in gray: the blue atoms are the 6 nearest neighbors, the red atoms are the 12 next-nearest neighbors, and the green atoms are the 8 next-next-nearest neighbors. On the right, an isolated image shows a calculation of the distance with right angles marked.

(f) *How many next-nearest neighbors do most atoms have? How far are they?*

The next-nearest neighbors are those that are two bonds away, labeled red in the above picture. Counting them, one finds that there are 12 next-nearest neighbors. Using the Pythagorean theorem, one sees that they are $\sqrt{2}r_0$ away.

(g) *How many next-next-nearest neighbors do most atoms have? How far are they?*

The next-nearest neighbors are those that are two bonds away, labeled green in the above picture. Counting them, one finds that there are 8 next-nearest neighbors. Using the Pythagorean theorem, one sees that they are $\sqrt{3}r_0$ away.

(h) *Recalculate the bond energy in a cube of size L using the next-nearest and next-next-nearest neighbors.*

We will need to use the values given for the potential at larger distances: $LJ(\sqrt{2}r_0) = -0.24\varepsilon$ aand $LJ(\sqrt{3}r_0) = -0.07\varepsilon$.

For each atom, we have 6 nearest neighbors, 12 next-nearest neighbors, and 8 next-next-nearest neighbors. Since each bond is shared between two atoms, we must divide these values by two, and we find the bond energy per atom is

$$E_{\text{bond,per atom}} = 3LJ(r_0) + 6LJ(\sqrt{2}r_0) + 4LJ(\sqrt{3}r_0) \simeq -47.2\varepsilon.$$

Multiplying by the number of atoms, we get

$$E_{\text{bond}} = -4.72\varepsilon L^3,$$

and for one mole of atoms, $N_{\text{atoms}} = L^3 = N_A$, we have $E_{\text{bond,molar}} = -4.72\varepsilon N_A$.

4 Models of Thermodynamics

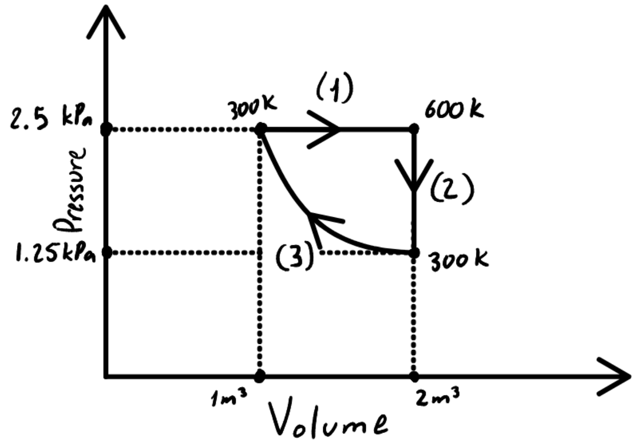
Question 4.1 ‘Cycle of constants’

(a) *Sketch a PV diagram of the process, labeling the relevant values for each of the states.*

We are given the volume and temperature before step 1: $1\ \text{m}^3$ and 300 K. We can calculate the pressure using the ideal gas law:

$$PV = nRT \implies P = \frac{nRT}{V} = \frac{1 \cdot 8.314 \cdot 300}{1}\ \text{Pa} = 2.5\ \text{kPa}.$$

Then, after step 1, we’ve double the temperature and kept pressure constant, so the volume must double. After step 2, we’ve halved the temperature and kept volume constant, so the pressure must be halved. Then, we return to the first point on a curve with constant temperature, so $P \propto 1/V$ gives us an approximate shape.



(b) *What is the work and heat corresponding to the constant pressure step?*

Work can be calculated using $W = -P\Delta V$:

$$W = -P\Delta V = -2.5 \cdot 1\ \text{kPa} \cdot \text{m}^3 = -2.5\ \text{kJ}.$$

In order to calculate heat, we need to calculate the change in internal energy, for which we use the formula in terms of the number of modes f:

$$\Delta U = \Delta E_{th} = \frac{nR}{2} f \Delta T = \frac{1 \cdot 8.314}{2} 3(300)\ \text{J} = 3.74\ \text{kJ}.$$

So,

$$Q = \Delta U - W = 5.26\ \text{kJ}.$$

(c) *What is the work and heat corresponding to the constant volume step?*

Since the volume does not change, the work is $W = 0$.

For the heat, we know we returned to the original temperature, so $\Delta U_{(\text{step 2})} = -\Delta U_{(\text{step 1})} = -3.74$ kJ. Since there is no work, we must also have that $Q = -3.74$ kJ.

(d) *What is the work for the constant temperature step? Hint: Recall* $P = \frac{nRT}{V}$, $W = \int PdV$, *and* $\int_a^b \frac{1}{x}dx = \ln(b/a)$.

We perform the suggested integral:

$$W = -\int_{2\text{ m}^3}^{1\text{ m}^3} PdV = -\int_{2\text{ m}^3}^{1\text{ m}^3} \frac{nRT}{V} dV = -nRT\ln(1/2) = 1 \cdot 8.314 \cdot 300 \cdot (0.693) = 1.73 \text{ kJ},$$

which is negative as expected, since the volume is decreasing.

(e) *What is the heat in the last step?*

In the last step, $\Delta U = \Delta E_{th} = 0$, since the temperature does not change. So,

$$\Delta U = Q + W = 0 \implies Q = -W \implies Q = -1.73 \text{ kJ}.$$

(f) *What is the entropy in each step? For the whole cycle?*

Recall that the constant pressure molar heat capacity is

$$c_{pm} = \left(\frac{f}{2} + 1\right) R,$$

where f is the number of modes per particle. Then, since we have one mole of monatomic particles,

$$\Delta S_1 = \left(\frac{3}{2} + 1\right) R\ln(600/300) = 14.41 \text{ J/K}.$$

Recall that the constant pressure molar heat capacity is

$$c_{vm} = \frac{f}{2}R,$$

where f is the number of modes per particle. Then,

$$\Delta S_2 = \frac{3}{2}R\ln(300/600) = -8.64 \text{ J/K}.$$

For the constant temperature step,

$$\Delta S_3 = \frac{Q}{T} = \frac{-1730}{300} = -5.77 \text{ J/K}.$$

The total change in entropy is

$$\Delta S_{\text{total}} = \Delta S_1 + \Delta S_2 + \Delta S_3 = 0 \text{ (due to rounding, one might be slightly off)},$$

as expected since we have completed a cycle and entropy is a state function.

Question 4.2 ‘Fridge’

(a) *What is the sign on the work in steps 1 and 3?*

In step 1, the fluid expands, i.e. $\Delta V > 0$. Since work is $W = -P\Delta V$, we must have $W < 0$.

By the same reasoning, one finds that $W > 0$ in step 3.

(b) *Explain why expanding adiabatically lowers temperature.*

An adiabatic expansion has $Q = 0$, while $\Delta V > 0 \implies W < 0$. Then, we can use the change in total energy to see that the thermal energy decreased, implying a lowered temperature:

$$\Delta U = Q + W = 0 + W < 0 \implies \Delta E_{th} = C\Delta T < 0 \implies \Delta T < 0.$$

(c) *What is the sign on ΔS in steps 2 and 4?*

Since heat is $Q = \int TdS$, when we have $Q > 0$, we must have $\Delta S > 0$. So, in step 2 we have an increasing entropy.

By the same reasoning, one finds that the entropy decreases in step 4.

(d) *What is the sign on ΔP in steps 2 and 4?*

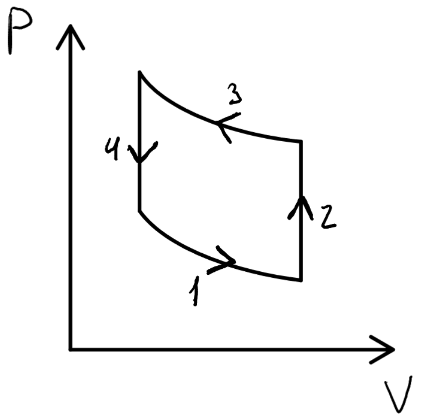
Using the ideal gas law, we have

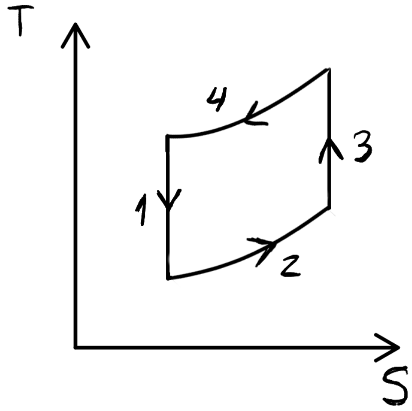
$$PV = nRT \implies \Delta(PV) = nR\Delta T.$$

In steps 2 and 4, there is no work, so volume is held constant, giving us $V\Delta P = nR\Delta T$, so the pressure changes in the same direction as the temperature.

Thus, in step 2 pressure increases, while in step 4 pressure decreases.

(e) *Sketch a PV and a TS diagram for the cycle.*





Note that the slopes on the non-vertical lines are not constant. Though it is not required to remember or necessarily apply, it can be nice to appreciate where the slopes come from:

- In the PV diagram, these slopes correspond to the case where $Q = 0$, where we have $W = \Delta E_{th}$. Then, one can set up the differential equation

$$-PdV = \frac{f}{2}nRdT \implies -PdV = \frac{f}{2}d(PV) \implies \left(-1 - \frac{f}{2}\right)\frac{dV}{V} = \frac{dP}{P}$$

$$\implies \left(1 - \frac{f}{2}\right)\ln(V) = \ln(P) + c \implies P \propto V^{-(1+\frac{f}{2})}$$

- In the TS, diagram one can use the formula

$$\Delta S = C\ln(T_f/T_i) \implies T_f = T_i e^{\frac{S_f - S_i}{C}}.$$

You can try plotting these using sample values using a graphing calculator, e.g. on `desmos.com`, to verify that the shapes above are correct.

(f) *Is the total heat positive or negative?*

There are two ways of calculating the sign of the heat.

One way is to find it directly from the TS diagram. The heat is positive when the entropy is increasing, and negative when the entropy is decreasing. The magnitude of the change in heat is larger when the temperature is larger, so the magnitude of negative heat from step 4 is greater than the magnitude of positive heat from step 2. So, the heat is negative.

We can also find it indirectly from the PV diagram by solving for work instead. The positive work from reducing the volume in step 3 is larger than the negative work of increasing the volume in step 1. So, the overall work is positive. Since it is a cycle, the total energy should not change, which means the heat is negative.

(g) *How is the sign on the heat related to $\Delta S_{closed} \geq 0$?*

When the room and the component exchange heat, we have $Q_{\text{room}} = -Q_{\text{step 2}}$.

$$\Delta S_{\text{room}} = \frac{Q_{\text{room}}}{T_{\text{room}}} = \frac{-Q_{\text{step 4}}}{T_{\text{room}}} > 0.$$

When the fridge and the component exchange heat, we have $Q_{\text{fridge}} = -Q_{\text{step 4}}$.

$$\Delta S_{\text{fridge}} = \frac{Q_{\text{fridge}}}{T_{\text{fridge}}} = \frac{-Q_{\text{step 2}}}{T_{\text{fridge}}} < 0.$$

In order for the total entropy to be $\Delta S \geq 0$, we must have

$$\begin{aligned}
\Delta S &= \Delta S_{\text{room}} + \Delta S_{\text{fridge}} \geq 0 \\
\implies & \frac{-Q_{\text{step 4}}}{T_{\text{room}}} + \frac{-Q_{\text{step 2}}}{T_{\text{fridge}}} \geq 0 \\
\implies & \frac{Q_{\text{step 4}}}{T_{\text{room}}} + \frac{Q_{\text{step 2}}}{T_{\text{fridge}}} \leq 0 \\
\implies & \frac{T_{\text{fridge}}}{T_{\text{room}}} Q_{\text{step 4}} + Q_{\text{step 2}} \leq 0 \\
\implies & (Q_{\text{step 4}} + Q_{\text{step 2}}) + \left(\frac{T_{\text{fridge}}}{T_{\text{room}}} - 1\right) Q_{\text{step 4}} \leq 0 \\
\implies & Q_{\text{total}} \leq \left(1 - \frac{T_{\text{fridge}}}{T_{\text{room}}}\right) Q_{\text{step 4}} < 0,
\end{aligned}$$

where the last step uses that $T_{\text{fridge}} < T_{\text{room}}$ and $Q_{\text{step 4}} < 0$.

So the negative total heat was actually required by the increasing entropy. This is related to how systems in the real world can never be perfectly efficient. In the process of removing some heat from inside the fridge, the component is forced to dump extra heat out into the room.

This extra energy actually come from the work done in the process: a fridge is a machine that turns work into the movement of heat, with some extra heat as a byproduct. The heat in the component is negative because the heat for the rest of the universe is positive with its use.