

NAME: _____

PHYSICS 314 – Thermodynamics and Statistical Physics (Spring 2018)

Instructor: Josh Weber

Final Exam

May 2018

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Instructions:

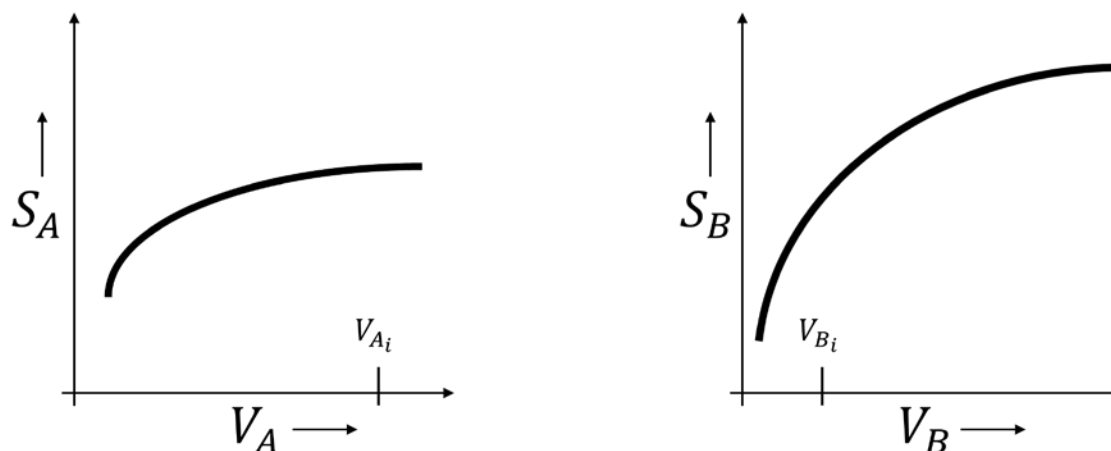
- 1) Please remember to write your name on this page.
- 2) You may need to use a calculator.
- 3) **Show all of your work and reasoning** to maximize your chances for partial credit. *Correct answers that are not supported by work and reasoning will not receive full credit.*
- 4) Keep track of **units**, and give a reasonable number of **significant figures**.
- 5) Please ask me if any questions or instructions are unclear.
- 6) You may use three pages of notes that are single-sided, hand-written, and written by you.

Please staple this sheet onto the front of your exam when you are finished.

1. [6 pts – 2 pts each]

Consider a thermally-isolated container containing two ideal gasses, A and B . The two gasses are separated by an impermeable, conducting, and moveable piston that allows them to exchange volume and energy, but not particles. Entropy versus volume plots for the sides are shown below.

Based on SCHROEDER 3.3



Both graphs use the same horizontal and vertical scales. The piston is initially locked in place such that the initial volumes of the two objects are V_{Ai} and V_{Bi} at the values shown.

a)

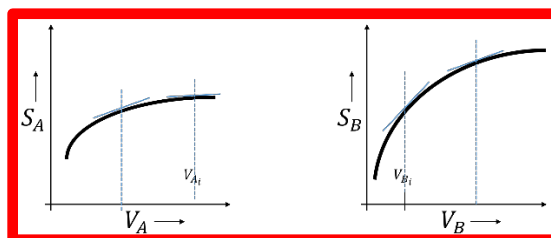
Use the plots to explain what happens to the two systems once the piston is allowed to move.

At the initial points, the slope of the plot of B is steeper than that of A . Thus, a transfer of volume from A to B results in gain in entropy for B that is larger in magnitude than the loss in entropy for A . Thus, the net entropy of the two objects increases. Thus, volume will spontaneously change. B loses volume, and A gains volume.

b)

Indicate on each plot above the equilibrium volume of the gas. *Explain.*

The systems will exchange volume until the slopes are the same. At that point, there is no gain in entropy to be had from further volume transfer. At this point the pressures are equal. The final volumes with equal slopes are shown below.



c)

Which system has more particles? *Explain.*

Use the ideal gas law to relate the pressure and the temperature to the other quantities.

$$PV = NkT$$

$$\frac{P}{kT} = \frac{N}{V}$$

The quantity on the left is the same for both gases once the system reaches (mechanical and thermal) equilibrium. Thus, the quantity on the right must also be the same for both sides.

$$\frac{N_A}{V_A} = \frac{N_B}{V_B}$$

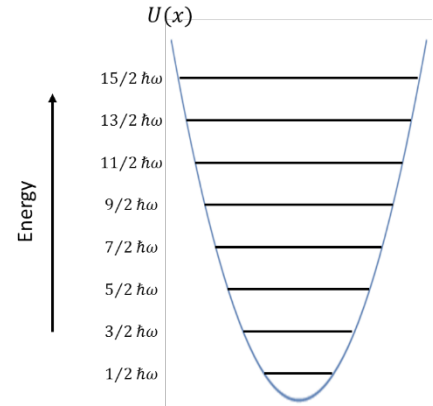
Based on the answer to part b), $V_B > V_A$ at equilibrium. Thus, to keep equality, it must be that $N_B > N_A$.

2. [12 pts – 3 pts each]

Consider a system of five particles trapped in a one-dimensional harmonic oscillator potential. In a harmonic oscillator potential, the energy levels are all non-degenerate and evenly spaced. The energy of the n th level is $E_n = \hbar\omega \left(n + \frac{1}{2}\right)$, with $n = 0, 1, 2, \dots$

Define $\epsilon = \hbar\omega$ as a unit of energy.

In this problem, you will consider how the allowed states for the system differ depending on the type of particle.



Based on SCHROEDER 7.10

a)

Describe the *ground state of the system* by listing the single-particle state of each of the five particles if the particles are...

- i. ... distinguishable particles.

With distinguishable particles, there are no restrictions on the number of particles in any single state. Thus, the lowest energy configuration is when **all five particles are in the lowest energy, $\frac{1}{2} \hbar\omega$, state.**

- ii. ... identical fermions.

With identical fermions, only one particle can be in each level due to the Pauli Exclusion Principle. Thus, the lowest energy configuration is when one of the five particles is in each of the five lowest energy states, $\frac{1}{2} \hbar\omega$, $\frac{3}{2} \hbar\omega$, $\frac{5}{2} \hbar\omega$, $\frac{7}{2} \hbar\omega$, and $\frac{9}{2} \hbar\omega$.

- iii. ... identical bosons.

As with distinguishable particles, for bosons, there are no restrictions on the number of particles in any single state. Thus, the lowest energy configuration is when **all five particles are in the lowest energy, $\frac{1}{2} \hbar\omega$, state.**

b)

Now suppose that the system has one unit of energy above the ground state. Describe the allowed states of the system. How many *system states* are possible if the particles are...

Adding another unit of energy allows for the “promotion” of one of the five particles to the level above its ground state level.

- i. ... distinguishable particles?

All particles are in the lowest level in the ground state. One unit of energy extra allows the promotion of any one of these particles to the second lowest level, $\frac{3}{2}\hbar\omega$. Any one of the five particles can be promoted, and since they are distinguishable, this leads to five possible different system states.

ii. ... identical fermions?

To promote a fermion up a level, the level above it must be vacant. Thus, there is only one possible system state with one extra unit of energy: the highest energy particle gets moved up a level. The configuration is thus $\frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{5}{2}\hbar\omega, \frac{7}{2}\hbar\omega$, and $\frac{11}{2}\hbar\omega$.

iii. ... identical bosons?

Like distinguishable particles, all bosons are in the lowest level in the ground state. One unit of energy extra allows the promotion of any one of these particles to the second lowest level, $\frac{3}{2}\hbar\omega$. Any one of the five particles can be promoted, but unlike distinguishable particles, promoting any one of them leads to the same resulting system. Thus, there is only one possible system state.

c)

Now suppose that the system has two units of energy above the ground state. Describe the allowed states of the system. How many *system states* are possible if the particles are...

i. ... distinguishable particles?

With two units of energy, one particle can move up two levels. Just like part b), there are five ways of doing this, moving one particle up to the third lowest level, $\frac{5}{2}\hbar\omega$.

Alternatively, two particles can each move up one level to $\frac{3}{2}\hbar\omega$. To find the number of ways to choose two out of the five to promote, calculate “five choose two.”

$$\binom{5}{2} = \frac{5!}{2! \times 3!} = 10$$

Thus, there are $5 + 10 = 15$ possible system states.

ii. ... identical fermions?

As with distinguishable particles, with fermions, either two particles can be promoted one level, or one can be promoted two levels. The restriction remains that a particle can only be promoted if there is an empty level above it. Thus, either the highest energy particle can be promoted two levels (to $\frac{13}{2}\hbar\omega$) or both the top two levels can be promoted (to $\frac{9}{2}\hbar\omega$ and to $\frac{11}{2}\hbar\omega$, respectively). There are two possible system states.

iii. ... identical bosons?

With two units of energy, one particle can move up two levels to the third lowest level, $\frac{5}{2}\hbar\omega$. Alternatively, two particles can each move up one level to $\frac{3}{2}\hbar\omega$. Unlike distinguishable particles, any particle promoted results in the same system state. Thus, both of these are only one system state each, and there are only two possible system states.

d)

For a given very low temperature, there is some small, but non-zero probability that the system has a few units of energy above the ground state. Under these conditions, consider the probability that the system is in an excited system state for each particle type: distinguishable particles, identical fermions, and identical bosons. Rank the probabilities from highest to lowest. *Explain.*

$$\mathcal{P}_{distinguishable}(excited) > \mathcal{P}_{bosons}(excited) = \mathcal{P}_{fermions}(excited)$$

The probability of finding the system in an excited state is proportional to the degeneracy of the excited state. Recall that the Boltzmann factor is multiplied by the degeneracy in the probability expression.

$$\mathcal{P}_s = \frac{n_s \times e^{-\frac{E_s}{kT}}}{Z}$$

As shown above, the multiplicity of the distinguishable particles is higher than that for the identical particle cases (which are equal to one another).

3. [12 pts]

In class, we derived the equipartition theorem for a *classical* quadratic degree of freedom.

$$E_{quad}(q) = cq^2 \quad \rightarrow \quad \overline{E_{quad}} = \frac{1}{2}kT$$

c is a constant, and q is a coordinate or momentum variable like x or p_x .

Now consider a *classical linear* degree of freedom. (As an example, the relativistic energy of a photon has this form.)

$$E_{lin}(q) = c|q|$$

Starting with the partition function, find the average energy of such a degree of freedom, $\overline{E_{lin}}$.

Based on SCHROEDER 6.31

The partition function is the sum of the Boltzmann factors.

$$Z = \sum_q e^{-\beta c|q|}$$

Multiply and divide by the spacing between states, Δq , which is a constant which can be taken out of the sum.

$$Z = \frac{1}{\Delta q} \sum_q e^{-\beta c|q|} \Delta q$$

This is a classical system, so the spacing between states is very small. Thus, one can approximate $\Delta q \approx dq$, and the sum becomes an integral. The integral runs over all possible q , from negative to positive infinity.

$$Z = \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta c|q|} dq$$

To help evaluate this, use the fact that the absolute value makes this an even function. The function has the same value for q as for $-q$. Thus, this is the same as twice the integral from zero to infinity. Also, with these new bounds, q is greater than zero, so the absolute value is no longer needed.

$$Z = \frac{2}{\Delta q} \int_0^{\infty} e^{-\beta c q} dq$$

Evaluate the integral.

$$Z = \frac{2}{\Delta q} \left(-\frac{1}{\beta c} e^{-\beta c q} \right)_{q=0}^{q=\infty}$$

$$Z = -\frac{2}{\Delta q \beta c} (e^{-\beta c q})_{q=0}^{q=\infty}$$

$$Z = -\frac{2}{\Delta q \beta c} (e^{-\infty} - e^0)$$

$$Z = -\frac{2}{\Delta q \beta c} (0 - 1)$$

$$Z = \frac{2}{\Delta q \beta c}$$

Now to find the average energy. Use the relationship from class involving the derivative of the partition function.

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

Insert the partition function from above.

$$\bar{E} = -\frac{\Delta q \beta c}{2} \frac{\partial}{\partial \beta} \left(\frac{2}{\Delta q \beta c} \right)$$

The constants cancel.

$$\bar{E} = -\beta \frac{\partial}{\partial \beta} \left(\frac{1}{\beta} \right)$$

Differentiate.

$$\bar{E} = -\beta \left(-\frac{1}{\beta^2} \right)$$

$$\bar{E} = \frac{1}{\beta} = kT$$

4. [6 pts – 1.5 each]

Below is a list of articles and presentations from homework reflection problems.

- *Negative temperatures that are hotter than the sun*
- *How strong can a hurricane get?*
- *Nobel Prize press release: Award for development of methods to cool and trap atoms with laser light*
- *Why diesel-powered cars are bigger in Europe than in the U.S.*
- *The shaky future of diesel fuel In America*
- *Hydrogen-powered vehicles: A chicken and egg problem*
- *What separates a liquid from a gas?*
- *Kamerlingh Onnes and the discovery of superconductivity*
- *Strange phenomena in matter's flatlands (Nobel Prize in Physics 2016)*
- *Lab-grown diamonds come into their own*
- *Big diamonds bring scientists a message from superdeep Earth*
- *Making CHILL, a new instrument for exploring the origin of our solar system*
- *Nature's ultimate sample return mission: seeing into stars by studying stardust in the laboratory*
- *Satyendra Nath Bose obituary*
- *New state of matter revealed: Bose-Einstein Condensate*

Choose any **two** from the list above, and for *each of the two*, list **two** substantial connections to topics from class (**for a total of four connections**). Be sure to indicate which article or presentation goes with which connections.

Superficial connections, or connections that could be drawn from the title alone will not earn full credit.

Examples of connections for a fictional article called 10 Shocking Reasons Classical Physicists Hate the Ultraviolet Catastrophe (#7 Will Blow Your Mind!):

10 Shocking Reasons:

Bad Example (no credit): *We talked about the ultraviolet catastrophe, which was discussed in the article.*

OK Example (partial credit): *We talked about the ultraviolet catastrophe in connection with blackbody radiation experiments, which was discussed in the article.*

Great Example (full credit): *The article discussed how the ultraviolet catastrophe, a disagreement between theory and experiment involving blackbody radiation, led to the idea of quantization of light, which is a topic we discussed in class.*

5. [12 pts - a) 6 pts, b) 2 pts, c) 1 pt, d) 2 pts, e), 1 pt]

In class, we derived the Maxwell speed distribution for the three-dimensional world in which we live. Suppose now that molecules are constrained to move in only two dimensions.

Based on SCHROEDER 6.41

a)

Derive a speed distribution formula for an ideal gas of particles constrained to move in two dimensions.

As in the three-dimension case, start out with reasoning through a form for the distribution.

$$\mathcal{D}(v) \propto (\text{probability of a molecule having velocity vector } \vec{v}) \\ \times (\text{number of vectors } \vec{v} \text{ that correspond to speed } |\vec{v}|)$$

Just as in the three-dimensional case, the probability is proportional to the Boltzmann factor. (The key idea is to leave just as a proportionality and to not worry about the value of the partition function.) The Boltzmann factor does not change moving from three to two dimensions.

$$e^{-\frac{E_v}{kT}}$$

In the three-dimensional case, the number of vectors was proportional to surface area of a sphere in velocity space.

$$SA = 4\pi v^2$$

In two dimensions, this translates to the circumference of a circle.

$$C = 2\pi v$$

Combine these into the expression above.

$$\mathcal{D}(v) \propto e^{-\frac{E_v}{kT}} \times 2\pi v$$

Plug in the expression for kinetic energy, $E_v = \frac{1}{2}mv^2$.

$$\mathcal{D}(v) \propto e^{-\frac{mv^2}{2kT}} \times 2\pi v$$

Define the unknown proportionality constant as C .

$$\mathcal{D}(v) = C e^{-\frac{mv^2}{2kT}} \times 2\pi v$$

To find this proportionality constant, use the fact that the integral of the distribution function is the probability. The integral overall all possible velocities is thus the probability that the particle has *any velocity*, and this must be equal to one.

$$\mathcal{P}(v_1, v_2) = \int_{v_1}^{v_2} \mathcal{D}(v) dv$$

$$\mathcal{P}(v_{all}) = \int_0^{\infty} \mathcal{D}(v) dv = 1$$

Plug in the distribution function.

$$\int_0^{\infty} C e^{-\frac{mv^2}{2kT}} \times 2\pi v dv = 1$$

Pull out constants.

$$2\pi C \int_0^{\infty} e^{-\frac{mv^2}{2kT}} v dv = 1$$

To integrate, use u substitution.

$$u = \sqrt{\frac{m}{2kT}} v \quad \rightarrow \quad \sqrt{\frac{2kT}{m}} u = v$$

$$du = \sqrt{\frac{m}{2kT}} dv \quad \rightarrow \quad \sqrt{\frac{2kT}{m}} du = dv$$

$$2\pi C \int_0^{\infty} e^{-u^2} \left(\sqrt{\frac{2kT}{m}} u \right) \left(\sqrt{\frac{2kT}{m}} du \right) = 1$$

Take the constants out front.

$$2\pi C \left(\frac{2kT}{m} \right) \int_0^{\infty} e^{-u^2} u du = 1$$

$$C \left(\frac{4\pi kT}{m} \right) \int_0^{\infty} e^{-u^2} u du = 1$$

This Gaussian integral can be solved with another u substitution.

$$x = u^2 \quad \rightarrow \quad dx = 2u \, du \quad \rightarrow \quad \frac{dx}{2} = u \, du$$

$$C \left(\frac{4\pi kT}{m} \right) \int_0^\infty e^{-x} \frac{dx}{2} = 1$$

Pull the constant out front and integrate.

$$C \left(\frac{4\pi kT}{m} \right) \frac{1}{2} \int_0^\infty e^{-x} \, dx = 1$$

$$C \left(\frac{2\pi kT}{m} \right) (-e^{-x} |_{x=0}^{x=\infty}) = 1$$

$$-C \left(\frac{2\pi kT}{m} \right) (e^{-\infty} - e^0) = 1$$

$$-C \left(\frac{2\pi kT}{m} \right) (0 - 1) = 1$$

$$C \left(\frac{2\pi kT}{m} \right) = 1$$

$$C = \frac{m}{2\pi kT}$$

Finally, plug this constant into the distribution function.

$$\mathcal{D}(v) = C e^{-\frac{mv^2}{2kT}} \times 2\pi v$$

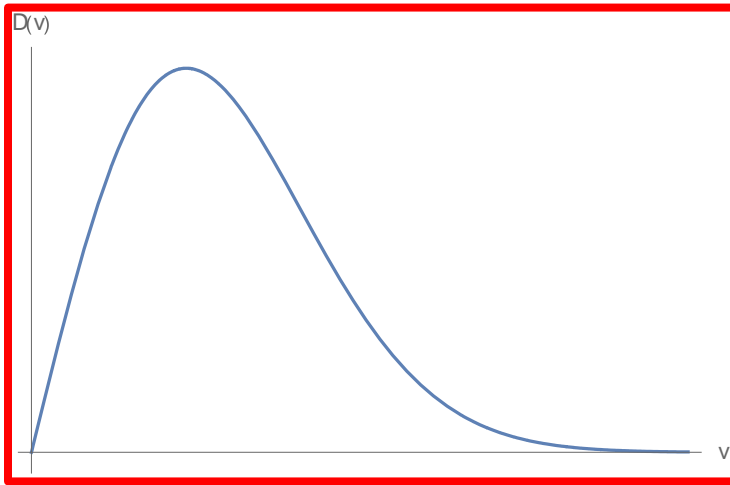
$$\mathcal{D}(v) = \left(\frac{m}{2\pi kT} \right) 2\pi v \times e^{-\frac{mv^2}{2kT}}$$

This could be slightly simplified, though the form above better emphasizes the different parts.

$$\mathcal{D}(v) = \left(\frac{m}{kT} \right) v \times e^{-\frac{mv^2}{2kT}}$$

b)

Qualitatively sketch the distribution from part a), and comment on how it differs from the three-dimensional case.



The exponential decay after the maximum looks similar to the three-dimensional case. However, the initial rise in this case (which occurs for low v , before the exponent dominates) is linear. (In the three-dimensional case it was parabolic.)

c)

For a gas constrained to move in two dimensions, what is the most probable *velocity*?

The most probable velocity vector is **zero**. It has the largest Boltzmann factor, $e^{-0} = 1$. This is the same as in three dimensions.

d)

For a gas constrained to move in two dimensions, what is the most probable *speed*?

Zero is not the most probable *speed* because with speed, the number of vectors with the speed need to be considered. Zero velocity only have one possible vector. This is essentially the multiplicity, and it corresponds to the second term in our distribution function from part a).

To find the most probable speed, take the derivative of the distribution function from part a) and find where it equals zero.

$$\frac{d}{dv} \mathcal{D}(v) = \frac{d}{dv} \left[\left(\frac{m}{2\pi kT} \right) 2\pi v \times e^{-\frac{mv^2}{2kT}} \right] = 0$$

The constants do not matter because it is equal to zero.

$$\frac{d}{dv} \left[v \times e^{-\frac{mv^2}{2kT}} \right] = 0$$

Differentiate using the product rule.

$$(1)e^{-\frac{mv^2}{2kT}} + v \frac{d}{dv} \left[e^{-\frac{mv^2}{2kT}} \right] = 0$$

$$e^{-\frac{mv^2}{2kT}} + v \left(-\frac{2mv}{2kT} e^{-\frac{mv^2}{2kT}} \right) = 0$$

$$e^{-\frac{mv^2}{2kT}} - \frac{mv^2}{kT} e^{-\frac{mv^2}{2kT}} = 0$$

Solve for v .

$$\left(1 - \frac{mv^2}{kT} \right) e^{-\frac{mv^2}{2kT}} = 0$$

The exponential is zero at $v = \infty$, but that is not the maximum based on the image. Thus, the maximum must be when the term in the parentheses vanishes.

$$1 - \frac{mv^2}{kT} = 0$$

$$\frac{mv^2}{kT} = 1$$

$$v^2 = \frac{kT}{m}$$

$$v = \sqrt{\frac{kT}{m}}$$

e)

For a gas constrained to move in two dimensions, write an expression that would allow you to calculate the average magnitude of momentum, \bar{p} . You do NOT need to evaluate the expression.

The average value of a property can be found by taking the integral of that property times the distribution function and then integrating over all states.

$$\bar{p} = \int_{p=0}^{p=\infty} p \mathcal{D}(v) dv$$

Rewrite momentum in terms of velocity to integrate, and then pull out the constant mass.

$$\bar{p} = m \int_{v=0}^{v=\infty} v \, \mathcal{D}(v) \, dv$$

6. [6 pts – a) 1 pt, b) 1 pt, c) 4 pts]

Consider the relative stability of two different phases, phase *A* and phase *B*, of a fictional substance *X*.

a)

Suppose substance *X* is held at a fixed volume in a container that is thermally isolated from its environment. (You may also assume that no work is done on the substance.) Which property of the phases determines whether *A* or *B* is more stable under these circumstances?

When energy and volume are held constant, the highest **entropy, *S***, phase is the most stable. This is the first way we looked at stability. (See page 162 in Schroeder.)

b)

Now suppose that substance *X* is held at a fixed volume in a container that is thermally conductive. The fixed-volume, thermally conductive container is allowed to reach equilibrium with a large reservoir at some temperature T_R . Which property of the phases determines whether *A* or *B* is more stable under these circumstances?

When *temperature* and volume are held constant, the **lowest Helmholtz free energy, *F***, phase is the most stable.

c)

Finally, suppose that substance *X* (no longer in a container) is exposed to a large reservoir at pressure P_R and temperature T_R .

The following table contains values for one mole of the substance *X* at $P = P_R$ and $T = T_R$.

<i>Phase</i>	<i>Description</i>	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	m (kg)	V (cm ³)
<i>A</i>	<i>crystalline solid (incompressible)</i>	–1500	95	85	0.52	40
<i>B</i>	<i>crystalline solid (incompressible)</i>	–1510	80	83	0.54	45

Suppose that the temperature is held fixed at $T = T_R$ and the pressure P_R is increased. If the pressure is increased to P_0 , a phase change occurs. Find $\Delta P \equiv P_0 - P_R$, and state which phase is most stable for pressures $P_R < P < P_0$ and which phase is more stable for pressures $P > P_0$.

Hint: $1 \frac{\text{kJ}}{\text{cm}^3} = 1 \times 10^9 \text{ Pa}$

Based on SCHROEDER 5.28 – HW9 #1

When *temperature* and *pressure* are held constant, the **lowest Gibbs free energy, *G***, phase is the most stable.

From the table, at P_R , *B* has a lower Gibbs free energy, and thus is more stable.

Use a procedure similar to our class discussion of graphite and diamond. In a plot of Gibbs free energy as a function of pressure, the slope is given by the volume.

$$\left. \frac{\partial G}{\partial P} \right|_{T,N} = V$$

As in class, assume that the volume of the crystalline solids, and therefore the slope of the plot, is constant. (This is the incompressibility assumption.) Gibbs free energy is then a linear function of pressure, with a slope of volume and some offset.

$$G = VP + \text{offset}$$

B has a lower Gibbs free energy at the conditions of the table. From the table, it also has a greater volume per mole.

$$V_{\text{calcite}} = 45 \frac{\text{cm}^3}{\text{mole}}$$

$$V_{\text{aragonite}} = 40 \frac{\text{cm}^3}{\text{mole}}$$

Thus, its slope is larger, and its Gibbs free energy increases faster as a function of pressure. Therefore, at some higher pressure, *B* will have a higher Gibbs free energy than (and thus be less stable than) *A*. The pressure at which the two linear plots cross is where the most stable phase switches to *A*. Find the intersection.

$$G_B = G_A$$

$$V_B P + \text{offset}_B = V_A P + \text{offset}_A$$

Solve for pressure.

$$(V_B - V_A)P = \text{offset}_A - \text{offset}_B$$

$$P = \frac{\text{offset}_A - \text{offset}_B}{V_B - V_A}$$

To make the math slightly easier, measure the pressure *change* from the given pressure where the difference in offsets is known.

$$\Delta P = \frac{\Delta_f G_A(P_R) - \Delta_f G_B(P_R)}{V_B - V_A}$$

Plug in the values, using the Gibbs free energies and volumes *per mole* from above.

$$\Delta P = \frac{-1500 - -1510}{45 - 40} \frac{\text{kJ}}{\text{cm}^3}$$

$$\Delta P = 2 \frac{\text{kJ}}{\text{cm}^3}$$

Use the hint about units.

$$\Delta P = 2 \times 10^9 \text{ Pa}$$

Phase B is most stable for pressures $P_R < P < P_0$ and phase A is more stable for pressures $P > P_0$.

7. [12 pts – a) 2 pts, b) 1 pt, c) 9 pts]

n moles of an ideal gas with f degrees of freedom are taken through the following cycle.

1 \rightarrow 2: *Adiabatic compression from V_1 to V_2*

2 \rightarrow 3: *Isochoric heating*

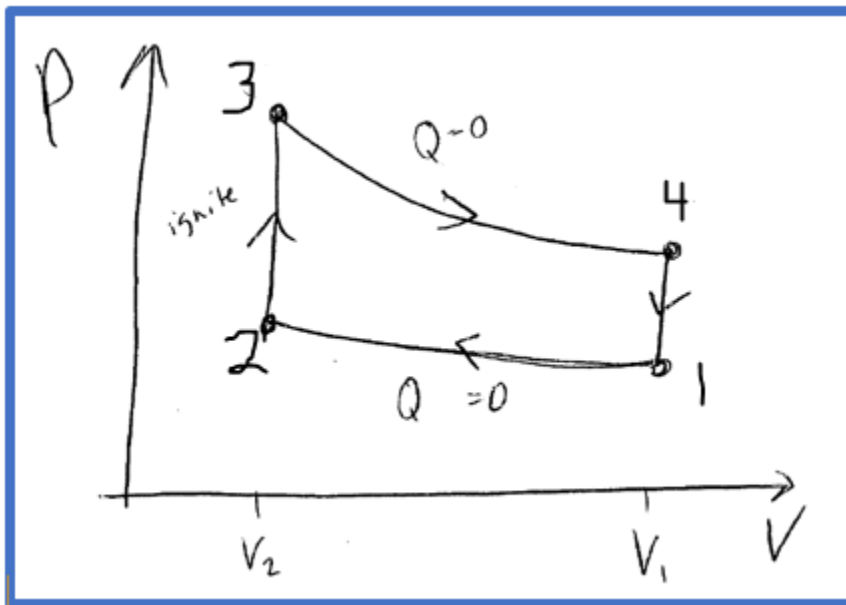
3 \rightarrow 4: *Adiabatic expansion*

4 \rightarrow 1: *Isochoric cooling*

a)

Sketch the process on a $P - V$ diagram.

This is the Otto cycle.



b)

Based on the $P - V$ diagram, explain how you can tell whether this process is an engine or a refrigerator.

The total area under the curve is the work done by the gas.

$$W_{by\ gas} = \int P\ dV$$

This area is positive, so the work done by the gas is positive. If the gas is outputting work, it must be an **engine** (as opposed to a refrigerator, which requires work to be done on the system).

c)

If this process is an engine, calculate the efficiency. If this process is a refrigerator, calculate the coefficient of performance. In either case, *answer in terms of given variables*. (Perform explicit calculations; do not just cite a known result.)

Based on SCHROEDER 4.18. See HW7 #1.

Update HW7 solution if there is a quicker way

Start with the general expression for efficiency.

$$e = \frac{W}{Q_{in}}$$

First find the heat, which comes from the ignition step, $2 \rightarrow 3$.

Because the volume change is zero during this step, work is zero. By the First Law, then, the heat is equal to the change in energy.

$$Q_{23} = \Delta U$$

Use the Equipartition Theorem to write the energy in terms of temperature.

$$Q_{23} = \frac{f}{2} n R \Delta T$$

$$Q_{23} = \frac{f}{2} n R (T_3 - T_2)$$

$$Q_{23} = \frac{f}{2} (n R T_3 - n R T_2)$$

Use the Ideal Gas Law to replace rewrite this in terms of pressure and volume.

$$Q_{23} = \frac{f}{2} (P_3 V_3 - P_2 V_2)$$

Rewrite the factor out front in terms of the adiabatic constant.

$$\gamma \equiv \frac{f+2}{f}$$

$$\gamma = 1 + \frac{2}{f}$$

$$\gamma - 1 = \frac{2}{f}$$

$$\frac{1}{\gamma - 1} = \frac{f}{2}$$

Plug this into the expression for heat.

$$Q_{23} = \frac{1}{\gamma - 1} (P_3 V_3 - P_2 V_2)$$

Note that the volume is constant for this step, and the value is V_2 .

$$Q_{BC} = \frac{1}{\gamma - 1} (P_3 V_2 - P_2 V_2)$$

$$Q_{BC} = \frac{V_2}{\gamma - 1} (P_3 - P_2)$$

Next find the net work done by the system. Because we are looking for the work done by the system (rather than on the system), the sign is the opposite of the usual convention.

$$W = +PdV$$

Because the volume change is zero during steps $2 \rightarrow 3$ and $4 \rightarrow 1$, work is zero during those steps. Thus, only the adiabatic steps ($3 \rightarrow 4$ and $1 \rightarrow 2$) need to be considered.

$$W_{net} = + \int_{V_3}^{V_4} PdV + \int_{V_1}^{V_2} PdV$$

Rewrite pressure in terms of volume to integrate. Use the fact that for an adiabat, PV^γ is constant. Call this constant K .

$$PV^\gamma = K$$

$$P = KV^{-\gamma}$$

Use this fact for each adiabat. Note that the constants are different.

$$W_{net} = + \int_{V_3}^{V_4} K_{34} V^{-\gamma} dV + \int_{V_1}^{V_2} K_{12} V^{-\gamma} dV$$

Pull the constants out of the integrals.

$$W_{net} = K_{34} \int_{V_3}^{V_4} V^{-\gamma} dV + K_{12} \int_{V_1}^{V_2} V^{-\gamma} dV$$

Note that the volumes at these points are known. See the diagram.

$$V_1 = V_4 = V_1$$

$$V_2 = V_3 = V_2$$

$$W_{net} = K_{34} \int_{V_2}^{V_1} V^{-\gamma} dV + K_{12} \int_{V_1}^{V_2} V^{-\gamma} dV$$

In order to combine the integrals, flip the bounds on the second integral and add a negative sign.

$$W_{net} = K_{34} \int_{V_2}^{V_1} V^{-\gamma} dV - K_{12} \int_{V_2}^{V_1} V^{-\gamma} dV$$

$$W_{net} = (K_{34} - K_{12}) \int_{V_2}^{V_1} V^{-\gamma} dV$$

Evaluate the integral.

$$W_{net} = (K_{34} - K_{12}) \frac{1}{-\gamma + 1} V^{-\gamma+1} \Big|_{V_2}^{V_1}$$

$$W_{net} = (K_{34} - K_{12}) \frac{1}{-\gamma + 1} (V_1^{-\gamma+1} - V_2^{-\gamma+1})$$

Now rewrite the constants in terms of the known pressures and volumes. Note either subscript could be chosen for the pressure and the volume.

$$K_{34} = P_3 V_3^\gamma$$

$$K_{12} = P_2 V_2^\gamma$$

Substitute in the known volumes. $V_2 = V_2 = V_2$

$$K_{34} = P_3 V_2^\gamma$$

$$K_{12} = P_2 V_2^\gamma$$

$$W_{net} = (P_3 V_2^\gamma - P_2 V_2^\gamma) \frac{1}{-\gamma + 1} (V_1^{-\gamma+1} - V_2^{-\gamma+1})$$

$$W_{net} = \frac{V_2^\gamma (P_3 - P_2) (V_1^{-\gamma+1} - V_2^{-\gamma+1})}{-\gamma + 1}$$

Now plug the calculated heat and work expressions into the efficiency expression.

$$e = \frac{W}{Q_{in}}$$

$$e = \frac{\frac{V_2^\gamma (P_3 - P_2) (V_1^{-\gamma+1} - V_2^{-\gamma+1})}{-\gamma + 1}}{\frac{V_2}{\gamma - 1} (P_3 - P_2)}$$

Simplify.

$$e = \frac{V_2^\gamma (P_3 - P_2) (V_1^{-\gamma+1} - V_2^{-\gamma+1}) (\gamma - 1)}{(-\gamma + 1) (P_3 - P_2) V_2}$$

Cancel pressure terms.

$$e = \frac{V_2^\gamma (V_1^{-\gamma+1} - V_2^{-\gamma+1}) (\gamma - 1)}{(-\gamma + 1) V_2}$$

Combine V_2 terms.

$$e = \frac{V_2^{\gamma-1} (V_1^{-\gamma+1} - V_2^{-\gamma+1}) (\gamma - 1)}{(-\gamma + 1)}$$

Note that $(-\gamma + 1) = -(\gamma - 1)$.

$$e = \frac{V_2^{\gamma-1} (V_1^{-(\gamma-1)} - V_2^{-(\gamma-1)}) (\gamma - 1)}{-(\gamma - 1)}$$

$$e = -V_2^{\gamma-1} \left(V_1^{-(\gamma-1)} - V_2^{-(\gamma-1)} \right)$$

Distribute the negative sign.

$$e = V_2^{\gamma-1} \left(V_2^{-(\gamma-1)} - V_1^{-(\gamma-1)} \right)$$

Distribute the term out front.

$$e = 1 - V_2^{\gamma-1} V_1^{-(\gamma-1)}$$

$$e = 1 - \left(\frac{V_2}{V_1} \right)^{\gamma-1}$$

Substitute in the definition of gamma.

$$e = 1 - \left(\frac{V_2}{V_1} \right)^{\left(\frac{f+2}{f} \right) - 1}$$

$$e = 1 - \left(\frac{V_2}{V_1} \right)^{\left(\frac{f+2}{f} \right) - \frac{f}{f}}$$

$$e = 1 - \left(\frac{V_2}{V_1} \right)^{\frac{2}{f}}$$

Here's an alternative approach.

Start with the general expression for efficiency, and eliminate work in favor of the heat using the conservation of energy.

$$e = \frac{W}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

$Q_{in} = Q_{23}$ was calculated above.

$$Q_{23} = \frac{V_2}{\gamma - 1} (P_3 - P_2)$$

Examine $Q_{out} = Q_{41}$. Because the step is isochoric, there is no change in volume, so there is no work done. Thus, the heat is equal to the change in internal energy by the First Law.

$$\Delta U = W + Q = 0 + Q = Q$$

$$Q_{41} = \Delta U_{41}$$

Use the equipartition theorem to calculate the change in internal energy.

$$Q_{41} = \Delta \left(\frac{f}{2} nRT \right)_{41}$$

$$Q_{41} = \frac{f}{2} (nRT_4 - nRT_1)$$

Rewrite this in terms of the pressures and volumes using the Ideal Gas Law.

$$Q_{41} = \frac{f}{2} (P_4 V_4 - P_1 V_1)$$

Note that these volumes are actually the same.

$$Q_{41} = \frac{f}{2} V_1 (P_4 - P_1)$$

Plug both heats into the efficiency expression.

$$e = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{Q_{41}}{Q_{23}}$$

$$e = 1 - \frac{\frac{f}{2} V_1 (P_4 - P_1)}{\frac{V_2}{\gamma - 1} (P_3 - P_2)}$$

$$e = 1 - \frac{\frac{f}{2}}{\frac{1}{\gamma - 1}} \frac{V_1 (P_4 - P_1)}{V_2 (P_3 - P_2)}$$

$$e = 1 - \frac{\frac{f}{2}}{\frac{1}{\gamma - 1}} \frac{V_1 (P_4 - P_1)}{V_2 (P_3 - P_2)}$$

As shown at the end of the last approach, $\gamma - 1 = \frac{2}{f}$ using the definition of gamma.

$$e = 1 - \frac{\frac{f}{2}}{\frac{1}{\frac{2}{f}}} \frac{V_1 (P_4 - P_1)}{V_2 (P_3 - P_2)}$$

$$e = 1 - \frac{\frac{f}{2}}{\frac{f}{2}} \frac{V_1 (P_4 - P_1)}{V_2 (P_3 - P_2)}$$

$$e = 1 - \frac{V_1 (P_4 - P_1)}{V_2 (P_3 - P_2)}$$

Rewrite pressure in terms of volume. Use the fact that for an adiabat, PV^γ is constant. Call this constant K .

$$PV^\gamma = K$$

$$P = KV^{-\gamma}$$

Use this fact for each adiabat. Note that the constants are different.

$$e = 1 - \frac{V_1(K_{34}V_1^{-\gamma} - K_{12}V_1^{-\gamma})}{V_2(K_{34}V_2^{-\gamma} - K_{12}V_2^{-\gamma})}$$

$$e = 1 - \frac{V_1V_1^{-\gamma}(K_{34} - K_{12})}{V_2V_2^{-\gamma}(K_{34} - K_{12})}$$

$$e = 1 - \frac{V_1V_1^{-\gamma}}{V_2V_2^{-\gamma}}$$

$$e = 1 - \frac{V_1^{1-\gamma}}{V_2^{1-\gamma}}$$

$$e = 1 - \left(\frac{V_1}{V_2}\right)^{1-\gamma}$$

Switch the fraction and the sign of the exponent to match what we had above.

$$e = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$e = 1 - \left(\frac{V_2}{V_1}\right)^{\frac{2}{\gamma}}$$

8. [6 pts – a) 3 pts, b) 3 pts, c) bonus]

a)

Start with the expression for the multiplicity of a two-state paramagnet with N dipoles below. Assume N is large. Derive an expression for the entropy in terms of N_{\uparrow} and N . Manipulate your expression so that it does not have any factorials, fractions, or exponents. You can use the form of Sterling's approximation that ignores large terms.

$$\Omega = \frac{N!}{N_{\uparrow}! N_{\downarrow}!}$$

Start with the definition of entropy.

$$S = k \ln \Omega = k \ln \left[\frac{N!}{N_{\uparrow}! N_{\downarrow}!} \right]$$

Rewrite using log rules for products and quotients.

$$S = k \ln \Omega = k(\ln[N!] - \ln[N_{\uparrow}!] - \ln[N_{\downarrow}!])$$

Since large terms can be ignored, use the Schroeder (2.16) version of Sterling's approximation.

$$S \approx k([N \ln N - N] - [N_{\uparrow} \ln N_{\uparrow} - N_{\uparrow}] - [N_{\downarrow} \ln N_{\downarrow} - N_{\downarrow}])$$

$$S \approx k(N \ln N - N_{\uparrow} \ln N_{\uparrow} - N_{\downarrow} \ln N_{\downarrow} - N + N_{\uparrow} + N_{\downarrow})$$

Use the fact that the total number of dipoles is fixed.

$$N = N_{\uparrow} + N_{\downarrow}$$

This leads to the non-log terms canceling.

$$S \approx k(N \ln N - N_{\uparrow} \ln N_{\uparrow} - N_{\downarrow} \ln N_{\downarrow})$$

Also use the fixed number to eliminate N_{\downarrow} .

$$N - N_{\uparrow} = N_{\downarrow}$$

$$S \approx k(N \ln N - N_{\uparrow} \ln N_{\uparrow} - (N - N_{\uparrow}) \ln[N - N_{\uparrow}])$$

b)

Suppose each of the 16 of us (15 students and me) flip a coin, and then the number of heads are counted. Find the most likely outcome, and calculate the probability of that outcome.

The probability is the multiplicity of the specific outcome (the number of heads) divided by the total multiplicity of the system.

Since the coin flips are independent of one another, the total multiplicity of the system is the number of possible outcomes per flip (two) raised to the power of the number of coins.

$$\Omega_{total} = 2^{16}$$

The multiplicity of any particular outcome can be calculated combinatorically taking (the number of coins) choose (the number of heads).

$$\Omega(N_{heads}) = \binom{N_{coins}}{N_{heads}} = \frac{N_{coins}!}{N_{heads}! (N_{coins} - N_{heads})!}$$

One could provide a more formal proof, but since the outcomes are equally likely, one can argue that the most likely outcome would be one half heads and one half tails, so eight heads. It is not necessary, but just to illustrate the point, the multiplicities for all outcomes are calculated below.

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{0} = 1$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{1} = 16$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{2} = 120$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{3} = 560$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{4} = 1820$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{5} = 4368$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{6} = 8008$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{7} = 11440$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{8} = 12870$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{9} = 11440$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{10} = 8008$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{11} = 4368$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{12} = 1820$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{13} = 560$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{14} = 120$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{15} = 16$$

$$\binom{N_{coins}}{N_{heads}} = \binom{16}{16} = 1$$

Calculate the probability.

$$\mathcal{P}(N_{heads}) = \frac{\Omega(N_{heads})}{\Omega_{total}}$$

$$\mathcal{P}(N_{heads}) = \frac{\binom{16}{8}}{2^{16}}$$

$$\mathcal{P}(N_{heads}) = \frac{12870}{65536}$$

$$\mathcal{P}(N_{heads}) \approx 19.6\%$$

c) [bonus!]

Write down either “heads” or “tails” below. I will count the number of heads in the class, and if the most probable outcome occurs, I will give everyone 1 bonus point.

I wrote down “tails”.

9. [12 pts – 3 each]

Assume your kitchen is 25°C. A 30.0-g ice cube at 0.0°C is left in the sink, where it eventually melts. The latent heat of water is $L_{H_2O} \approx 333 \text{ J/g}$.

d)

Calculate the change in entropy for the phase change of the ice cube as it melts into water at 0°C. Ignore the small change in volume that happens with the phase change.

The entropy can be calculated from the heat and temperature using Schroeder (3.17).

$$\Delta S = \frac{Q}{T}$$

The heat is the latent heat of the phase change.

$$\Delta S = \frac{mL}{T}$$

Substitute in values. Remember to convert temperature to K.

$$\Delta S \approx \frac{(30.0 \text{ g})(333 \text{ J/g})}{273 \text{ K}}$$

$$\Delta S \approx 36.6 \text{ J/K}$$

e)

Calculate the change in entropy of the resulting water as its temperature rises from 0°C to 25°C. You can assume that the heat capacity of water is constant over this range, which is a pretty good assumption. The specific heat capacity of water is approximately $c \approx 4.2 \frac{\text{J}}{\text{g K}}$.

To calculate the entropy increase from the heat capacity and the temperature change, use Schroeder (3.19).

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT$$

Pull out the nearly constant C_V and then integrate.

$$\Delta S \approx C_V \int_{T_i}^{T_f} \frac{dT}{T}$$

$$\Delta S \approx C_V \ln T \Big|_{T_i}^{T_f}$$

$$\Delta S \approx C_V (\ln T_f - \ln T_i)$$

Use log rule for differences.

$$\Delta S \approx C_V \ln \left(\frac{T_f}{T_i} \right)$$

Replace the heat capacity with the specific heat times the mass. Do so in order to use the value for specific heat of water from Schroeder page 28.

$$\Delta S \approx cm \ln \left(\frac{T_f}{T_i} \right)$$

Plug in values, again remembering to convert to kelvin.

$$\Delta S \approx (4.2 \text{ J/g K}) (30 \text{ g}) \ln \left(\frac{298 \text{ K}}{273 \text{ K}} \right)$$

$$\Delta S \approx 11 \text{ J/K}$$

f)

Calculate the change in entropy *of the kitchen* as it gives up heat to the melt ice and warm the water to room temperature.

The heat lost by the kitchen must be the same as the heat gained by the melting ice and warming water. This is true by conservation of energy and the First Law with zero work.

$$\Delta U_{total} = 0 \rightarrow \Delta U_{H_2O} = -\Delta U_{kitchen}$$

$$\Delta U_{H_2O} = -\Delta U_{kitchen} \rightarrow Q_{H_2O} = -Q_{kitchen}$$

Calculate the change in entropy as in part a).

$$\Delta S = \frac{Q_{kitchen}}{T} = \frac{-Q_{H_2O}}{T}$$

The heat for melting is from part a). The heat for warming the water is given by the expressions for specific heat and heat capacity (Schroeder (1.41) and (1.42)). Plug in these heat expressions

$$\Delta S = \frac{-[mL + mc\Delta T]}{T}$$

$$\Delta S = \frac{-m[L + c\Delta T]}{T}$$

Plug in the values.

$$\Delta S \approx \frac{-(30 \text{ g}) \left[(333 \text{ J/g}) + (4.2 \text{ J/g K}) (25 \text{ K}) \right]}{298 \text{ K}}$$

$$\Delta S \approx -44.1 \text{ J/K}$$

g)

Calculate the net change in entropy of the universe during the process. Comment on the meaning of the sign of your answer.

The net change in entropy is the sum of the change in entropies from a), b), and c).

$$\Delta S = \Delta S_{\text{kitchen}} + \Delta S_{\text{melting}} + \Delta S_{\text{raise temperature}}$$

Plug in the values.

$$\Delta S \approx -44.1 \text{ J/K} + 36.6 \text{ J/K} + 11 \text{ J/K}$$

$$\Delta S \approx 3.5 \text{ J/K}$$

The net change is positive, which is what we expect for an irreversible process.

10. [1 pt]

Which number is larger?

This one was just supposed to be a joke. Any reasonable answer given was correct.

$$1.03 \times 10^{-9.0}$$

Or

$$1.03 \times 10^{-9.0}$$

11. [12 pts – a) 7 pts (1 pt for each non-given value), b) 5 pts]

A cylinder with thermally insulating walls is divided into two sides, A and B . Each one contains one mole of a monatomic ideal gas. The separating wall between A and B is a non-permeable, thermally conductive piston that is free to move. Initially the temperatures and pressures of both sides are equal.

$$T_{Ai} = T_{Bi} \equiv T_i = 273 \text{ K}$$

$$P_{Ai} = P_{Bi} \equiv P_i = 105 \text{ Pa}$$

In side A , there is a small heater (of negligible heat capacity) that is turned on, and this slowly heats the gas. At some *long time* after the heater is turned on, t_f , a thermometer is placed in side B , indicating its final temperature, $T_{Bf} = 321 \text{ K}$.

a)

Make a table containing the initial and final temperatures, pressures, and volumes of each of the two sides.

The initial temperatures and pressures are given.

$$T_{Ai} = T_{Bi} \equiv T_i = 273 \text{ K}$$

$$P_{Ai} = P_{Bi} \equiv P_i = 105 \text{ Pa}$$

The initial volumes can be calculated using the ideal gas law and $n = 1$ mole for both sides. Because the initial temperatures, pressures, and number of mole are the same for both sides, the initial volumes will be the same, V_i .

$$V_i = \frac{nRT_0}{P_0}$$

$$V_i = \frac{1 \text{ mol} \left(8.314 \frac{\text{J}}{\text{mol K}} \right) 273 \text{ K}}{105 \text{ Pa}}$$

$$V_{Ai} = V_{Bi} \equiv V_i \approx 21.6 \text{ m}^3$$

The piston is diathermal and thus conducts heat readily, so the two temperatures must be the same after a long time. In the final state, they are in thermal equilibrium.

$$T_{Af} = T_{Bf} \equiv T_f = 321 \text{ K}$$

Similarly, after a long time, they will move the piston to be in mechanical equilibrium.

$$P_{Af} = P_{Bf}$$

Use the ideal gas law. T_f is the same for both, as mentioned above.

$$\frac{nRT_f}{V_{Af}} = \frac{nRT_f}{V_{Bf}}$$

$$V_{Af} = V_{Bf} \equiv V_f$$

The overall volume of the system cannot change, and above it is shown that the volumes of the two sides are equal in both cases. Thus all for volumes must be the same.

$$V_{Ai} = V_{Bi} = V_{Af} = V_{Bf} \approx 21.6 \text{ m}^3$$

Plug the volumes and temperatures back in to the ideal gas law to find the common final pressure.

$$P_{Af} = P_{Bf} = \frac{nRT_f}{V_f}$$

$$P_{Af} = P_{Bf} \approx \frac{1 \text{ mol} (8.314 \text{ J/mol K}) 321 \text{ K}}{21.6 \text{ m}^3}$$

$$P_{Af} = P_{Bf} \approx 124 \text{ Pa}$$

$T_{Ai} = 273 \text{ K}$	$T_{Bi} = 273 \text{ K}$	$T_{Af} = 321 \text{ K}$	$T_{Bf} = 321 \text{ K}$
$P_{Ai} = 105 \text{ Pa}$	$P_{Bi} = 105 \text{ Pa}$	$P_{Af} \approx 124 \text{ Pa}$	$P_{Bf} \approx 124 \text{ Pa}$
$V_{Ai} \approx 21.6 \text{ m}^3$	$V_{Bi} \approx 21.6 \text{ m}^3$	$V_{Af} \approx 21.6 \text{ m}^3$	$V_{Bf} \approx 21.6 \text{ m}^3$

b)

Calculate the energy provided by the heater during the time between the initial and final temperature measurements.

Now consider the energy provided by the heater. There is no change in volume, and so there is no work done. Use the first law for the overall system (that is, the two compartments considered together).

$$\Delta U = Q + W = Q$$

Note that this heat comes from the heater. Use the Equipartition Theorem. The number of moles, n , does change from its initial value of two.

$$Q = \Delta U = \frac{f}{2} n R \Delta T$$

The gasses are monatomic, so $f=3$. Plug in the temperature change values.

$$Q = \frac{3}{2} \times 2 \text{ mol} (8.314 \text{ J/mol K}) (321 - 273) \text{ K}$$

$$Q_{\text{heater}} \approx 1,197 \text{ J}$$