NAME: _____

PHYSICS 314 – Thermodynamics and Statistical Physics (Spring 2018)

Instructor: Josh Weber

Test #2

April 17th, 2018

8:00 – 9:20 AM

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 one page of notes that is double-sided, hand-written, and written by you.

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

Problem 1	/ 6
Problem 2	/ 6
Problem 3	/ 6
Problem 4	/ 1
Problem 5	/ 6
Problem 6	/ 12
Problem 7	/12
Total	/ 49

1. [6 pts]

Starting from the definition of Helmholtz free energy, show that the following statement is true.

$$dF = -S \, dT - P \, dV + \mu \, dN$$

As instructed, start with the definition of Helmholtz free energy.

$$F \equiv U - TS$$

Look at an infinitesimal change, and use the product rule.
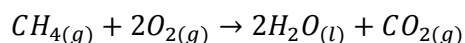
$$dF = dU - S \, dT - T \, dS$$

Substitute in the thermodynamic identity for energy.

$$dF = (T \, dS - P \, dV + \mu \, dN) - S \, dT - T \, dS$$

$$dF = -P \, dV + \mu \, dN - S \, dT$$

2. [6 pts]

Consider the reaction that powers natural gas (methane) fuel cells.

$$CH_{4(g)} + 2O_{2(g)} \rightarrow 2H_2O_{(l)} + CO_{2(g)}$$

Assume that the reaction takes place in a constant pressure and constant temperature environment, $P = 1\ atm$ and $T = 298\ K$. For the ideal case, find the maximum work that you can recover from this reaction for one mole of methane ($CH_{4(g)}$) reacted.

The following table contains values for one mole of the substance at $P = 1\ atm$ and $T = 298\ K$.

Substance	$\Delta_f H$ (kJ)	$S\ (^J/_K)$
$CH_{4(g)}$	-75	186
$CO_{2(g)}$	-394	214
$H_2O_{(l)}$	-286	70
$O_{2(g)}$	0	205

The energy that you can recover from this reaction is the opposite of the change in Gibbs free energy. In the ideal case, this is equal to the work that can be recovered.

The Gibbs free energy is not given in the table, so calculate it from the enthalpies and entropies given. For constant temperature and pressure, the Gibbs free energy change can be calculated from the change in enthalpy and the change in entropy.

$$\Delta G = \Delta H - T\ \Delta S$$

First calculate the change in enthalpy. Examine the difference between the enthalpies of formation for the products and the reactants. Remember to consider the number of moles.

$$\Delta H = \Delta_f H_{products} - \Delta_f H_{reactants}$$

$$\Delta H = \left[2 \times \Delta_f H\left(H_2O_{(l)}\right) + \Delta_f H\left(CO_{2(g)}\right)\right] - \left[\Delta_f H\left(CH_{4(g)}\right) + 2 \times \Delta_f H\left(O_{2(g)}\right)\right]$$

$$\Delta H = [2 \times -286\ kJ + -394\ kJ] - [-75\ kJ + 2 \times 0\ kJ]$$

$$\Delta H = -891\ kJ$$

Now calculate the change in entropy. Examine the difference of entropies between the products and the reactants. Remember to consider the number of moles.

$$\Delta S = S_{products} - S_{reactants}$$

$$\Delta S = \left[2 \times S\left(H_2O_{(l)}\right) + S\left(CO_{2(g)}\right)\right] - \left[S\left(CH_{4(g)}\right) + 2 \times S\left(O_{2(g)}\right)\right]$$

$$\Delta H = \left[2 \times 70\ ^J/_K + 214\ ^J/_K\right] - \left[186\ ^J/_K + 2 \times 205\ ^J/_K\right]$$

$$\Delta S = -242\ ^J/_K$$

Finally plug the calculated values and the temperature into the expression for the Gibbs free energy.

$$\Delta G = \Delta H - T\,\Delta S$$

$$\Delta G = -891\ kJ - (298\ K)\left(-242\ ^J/_K\right)$$

$$\Delta G = -891{,}000\ J - (298\ K)\left(-242\ ^J/_K\right)$$

$$\Delta G = -818{,}884\ J$$

The ideal recoverable work is the opposite of this change in Gibbs free energy.

$$W \approx 819\ kJ$$

3. [6 pts – 3 pts each]

a)
Below is an energy-flow diagram for a proposed heat engine. The idea is to use the heat from the environment to add to the heat from the hot reservoir to improve efficiency. Based on the laws of thermodynamics, decide whether the design is fundamentally possible or not. Depending on your response, respond address the appropriate issues.
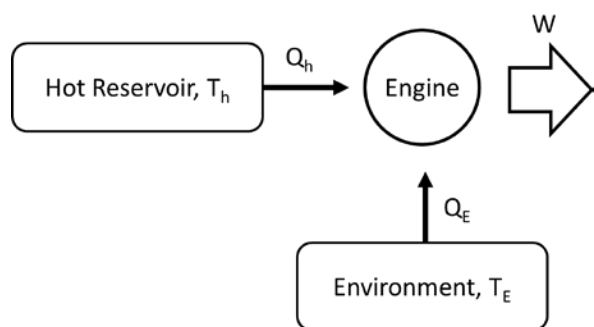
If this design is fundamentally <u>possible</u>, calculate its efficiency, e, in terms of the given variables. By how much is the efficiency improved over that of a conventional heat engine? *Explain*.

If this design is fundamentally <u>impossible</u>, *argue why it is not possible*, and explain how the design needs to be modified to make it possible.

As shown, the design is <u>impossible</u>. The engine gains entropy with the heat from both the hot reservoir and the environment. Engines rely on cyclic processes, so the entropy needs to be expelled somehow to return the system to its original state before the cycle can start over. For this design to work, a cold reservoir could be added so that the entropy could be dumped to the cold reservoir as waste heat.

b)
Below is an energy-flow diagram for a proposed hybrid absorption refrigerator that cools the cold reservoir. The hybrid refrigerator is powered by a combination of electrical work (W) and heat from burning fuel, Q_h.
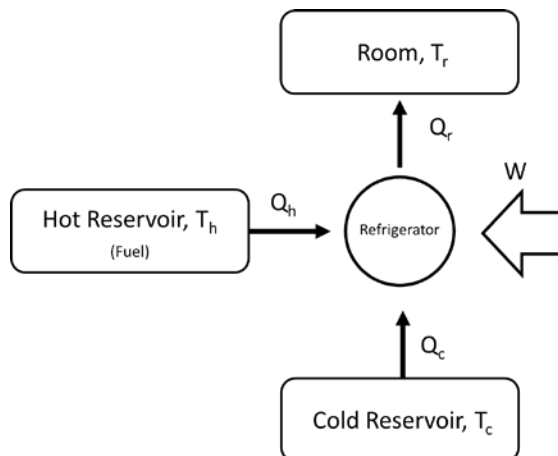
i)
Define the coefficient of performance for this refrigerator using the given variables. Briefly explain.

ii)
Using the given variables, write an equation that expresses conservation of energy for the system.

iii)
Using the given variables, write an expression of the second law of thermodynamics for the system. *You do <u>not</u> need to simplify the expression.*

i)
The coefficient of performance is the ratio of benefit to cost. The benefit is the heat extracted from the cold reservoir. The cost is the sum of the electrical work and the heat from the burning fuel.

$$COP = \frac{benefit}{cost} = \frac{Q_c}{W + Q_h}$$

ii)
Conservation of energy connects the three heat values and the electrical work. The energy in equals the energy out.

$$Q_h + W + Q_c = Q_r$$

iii)
The second law requires that overall entropy stay the same or increase. The refrigerator itself cannot gain or lose entropy because it the process must be cyclic. Thus, the second law requires that the entropy expelled must be greater than or equal to the amount absorbed. The room must gain more entropy than the cold and hot reservoirs lose.

$$\Delta S_r \geq \Delta S_c + \Delta S_h$$

Note that because the mechanical work carries no entropy, this is the same result as for the standard absorption refrigerator. Express the entropies in terms of the given heat values and temperatures using the expression connecting those quantities for constant temperature.

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

$$\frac{Q_r}{T_r} \geq \frac{Q_c}{T_c} + \frac{Q_h}{T_h}$$

4. [1 pt]

Which number is larger?

$$1.03 \times 10^{-8} \quad or \quad 7.21 \times 10^{-9}$$

1.03×10^{-8} is a larger number.

5. [6 pts – 1 pt each for a and b, 2 pts each for c and d]

Two systems, A and B, are free to exchange both energy and particles with one another. The systems are isolated from the environment so that they can only interact with one another. Assume the volume *of each system* remains constant. Assume both systems initially have finite and non-negative temperatures. Below is a qualitative plot of the <u>total</u> entropy of the combined system, S_{total}, as a function of the energy and the number of particles <u>of system A</u>, U_A and N_A.
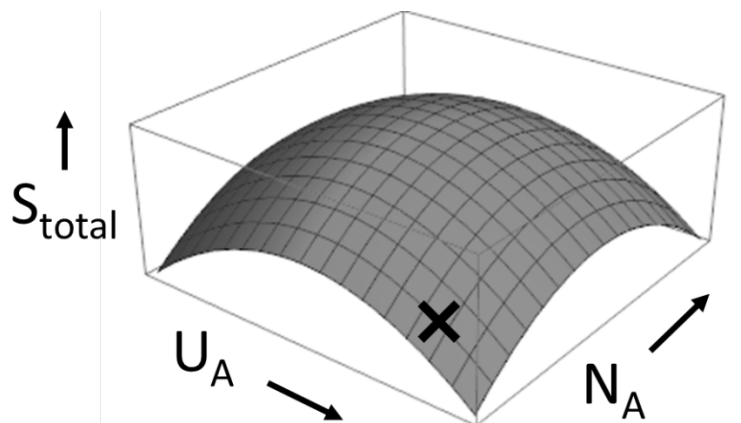
When the systems are initially brought into contact, system A is in a state $A_{initial} = (U_{A_i}, N_{A_i})$ at the point indicated by the X.

a)
On the plot, indicate the equilibrium state of the combined system. Describe the position in a few words (because 2-D representations of 3-D plots are sometimes difficult to interpret).

The equilibrium state is at the center of the plot, the point with the highest total entropy.

b)
In moving from the initial point to the equilibrium point indicated, which type(s) of equilibrium has the combined system achieved? *Briefly explain.*

Energy was exchanged, so thermal equilibrium was reached.

Particles were exchanged, so diffusive equilibrium was reached.

c)
Compare the initial chemical potential of system A, μ_{A_i}, to that of system B, μ_{B_i}. *Briefly explain.*
From the plot, to reach equilibrium, system A must gain particles. The total number of particles of the combined system is fixed, so if N_A increases, N_B decreases; particles flow from system B to system A. Particles tend to flow towards lower values of chemical potential, so system A must have a lower chemical potential.

$$\mu_{A_i} < \mu_{B_i}$$

d)

Compare the initial temperature of system A, T_{A_i}, to that of system B, T_{B_i}. *Briefly explain.*

From the plot, to reach equilibrium, system A must lose energy. The total energy of the combined system is fixed, so if U_A decreases, U_B increases; energy flows from system A to system B.

The problem says to assume the temperature of system A is positive. Energy flows from out of a positive temperature system to a system with lower (positive) temperature, so system A must initially have a higher temperature.

$$T_{A_i} > T_{B_i} \quad (T_{A_i} > 0)$$

Aside: If the temperature of system A were negative, things would be more complicated. Energy flows from negative temperature systems to systems with less negative temperatures and to any system with a positive temperature.

Aside:
One might (incorrectly) argue based on the negative slope of entropy as a function of energy that the temperature of system A is negative

$$\left.\frac{\partial S_{total}}{\partial U_A}\right|_{N,V} = \frac{1}{T_A} \text{ (incorrect)}$$

However, the proper derivative to define temperature is the entropy *of system A only*, which is not the same as the slope shown.

$$\left.\frac{\partial S_A}{\partial U_A}\right|_{N,V} = \frac{1}{T_A} \text{ (correct)}$$

6. [12 pts]

In class, we found an expression for the multiplicity of a monatomic ideal gas.

$$\Omega = \mathcal{F}(N)\, V^N\, U^{3N/2}$$

$\mathcal{F}(N)$ is some function of N. Starting with this expression for multiplicity, derive an expression for the energy of a monatomic ideal gas that is identical to a statement of the equipartition theorem.

Begin with the definition of temperature.

$$\frac{1}{T} \equiv \left.\frac{\partial S}{\partial U}\right|_{N,V}$$

In order use this, find an expression for entropy from the expression for multiplicity. Calculate the entropy from the multiplicity.

$$S = k \ln \Omega$$

$$S = k \ln \left[\mathcal{F}(N)\, V^N\, U^{3N/2}\right]$$

Apply the log rule for products.

$$S = k \left[\ln[\mathcal{F}(N)\,] + \ln[V^N\,] + \ln\left[U^{3N/2}\right]\right]$$

Apply the long rule for exponents.

$$S = k \left[\ln[\mathcal{F}(N)\,] + N \ln[V\,] + \frac{3}{2} N \ln[U]\right]$$

$$S = k \ln[\mathcal{F}(N)\,] + Nk \ln[V\,] + \frac{3}{2} Nk \ln[U]$$

Plug in the expression for entropy into the temperature definition.

$$\frac{1}{T} = \left.\frac{\partial}{\partial U}\right|_{N,V} \left[k \ln[\mathcal{F}(N)\,] + Nk \ln[V\,] + \frac{3}{2} Nk \ln[U]\right]$$

Consider the derivative. Only the last term contributes because it contains all the explicit energy dependence.

$$\frac{1}{T} = \left.\frac{\partial}{\partial U}\right|_{N,V} \left[\frac{3}{2} Nk \ln[U]\right]$$

Pull out the constant terms.

$$\frac{1}{T} = \frac{3}{2} Nk \left.\frac{\partial}{\partial U}\right|_{N,V} [\ln(U)]$$

Evaluate the derivative.

$$\frac{1}{T} = \frac{3}{2} Nk \left.\frac{\partial}{\partial U}\right|_{N,V} [\ln(U)]$$

$$\frac{1}{T} = \frac{\frac{3}{2}Nk}{U}$$

Solve for energy.

$$U = \frac{3}{2}NkT$$

This is the equipartition theorem for a monatomic ideal gas, which has three degrees of freedom, $f = 3$.

$$U = \frac{f}{2}NkT$$

7. [12 pts]

Consider a heat engine that consists of n moles of an ideal gas that are taken through the cyclic process shown. The cycle consists of the following steps.

$A \rightarrow B$:   Adiabatic compression
$B \rightarrow C$:   Isobaric heating at $P = P_2$
$C \rightarrow D$:   Adiabatic expansion
$D \rightarrow A$:   Isobaric cooling at $P = P_1$
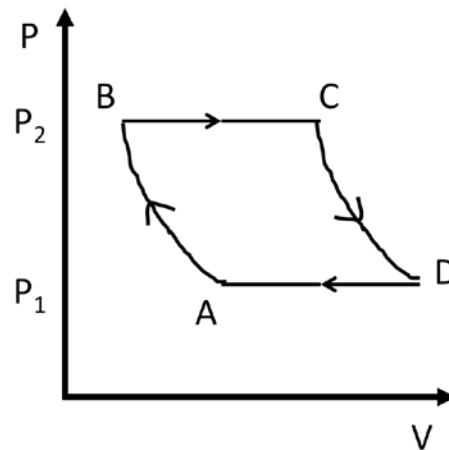
Calculate the efficiency of this engine cycle in terms of the temperatures T_A, T_B, T_C, and T_D, the temperatures at the four corners of the cycle.
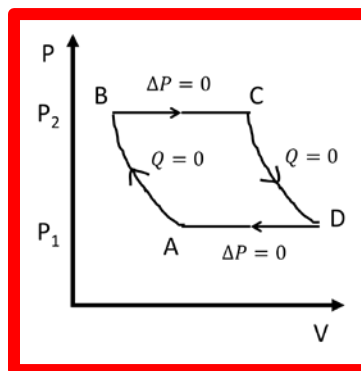
The efficiency is the benefit over the cost, the work done by the cycle divided by the heat taken from the hot reservoir.

$$e = \frac{benefit}{cost} = \frac{W_{by\ cycle}}{Q_h}$$

First find the work done BY the cycle. To do so, find the work done on the gas (to keep with the normal sign conventions), and then negate it.

For the adiabats, $Q = 0$, and thus by the First Law, the work is equal to the change of energy.

$$\Delta U = W + Q$$

$$W = \Delta U$$

To calculate the change in energy, use the Equipartition Theorem to rewrite in terms of the change in temperature.

$$W = \frac{f}{2}nR\Delta T$$

$$W = \frac{f}{2}nR(T_f - T_i)$$

Apply this to the two adiabats.

$$W_{AB} = \frac{f}{2}nR(T_B - T_A)$$

$$W_{CD} = \frac{f}{2}nR(T_D - T_C)$$

Examine the constant pressure processes.

$$W_{P\ constant} = -\int P dV = -P\int dV$$

$$W_{P\ constant} = -PV_f + PV_i$$

Rewrite this in terms of temperature using the Ideal Gas Law.

$$W_{P\ constant} = -nRT_f + nRT_i$$

$$W_{P\ constant} = nR(-T_f + T_i)$$

Apply this to the two constant pressure processes.

$$W_{BC} = nR(-T_C + T_B)$$

$$W_{DA} = nR(-T_A + T_D)$$

Sum the work contributions for all the sections to get the work of the cycle.

$$W_{on\ cycle} = W_{AB} + W_{BC} + W_{CD} + W_{DA}$$

$$W_{on\ cycle} = \frac{f}{2}nR(T_B - T_A) + nR(-T_C + T_B) + \frac{f}{2}nR(T_D - T_C) + nR(-T_A + T_D)$$

$$W_{on\ cycle} = nR\left[\frac{f}{2}(T_B - T_A) + (-T_C + T_B) + \frac{f}{2}(T_D - T_C) + (-T_A + T_D)\right]$$

$$W_{on\ cycle} = nR\left(\frac{f}{2} + 1\right)(T_B + T_D - T_A - T_C)$$

This is the work done ON the gas. For the work done BY the gas, add a negative sign.

$$W_{by\ cycle} = -W_{on\ cycle} = -nR\left(\frac{f}{2} + 1\right)(T_B + T_D - T_A - T_C)$$

$$W_{by\ cycle} = nR\left(\frac{f}{2} + 1\right)(T_A + T_C - T_B - T_D)$$

$$e = \frac{benefit}{cost} = \frac{W_{by\ cycle}}{Q_h}$$

Now look at the heat taken from the hot reservoir.

Examine Q_h, the heat transferred during the process $B \rightarrow C$. By the first law, the heat can be written in terms of the energy change and the work done.

$$Q_h = \Delta U_{BC} - W_{BC}$$

To calculate the change in energy, use the equipartition theorem to rewrite in terms of the change in temperature.

$$Q_h = \frac{f}{2}nR\Delta T_{BC} - W_{BC}$$

$$Q_h = \frac{f}{2}nR(T_C - T_B) - W_{BC}$$

Plug in the expression for work from part b).

$$Q_h = \frac{f}{2}nR(T_C - T_B) - nR(-T_C + T_B)$$

$$Q_h = \frac{f}{2}nR(T_C - T_B) + nR(T_C - T_B)$$

$$Q_h = \left(\frac{f}{2} + 1\right)nR(T_C - T_B)$$

Use this expression and the expression for the work of the cycle from part b) to calculate the efficiency.

$$e = \frac{W_{by\ cycle}}{Q_h}$$

$$e = \frac{nR\left(\frac{f}{2}+1\right)(T_A + T_C - T_B - T_D)}{\left(\frac{f}{2}+1\right)nR(T_C - T_B)}$$

$$e = \frac{T_A + T_C - T_B - T_D}{T_C - T_B}$$