Instructions: There are 5 questions for a total of 100 points. Please make sure to present your solutions in a clear, logical, and legible manner. Indicate your final answer(s) where appropriate. Indicate clearly any approximations or assumptions you make and provide your justification(s) for them. If you use scratch paper, remember to transfer answers to the exam; answers on scratch paper will not be considered. You are allowed use of only pen/pencil, equations handbook, and calculator.

1. (**15 Points**) The mean solar flux at the Earth's surface is about 2.0 J cm-2 min-1. Using a non-focusing solar collector, the temperature of the device can reach 85.0 Celsius. A heat engine is operated using the collector as the hot reservoir and a cold reservoir at 298K. What area of the collector is needed to produce one horsepower (746 Watts)? Assume the engine operates at the maximum Carnot efficiency. Recall that $Carnot\ Efficiency = 1 - \dfrac{T_{Cold}}{T_{Hot}}$.

$$1 - \frac{T_C}{T_H} = \frac{w}{q}$$

$$q = w\left(\frac{T_H}{T_H - T_C}\right) = (SA)(FLUX)$$

$$SA = \left(\frac{w}{FLUX}\right)\left(\frac{T_H}{T_H - T_C}\right) = \left(\frac{w}{FLUX}\right)\left(\frac{T_H}{T_H - T_C}\right)$$

$$= \left(\frac{746\dfrac{J}{sec}\dfrac{60\,sec}{min}}{2.0\dfrac{J}{cm^2\,min}}\right)\left(\frac{358.15K}{358.15K - 298K}\right) = 13.3m^2$$

2. (20 Points) The volume coefficient of expansion of mercury at 0°C is 18 x 10^{-5} $(°C)^{-1}$. The coefficient of compressibility β is 5.32 x 10^{-6} bar^{-1}. If mercury were heated from 0°C to 1°C in a constant volume system, what pressure would be developed? Consider that volume is a state function, and this being so, how you would express the total differential of volume taking it be a function of temperature and pressure. Furthermore, think back to the Joule Free Expansion or Joule-Thomson Expansion experiments to consider how we can arrive at auxiliary differential relations when certain state variables or functions have zero total differentials.

$$dV = \left(\frac{\partial V}{\partial T}\right)_P \partial T + \left(\frac{\partial V}{\partial P}\right)_T \partial P$$
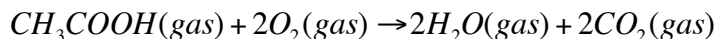
Constant V; $\partial V = 0$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$
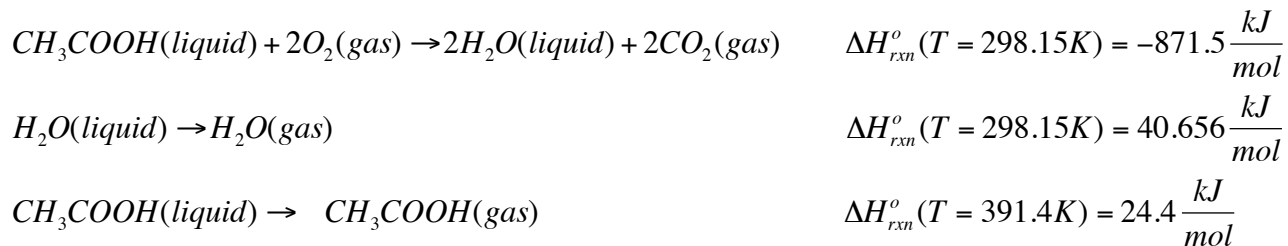
$$0 = V\alpha\partial T - V\beta\partial P$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta} = \frac{18x10^{-5}\,°C^{-1}}{5.32x10^{-6}bar^{-1}} = 33.8 \text{ bar/°C}$$

3. **(20 Points)** From the following data, calculate the standard enthalpy at 391.4 Kelvin for the following reaction:

$$CH_3COOH(gas) + 2O_2(gas) \rightarrow 2H_2O(gas) + 2CO_2(gas)$$

Data:

$CH_3COOH(liquid) + 2O_2(gas) \rightarrow 2H_2O(liquid) + 2CO_2(gas)$ $\Delta H^o_{rxn}(T = 298.15K) = -871.5\dfrac{kJ}{mol}$

$H_2O(liquid) \rightarrow H_2O(gas)$ $\Delta H^o_{rxn}(T = 298.15K) = 40.656\dfrac{kJ}{mol}$

$CH_3COOH(liquid) \rightarrow CH_3COOH(gas)$ $\Delta H^o_{rxn}(T = 391.4K) = 24.4\dfrac{kJ}{mol}$

Substance	CH₃COOH(liquid)	O₂(gas)	CO₂(gas)	H₂O(liquid)	H₂O(gas)
$\dfrac{\overline{C}_P}{R}$	14.9	3.53	4.46	9.055	4.038

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T1}^{T2} \Delta \overline{C}_P(T)dT$$

$$= 40.656\frac{kJ}{mol} + R \int_{298.15K}^{391.4K}(4.038 - 9.055)dT = 40.656 + (8.314\frac{J}{mol-K})(0.001kJ/J)(-5.017)(93.25K)$$

$$= 36.766\frac{kJ}{mol}$$

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T1}^{T2} \Delta \overline{C}_P(T)dT$$

$$= -871.5\frac{kJ}{mol(EtOH)} + \left[\int_{T1}^{T2}\Delta\overline{C}_P(T)dT\right] = -871.5\frac{kJ}{mol(EtOH)} + R\left[\int_{298.15K}^{391.4K}((2)(9.055) + (2)(4.46) + (-1)(14.9) + (-2)(3.53))dT\right]$$

$$= -871.5\frac{kJ}{mol(EtOH)} + R((2)(9.055) + (2)(4.46) + (-1)(14.9) + (-2)(3.53))(391.4K - 298.15K)$$

$$= -867.57kJ/mol(EtOH)$$

So the reaction enthalpy at 391.4K is simply the sum of the individual enthalpies (the stoichiometry is straightforward, and enthalpy is a state function)

$$\Delta H(391.4K) = -24.4 - 867.57 + 2(36.766) = -818.44kJ/mol(EtOH)$$

4. (**10 Points**) For each statement or question in the **left** column, find the appropriate response in the **right** column and place the letter of the response in the blank line provided in the **left** column.

1. The reversible work needed to compress a gas is ____H___ that needed in an irreversible process leading to the same change.	A. equal to
2. An extensive thermodynamic property is independent of the amount of substance or system size. (True or False?)_____False, L_____	B. amount
	C. volume, and pressure.
3. The Second Law of Thermodynamics allows us to formulate bounds on the amount of internal energy that can be converted to work. (True or False) _False, L__	D. isoenergetic
4. The internal energy of an ideal gas depends only on _____G_____.	E. greater than
5. We can write the standard enthalpy of reaction in a general form as: $$\Delta H^0_{reaction}(T) = \sum_{products,i} v_i \Delta H^o_{f,i} - \sum_{react,j} v_j \Delta H^o_{f,j}$$ because enthalpy has the quality of being a(n) _____I_____.	F. isenthalpic
	G. temperature
	H. less than
	I. state function
	J. inexact integral
	K. natural variable
	L. false
	M. true

5. (35 Points). Consider the following 2-state model: a system of N (with N→∞) non-interacting particles that can occupy one of two energy levels. This is analogous to non-interacting spin ±½ particles in a magnetic field (i.e., NMR). The energies associated with the two states are 0 and 'b', respectively. In this model, there will be a certain number of "up" spins (denoted, U), and some number of "down" spins (denoted, D). Consider no external constraints on the system (i.e. thermal or pressure baths) and that the system is isolated.
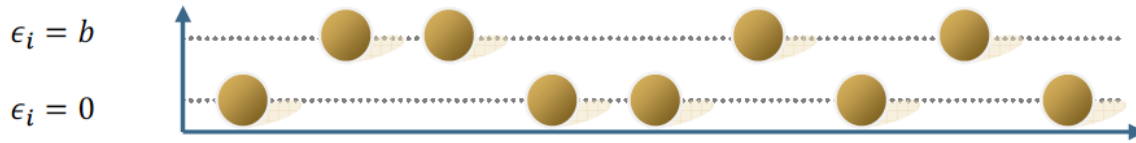
5A. (30 Points) Determine the condition at which the entropy of this system is maximized. That is, carefully show the relation between D and U that maximizes the entropy of the system. **Explicitly state any assumptions that you make/invoke.**

$$W = \frac{N!}{U!D!} = \frac{N!}{(N-D)!D!}$$

$\ln W = \ln(N!) - \ln((N-D)!) - \ln(D!)$

As N, U, D go to infinity (approximation for thermodynamic limit)

$\ln W = N\ln N - N - [(N-D)\ln(N-D) - (N-D)] - [D\ln(D) - D]$

Entropy

$S = k_B \ln W$

Maximum Entropy

$\frac{d\ln W}{dD} = 0 = \ln(N-D) - \ln(D)$

$\ln(N-D) = \ln(D)$

$N - D = D$

$D = N/2$

$D = U$

Entropy is maximized for this case when half of the particles are in the upper level and the remaining half are in the lower level.

5B. (2.5 Points) What is the value of entropy associated with the state where D = 0 and U = N?
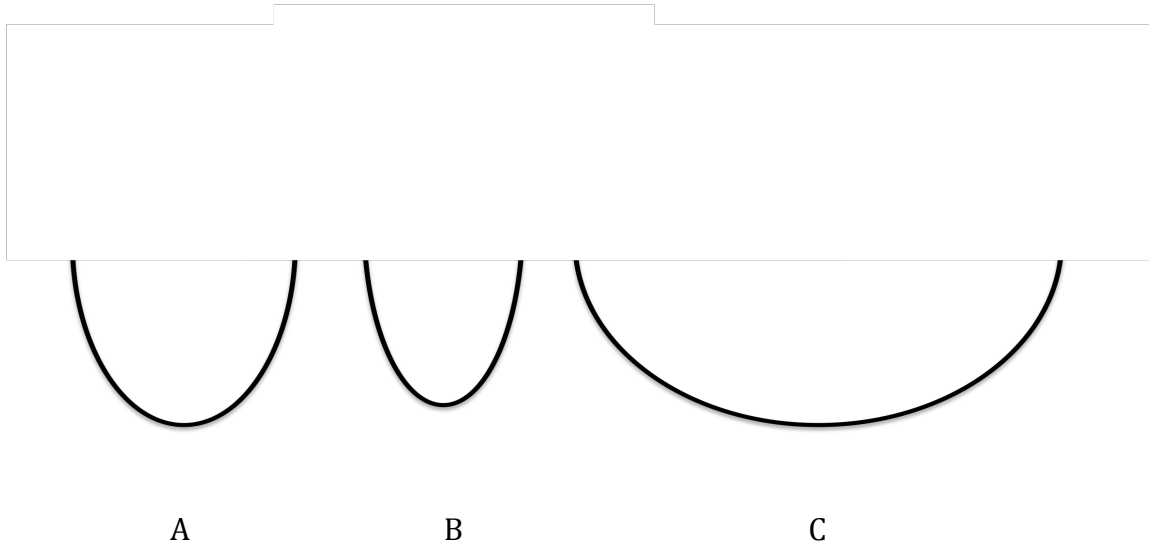
Entropy

$S = k_B \ln W = k_B \ln(1) = 0$

5C. (2.5 Points) What is the value of entropy associated with the state where D = N and U = 0?

Entropy

$S = k_B \ln W = k_B \ln(1) = 0$

6. Bonus (5 Points) Consider a system (i.e., a particle, or a harmonic oscillator) that is confined in a harmonic potential well in one dimension (see figure). Given the same internal energy, which system will have the largest entropy and why?

A   B   C

Answer:

system C because the accessible region of space is the largest in this case. Since the accessible space is largest, there are the most possible ways for realizing a system with this "soft" potential.