ME-351 THERMODYNAMICS AND ENERGETICS II

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SPRING 2025

NAME :
Solutions

SCIPER :

Question	Points	Score
1	20	
2	15	
3	20	
4	15	
5	15	
6	15	
Total:	100	

This is a *closed book* examination. No extra papers, calculators, books etc. are permitted for use during the exam. Answer the questions in the space provided. Please ensure you show all your work and your answers are legible. Keep your answers to the point. When appropriate, include sufficient information to indicate reasoning. This will allow us to give you partial credit, even if you do not answer the question completely. If you need additional space, continue on the back of the page. You have 3 hours to complete the exam. **Good Luck!**

Difficult to remember formulas

1. Reciprocal Rule : $\left(\frac{\partial x}{\partial y}\right) = \frac{1}{\left(\frac{\partial y}{\partial x}\right)}$
2. Cyclical Relation : $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$
3. Chain Rule : $\left(\frac{\partial x}{\partial z}\right)_\phi = \left(\frac{\partial x}{\partial y}\right)_\phi \left(\frac{\partial y}{\partial z}\right)_\phi$
4. $\left(\frac{\partial x}{\partial \phi}\right)_z = \left(\frac{\partial x}{\partial \phi}\right)_y + \left(\frac{\partial x}{\partial y}\right)_\phi \left(\frac{\partial y}{\partial \phi}\right)_z$
5. Maxwell relations : $\left(\frac{\partial A}{\partial B}\right)_{\mathrm{conjugate}(A)} = \pm \left(\frac{\partial(\mathrm{conjugate}(B))}{\partial(\mathrm{conjugate}(A))}\right)_B$

1. Are the following statements true or false? *No credit will be given if the answer is not justified based on rigorous thermodynamic arguments.*

   (a) (3 points) The volume of a system is held constant in a reversible process. The work done on the system by the environment is zero.

   ○ True ● False

   Other kinds of work could be done on the system: (eg) shear work or electro-magnetic work.

   (b) (3 points) Heat transfer from a system at a high temperature to a system at a lower temperature can only be achieved through an irreversible process.

   ○ True ● False

   (eg) Carnot cycle

   (c) (3 points) During the adiabatic expansion of a material, the temperature of the material must decrease.

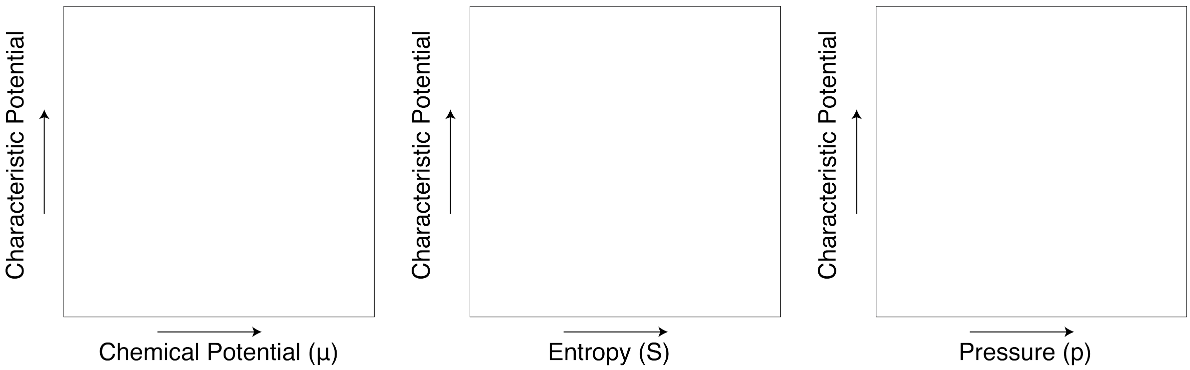
   ○ True ● False

   (eg) The temperature of an ideal gas does not change during an adiabatic process.

   (d) (2 points) Enthalpy is a conserved quantity ○ True ● False

   (eg) When S, and p are the natural variables of a system H is the char. potential ⇒ Will be minimized & not conserved.

   (e) (9 points) Consider the characteristic potential, denoted Λ, of a pure element that has as its natural variables, μ, S and p. Here, μ is the chemical potential of the element, S is the entropy, and p is the pressure. Sketch Λ as a function of its natural variables in the below plots. Provide a thermodynamic reason for the shapes of each of your schematic curves.



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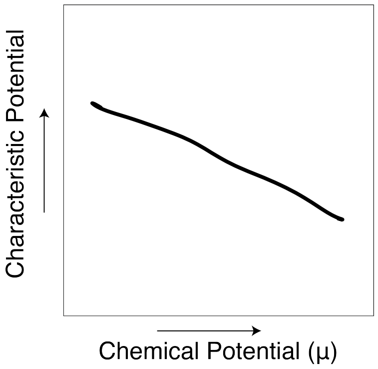
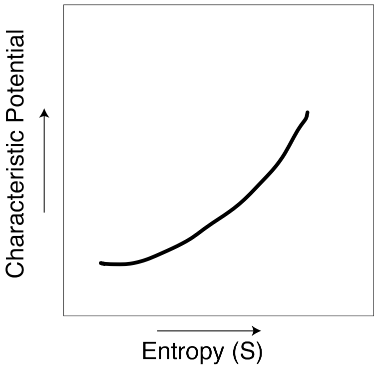
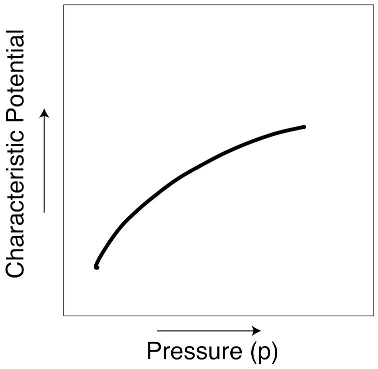






$$\Lambda = U + pV - \mu N$$

$$d\Lambda = TdS + Vdp - Nd\mu \Rightarrow \underset{+ve.}{\left(\frac{\partial \Lambda}{\partial S}\right)_{p,\mu} = T \, ; \left(\frac{\partial^2 \Lambda}{\partial S^2}\right)} = \left(\frac{\partial T}{\partial S}\right)_{p,\mu} = \frac{T}{C_p}$$

$$\underset{\underset{+ve}{\uparrow}}{\left(\frac{\partial \Lambda}{\partial p}\right)_{\mu,S}} = V \, ; \underset{\underset{-ve}{\uparrow}}{\left(\frac{\partial^2 \Lambda}{\partial p^2}\right)} = \left(\frac{\partial V}{\partial p}\right)_{\mu,S} = -V\underline{\kappa} \xrightarrow{} \text{Compressibility}$$

$$\left(\frac{\partial \Lambda}{\partial \mu}\right)_{S,p} = \underset{\underset{-ve.}{\uparrow}}{-N} \qquad \left(\frac{\partial^2 \Lambda}{\partial \mu^2}\right) = -\left(\frac{\partial N}{\partial \mu}\right)_{S,p} \xrightarrow{} \text{at this point difficult to guess the sign.}$$

2. The Helmholtz free energy per atom of a system is given by:

$$F = U - TS = \sum_{ij} v_0 A_{ij} (\epsilon_{ij} - \frac{1}{2})^2 \tag{1}$$

where v_0 is the volume per atom of the system, A_{ij} is a constant, ϵ_{ij} is the strain of the system relative to a reference state, and ij refers to the components of the strain tensor. The above relation holds at constant temperature. You can assume that the temperature is held to be a constant for the following questions.

(a) (5 points) Compute a relationship between stress (σ_{ij}) and strain (ϵ_{ij}) for this system.

(b) (2 points) Does the material follow Hooke's law?

(c) (3 points) Compute the elasticity (also called the stiffness) tensor for this system

(d) (5 points) Compute the value of strain that is attained by the system if it is allowed to equilibrate against an environment where all the stresses are zero.

a) $dU = TdS + \sum_{ij} v_0 \sigma_{ij} d\epsilon_{ij}$

$F = U - TS \Rightarrow df = -SdT + \sum_{ij} v_0 \sigma_{ij} d\epsilon_{ij}$

EOS: $\left(\frac{\partial f}{\partial \epsilon_{ij}}\right)_{T, \epsilon_{kl \neq ij}} = v_0 \sigma_{ij} = v_0 A_{ij} 2 (\epsilon_{ij} - \frac{1}{2})$

$$\Rightarrow \boxed{\sigma_{ij} = 2 A_{ij} (\epsilon_{ij} - \frac{1}{2})}$$

b) Formally:

Hookes Law: $\sigma_{ij} = \sum_{kl} C_{ijkl} \epsilon_{kl}$

This is equivalent to the above expression if $C_{ijkl} = 0$, for all $ij \neq kl$ and $C_{ijij} = 2A_{ij}$ and the strain reference state is shifted.

c) Elasticity tensor is $C_{ijkl} = \left(\frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}}\right)$

$$C_{ijkl} = \begin{cases} 2A_{ij}, & \text{if } kl = ij \\ 0, & \text{if not} \end{cases}$$

d) When the system equilibrates with an environment at zero stress, the system stress is zero,

(ie) $\sigma_{ij} = 0$ @ eq^m.

from <u>above</u>:

$$\sigma_{ij} = 2A_{ij}\left(\epsilon_{ij} - \frac{1}{2}\right)$$

$$\Rightarrow \boxed{\epsilon_{ij}^{eq^m} = \frac{1}{2}}$$ when the environment imposes zero stress on the system

3. Consider a hypothetical universe that is entirely made of a single element called *universium*. This element is found to occur in one of three possible phases: α, β, γ. The internal energies of these phases are:

$$U^\alpha = AS + BV \tag{2}$$

$$U^\beta = \frac{A}{2}S + \frac{B}{2}V \tag{3}$$

$$U^\gamma = 2AS + 2BV \tag{4}$$

where $U^\alpha, U^\beta, U^\gamma$ are the internal energies of α, β, and γ respectively, S and V are the entropy and volume. B is a positive constant and A is another constant.

The universe is initially prepared, such that all the universium is in the α phase and has an initial entropy and volume of S_0, V_0.

(a) (3 points) What is the sign of A? Justify your answer based on a rigorous thermodynamic argument.

(b) (5 points) After the universe attains equilibrium, what phases of universium can be found in the universe?

(c) (10 points) Compute all state variables (S, U, p, T, V) of the universe after it reaches equilibrium. Express all your answers in terms of S_0, V_0, A, B.

(d) (2 points) Did the temperature of the universe at equilibrium increase or decrease as compared with its initial temperature?

(a) $dU = TdS - pdV$

$\left(\frac{\partial U}{\partial S}\right)_V = T \Rightarrow A > 0$ since $T > 0$

(b) System $\longrightarrow$ isolated $\Rightarrow$ U and V are conserved. ; ENTROPY of the system is maximized @ eq^m.

initial state:

$U^\alpha = AS_0 + BV_0 = U_0 \; ; \; V_0$

final state:

System could have one of three possible entropies:

$S^\alpha = \frac{U_0 - BV_0}{A} \; ; \; S^\beta = \frac{U_0 - \frac{B}{2}V_0}{A/2} \; ; \; S^\gamma = \frac{U_0 - 2BV_0}{2A_0}$

$S^\alpha = S_0 \; ; \; S^\beta = S_0 + \frac{U_0}{A} \; ; \; S^\gamma = S_0 - \frac{U_0}{2A_0}$

$U_0 > 0$ [$\because A, B, S_0, V_0 > 0$]

$\Rightarrow S^\beta > S^\alpha > S^\gamma \Rightarrow$ @ eq^m system maximizes entropy by forming β

(c) $S = S_o + \frac{AS_o + BV_o}{A} = 2S_o + \frac{B}{A}V_o$

$V = V_o$

$U = U_o$

$T = \left(\frac{\partial U^{\beta}}{\partial S}\right)_V = \frac{A}{2}$

$p = -\left(\frac{\partial U^{\beta}}{\partial V}\right)_S = -\frac{B}{2}$

d) Initial temp. of universe: A
final T : $A/2$
$\Rightarrow$ Temp. decreased, universe has cooled.

$V_0 \longrightarrow V_1$ $V_1 \longrightarrow V_2$

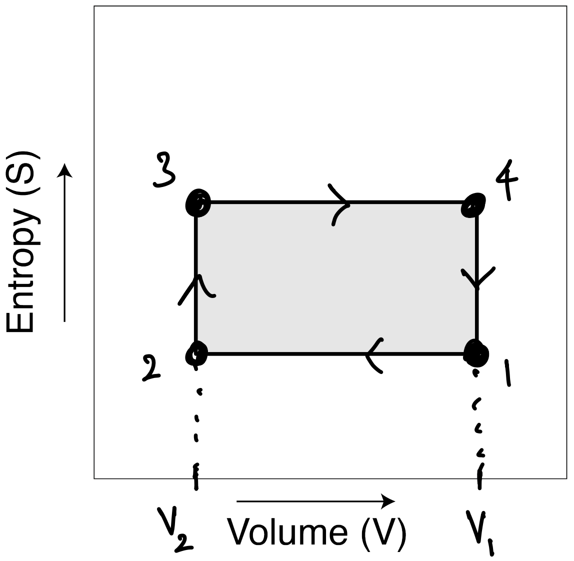
4. The *Otto cycle* is a convenient approximation to the operation of a gasoline engine. An ideal gas is first compressed adiabatically from an initial volume of V_0 to V_1. It is then heated at constant volume. In the third step of the cycle, the ideal gas is expanded adiabatically to a volume of V_0. Finally the ideal gas is cooled at constant volume back to its initial state. All steps of the Otto cycle are performed reversibly.

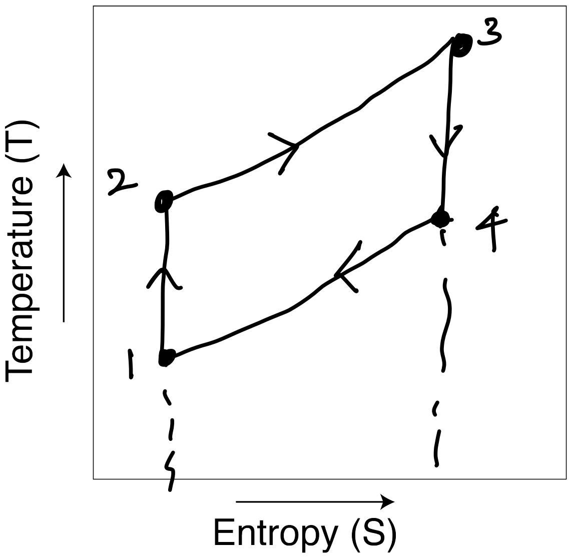
   (a) (6 points) Sketch the various steps of the Otto cycle on the $S-V$ and $T-S$ graphs provided below. Clearly label the four states of the ideal gas as 1, 2, 3, and 4. Where 1 is the initial state of the ideal gas.

   (b) (9 points) Show that the efficiency of the Otto cycle is given by:

$$\eta_{\text{Otto}} = 1 - \cancel{\left(\frac{V_1}{V_0}\right)^{\frac{C_p-C_v}{C_v}}} = 1 - \left(\frac{V_2}{V_1}\right)^{\frac{C_p-C_v}{C_v}} \qquad (5)$$

C_p and C_V are the constant pressure and constant volume heat capacities of an ideal gas. Both heat capacities are constant and independent of temperature. For an ideal gas, along an adiabatic path, $pV^\gamma = \text{constant}$, where $\gamma = \frac{C_p}{C_V}$





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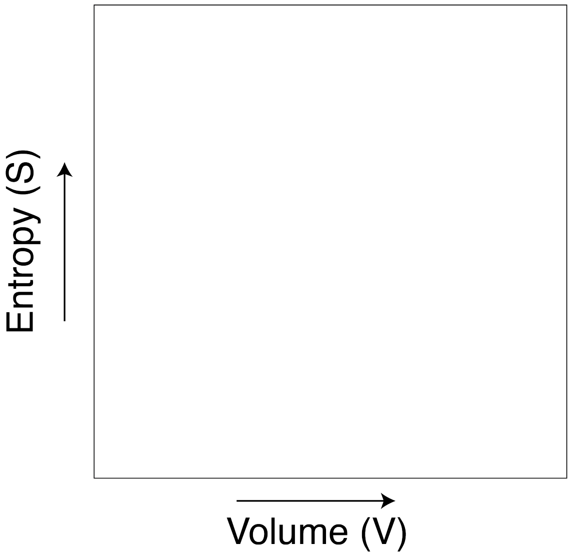
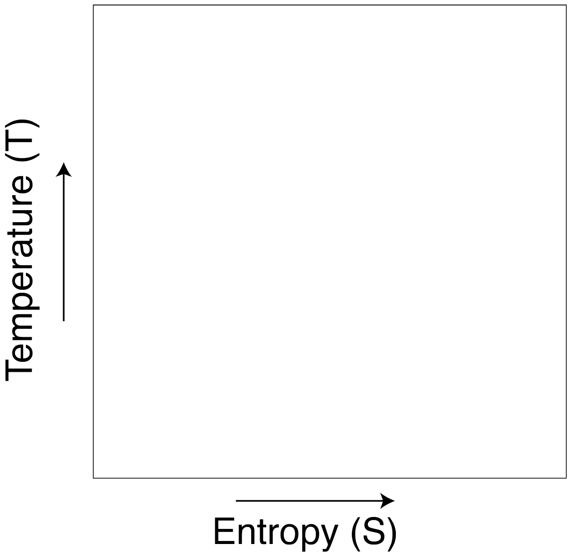




Otto cycle efficiency

$\Delta U_{cycle} = q_H + q_L + W = 0$; $q_H \longrightarrow$ heat into the system when going from $2 \to 3$

$\Rightarrow W = -(q_H + q_L)$ $q_L \longrightarrow$ heat out of the system when going from $4 \to 1$

$$\eta_{otto} = \frac{-\boxed{} \leftarrow \text{what we get}}{\boxed{} \leftarrow \text{what we input}} = \frac{-W}{q_H} = 1 + \frac{q_L}{q_H}$$

Heat input/out of the system happens reversibly AND @ const. volume.

$$\left.\begin{aligned} \Rightarrow q_H &= C_v \Delta T_{2\to 3} = C_v (T_3 - T_2) \\ q_L &= C_v (T_1 - T_4) \end{aligned}\right] \Rightarrow \eta = 1 + \frac{T_1 - T_4}{T_3 - T_2}$$

$1 \to 2$ is an adiabat & $3 \to 4$ is an adiabat

$$\Rightarrow p_1 V_1^{\gamma} = p_2 V_2^{\gamma} \text{ and } p_3 V_3^{\gamma} = p_4 V_4^{\gamma}$$

ideal gas law: $pV = nRT$

$$\Rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \text{ and } T_3 V_3^{\gamma-1} = T_4 V_4^{\gamma-1}$$

$4 \to 1$ and $2 \to 3$ are constant volume.

$$\Rightarrow V_1 = V_4 \text{ and } V_2 = V_3$$

$$\Rightarrow T_1 V_4^{\gamma-1} = T_2 V_3^{\gamma-1} \text{ and } T_3 V_3^{\gamma-1} = T_4 V_4^{\gamma-1}$$

$$\Rightarrow (T_1 - T_4) V_4^{\gamma-1} = (T_2 - T_3) V_3^{\gamma-1}$$

$$\Rightarrow \frac{T_1 - T_4}{T_2 - T_3} = \left(\frac{V_3}{V_4}\right)^{\gamma-1} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$\boxed{\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} = 1 - \left(\frac{V_2}{V_1}\right)^{\frac{C_p - C_v}{C_v}}}$$

5. (15 points) You are asked to explore whether a material that is under an applied hydrostatic stress can be used to cool its environment. The idea would be to place the material in an environment where it is subject to a hydrostatic stress given by p. When cooling is required, the applied stress would be suddenly removed. The hope is that the resultant relaxation of the total volume would be accompanied by an absorption of heat.

   Derive an expression for the amount of heat absorbed by the material at constant temperature after an initial pressure with value p_1 is suddenly removed. The temperature T of the material is less than T_c

   The following relationships between thermodynamic state variables, and response functions are known for the material:

$$V(T,p) = A(T_C - T)^{\frac{1}{2}} + \chi p^2 \tag{6}$$

   where V, p and T are the volume, pressure and temperature of the material, A, χ, and T_C are constants.

Char. potential for the system: Control T, p.

$$G(T,p) = U - TS + pV \Rightarrow dG = Vdp - SdT$$

To compute: $q = ?$

I Law: $\Delta U = q + W$

$W = 0$, since $p = 0$ when the material is absorbing heat from the environment.

$$\Rightarrow q = \Delta U = U(p=0,T) - U(p=p_1,T) = \int_{p_1}^{0} \left(\frac{\partial U}{\partial p}\right)_T dp$$

fundamental eqn. of thermo:

$$dU = TdS - pdV$$

$$\Rightarrow \left(\frac{\partial U}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T$$

from $dG = Vdp - SdT$

Maxwell: $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

$$\left(\frac{\partial U}{\partial p}\right)_T = -\left[T\left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial p}\right)_T\right]$$

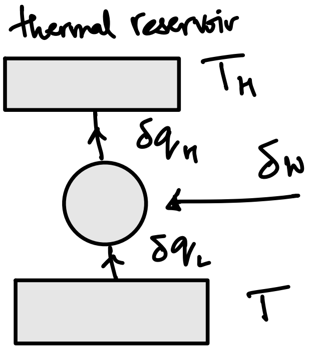
$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{-A}{2(T_c - T)^{1/2}} \qquad \left(\frac{\partial V}{\partial p}\right)_T = 2\chi p$$

$$\boxed{\left(\frac{\partial U}{\partial p}\right)_T = +\frac{AT}{2(T_c - T)^{1/2}} - 2\chi p^2}$$

$$q = \int_{p_1}^{0} \left(\frac{\partial u}{\partial p}\right)_T dp = -\frac{ATp_1}{2(T_c - T)^{1/2}} + 2\chi p_1^3$$

$$\boxed{q = 2\chi p_1^3 - \frac{ATp_1}{2(T_c - T)^{1/2}}}$$

6. (15 points) The enthalpy of a material is found to be $H = CT$, where C is a positive constant with units J/K. The material is cooled from a high temperature (T_H) to a low temperature (T_L) by operating a refrigerator that releases its heat to a thermal reservoir at T_H and absorbs heat from the material during the low temperature heat absorption. The refrigerator operates in a cycle, and work is done on the refrigerator during the course of the cycle. What is the minimum work that must be performed on the refrigerator to cool the material from T_H to T_L?



<u>I Law:</u> $\delta q_H + \delta q_L + \delta w = 0$

$$\Rightarrow \delta w = -(\delta q_H + \delta q) \text{ — ①}$$

<u>II Law:</u> $$\frac{\delta q_H}{T_H} + \frac{\delta q}{T} = 0 \quad \left[\text{All steps performed reversibly}\right]$$

$$\Rightarrow \delta q_H = -\delta q \left(\frac{T_H}{T}\right) \text{ — ②}$$

② in ① $\Rightarrow$ $$\delta w = -\delta q \left(1 - \frac{T_H}{T}\right)$$

$$\delta q = -dH = -CdT$$

$$\delta w = CdT\left(1 - T_H/T\right)$$

$$W = \int_{T_H}^{T_L} C\left(1 - \frac{T_H}{T}\right) dT = C(T_L - T_H) - CT_H \log\left(\frac{T_L}{T_H}\right)$$

$$\boxed{W = CT_H \log\left(\frac{T_H}{T_L}\right) - C(T_H - T_L)}$$