ME-351 THERMODYNAMICS AND ENERGETICS II

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NAME :

SCIPER :

Question	Points	Score
1	10	
2	20	
3	20	
4	15	
5	15	
6	20	
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 2 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 : $\left(\frac{\partial A}{\partial B}\right)_{\text{conjugate}(A)} = \pm \left(\frac{\partial(\text{conjugate}(B))}{\partial(\text{conjugate}(A))}\right)_B$

1. Short questions

(a) (4 points) List the conjugate variables for the following quantities:

1. Pressure (p) : Volume (V)
2. Magnetic Field (H) : Magnetization (M)
3. Entropy (S) : Temperature (T)
4. Stress (σ_{ij}) : $V_0 \varepsilon_{ij}$ [has to be extensive!]

(b) (4 points) A material is held in an environment at constant temperature (T) and pressure (p). Sketch the variation of the characteristic potential of this material under these boundary conditions:

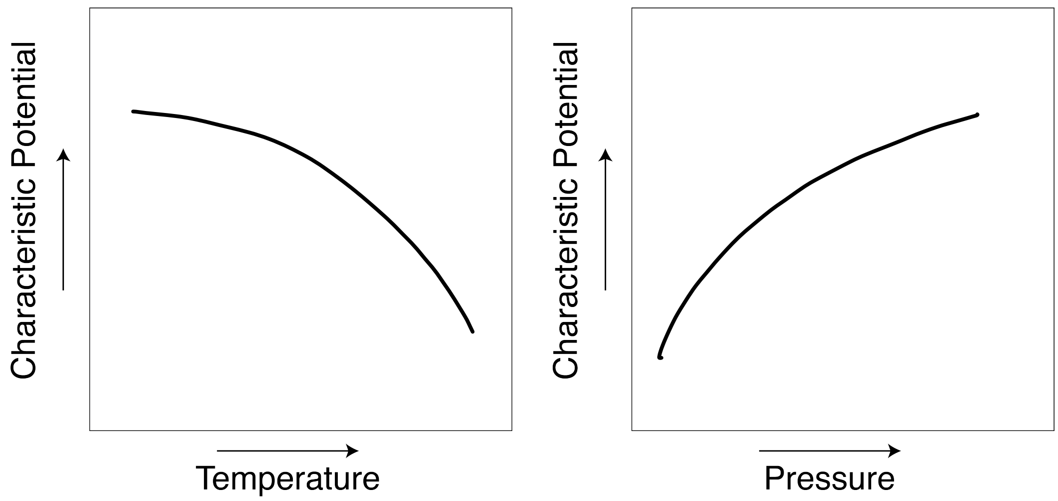


Figure 1

$$G = U - TS + pV$$
$$dG = Vdp - SdT \Rightarrow \left(\frac{\partial G}{\partial p}\right)_T = V > 0 \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S < 0$$

$$\frac{\partial^2 G}{\partial T^2} = -\left(\frac{\partial S}{\partial T}\right)_p = -C_p/T < 0$$

(c) (2 points) The entropy of a system can decrease (Justify your answer)

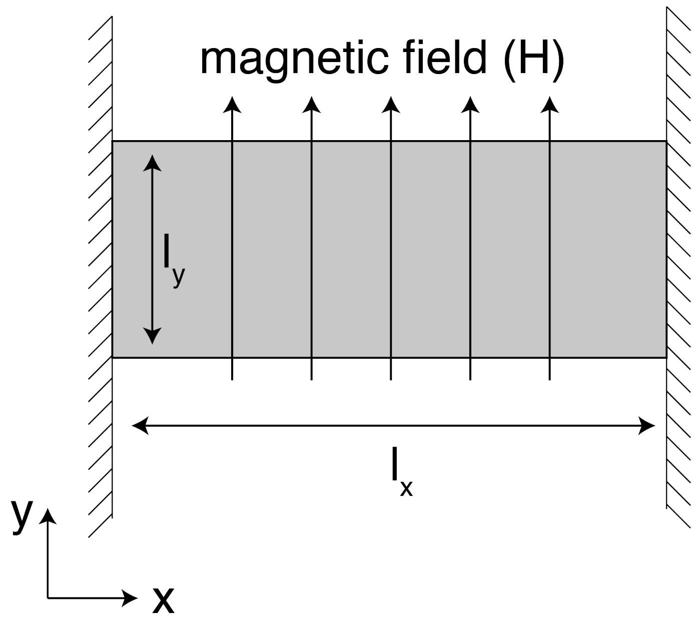
◯ True ◯ False

$dS \geq 0$ for an isolated universe

$\Rightarrow \Delta S_{total} \geq 0 \Rightarrow \Delta S_{system} + \Delta S_{surrounding} \geq 0$

can be negative if $\Delta S_{surrounding}$ is sufficiently positive.

2. A rod, made of a ferromagnetic material is clamped between two walls in an atmosphere at temperature T and pressure p. as illustrated in the figure. A magnetic field H is imposed along the y direction.



(a) (2 points) Write down the experimentally controlled state variables

(b) (3 points) Write down the fundamental equation of thermodynamics for this system

(c) (4 points) Derive an expression for the characteristic potential for this system and its differential form

(d) (5 points) Write down the equations of state for this system

(e) (2 points) How many independent response functions can be defined for this system? Justify your answer.

(f) (4 points) Experiments have shown that the length of the material along the y and z directions increase when the magnetic field is increased. For design reasons, you are asked to increase the magnetization of the material without increasing the magnetic field applied to the material. Propose a way to achieve this and justify your answer with rigorous thermodynamic arguments.

(a) Controlled: $T,\ H,\ \varepsilon_{xx}V_0,\ \sigma_{yy},\ \sigma_{zz}$

(b) fundamental eqn of thermo: (shear strains can be ignored).

$$dU = TdS + V_0\sigma_{xx}d\varepsilon_{xx} + V_0\sigma_{yy}d\varepsilon_{yy} + V_0\sigma_{zz}d\varepsilon_{zz} + HdM$$

(c) $$U(S, V_0\varepsilon_{xx}, V_0\varepsilon_{yy}, V_0\varepsilon_{zz}, M) \longrightarrow \Lambda(T, V_0\varepsilon_{xx}, \sigma_{yy}, \sigma_{zz}, H)$$

$$\Lambda = U - TS - V_0\sigma_{yy}\varepsilon_{yy} - V_0\sigma_{zz}\varepsilon_{zz} - MH$$

$$d\Lambda = -SdT + V_0\sigma_{xx}d\varepsilon_{xx} - V_0\varepsilon_{yy}d\sigma_{yy} - V_0\varepsilon_{zz}d\sigma_{zz} - MdH$$

d) EoS:

$$\left(\frac{\partial\Lambda}{\partial T}\right)_{\varepsilon_{xx},\ldots} = -S \qquad \left(\frac{\partial\Lambda}{\partial\varepsilon_{xx}}\right) = V_0\sigma_{xx} \qquad \left(\frac{\partial\Lambda}{\partial\sigma_{yy}}\right) = -V_0\varepsilon_{yy}$$

$$\left(\frac{\partial \Lambda}{\partial \sigma_{zz}}\right) = -V_0 \varepsilon_{zz} \quad \left(\frac{\partial \Lambda}{\partial H}\right) = -M$$

(e) 25 second derivatives of Λ; 5 of them of the form $\left(\frac{\partial^2 \Lambda}{\partial X^2}\right)$

of the remaining 20: 10 are related by Maxwell relations:

$$\frac{\partial^2 \Lambda}{\partial X \partial Y} = \frac{\partial^2 \Lambda}{\partial Y \partial X}$$

$\Rightarrow (10 + 5)$ independent response functions.

f) Given: $\frac{\partial \varepsilon_{yy}}{\partial H} > 0$ and $\frac{\partial \varepsilon_{zz}}{\partial H} > 0$

Maxwell Relation $\Rightarrow V_0 \frac{\partial \varepsilon_{yy}}{\partial H} = \frac{\partial M}{\partial \sigma_{yy}}$ and $V_0 \frac{\partial \varepsilon_{zz}}{\partial H} = \frac{\partial M}{\partial \sigma_{zz}}$

$\because \frac{\partial \varepsilon_{yy}}{\partial H} > 0 \Rightarrow$ M can be increased by increasing σ_{yy} & σ_{zz}

3. The characteristic potential (A) for a block of material at constant length and temperature is given by:

$$A(T, L) = (L - L_0)^4(\lambda + T\theta) + \kappa T^2 \tag{1}$$

where the length of the material is L, temperature is T, $L_0, \lambda, \theta, \kappa$ are constants. The constants are such that $\lambda > 0$ and $\theta < 0$. The free energy is found to characterize the behavior of the material at low temperatures.

(a) (2 points) What is the sign of κ?

(b) (2 points) Derive an equation for the force on the rod as a function of the length of the rod. Express the force in terms of the constants $\theta, \lambda, \kappa, L_0$, temperature ($T$) and length ($L$).

(c) (6 points) Derive an expression for the characteristic potential (G) of the material at constant temperature and force (F). The free energy should be expressed in terms of its natural variables F, T and material constants ($\theta, \lambda, \kappa, L_0$).

(d) (6 points) Use the characteristic potential, $G(T, F)$ to calculate the length of the material when no force is applied to it at a temperature T.

(e) (4 points) The force and length of a material are proportional to each other in linear elastic materials, i.e. $F \propto (L - L_0)$. Is the material with the free energy function shown in eq. (1) a linear elastic material? If not, propose a free energy function ($B(T, L)$) that could represent a linear elastic material.

(a) $A(T,L) \Rightarrow dA = -SdT + fdL$

$$\left(\frac{\partial A}{\partial T}\right)_L = -S$$

$$\theta(L-L_0)^4 + 2\underline{\kappa}T = -S$$

$\Rightarrow \underline{\kappa} < 0$ if $S >$ for $L = L_0$

b) $$f = \left(\frac{\partial A}{\partial L}\right)_T = 4(L-L_0)^3(\lambda + \theta T)$$

c) $$L = \left[\frac{F}{4(\lambda + \theta T)}\right]^{1/3} + L_0$$

$$G = A - fL = (L-L_0)^4(\lambda + \theta T) + \underline{\kappa}T^2 - fL$$

$$\Rightarrow G = \left[\frac{f}{4(\lambda+\theta T)}\right]^{4/3}(\lambda + \theta T) + \underline{\kappa}T^2 - fL_0 - \frac{f^{4/3}}{(4(\lambda+\theta T))^{1/3}}$$

$$G = \frac{f^{4/3}}{(4(\lambda+\theta T))^{1/3}}\left(-\frac{3}{4}\right) - fL_0 + \underline{\kappa}T^2$$

(d) $L = -\left(\frac{\partial G}{\partial f}\right)_T$

$$= \frac{f^{1/3}}{\left(4(\lambda+\theta T)\right)^{1/3}} + L_0$$

when $f=0$

$$\boxed{L = L_0}$$

(e) The material is not linear elastic since $f \propto (L-L_0)^3$

linear elastic material:

$$\boxed{B(T,L) = (L-L_0)^2(\lambda+\theta T) + \underline{K}\,T^2}$$

4. One mole of an ideal gas has the following equations of state:

$$pV = RT$$

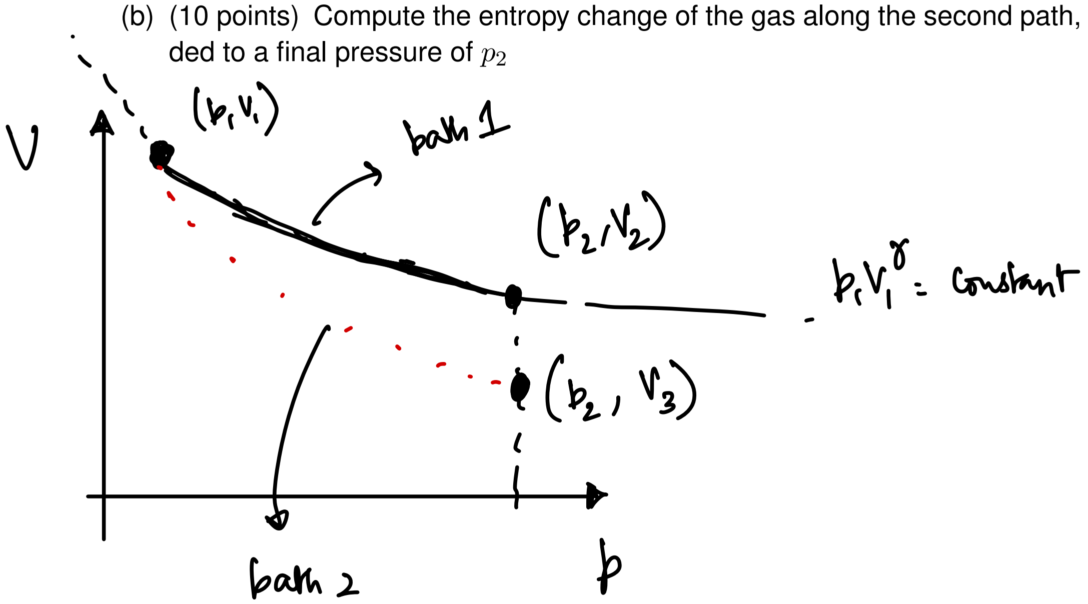
$$U = C_V T$$

where $p, V, T, U,$ and C_V are the pressure, volume, temperature, internal energy and heat capacity at constant volume respectively. C_V of the ideal gas is $\frac{3}{2}R$ and adiabats of this gas are found to follow $pV^\gamma = constant$, where γ is a constant number.

The gas,held in an adiabatic chamber, is prepared in an initial state (p_1, T_1) and is transformed along two different paths. Along the first path, the pressure of the gas is reversibly decreased to p_2. Along the second path, the gas is suddenly expanded such that the final pressure of the gas is p_2 and some work (denoted $w_{1\to 2}$) is extracted from the gas.

(a) (5 points) What is the final temperature of the system along path 1 and path 2? Is the final temperature of the gas higher for path 1 or path 2?

(b) (10 points) Compute the entropy change of the gas along the second path, where it is suddenly expanded to a final pressure of p_2



path 2
(can't be drawn on the p-V diagram as it is sudden)

path 1: reversible

$p_1 V_1 = RT_1 \Rightarrow V_1 = RT_1/p_1$

$$\Rightarrow p_1 V_1^\gamma = p_2 V_2^\gamma$$

$$\boxed{V_2 = \left(\frac{p_1}{p_2}\right)^{\frac{1}{\gamma}} V_1 = \left(\frac{p_1}{p_2}\right)^{\frac{1}{\gamma}} \frac{RT_1}{p_1}}$$

$$\Rightarrow T_2 = \frac{p_2 V_2}{R} = \frac{R p_2 T_1}{p_1 R}\left(\frac{p_1}{p_2}\right)^{1/\gamma} = T_1 \left(\frac{p_1}{p_2}\right)^{1/\gamma - 1}$$

along path 2 : $\Delta U = q + W = W$ [Adiabatic path]

$$\Delta U = C_v (T_3 - T_1) = W_{1\to 2} \Rightarrow \boxed{T_3 = \frac{W_{1\to 2}}{C_v} + T_1}$$

(b) Entropy change for path 2

Construct a reversible path going from (p_1, T_1) to (p_2, T_3)

$$(p_1, T_1) \xrightarrow{ⓐ} (p_3, T_3) \xrightarrow{ⓑ} (p_2, T_3)$$

constant volume. constant temperature

path ⓐ:

$$dU = \delta q + \delta w$$

$$dW = -p\,dV \Rightarrow W = 0$$

$$\Rightarrow dU = T\,dS \Rightarrow dS = \frac{dU}{T} = \frac{C_v\,dT}{T}$$

$$\Delta S_a = \int_{T_1}^{T_3} \frac{C_v\,dT}{T} = C_v \log\left(\frac{T_3}{T_1}\right)$$

path ⓑ: constant temperature

$$dU = dq + dW = 0 \Rightarrow dq = -dW = p\,dV$$

$$\Rightarrow dS = \frac{p\,dV}{T} = \frac{R\,dV}{V} \Rightarrow \Delta S_b = R \log\left(\frac{V_3}{V_1}\right)$$

$$\Delta S_{total} = \Delta S_a + \Delta S_b = C_v \log\left(\frac{T_3}{T_1}\right) + R \log\left(V_3/V_1\right)$$

$$V_3 = \frac{RT_3}{p_2} \quad V_1 = \frac{RT_1}{p_1} \Rightarrow \log\left(V_3/V_1\right) = \log\left(\frac{T_3}{T_1}\right) + \log\left(\frac{p_1}{p_2}\right)$$

$$\Delta S_{total} = (C_v + R)\log\left(T_3/T_1\right) + \log\left(\frac{p_1}{p_2}\right)$$

$$\boxed{\Delta S_{total} = (C_v + R)\log\left(\frac{W_{1\to2}}{C_v T_1} + 1\right) + \log\left(\frac{p_1}{p_2}\right)}$$

5. (15 points) The adiabatic bulk modulus is defined as:

$$\beta_S = -V\left(\frac{\partial p}{\partial V}\right)_S$$

Express the adiabatic bulk modulus in terms of the heat capacities at constant pressure and volume (C_p, C_V), and compressibility ($\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$)

$$\beta_S = -V\left(\frac{\partial p}{\partial V}\right)_S$$

$$\left(\frac{\partial p}{\partial V}\right)_S\left(\frac{\partial V}{\partial S}\right)_p\left(\frac{\partial S}{\partial p}\right)_V = -1 \longrightarrow \text{Cyclical relation}$$

$$\Rightarrow -V\left(\frac{\partial p}{\partial V}\right)_S = \frac{V\left(\frac{\partial S}{\partial V}\right)_p}{\left(\frac{\partial S}{\partial p}\right)_V}$$

$$\left(\frac{\partial S}{\partial V}\right)_p = \underbrace{\left(\frac{\partial S}{\partial T}\right)_p}_{=C_p/T}\left(\frac{\partial T}{\partial V}\right)_p = \frac{C_p}{T}\left(\frac{\partial T}{\partial V}\right)_p \text{ --- } (1)$$

$$\left(\frac{\partial S}{\partial p}\right)_V = \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{C_V/T}\left(\frac{\partial T}{\partial p}\right)_V = \frac{C_V}{T}\left(\frac{\partial T}{\partial p}\right)_V \quad ;$$

Cyclical relation between $p, T, V \Rightarrow \left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial T}{\partial V}\right)_p = -1$

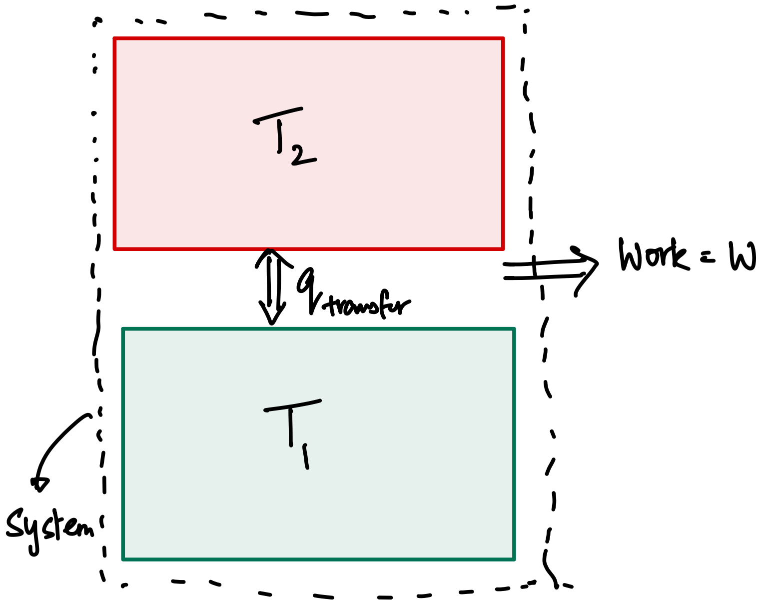
$$\Rightarrow \left(\frac{\partial T}{\partial p}\right)_V = \underbrace{-\left(\frac{\partial V}{\partial p}\right)_T}_{=V\underline{K}}\left(\frac{\partial T}{\partial V}\right)_p$$

$$\left(\frac{\partial S}{\partial p}\right)_V = \frac{C_V}{T}V\underline{K}\left(\frac{\partial T}{\partial V}\right)_p \text{ --- } (2)$$

Using (1) & (2) $\Rightarrow \beta_S = \left[\frac{C_p V}{T}\left(\partial T/\partial V\right)_p\right] \Big/ \left[\frac{C_V V\underline{K}}{T}\left(\frac{\partial T}{\partial V}\right)_p\right]$

$$\Rightarrow \boxed{\beta_s = \frac{C_p}{C_v \kappa}}$$

6. (20 points) Two bodies have heat capacities (at constant volume) of $C_1 = aT$ and $C_2 = 2bT$. The initial temperatures of the two bodies are T_1 and T_2, where $T_2 > T_1$. The two bodies are to be brought to thermal equilibrium (at constant volume) while delivering as much work as possible to a reversible work source. Compute the final equilibrium temperature and the maximum work that can be extracted from the two bodies by the reversible work source.



Let the final temperature of the two bodies be T_f. The process is done reversibly for maximum work extraction:

$$\Rightarrow \quad dS_{system} = \frac{\delta q}{T} \longrightarrow \text{II Law \& reversible.}$$

$$\delta q = 0 \Rightarrow \boxed{\Delta S_{system} = 0}$$

$$\Delta S_{system} = \Delta S_1 + \Delta S_2$$

$$\Delta S_1 = \int_{T_1}^{T_f} \frac{dq}{T} = \int_{T_1}^{T_f} \frac{C_1\,dT}{T} = \int_{T_1}^{T_f} a\,dT = a(T_f - T_1)$$

$$\Delta S_2 = \int_{T_2}^{T_f} \frac{C_2\,dT}{T} = \int_{T_2}^{T_f} 2b\,dT = 2b(T_f - T_2)$$

$$\Delta S_{system} = a(T_f - T_1) + 2b(T_f - T_2) = 0$$

$$\Rightarrow T_f(a+2b) = aT_1 + 2bT_2$$

$$\boxed{T_f = \frac{aT_1 + 2bT_2}{a+2b}}$$

$$\Delta U_{System} = q_{System} + W_{System} = W_{System}$$

$$W_{System} = \Delta U_1 + \Delta U_2 = \int_{T_1}^{T_f} C_1\, dT + \int_{T_2}^{T_f} C_2\, dT$$

$$= \left[\frac{aT^2}{2}\right]_{T_1}^{T_f} + \left[\frac{2bT^2}{2}\right]_{T_2}^{T_f}$$

$$= \frac{aT_f^2}{2} - \frac{aT_1^2}{2} + \frac{2bT_f^2}{2} - \frac{2bT_2^2}{2} = T_f^2\left(\frac{a+2b}{2}\right) - \left[\frac{aT_1^2 + 2bT_2^2}{2}\right]$$

$$\boxed{W = \frac{(aT_1 + 2bT_2)^2}{2(a+2b)} - \frac{aT_1^2 + 2bT_2^2}{2}}$$