

**Q4001 Thermodynamics of Materials
Homework 2**

August, 2019

1. Indicate whether the following statements are true or false. Justify your reasoning.

- (a) In an isobaric compression, $\Delta H = 0$.
- (b) In an isocoric process, $\Delta H = 0$.
- (c) For a perfect gas, $\Delta U = n\bar{C}_P\Delta T$, in an isobaric process.
- (d) During an adiabatic expansion against a vacuum, $w = 0$
- (e) For an adiabatic process $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

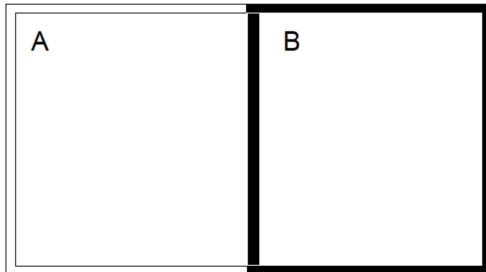
2. Demonstrate that for a adiabatic reversible process

$$w_{ad} = \frac{1}{\gamma - 1} [P_f V_f - P_i V_i]$$

3. One mole of N₂ gas is contained at 273 K and pressure of 1 atm. The addition of 3000 J of heat to the gas at constant pressure causes -832 J of work to be done during the expansion. Calculate:

- (a) The final state of the gas.
- (b) The values of ΔU and ΔH for the change of the state.
- (c) The values of \bar{C}_V and \bar{C}_P for N₂.

4. A semi-insulated system, as shown bellow, is formed by a container that has two compartments, A and B, separated by an movable adiabatic wall. Each compartment has an initial volume of 5 L and 1 atm of pressure. Each contains 0.5 mole of a perfect monoatomic gas.



In the beginning, the temperatures of A and B are the same. Then, the gas A expands and displaces the gas B is compressed in a reversible and adiabatic way until it reaches a final volume of 2 L.

- (a) Draw a PV diagram for this process to indicate the behavior corresponding to the subsystems A and B.
- (b) With this information, calculate ΔU and ΔH for A, B, the surroundings and the universe. In addition, calculate the final pressures and temperatures of A and B.

5. The molar heat capacity, C_V , of solids at low temperature is given by the Debye's law:

$$C_V = A \left(\frac{T}{\theta} \right)^3$$

The quantity A is a constant equal to $3.7 \times 10^3 \text{ J/mol K}$, and θ is the Debye temperature, equal to 230 K for KCl.

- (a) What is the molar heat capacity at constant volume of KCl at 5 K and at 30 K?
- (b) How much heat is required to raise the temperature of 2 moles of KCl from 5 K to 30 K at constant volume?

6. Paramagnetic materials present a magnetic behavior described by Curie's equation:

$$\frac{M}{H} = \frac{C}{T}$$

where M is the magnetization of the material, H is the external magnetic field in Tesla, C is a constant and T is the temperature.

- (a) Indicate whether M and H are intensive or extensive properties. Explain.
- (b) Write the form of the configuration work, dw , for this system.
- (c) Find an expression for the work that has to be done on the system to change its magnetization from 0 to M .

Due date: Tuesday, august 27th.

For adiabatic processes,

$$W = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{k}{V^\gamma} dV = k \left[\frac{V^{(1-\gamma)}}{1-\gamma} \right]_{V_1}^{V_2}$$

$$W = P_i V_1^\gamma \left[\frac{V^{(1-\gamma)}}{1-\gamma} \right]_{V_1}^{V_2}$$

$$W = \frac{P_i V_1^\gamma}{1-\gamma} \left[V_2^{(1-\gamma)} - V_1^{(1-\gamma)} \right]$$

$$W = \frac{(1.5 \times 10^6)(60 \times 10^{-3})^{1.125}}{1 - 1.125} \left[150 \times 10^{-3}^{(1-1.125)} - 60 \times 10^{-3}^{(1-1.125)} \right] \text{ Pa.m}^3$$

$W = 77,918,739 \text{ J}$
is the work done by the system

$$\text{Pa} = \frac{\text{kg}}{\text{m.s}^2} \quad \& \quad \text{J} = \frac{\text{kg.m}^2}{\text{s}^2}$$

1a) False. Isobaric process is a thermodynamic process in which the pressure stays constant $\Delta P = 0$. The heat transferred to the system does work, but also changes the internal energy of the system; hence the enthalpy changes.

1b) False. Since the volume is constant, the system does no work, however the internal energy can change and that affect the enthalpy.

1c) False. the change in internal energy is given by: $\Delta U = nC_V \Delta T$

1d) False. The energy is transferred only by work; and it's given by $W = \Delta H$

1e) ~~False~~ For adiabatic processes: ~~False~~ True

$Q=0 ; pdV + Vdp = nRdT ; n \frac{f}{2} RdT = -pdV$; where f is the number of degrees of freedom.

$$\rightarrow pdV + Vdp = -\frac{2}{f} pdV$$

$$Vdp + \left(1 + \frac{2}{f}\right) pdV = 0 ; \gamma = 1 + \frac{2}{f}$$

$$Vdp + \gamma pdV = 0$$

$$\frac{Vdp}{pV} + \gamma \frac{pdV}{pV} = 0$$

$$\frac{dp}{P} + \gamma \frac{dV}{V} = 0$$

$$\int_{P_i}^{P_f} \frac{1}{P} dp + \gamma \int_{V_i}^{V_f} \frac{dV}{V} = 0$$

$$\ln \frac{P_f}{P_i} + \gamma \ln \frac{V_f}{V_i} = 0$$

$$\ln \frac{P_f V_f^\gamma}{P_i V_i^\gamma} = 0$$

$$P_f V_f^{\gamma-1} = P_i V_i^{\gamma-1} = \text{constant}$$

$$P_i V_i = n R T_i \quad \& \quad P_2 V_2 = n R T_2$$

$$\frac{P_i V_i}{P_2 V_2} = \frac{T_i}{T_2}$$

$$P_i V_i^{\gamma-1} = P_2 V_2^{\gamma-1}$$

$$\frac{P_i}{P_2} = \frac{V_2^{\gamma-1}}{V_i^{\gamma-1}}$$

$$\frac{V_2^{\gamma-1}}{V_i^{\gamma-1}} = \frac{T_i}{T_2}$$

$$T_i V_i^{\gamma-1} = T_2 V_2^{\gamma-1}$$

2 for adiabatic processes,

$$W = -\Delta U = -n C_V \Delta T$$

$$= n C_V (T_i - T_2)$$

$$= \frac{C_V}{R} (P_i V_i - P_2 V_2)$$

$$= \frac{1}{\gamma-1} (P_i V_i - P_2 V_2)$$

3 $n = 1$; $T_i = 273 \text{ K}$; $P_i = 1 \text{ atm}$; $q = 3000 \text{ J}$; $w = 832 \text{ J}$

 $P_2 = 1 \text{ atm} \rightarrow \text{constant pressure}$
 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
 $= 0.08206 \text{ L atm K}^{-1}$

3a $V_i = \frac{n R T_i}{P_i} = \frac{1 \text{ mol} (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (273 \text{ K})}{1 \text{ atm}}$

 $V_{i,\text{approx}} = 22.402 \text{ L}$

$$\Delta U = q - w = 3000 \text{ J} - 832 \text{ J} = 2168 \text{ J}$$

$$w = 832 \text{ J}$$

$$= \int P dV = P(V_2 - V_i)$$

$$832 \text{ J} = (1 \text{ atm})(V_2 - 22.402 \text{ L})$$

$$V_2 = \frac{832 \text{ J}}{1 \text{ atm}} + 22.402 \text{ L}$$

$$V_2 = 8.211 \times 10^{-3} \text{ m}^3 + 22.402 \text{ L}$$

$$V_2 = 30.613 \text{ L}$$

$$J = \frac{\text{kg m}^2}{\text{s}^2}; P_a = \frac{\text{kg}}{\text{m s}^2}$$

$$1 \text{ atm} = 101325 \text{ Pa}$$

$$T_2 = \frac{P_2 V_2}{n R} = \frac{(1 \text{ atm})(30.613 \text{ L})}{(1 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})}$$

$$T_2 = 373.056 \text{ K}$$

$$[3b] \Delta U = 2168 \text{ J}$$

$$\begin{aligned}
 H &= U + PV \\
 \Delta H &= \Delta(U + PV) \\
 &= \Delta U + \cancel{PV} + P\Delta V + V\Delta P \\
 &= 2168 \text{ J} + (30.613 \cancel{\text{J}} - 22.402 \text{ L}) (1 \text{ atm}) + 0 \quad / \text{ as } \Delta P = 0 \\
 &= 2168 \text{ J} + (30.613 \text{ L} - 22.402 \text{ L}) (101325 \text{ Pa}) \\
 \Delta H &= 2168 \text{ J} + (8.211 \times 10^{-3} \text{ m}^3)(101325 \text{ Pa}) \\
 \Delta H &= 2999.980 \text{ J}
 \end{aligned}$$

$$\Delta U = n \int C_v dT$$

$$2168 \text{ J} = (1) \cancel{C_v} (373.056 - 273 \text{ K}) / 101325 \text{ Pa}$$

$$C_v = \frac{2168 \text{ J}}{100.056 \text{ K}}$$

$$C_v = 21.68 \frac{\text{J}}{\text{K}}$$

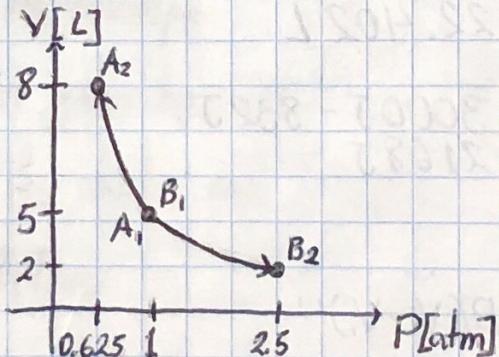
$$\Delta H = n \int C_p dT$$

$$2999.980 \text{ J} = (1) C_p (373.056 - 273 \text{ K})$$

$$C_p = 29.983 \frac{\text{J}}{\text{K}}$$

$$\begin{array}{ll}
 [4a] \quad P_{A1} = 1 \text{ atm} & / \quad P_{B1} = 1 \text{ atm} \\
 V_{A1} = 5 \text{ L} & V_{B1} = 5 \text{ L} \\
 V_{A2} = 8 \text{ L} & V_{B2} = 2 \text{ L}
 \end{array}$$

$$\begin{array}{ll}
 P_{A2} = \frac{P_{A1} V_{A1}}{V_{A2}} & P_{B2} = \frac{P_{B1} V_{B1}}{V_{B2}} \\
 P_{A2} = 0.625 \text{ atm} & P_{B2} = 2.5 \text{ atm}
 \end{array}$$



[4b] Assuming isothermal processes,

AU for A & B is \emptyset (no change in internal energy)
AH for A & B is \emptyset (no change in enthalpy)

Final pressure of A $P_{A2} = 0.625 \text{ atm}$
Final pressure of B $P_{B2} = 2.5 \text{ atm}$

From $p\delta V$ Work equations for isothermal processes,

$$w = nRT \ln\left(\frac{V_2}{V_1}\right) = P_2 V_2 \ln\left(\frac{V_2}{V_1}\right)$$

$$nRT = P_2 V_2$$

$$T = \frac{P_2 V_2}{nR}$$

$$T_A = \frac{(0.625 \text{ atm})(8L)}{(0.5 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})}$$
$$T_A = 121.862 \text{ K}$$

$$T_B = \frac{(2.5 \text{ atm})(2L)}{(0.5 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})}$$
$$T_B = 121.862 \text{ K}$$

5a) $C_V = A \left(\frac{T}{\theta}\right)^3$

$$C_{V1}(5K) = 3.7 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1} \left(\frac{5K}{230K}\right)^3$$

$$C_{V1}(5K) = 80.435 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_{V2}(30K) = 3.7 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1} \left(\frac{30K}{230K}\right)^3$$

$$C_{V2}(30K) = 482.609 \text{ J mol}^{-1} \text{ K}^{-1}$$

5b) $Q_1 = nC_V(T_2 - T_1)$

$$Q_1 = (2 \text{ mol})(80.435 \text{ J mol}^{-1} \text{ K}^{-1})(30K - 5K)$$

$$Q_1 = 4021.75 \text{ J}$$

$$Q_2 = (2 \text{ mol})(482.609 \text{ J mol}^{-1} \text{ K}^{-1})(30K - 5K)$$

$$Q_2 = 24130.45 \text{ J}$$

$$\Delta Q = 20108.7 \text{ J}$$

6a) M & H are intensive properties as they are independent of mass.

6b) The work done on a material by an external magnetic field is given by

$$dw = -C H dM$$
, where: $\begin{cases} Y = \text{volume of the magnetic field in m}^3 \\ \mu_0 = \text{permittivity of vacuum in N amp}^{-2} \\ H \text{ and } M \text{ are in amp m}^{-1} \end{cases} \} C = Y \mu_0$

6c

$$W = -C \int_{M_1}^{M_2} H dM$$

$$W = -C \int_0^M H dM = [HM]_0^M (-C)$$

$$= -CHM \text{ Joules}$$

Exercise 4 - 2nd attempt

→ After some discussion, the following assumptions were made:

- i) The thermodynamic process of compartment A is undefined
- ii) The thermodynamic process of compartment B is adiabatic
- iii) The pressure of both compartments are equal to each other but not constant.

→ Let's analyze compartment B.

- For an adiabatic process in an ideal monatomic gas, the polytropic index n is $3/2$.
 if $n = \frac{1}{\gamma-1} \Rightarrow \gamma = \frac{5}{3}$; where γ is the ratio of specific heats.

- Therefore, PV^n is constant

$$P_1 V_1^n = P_2 V_2^n$$

$$(1 \text{ atm})(5L)^n = P_2 (2L)^n$$

$$(101325 \text{ Pa})(5 \times 10^{-3} \text{ m}^3)^n = P_2 (2 \times 10^{-3} \text{ m}^3)^n$$

$$P_2 = 400522.2299 \text{ Pa or } 3.953 \text{ atm}$$

- As the heat transfer is 0, then

$$\Delta U = W$$

$$= PdV$$

$$= PV^\gamma \int_{V_1}^{V_2} \frac{1}{V^\gamma} dV$$

$$= \frac{P_1 V_1^\gamma (V_2^{1-\gamma} - V_1^{1-\gamma})}{1-\gamma}$$

$$\Delta U = -639.879 \text{ J}$$

- Let's compute the temperatures of compartment B

$$PV = nRT$$

$$(101325 \text{ Pa})(5 \times 10^{-3} \text{ m}^3) = (0.5 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) T_1$$

$$T_1 = 121.873 \text{ K}$$

$$(400522.2299 \text{ Pa})(2 \times 10^{-3} \text{ m}^3) = (0.5 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) T_2$$

$$T_2 = 192.698 \text{ K}$$

→ Let's analyze compartment A

- Due to assumption iii), $P_2 = 400522.2299 \text{ Pa}$

$$P_1 V_1^n = P_2 V_2^n$$

$$(1 \text{ atm})(5L)^n = (3.953 \text{ atm})(8L)^n$$

$$n = 2.92439$$

$$\gamma = 1 + \frac{1}{n} = 1.34195$$

$$PV = nRT$$

$$\frac{(101325 \text{ Pa})(5 \times 10^{-3} \text{ m}^3)}{T_1} = (0.5 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) T_1$$

$$\frac{(400522.2299 \text{ Pa})(8 \times 10^{-3} \text{ m}^3)}{T_2} = 194.996 \text{ K}$$

- For an ideal monoatomic gas:

$$Q = C_V n \Delta T ; \quad Q = \Delta U + P \Delta V = \Delta U$$

$$C_V = \frac{1}{n} \frac{\Delta U}{\Delta T} = \frac{3}{2} R = 12.471 \frac{\text{J}}{\text{K mol}}$$

$$\left. \begin{array}{l} C_p = C_V + R \\ C_p = 20.785 \text{ J K}^{-1} \text{ mol}^{-1} \end{array} \right.$$

$$\Delta U = (12.471 \text{ J K}^{-1} \text{ mol}^{-1})(0.5 \text{ mol})(T_2 - T_1)$$

$$= 455.958 \text{ J}$$

$$\Delta U = \Delta Q - P \Delta V ; \quad \text{where } P \Delta V = \frac{(101325 \text{ Pa})(5 \times 10^{-3} \text{ m}^3)^{\gamma}[(8 \times 10^{-3} \text{ m}^3)^{\gamma-1} - (5 \times 10^{-3} \text{ m}^3)^{\gamma-1}]}{1-\gamma}$$

$$P \Delta V = 219.966 \text{ J}$$

→ Let's calculate ΔH for compartments A & B

$$\text{for A, } \Delta H = \Delta Q - V dP$$

$$= \Delta Q - m C_p (T_2 - T_1)$$

$$= 675.924 - (0.5 \text{ mol})(20.785 \text{ J K}^{-1} \text{ mol}^{-1})(194.996 \text{ K} - 121.873 \text{ K})$$

$$\Delta H = -84.007 \text{ J}$$

$$\text{for B, } \Delta H = \Delta Q - V dP$$

$$= 0 - m C_p (T_2 - T_1)$$

$$= (0.5 \text{ mol})(20.785 \text{ J K}^{-1} \text{ mol}^{-1})(192.698 \text{ K} - 121.873 \text{ K})$$

$$= -60.125 \text{ J}$$

→ Let's analyze the surroundings.

$$\begin{aligned}\Delta U_{\text{surr}} &= \Delta U_A + \Delta U_B \\ &= 455.958 \text{ J} + (-639.879 \text{ J}) \\ &= -183.921 \text{ J}\end{aligned}$$

$$\begin{aligned}\Delta H_{\text{surr}} &= \Delta H_A - \Delta H_B \\ &= -84.007 \text{ J} + (-60.125 \text{ J}) \\ &= -144.132 \text{ J}\end{aligned}$$

→ For the universe,

$$\Delta U = \emptyset \quad \& \quad \Delta H = \emptyset$$

→ So:

-Initial State

-Compartment A
 $P = 1 \text{ atm}$
 $V = 5L$
 $T = 121.873 \text{ K}$

-Compartment B
 $P = 1 \text{ atm}$
 $V = 5L$
 $T = 121.873 \text{ K}$

-Surroundings
 $\Delta U = -183.921 \text{ J}$
 $\Delta H = -144.132 \text{ J}$

- Universe
 $\Delta U = \emptyset$
 $\Delta H = \emptyset$

-Final State

- Compartment A
 $P = 3.953 \text{ atm}$
 $V = 8L$
 $T = 194.996 \text{ K}$
 $\Delta U = 455.958 \text{ J}$
 $\Delta H = -84.007 \text{ J}$

- Compartment B
 $P = 3.953 \text{ atm}$
 $V = 2L$
 $T = 192.698 \text{ K}$
 $\Delta U = -639.879 \text{ J}$
 $\Delta H = -60.125 \text{ J}$

