

**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 $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

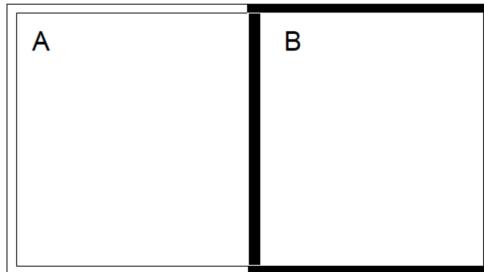
2. Demonstrate that for a adiabatic reversible process

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

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,

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

$$W = P_1 V_1^\gamma \left[\frac{V^{(1-\gamma)}}{1-\gamma} \right]_{V_1}^{V_2}$$

$$W = \frac{P_1 V_1^\gamma}{1-\gamma} \left[V_2^{(1-\gamma)} - V_1^{(1-\gamma)} \right]$$

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

$W = 77,918,739 \text{ J}$
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 $V_i = \frac{n R T_i}{P_i} = \frac{1 \text{ mol} (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (273 \text{ K})}{1 \text{ atm}}$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

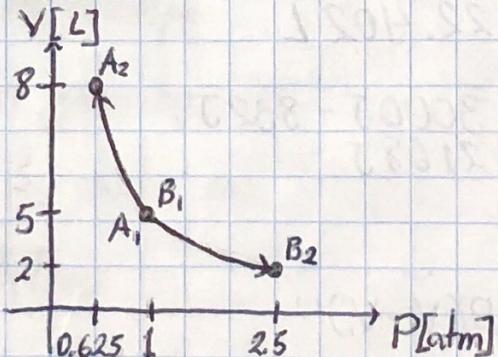
$$\Delta H = n \int C_p dT$$

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

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

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

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



[4b] Assuming isothermal processes,

ΔU for A & B is \emptyset (no change in internal energy)
 ΔH 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), $P_2 = 400522.2299 \text{ Pa}$

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

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

$$n = 2.92439$$

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

$$PV = nRT$$

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

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

$$(400522.2299 \text{ Pa})(8 \times 10^{-3} \text{ m}^3)$$

$$T_2 = 194.996 \text{ K}$$

- 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

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

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

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

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

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

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

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

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

→ 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
 $P = 1 \text{ atm}$
 $V = 5L$
 $T = 121.873 \text{ K}$

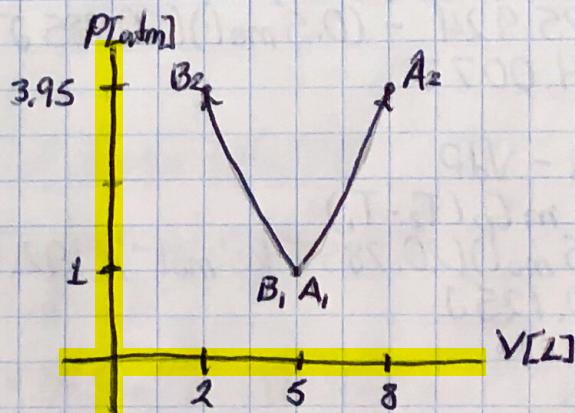
-Surroundings
 $\Delta U = -183.921 \text{ J}$
 $\Delta H = -144.132 \text{ J}$

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



Comment Summary