

Thermodynamics exam answers
1st year Common trunk state engineer, S II

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Exercise 1: 5 points

1) Heat capacity of calorimeter:

- Cold water = $Q_1 = m_1 C_{\text{water}} (\theta_e - \theta_1)$

- Hot water = $Q_2 = m_2 C_{\text{water}} (\theta_e - \theta_2)$

- Calorimeter = $Q_{\text{cal}} = C_{\text{cal}} (\theta_e - \theta_1)$

* The system { water 1 + water 2 + calorimeter } is isolated:

$\sum Q_i = 0 \Rightarrow Q_1 + Q_{\text{cal}} + Q_2 = 0$ ----- (1)

$m_1 C_{\text{water}} (\theta_e - \theta_1) + C_{\text{cal}} (\theta_e - \theta_1) + m_2 C_{\text{water}} (\theta_e - \theta_2) = 0$ --- (1)

$C_{\text{cal}} = \frac{m_1 C_{\text{water}} (\theta_e - \theta_1) + m_2 C_{\text{water}} (\theta_e - \theta_2)}{\theta_1 - \theta_2} = \frac{0,1 \times 4185 (35,9 - 18) + 0,08 \times 4185 (35,9 - 60)}{18 - 35,9} = 32,265 \cdot K$

$C_{\text{cal}} = 32,265 \text{ J/K}$ ----- (1)

2) The equilibrium temperature if the calorimeter capacity is negligible

- Cold water = $Q_1 = m_1 C_{\text{water}} (\theta_e - \theta_1)$ ----- (0,25)

- Hot water = $Q_2 = m_2 C_{\text{water}} (\theta_e - \theta_2)$ ----- (0,25)

$\sum Q_i = 0 \Rightarrow Q_1 + Q_2 = 0$ ----- (0,25)

$m_1 C_{\text{water}} (\theta_e - \theta_1) + m_2 (\theta_2 - \theta_e) = 0 \Rightarrow \theta_e = \frac{m_1 \theta_1 + m_2 \theta_2}{m_1 + m_2}$ ----- (0,5)

$= \frac{0,1 \times 18 + 0,08 \times 60}{0,1 + 0,08} = 36,66^\circ C$ ----- (0,5)

$\theta_e = 36,66^\circ C$

3) Conclusion:

We can see clearly that the neglect of calorimeter capacity didn't affect

The equilibrium temperature: $\theta_e = 35,9^\circ C$ and $\theta'_e = 36,66^\circ C$
 $\Rightarrow \theta_e \approx \theta'_e$

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Exercise 2 (8 points)

1) We complete the table by determining the parameters of each state. We first calculate the nbr of moles:

$$\text{State A} = n? = P_A \cdot V_A = nRT_A \Rightarrow n = \frac{P_A V_A}{RT_A} = \frac{1 \text{ bar}}{0,082 \times 300} = 0,413 \times 10^{-2} \text{ mol}$$

$n = 0,13 \times 10^{-2} \text{ mol}$ ----- (0,25)

state B: A \rightarrow B Isochoric transformation: $V_A = V_B = 2 \text{ L}$ (0,25)

$$T_B = ? P_B \cdot V_B = nRT_B \Rightarrow T_B = \frac{P_B V_B}{nR} = \frac{3,5 \times 2}{0,13 \times 10^{-2} \times 0,082} = 1050 \text{ K}$$
 (0,25)

state C: C \rightarrow A = isobare transformation $P_C = P_A = 1 \text{ atm}$ (0,25)

V_C et $T_C = ?$

B \rightarrow C = Adiabatic transformation: $P_B \cdot V_B^\gamma = P_C \cdot V_C^\gamma$ ----- (0,25)

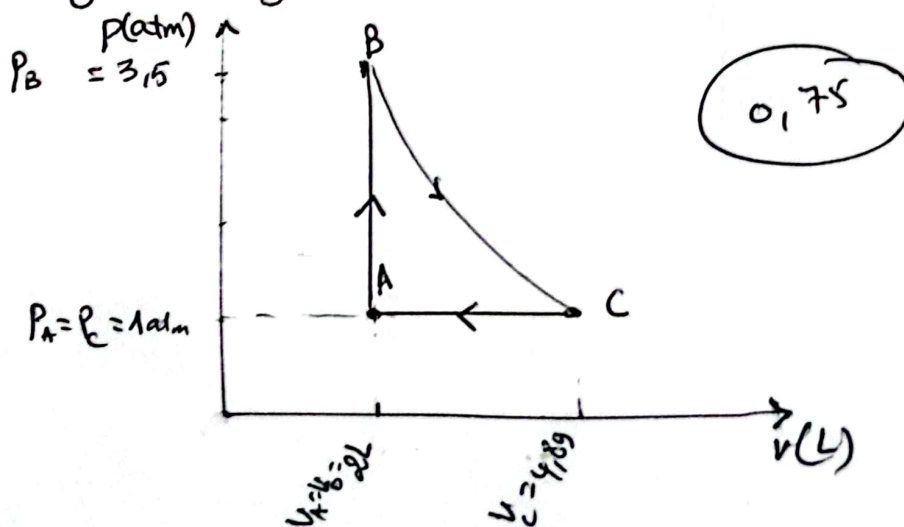
$$V_C = V_B \sqrt[\gamma]{\frac{P_B}{P_C}} = 2 \left(\frac{3,5}{1}\right)^{\frac{1}{1,4}} = 4,89 \text{ L}$$
 (0,25)

$$T_C = \frac{P_C \cdot V_C}{nR} = \frac{1 \times 4,89}{0,13 \times 10^{-2} \times 0,082} = 733,5 \text{ K}$$
 (0,25)

2)

	State A	State B	State C
P(atm)	1	3,5	1
V(L)	2	2	4,89
T(K)	300	1050	733,5

Clayton diagram



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3) The work W , Heat Q for each transformation:

• A $\xrightarrow{v=cte}$ B \Rightarrow isovolumetric $\Delta U_{A-B} = W_{AB} + Q_{AB} \dots (0,25)$

$W_{A-B} = 0 \text{ J} \dots (0,25)$

$Q_{AB} = nC_v (T_B - T_A) = \frac{nR}{\gamma - 1} (T_B - T_A)$

$Q_{A-B} = \frac{8,13 \times 10^{-2} \times 8,31}{1,4 - 1} (1050 - 300) = 1266,75 \text{ J} \dots (0,15)$

$\left. \begin{array}{l} \frac{C_p}{C_v} = \gamma \dots (1) \Rightarrow C_p = \gamma C_v \\ C_p - C_v = R \dots (2) \\ \gamma C_v - C_v = R \dots (3) \\ C_v(\gamma - 1) = R \dots (4) \\ C_v = \frac{R}{\gamma - 1} \end{array} \right\}$

• B $\xrightarrow{\text{Adiabatic}}$ C $\Delta U_{B-C} = W_{B-C} + Q_{BC}, Q_{BC} = 0 \dots (0,25)$

$\Delta U_{BC} = W_{BC} \dots (0,25)$

$W_{BC} = nC_v (T_C - T_B) = \frac{nR}{\gamma - 1} (T_C - T_B) = \frac{8,13 \times 10^{-2} \times 8,31}{1,4 - 1} =$
 $= (733,5 - 1050) = -534,57 \text{ J} \dots (0,15)$

or $W_{BC} = \frac{P_C V_C - P_B V_B}{\gamma - 1} = -534,57 \text{ J}$

• C $\xrightarrow{P=cte}$ A Isobaric transformation $\dots (0,15)$

$W_{C-A} = -P (V_A - V_C) = -1,013 \times 10^5 (2 - 4,89) \times 10^{-3} = 292,75 \text{ J}$

$Q_{C-A} = nC_p (T_A - T_C) = \frac{n\gamma R}{\gamma - 1} (T_A - T_C)$

$Q_{CA} = 8,13 \times 10^{-2} \times \frac{1,4 \times 8,31}{1,4 - 1} (300 - 733,5) = -1025,05 \text{ J} \dots (0,25)$

1) The internal energy ΔU_{AB} and the enthalpy ΔH_{CA}

• The transformation A $\xrightarrow{v=cte}$ B $\Rightarrow \Delta U_{AB} = Q_{AB} \dots (0,25)$

$\Delta U_{AB} = Q_{AB} = nC_v (T_B - T_A) = 1266,75 \text{ J} \dots (0,25)$

• The transformation C $\xrightarrow{P=cte}$ A $\Rightarrow \Delta H_{C-A} = Q_{CA} \dots (0,25)$

$\Delta H_{C-A} = nC_p (T_A - T_C) = -1025,05 \text{ J} \dots (0,25)$

5) Nature of the thermodynamic cycle

0,25

$$W_{\text{cycle}} = W_{AB} + W_{BC} + W_{CA} = 0 - 534,57 + 292,75 = -241,82 \text{ J}$$

$W_{\text{cycle}} < 0$ therefore the cycle is driving \equiv le cycle est moteur

Exercise 3: (7 points)



1) The variation of st enthalpy of the reaction at 298K:

* we apply Hess's Law:

$$\Delta H_R^{\circ} = \sum \varepsilon_i \Delta H_f^{\circ}(\text{Products}) - \sum \varepsilon_j \Delta H_f^{\circ}(\text{Reactifs}) \quad \text{--- } (0,25)$$

$$\Delta H_R^{\circ} = \left(2\Delta H_f^{\circ}(\text{CO}_2(\text{g})) + \Delta H_f^{\circ}(\text{H}_2\text{O}(\text{l})) \right) - \left(\Delta H_f^{\circ}(\text{C}_2\text{H}_2(\text{g})) + \frac{5}{2} \Delta H_f^{\circ}(\text{O}_2(\text{g})) \right) \quad (0,25)$$

$$\Delta H_R^{\circ} = 2(-393) - 285 - \left(226 + \frac{5}{2} \times 0 \right) \quad \text{--- } (0,25)$$

$$\Delta H_R^{\circ} = -1297 \text{ kJ/mol} \quad \text{--- } (0,15)$$

2) ΔU_R°

$$\Delta H_R^{\circ} = \Delta U_R^{\circ} + \Delta n_{(\text{g})} RT \Rightarrow \Delta U_R^{\circ} = \Delta H_R^{\circ} - \Delta n_{(\text{g})} RT \quad (0,15)$$

$$\Delta n_{(\text{g})} = \sum n(\text{Produits gazeux}) - \sum n(\text{reactifs gazeux})$$

$$\Delta n = (n_{\text{CO}_2}) - (n_{\text{C}_2\text{H}_2} + n_{\text{O}_2}) \quad \text{--- } (0,25)$$

$$\Delta n = 2 - \left(\frac{5}{2} + 1 \right) = -1,5 \text{ mol}$$

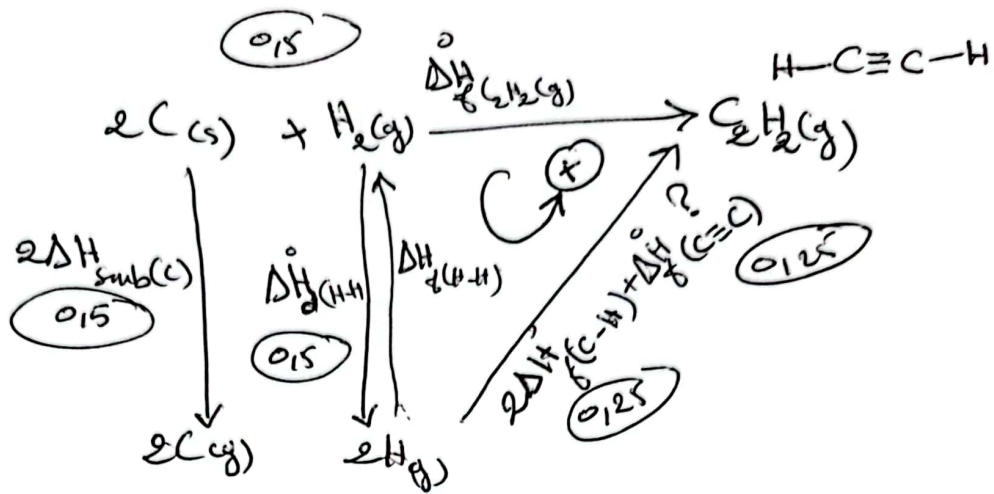
$$\Delta U_R^{\circ} = \Delta H_R^{\circ} - \Delta n RT = -1297 - (-1,5 \times 8,31 \times 10^{-3} \times 298) = -1293,28 \text{ kJ/mol} \quad \text{--- } (0,15)$$

3) The variation in enthalpy of the reaction at 348K \equiv Kirchhoff Law:

$$\Delta H_{R,T_2}^{\circ} = \Delta H_{R,T_1}^{\circ} + \Delta C_p (T_2 - T_1) \quad \text{--- } (0,25)$$

$$\Delta H_{R,T_2}^{\circ} = -1297 + 32 \times 10^{-3} (348 - 298) = -1295,4 \text{ kJ/mol} \quad \text{--- } (0,15)$$

4) The bond (C≡C) energy in acetylene $C_2H_2(g)$



$$\Delta H_f^\circ(C_2H_2(g)) = 2\Delta H_{sub}^\circ(C) - \Delta H_f^\circ(H-H) + 2\Delta H_f^\circ(C-H) + \Delta H_f^\circ(C\equiv C) \quad (015)$$

$$\Delta H_f^\circ(C\equiv C) = \Delta H_f^\circ(C_2H_2) - 2\Delta H_{sub}^\circ(C) + \Delta H_f^\circ(H-H) - 2\Delta H_f^\circ(C-H) \quad (0125)$$

$$\begin{aligned} \Delta H_f^\circ(C\equiv C) &= 226 - 2 \times (720) - 435 - 2 \times (-415) \quad (0125) \\ &= -819 \text{ kJ/mol} \quad (015) \end{aligned}$$

End