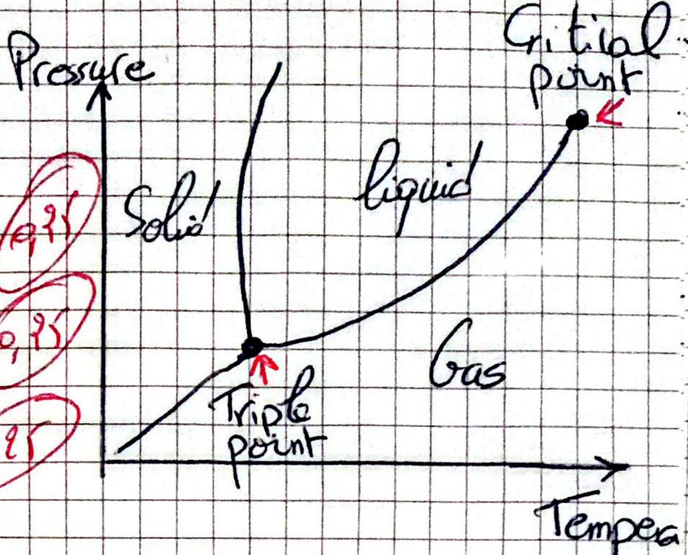
Thermodynamic Exam Correction 2025-2026

Exercise 1 (3 pts)



1- Definition of each section:

- Solid : low T°, relatively high Pr (0,25)
- liquid : intermediate T° and P (0,25)
- Gas : high T° and or low P (0,25)

Equilibrium Curves :

- Solid - liquid Curve : equilibrium between solid and liq (0,25)
- Solid - Gas Curve : " " " " Vapor (0,25)
- liquid - Gas Curve : " " liq and Vapor (0,25)

Special Points :

- Triple Point : intersection between the three curves, Coexistance of solid, liq and gas (0,25)
- Critical Point : end of the liq - Gas Curve, beyond this, no distinction between liq and gas (0,25)

2 - a - No, a liquid can not exist at 0,01 atm (0,25)

justification : Triple point pressure is 0,02 atm, below this P liq phase is impossible (0,25) b – Transformations when heated at 1 atm

at 1 atm = P (> 0,02 atm).

as T° increases : Solid → liq (fusion) 0,25

0,25 liq → Gas (Vaporization)

So, we have melting after boiling.

Exercise 2 (7 pts)

1- $2PbS_{(s)} + 3O_{2(g)} \rightleftharpoons 2PbO_{(s)} + 2SO_2$ 0,75

or

$PbS_{(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons PbO_{(s)} + SO_{2(g)}$

2- $\Delta H^\circ_{r\,298K} = ?$

Hess Law : $\Delta H^\circ_{r\,298K} = \sum n_i \Delta H^\circ_{f\,Products} - \sum n_j \Delta H^\circ_{f\,reactan}$ 0,5

$\Delta H^\circ_{r\,298K} = 2\Delta H^\circ_{f(PbO)} + 2\Delta H^\circ_{f(SO_2)} - 2\Delta H^\circ_{f(PbS)} - 3\Delta H^\circ_{f\,O_2}$ 0,5

$= 2(-217,4) + 2(-296,8) - 2(-100,4)$

$\Delta H^\circ_{r\,298K} = -827,6\ KJ$ 0,25

$\Delta H^\circ_{r\,298K} < 0 \Rightarrow$ exothermic reaction

Or $\Delta H^{\circ}_{r\,298K} = \Delta H^{\circ}_{f}(PbO) + \Delta H^{\circ}_{f}(SO_2) - \Delta H^{\circ}_{f}(PbS)$

$= -217,4 - 296,8 + 100,4$

$\Delta H^{\circ}_{r\,298K} = -413,8 \text{ KJ}$

3- $\Delta H^{\circ}_{r\,1223K} = ?$

Kirchoff Law: $\Delta H^{\circ}_{r\,1223K} = \Delta H^{\circ}_{r\,298K} + \int_{298}^{1223} \Delta C_p \, dT$ (0,5)

$\Delta C_p = \sum n_i C_{p\,Products} - \sum n_j C_{p\,reactants}$ (0,5)

(0,5) $= 2C_p(PbO) + 2C_p(SO_2) - 2C_p(PbS) - 3C_p(O_2)$

$= 2(45,8) + 2(39,9) - 2(49,5) - 3(29,4)$

$\Delta C_p = -15,8 \text{ J/K}$ (0,25)

So, $\Delta H^{\circ}_{r\,1223K} = -827,6 - 15,8 \cdot 10^{-3}(1223 - 298)$

$\Delta H^{\circ}_{r\,1223K} = -842,215 \text{ KJ}$ (0,25)

Or : $\Delta C_p = C_p(PbO) + C_p(SO_2) - C_p(PbS) - \frac{3}{2} C_p(O_2)$

$= 45,8 + 39,9 - 49,5 - \frac{3}{2}(29,4)$

$\Delta C_p = -7,9 \text{ J/K}$

$\Delta_r H^{\circ}_{1223K} = -413,8 - 7,9 \cdot 10^{-3}(1223 - 298)$

$\Delta_R H^\circ_{1223K} = -421,107\ KJ$

4 - Expression of the K_p costant:

(0,5) $K_p = \frac{P^2_{SO_2}}{P^3_{O_2}}$ or $K_p = \frac{P_{SO_2}}{P^{3/2}_{O_2}}$

$\Delta G^\circ = -RT \ln K_p \Rightarrow K_p = e^{-\frac{\Delta G^\circ}{RT}}$ (0,5)

5 - a - If we increase T°, the equilibrium move (0,25) in the endothermic direction, So, for this reaction $\Delta_r H^\circ < 0 \Rightarrow T \nearrow$ the sens ② is favored (0,25)

b - If we decrease the Total Pressure:

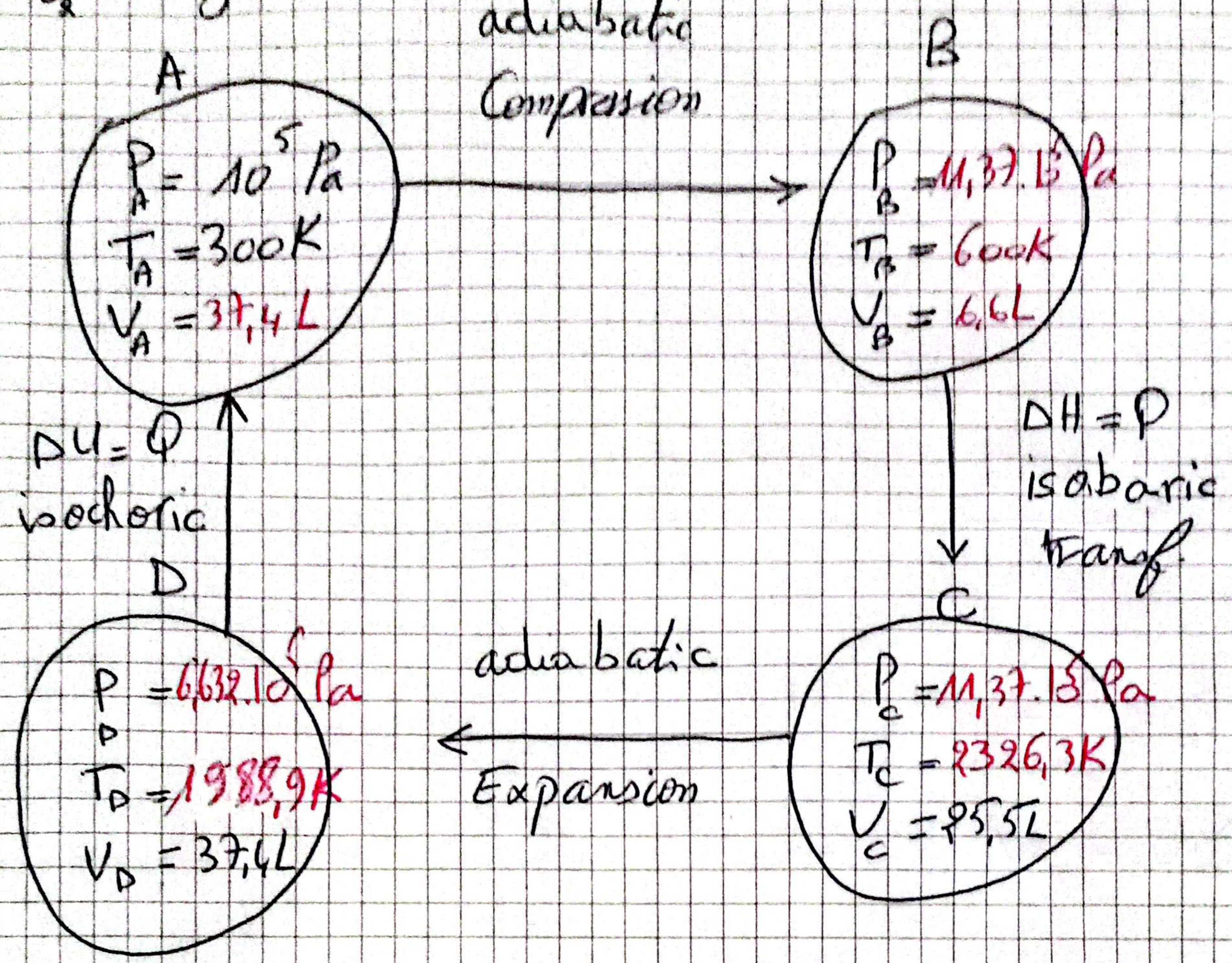
$\Delta n = 2 - 3 = -1 < 0$ (0,25)

$\Rightarrow P \nearrow \Rightarrow \Delta n < 0 \Rightarrow$ sens ① is favored (0,25)

c - If we added $PbS_{(s)}$: the equilibrium doesn't move because it is a solid $\Rightarrow$ So no effect (0,25) (0,25)

Exercice 3 (10 pts)

$m_{O_2} = 48\,g$



On donne : $\gamma = 1,4$

$Q_{BC} = 75\ KJ$

1. <u>states Variables</u> :

$$n_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{48}{16.2} = 1,5\ mol \quad (0,25)$$

$$\frac{T_A}{T_B} = \frac{1}{2} \Rightarrow T_B = 2T_A = 600\ K \quad (0,25)$$

$$P_A V_A = nRT_A \Rightarrow V_A = \frac{nRT_A}{P_A} = \frac{1,5 \cdot 8,314 \cdot 300}{10^5}$$

$V_A = 0{,}0374\ m^3 = 37{,}4\ L$ (0,25)

$A \rightarrow B$ adiabatic S0, $TV^{\gamma-1} = cst$

$T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1} \Rightarrow V_B = \left(\frac{T_A}{T_B}\right)^{\frac{1}{\gamma-1}} \cdot V_A$ (0,5)

$= \left(\frac{1}{2}\right)^{\frac{1}{0{,}4}} \cdot 37{,}4$

$V_B = 6{,}6\ L$ (0,25)

$P_B = \frac{nRT_B}{V_B} = \frac{1{,}5 \cdot 8{,}314 \cdot 600}{6{,}6 \cdot 10^{-3}} = 11{,}377 \cdot 10^5\ Pa$ (0,25)

$P_C = P_B = 11{,}377 \cdot 10^5\ Pa$ (0,25)

$P_C V_C = nRT_C \Rightarrow T_C = \frac{P_C \cdot V_C}{nR} = \frac{11{,}377 \cdot 10^5 \cdot 25{,}5 \cdot 10^{-3}}{1{,}5 \cdot 8{,}314}$

$T_C = 2326{,}3\ K$ (0,25)

$C \rightarrow D$: adiabatic, S0, $PV^{\gamma} = cst$ (0,5)

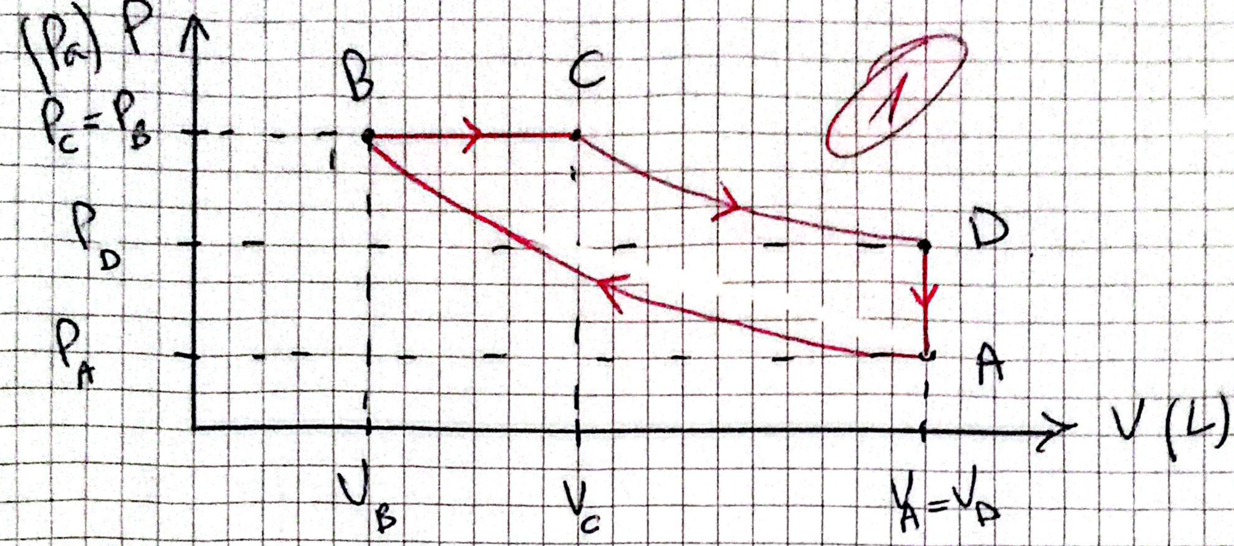
$P_C V_C^{\gamma} = P_D V_D^{\gamma} \Rightarrow P_D = P_C \cdot \left(\frac{V_C}{V_D}\right)^{\gamma}$

$= 11{,}377 \cdot 10^5 \left(\frac{25{,}5}{37{,}4}\right)^{1{,}4}$

$P_D = 6{,}632 \cdot 10^5\ Pa$ (0,25)

$$T_D = \frac{P_D V_D}{nR} = \frac{6{,}632 \cdot 10^5 \cdot 37{,}4 \cdot 10^{-3}}{1{,}5 \cdot 8{,}314} = 1988{,}9\ K$$ (0,25)

2 - Clapeyron Diagram :



3 - Q, W, ΔU for each transformation :

• A → B : adiabatic

$Q_{AB} = 0$ (0,25)

$W_{AB} = \Delta U_{AB} = n C_v \Delta T = n \cdot \frac{5}{2} \cdot R \cdot (T_B - T_A)$ (0,25) (0,25)

$= 1{,}5 \cdot \frac{5}{2} \cdot 8{,}314 \, (600 - 300)$

$\Delta U_{AB} = W_{AB} = 9353{,}25\ J = 9{,}35\ KJ$ (0,25)

• B → C : isobaric transf. $(P_C = P_B)$

$Q_{BC} = 75\ KJ$ (0,5)

$W_{BC} = -\int_{V_B}^{V_C} P_{ext}\, dV = -P(V_C - V_B) = -11{,}35 \cdot 10^5 (21{,}5 - 6{,}6 \ldots) \cdot 10^{-3}$ (0,25)

$W_{BC} = -21486,93\,J = -21,486\,KJ$ (0,25)

(0,25)

$\Delta U_{BC} = Q_{BC} + W_{BC} = 75 - 21,486$

$\Delta U_{BC} = 53,514\,KJ$ (0,25)

- $C \rightarrow D$: adiabatic

$Q_{CD} = 0$ (0,25)

(0,25)

$W_{CD} = \Delta U_{CD} = n C_v \Delta T = n \cdot \frac{5}{2} \cdot R (T_D - T_C)$

$= 1,5 \cdot \frac{5}{2} \cdot 8,314 \cdot (1988,9 - 2326,3)$

$W_{CD} = \Delta U_{CD} = -10\,528,6\,J$

$= -10,528\,KJ$ (0,25)

- $D \rightarrow A$: isochoric transf.

$Q_{DA} = n C_v \Delta T = n \frac{5}{2} R . (T_A - T_D) = 1,5 . 8,314 . \frac{5}{2} .$

$(300 - 1988,9)$

$Q_{DA} = -52,65\,KJ$ (0,25)

$W_{DA} = -\int P dV = 0$ So, $\Delta U_{DA} = Q_{DA}$ (0,25)

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4- ΔS for the cycle:

$\Delta S_{AB} = 0$ (0,25) $\Delta S = \frac{Q}{T}$ (0,25)

$\Delta S_{CD} = 0$ (0,25)

$\Delta S_{BC} = n C_p \ln \frac{T_C}{T_B} = n \cdot \frac{7}{2} \cdot R \ln \frac{T_C}{T_B}$ (0,25)

$= 1,5 \cdot \frac{7}{2} \cdot 8,314 \cdot \ln \frac{2326,3}{600}$

$\Delta S_{BC} = 58,99 \ J.K^{-1}$ (0,25)

$\Delta S_{DA} = n C_v \ln \frac{T_A}{T_D} = n \cdot \frac{5}{2} \cdot R \ln \frac{T_A}{T_D}$ (0,25)

$= 1,5 \cdot \frac{5}{2} \cdot 8,314 \ln \frac{300}{1988,9}$

$\Delta S_{DA} = -58,97 \ J.K^{-1}$ (0,25)

So, $\Delta S_{cycle} = \Sigma \Delta S_i = 0$ (0,25)

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