Exer1 :

1) $Cl_2(g) + H_2O(l) \longrightarrow HCl_{aq}(l) + HClO_{aq}(l)$.

g + l $\quad \Delta S < 0 \quad$ l + l

$Ca_3(PO_4)_2(s) \longrightarrow 3Ca^{2+}_{aq}(l) + 2PO_4^{3-}{}_{aq}(l)$

$\Delta S > 0$

$SO_2(g) + Br_2(g) + 2H_2O(l) \longrightarrow H_2SO_{4\,aq}(l) + HBr(g)$

2g + 2l $\quad$ l + g.

$\Delta S < 0$.

$2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$.

2s+3g $\quad$ 2s

$\Delta S > 0$.

2) $\Delta S^0_{25°C} = ?$

a) $NO_2 \xrightarrow{\Delta S^0_{25°}} O_2 + \frac{1}{2}N_2$.

$\Delta S^0_{25°C} = \Delta S^0_{disso.} = S^0_{O_2} + \frac{1}{2}S^0_{N_2} - S^0_{NO_2}$

$\Delta S^0_{25°C} = 49 + \frac{1}{2} 45{,}77 - 14{,}35$.

$\Delta S^0_{25°C} = 57{,}535$ cal/K.

b) $CaCO_3 \longrightarrow CO_2 + CaO$.

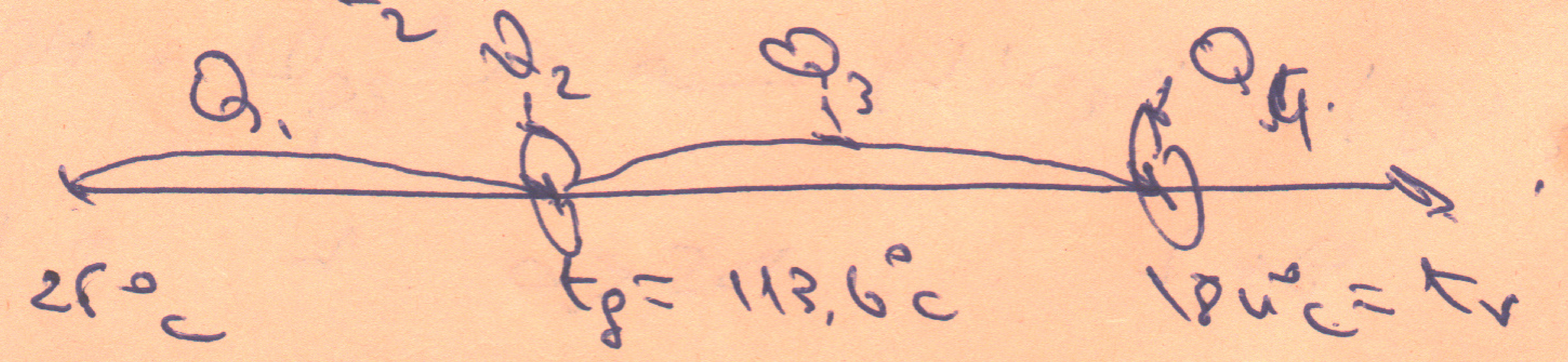
$\Delta S^0_{25°C} = S^0_{CO_2} + S^0_{CaO} - S^0_{CaCO_3}$.

$\Delta S^0_{25°C} = 51{,}1 + 9{,}5 - 22{,}2$

$\Delta S^0 = 38{,}4$. cal/K

Exo2 :

$\Delta S^\circ_{T_2}$ (25°C → 184°C).



$$\Delta S^\circ_{T_2}(25°C \to 184°C) = \Delta S_1 + \Delta S_f + \Delta S_3 + \Delta S_4.$$

$$\Delta S_1 = \Delta S_{25 \to 113,6} = \int \frac{\delta Q}{T}.$$

$$\delta Q_p = \delta H_p = n c_p \, dT.$$

$n = 1$ mole.

$$\Delta S_1 = \int_{298,15}^{386,75} n c_{p_s} \frac{dT}{T} = n c_{p_s} \ln \frac{386,75}{298,15}$$

$$\Delta S_1 = 54,6 \ln \frac{386,75}{298,15} = 14,21 \text{ J/K}.$$

$$\Delta S_2 = \Delta S_{t_f} = \frac{Q_f}{T_f} = \frac{n L_f}{T_f} = \frac{n \Delta_f H}{T_f}.$$

$$\Delta S_f = \frac{15,633 \cdot 10^3}{386,75} = 40,42 \text{ J/K}.$$

$$\Delta S_3 = n c_{p_L} \ln \frac{457,15}{386,75} = 13,63 \text{ J/K}$$

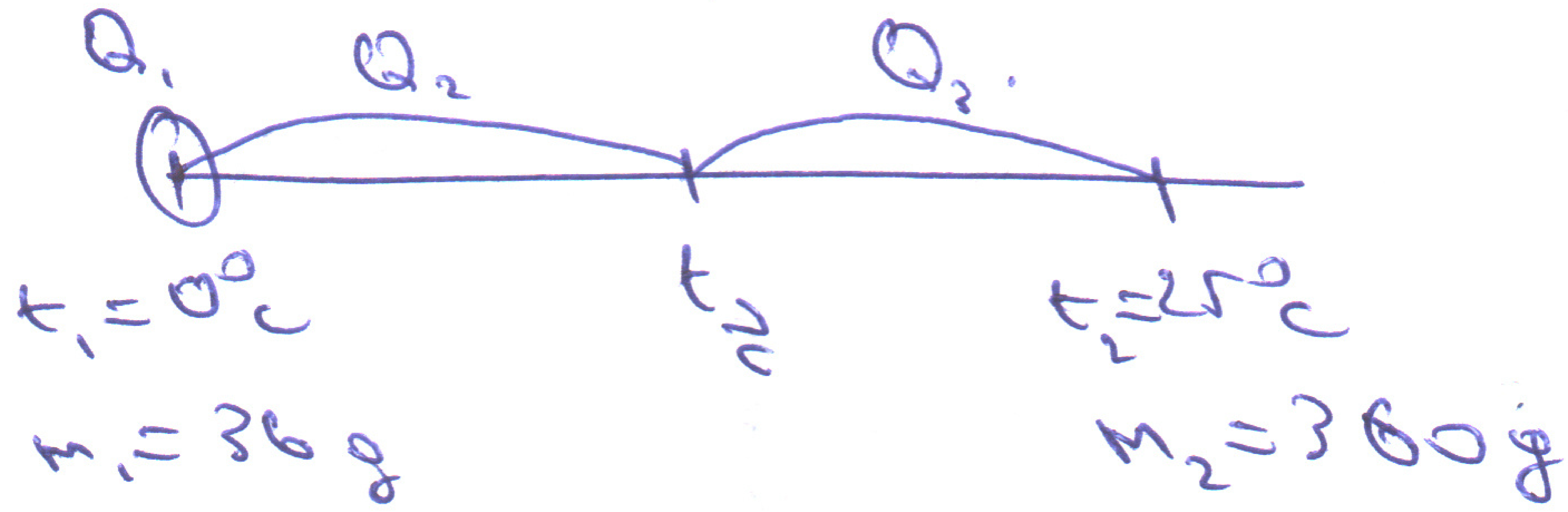
$$\Delta S_4 = \frac{Q_v}{T_v} = \frac{n L_v}{T_v} = \frac{n \Delta_v H}{T_v} = \frac{25,498 \cdot 10^3}{457,15}$$

$$\Delta S_4 = 55,78 \text{ J/K}.$$

$$\Delta S^\circ_T = \Delta S^\circ \ldots = 124,04 \text{ J/K}$$

Exo3 :

1) Enceinte adiabatique $\Rightarrow \sum Q_i = 0$.



$$Q_{glace} + Q_{H_2O}^{25°} = 0$$

$$Q_{glace} = Q_1 + Q_2 \text{ donc } Q_1 + Q_2 + Q_{H_2O}^{25°C} = 0.$$

$$Q_1 = m_1 L_f = \frac{m_1}{M_{H_2O}} \cdot \Delta_f H° = \frac{36}{18} \cdot 5{,}94 \cdot 10^3 = 11{,}88 \text{ kJ}.$$

$$Q_2 = m_1 c_{p\,e.l} (T_f - T_1).$$

$$Q_3 = Q_{H_2O}^{25°C} = m_2 c_{p\,e.l} (T_f - T_2).$$

$$m_1 c_{p\,e.l} (T_f - T_1) + m_2 c_{p\,e.l} (T_f - T_2) = -11{,}88 \cdot 10^3.$$

$$T_f = \frac{c_{p\,e.l}(m_1 T_1 + m_2 T_2) - 11{,}88 \cdot 10^3}{(m_1 + m_2)\, c_{p\,e.l}}$$

$$T_f = \frac{4{,}18\,(36 \cdot 273{,}15 + 360 \cdot 298{,}15) - 11{,}88 \cdot 10^3}{(36 + 360)\, 4{,}18}$$

$$T_f = \frac{477873{,}732}{1655{,}28} \Rightarrow T_f = 288{,}70 \text{ K}.$$

$$\Rightarrow t_f = 15{,}55 \,°C.$$

2) $\Delta S = ??$

$$\Delta S = \Delta S_1 + \Delta S_2 .$$

$\Delta S_1 \rightarrow$ glace. , $\Delta S_2 \rightarrow H_2O\ (25°C)$.

$$\Delta S_1 = \frac{Q_1}{T_f} + \int \frac{dQ_2}{T}$$

$$\Delta S_1 = \frac{n_1 \Delta_f H}{T_f} + \int_{273,15}^{288,70} n_1 C_{p_{e.L}} \frac{dT}{T} .$$

$$\Delta S_1 = \frac{n_1 \Delta_f H}{T_f} + n_1 C_{p_{e.L}} \ln \frac{288,70}{273,15} .$$

$$\Delta S_1 = \frac{36 \cdot 5,94 \cdot 10^3}{18 \cdot 273,15} + \frac{36}{18} \cdot 75,25 \ln \frac{288,70}{273,15}$$

$$\Delta S_1 = 43,49 + 8,33 = 51,82 \text{ J/K} .$$

$$\Delta S_2 = \int \frac{dQ_3}{T} = \int_{298,15}^{288,70} n_2 C_{p_{e.L}} \frac{dT}{T}$$

$$\Delta S_2 = n_2 C_{p_{e.L}} \ln \frac{288,70}{298,15} = \frac{360}{18} \cdot 75,25 \ln \frac{288,70}{298,15}$$

$$\Delta S_2 = -48,47 \text{ J/K} .$$

$$\Delta S = \Delta S_1 + \Delta S_2 = 51,82 - 48,47 .$$

$$\Delta S = 3,35 \text{ J/K}$$

Exo4 :

1) $\Delta_r S^\circ_{298} = ??$

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g).$$

Loi de Hess :

$$\Delta_r S^\circ_{298} = 2.S^\circ_{298}(HCl) - S^\circ_{298}(Cl_2) - S^\circ_{298}(H_2).$$

$$\Delta_r S^\circ_{298} = 2.186,91 - 223,07 - 130,68.$$

$$\Delta_r S^\circ_{298} = 20,07 \text{ J/K}.$$

2). relation de Kirchhoff :

$$\Delta_r S^\circ_{1000°C} = \Delta_r S^\circ_{298} + \int_{298}^{1273,15} \frac{dQ}{T}$$

$$\Delta_r S^\circ_{1000°C} = \Delta_r S^\circ_{298} + \Delta C_p \ln \frac{1273,15}{298}$$

$$\Delta_r S^\circ_{1000°C} = 20,07 + (2 \times 28,13 - 31,66 - 29,03) \ln \frac{1273}{298}$$

$$\Delta_r S^\circ_{1000°C} = 13,64 \text{ J/K}.$$

Exo 5 : Température de flamme.

$$CO_{(g)} + \frac{1}{2} O_2(g) + 2N_2(g) \longrightarrow CO_2(g) + 2N_2(g)$$

Enceinte adiabatique $\Rightarrow \sum Q_i = 0$.
On travail à pression constante $\Rightarrow Q_p = \Delta H$.

$$\Delta_r H^\circ_{298} = \Delta_f H^\circ_{CO_2(g)} + \cancel{2\Delta_f H^\circ_{N_2(g)}} - \Delta_f H^\circ_{CO(g)} - \frac{1}{2}\cancel{\Delta_f H^\circ_{O_2(g)}} \; 0$$

$$\cancel{2\Delta_f H^\circ_{N_2(g)}}$$

$$\Delta_r H^\circ_{298} = \Delta_f H^\circ_{CO_2(g)} - \Delta_f H^\circ_{CO(g)}$$

$$\Delta_r H^\circ_{298} = -94,05 - (-26,4)$$

$$\Delta_r H^\circ_{298} = -67,65 \text{ Kcal}$$

réactifs: $CO(g)$, $\frac{1}{2} O_2(g)$, $2N_2(g)$ $\xrightarrow{\Delta_r H^\circ_{298}}$ produits: $CO_2(g)$, $2N_2(g)$ à 298K

on chauffe les produits à T_f $\quad \Delta_r H_{T_f}$

$CO_2(g)$, $2N_2(g)$ $\quad T$ flamme.

$\sum Q_i = 0 \Rightarrow \Delta_r H^0_{298} + \Delta_r H_{T_f} = 0$.

$$\boxed{\Delta_r H_{T_f} = -\Delta_r H^0_{298} = \int_{298}^{T_f} \Delta C_p \, dT}$$

$\Delta C_p = C_{p_{N_2,g}} + C_{p_{CO_2,g}}$.

$\Delta C_p = (7,3 + 47,8.10^{-4}\,T) + (6,5 + 10^{-3}\,T)$.

$\Delta C_p = 13,8 + 5,78.10^{-3}\,T$.

$$\Delta_r H_{T_f} = \int_{298}^{T_f} (13,8 + 5,78.10^{-3}\,T)\, dT.$$

$$\Delta_r H_{T_f} = \left(13,8\,[T_f - 298]\right) - \left(\frac{5,78.10^{-3}}{2}\,[T_f - 298)\right)$$

$\Delta_r H_{T_f} = 13,797\, T_f - 4111,54 = -\Delta_r H^0_{298}$.

$= 67,65$ <u>kcal</u>.

Donc : $13,797\, T_f = 4111,51 + 67,65.10^3$.

$$\Rightarrow T_f = \frac{71761,51}{13,797} = 5201,24\ K.$$

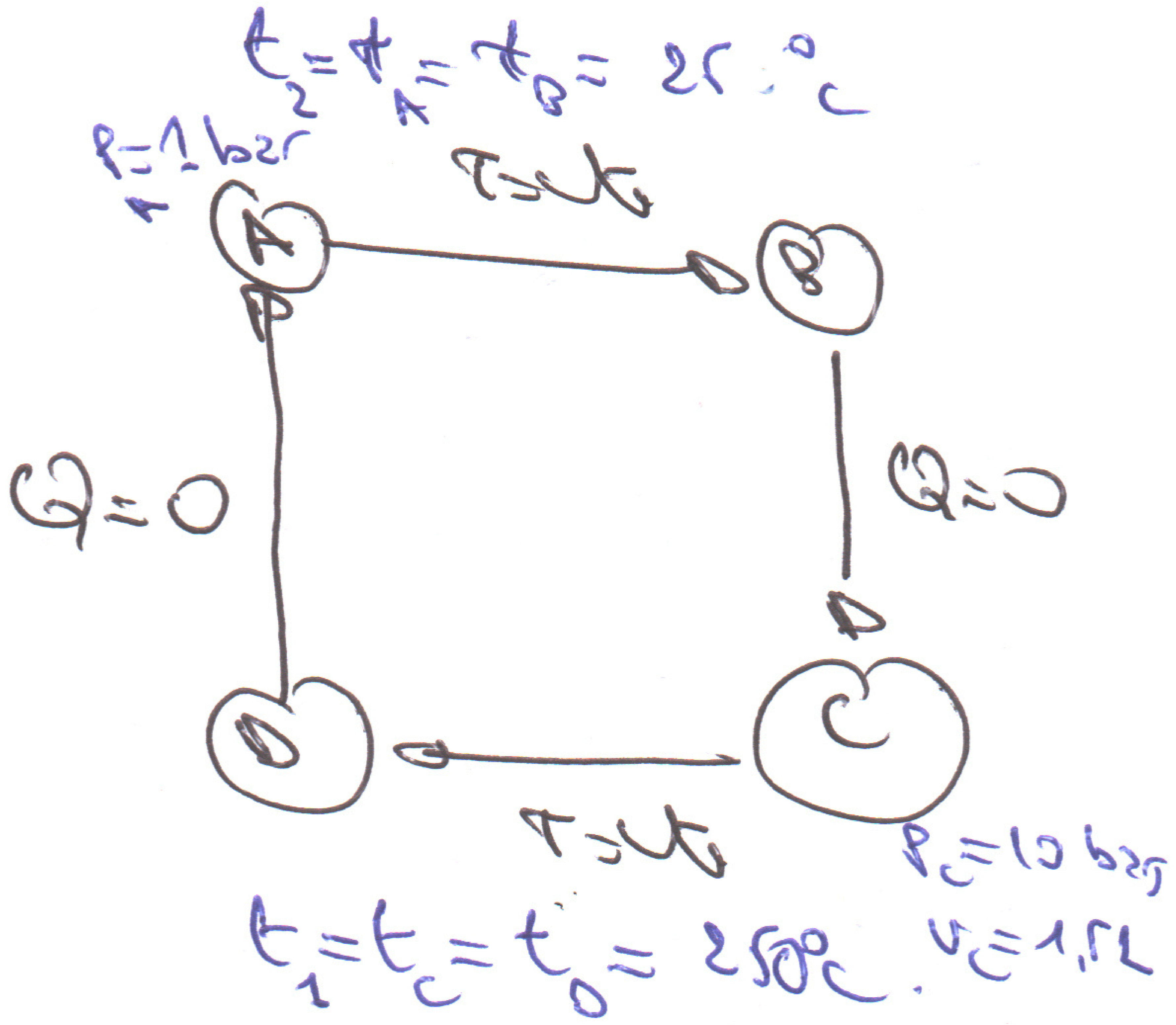
$$\Rightarrow T_f = 5201,24\ K.$$

Exo 6 :

Gaz diatomique : $\gamma = \frac{7}{5} = 1,4$.

1) paramètres d'état.

$$n = \frac{P_A V_A}{R T_A} = \frac{P_C V_C}{T_C}.$$



$$\Rightarrow V_A = \frac{P_C}{P_A} \cdot \frac{T_A}{T_C} \cdot V_C.$$

$$V_A = \frac{10}{1} \cdot \frac{298}{523} \cdot 1,5 = 8,5\,L.$$

$A \xrightarrow{T=cte} B \Rightarrow$ isotherme

$$\Rightarrow P_A V_A = P_B V_B. \Rightarrow P_B = \frac{P_A V_A}{V_B} = \frac{1 \cdot 8,5}{6,1}$$

et $B \rightarrow C \Rightarrow$ adiabatique $\Rightarrow P_B = 1,4$ Bar.

$$T_B (V_B)^{\gamma - 1} = T_C (V_C)^{\gamma - 1} \Rightarrow V_B = V_C \left(\frac{T_C}{T_B}\right)^{\frac{1}{\gamma - 1}}$$

$$V_B = 1,5 \left(\frac{523}{298}\right)^{\frac{1}{0,4}} \Rightarrow V_B = 6,1\,L$$

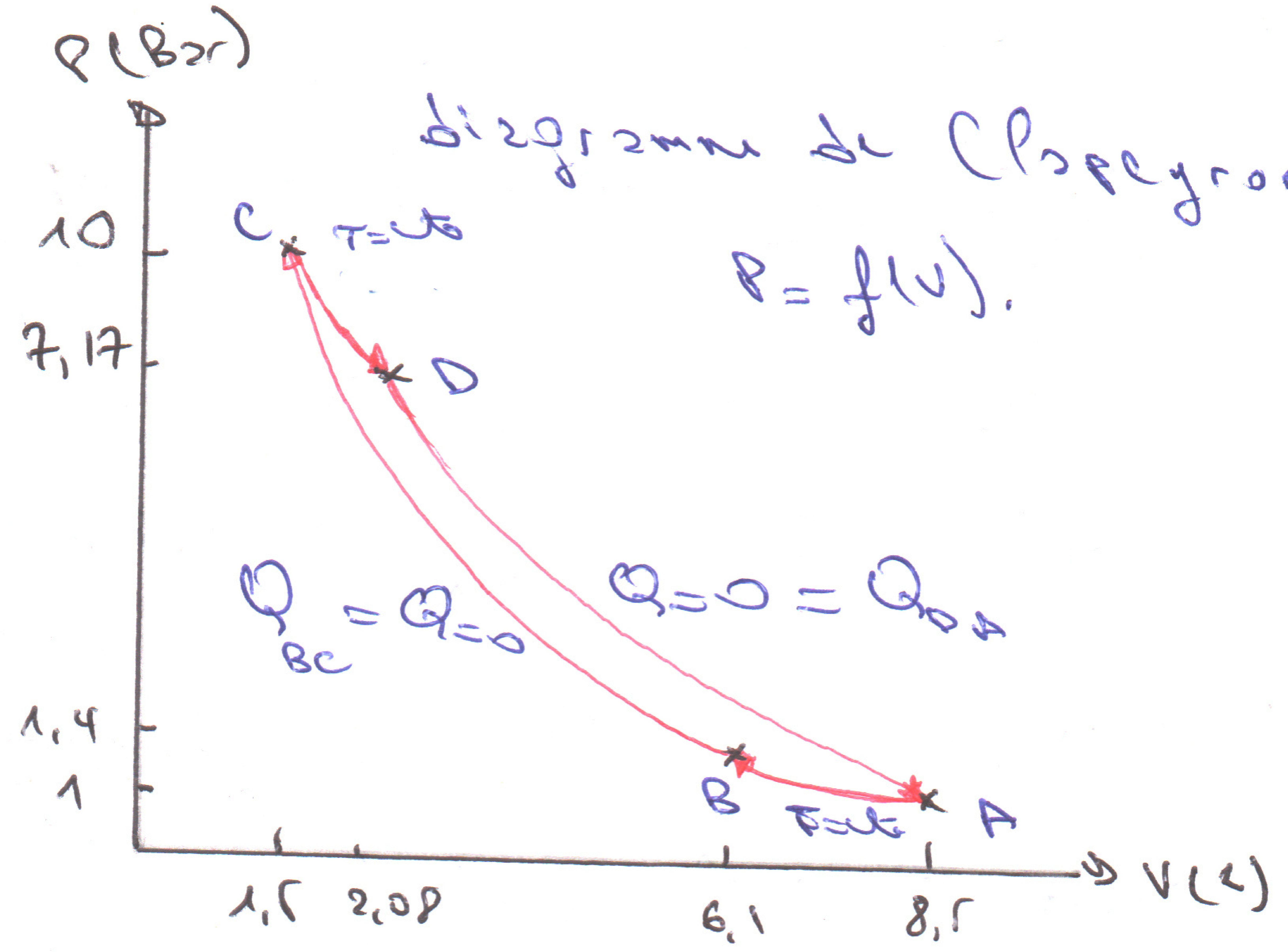
et $D \rightarrow C \Rightarrow$ adiabatique.

$$V_D = V_A \left(\frac{T_A}{T_D}\right)^{\frac{1}{\gamma - 1}} \Rightarrow V_D = \left(\frac{298}{523}\right)^{\frac{1}{0,4}}$$

$$\Rightarrow V_D = 2,08\,L.$$

et $P_D = P_A \left(\frac{V_A}{V_D}\right)^{\gamma} = 1 \cdot \left(\frac{8,5}{2,08}\right)^{1,4} = 7,17$ Bars.

2)



3)

(A) ⟶ (B) ⟹ isotherme $\Delta U = 0 = Q + W$.

$$Q_{AB} = -W_{AB} = \int P\,dV = nRT_2 \ln \frac{V_B}{V_A}.$$

$$Q_{AB} = P_A V_A \ln \frac{V_B}{V_A} = 1 \cdot 1{,}013 \cdot 10^5 \cdot 8{,}5 \cdot 10^{-3} \ln \frac{6{,}1}{8{,}5}$$

$Q_{AB} = -285{,}68\ J$ chaleur cédée par le Gaz.

(C) ⟶ (D) ⟹ isotherme.

$$Q_{CD} = -W_{CD} = nRT_1 \ln \frac{V_D}{V_C} = P_C V_C \ln \frac{V_D}{V_C}.$$

$$Q_{CD} = 10 \cdot 1{,}013 \cdot 10^5 \cdot 1{,}5 \cdot 10^{-3} \ln \frac{2{,}08}{1{,}5}$$

$Q_{CD} = 511\ J$ chaleur reçue par le Gaz.

Le Travail reçu par le gaz :

$$\Delta U_T = \Delta U_{cycle} = Q_T + W_T = 0 \text{ (cycle)}.$$

$$W_T = -Q_T = -(Q_{AB} + Q_{CD}).$$

avec $(Q_{BC} = Q_{DA} = 0$ (adiab)).

$$W_T = -(511,00 - 285,68) = -225,32 \text{ J}.$$

$W_T < 0 \Rightarrow$ Travail négatif.

Donc cette machine est un moteur thermique car le travail est fourni par le gaz au cours du cycle.

Sér 4) Le rendement ou l'efficacité :

$$\eta = 1 - \frac{T_f}{T_{ch}} = 1 - \frac{298}{523} = 0,43$$

$$\eta = 43\ \%.$$