Exercice 3 :

(R_1): **CO (g) + 1/2O_2 (g) → CO_2 (g)** $\Delta H^0_{R1,298K} = -283\ \text{kJ.mole}^{-1}$

(R_2): **3 x[H_2 (g) + 1/2O_2 (g) → H_2O (l)]** $3\Delta H^0_{R2,298K} = 3 \times (-285{,}8)\text{kJ.mole}^{-1}$

(R_3): **$CO_{2(g)}$ + 2$H_2O_{(l)}$ → $CH_{4(g)}$ + 2$O_{2(g)}$** $-\Delta H^0_{R3,298K} = +890\ \text{kJ.mole}^{-1}$

$CO_{(g)}$+ 3$H_{2(g)}$ → $CH_{4(g)}$ + $H_2O_{(l)}$ $\Delta H^0_{R,298K} = \Delta H^0_{R1,298K} + 3\Delta H^0_{R2,298K} - \Delta H^0_{R3,298K}$

Donc :

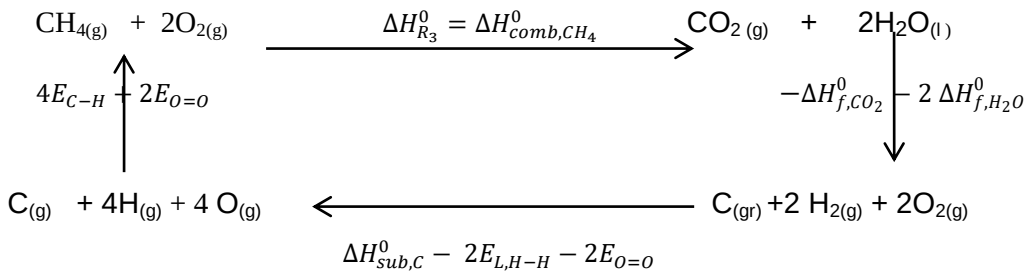
$$\Delta H^0_{R,298K} = \Delta H^0_{R1,298K} + 3\Delta H^0_{R2,298K} - \Delta H^0_{R3,298K} = -283 + 3 \times (-285{,}8) + 890{,}2$$

$$\Delta H^0_{R,298K} = -250{,}4\ \text{kJ.mole}^{-1}$$

$\Delta H^0_{R,298K} < 0$ ⟹ la réaction est exothermique.

($\Delta H^0_{R,298K} > 0$ ⟹ la réaction est endothermique)

b)-



Les données :

$\Delta H^0_{Sub,C_{gr}} = 171{,}7\ kcal.mol^{-1}$, $\Delta H^0_{L,H-H} = -104{,}2\ kcal.mol^{-1}$,

$\Delta H^0_{f,CO_{2(g)}} = -94{,}1\ kcal.mol^{-1}$,

$\Delta H^0_{f,H_2O} = \Delta H^0_{R_2,298K} = -285{,}8\text{kJ.mole}^{-1} = -68{,}4\ \boldsymbol{kcal.mol^{-1}}$,

$\Delta H^0_{R_3} = \Delta H^0_{comb,CH_4} = -890\ \text{kJ.mole}^{-1} = -212{,}9\boldsymbol{kcal.mol^{-1}}$

L'enthalpie H est une fonction d'état, $\boldsymbol{\Delta H_{cycle} = 0}$

$$\Delta H_{cycle} = \sum \Delta H = \Delta H^0_{comb,CH_4} - \Delta H^0_{f,CO_2} - 2\,\Delta H^0_{f,H_2O} + \Delta H^0_{sub,C} - 2E_{L,H-H} + 4E_{C-H} = 0$$

$$E_{C-H} = \frac{-\Delta H^0_{comb,CH_4} + \Delta H^0_{f,CO_2} + 2\,\Delta H^0_{f,H_2O} - \Delta H^0_{sub,C} + 2E_{L,H-H}}{4}$$

$$E_{C-H} = \frac{212{,}9 - 94{,}1 + 2 \times (-68{,}4) - 171{,}7 + 2 \times (-104{,}2)}{4} = \boldsymbol{-99{,}53 kcal.mol^{-1}}$$

Exercice 04 :

1)- On applique la loi de Kirchhoff pour calculer $\Delta H^0_{R,723K}$:

à P=cst $\longrightarrow$ $Q_P = \Delta H^0_{R,723K}$

donc : $\Delta \boldsymbol{H^0_{R,723K}} = \Delta H^0_{R,273} + \int_{T_1}^{T_2} \Delta C_P dT = \Delta_R H^0_{298} + \int_{T_1}^{T_2} \Delta C_P dT$

on calcule ΔC_P

$$\Delta C_P = \sum \Delta C_{P\,p} - \sum \Delta C_{P\,r} = \left(C_{P(NH_3)}\right) - \left(\frac{3}{2} C_{P(H_2)} + \frac{1}{2} C_{P_{(N_2)}}\right)$$

Application numérique : $\Delta C_P = (8{,}3 + 10^{-4}T) - 2(6{,}5 + 10^{-3}T)$

$\Delta C_P = -4{,}7 - 0{,}8\,.\,10^{-3}T \qquad = \boldsymbol{a + bT}$

$$\Delta \boldsymbol{H^0_{R,723}} = \Delta H^0_{R,273} + \int_{T_1}^{T_2} (a + bT) dT = \Delta H^0_{R,273} + \int_{T1}^{T2} a dT + \int_{T1}^{T2} bT dT$$

$$\Delta \boldsymbol{H^0_{R,723}} = \Delta H^0_{R,273} + a[T] + \frac{b}{2}\left[T^2\right] = \Delta H^0_{R,273} + a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2)$$

A.N: $\Delta H^0_{R,723} = -12{,}2.\,10^3 - 4{,}7(723 - 273) - \frac{0{,}8.10^{-3}}{2}(723^2 - 273^2)$

$\Delta H^0_{R,723} = -12{,}82\ k\ cal.mol^{-1}$

2)- Calcul de Q_V :

$\Delta U^0_{comb,298} = \Delta H^0_{comb,298} - \Delta n_g RT$

$\Delta U^0_{comb,298} = Q_V$ et $\Delta H^0_{comb,298} = Q_P$

$\boldsymbol{Q_{V,comb} = Q_{P,comb,298} - \Delta n_g RT}$

$\Delta n_{gaz} = \sum n_{produits} - \sum n_{réactifs} = 1 - 2 = \boldsymbol{-1\ mole}$

Donc : $\boldsymbol{Q_{V,comb}} = -11{,}37\ kJ.mol^{-1}$