

Thermochimie: premier principe

Exercice 1.

La loi de Kirchhoff donne: $\frac{d\Delta_r H^\circ}{dT} = \Delta_r C_p^\circ = \sum_i \nu_i C_{p,m}^\circ$

$$\begin{aligned}\Delta_r H^\circ(T_2) &= \Delta_r H^\circ(T_1) + \Delta_r C_p^\circ (T_2 - T_1) \\ &= \Delta_r H^\circ(T_1) + (C_{p,m}(\text{O}_2, g) - C_{p,m}(\text{O}_2, g) - C_{p,m}(\text{C}_s)) (T_2 - T_1) \\ &= -393,5 + (37,1 - 2,4 - 8,5) \cdot 10^{-3} (1000 - 298)\end{aligned}$$

$$\Delta_r H^\circ(T_2) = -394,1 \text{ kJ} \cdot \text{mol}^{-1}$$

On pourra bien considérer $\Delta_r H^\circ$ indépendant de T
(approximation d'Ellingham)

Exercice 2



Etat
initial

n_0 5 m_0

$m_0 = 1 \text{ mmol}$.

Etat
final

$m_0 - 3\zeta_f$ 5 $m_0 - 3\zeta_f$ 2 $\zeta_f = 0,4 m_0$
" " " " "
0,8 m_0 4,4 m_0 ($\zeta_f = 0,2 m_0$)

La transformation étant réalisée à $P = \text{cst}$.

$$Q = Q_p = \Delta H = \int_{\xi_i}^{\xi_f} \left. \frac{\partial H}{\partial \xi} \right|_{T,P} d\xi = \int_{\xi_i}^{\xi_f} \Delta_r H d\xi = \int_{\xi_i}^{\xi_f} \Delta_r H^\circ d\xi.$$

$$\begin{aligned}Q &= \Delta_r H^\circ \xi_f = \Delta_r H^\circ \times 0,2 \cdot m_0 \\ &= -105 \times 10^3 \times 0,2 \times 10^{-3} \\ &= -21,0 \text{ J}.\end{aligned}$$

Exercice 3.

(2)

Réaction de combustion de l'éthane.



Conservation des él^e -

$$\begin{aligned} \beta &= 2 \\ \gamma &= 3 \\ \alpha &= \frac{7}{2} \end{aligned}$$

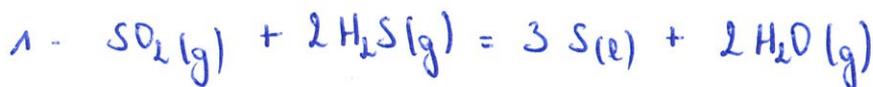


Loi de Hess: $\Delta_r H^\circ = 2 \Delta_f H^\circ(CO_2) + 3 \Delta_f H^\circ(H_2O) - \Delta_f H^\circ(C_2H_6) - \frac{7}{2} \Delta_f H^\circ(O_2)$

$$= 2(-393,5) + 3(-285,8) - (-84,7)$$

$$\Delta_r H^\circ = -1559,7 \text{ kJ} \cdot \text{mol}^{-1}$$

Exercice 4:



$$\begin{aligned} \Delta_r H^\circ &= 2 \Delta_f H^\circ(H_2O) + 3 \Delta_f H^\circ(S) - \Delta_f H^\circ(SO_2) - 2 \Delta_f H^\circ(H_2S) \\ &= 2(-241,8) + 3(0) - (-296,8) - 2(-20,6) \\ &= -110,6 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$



$$\begin{aligned} \Delta_r H^\circ(298K) &= 2 \Delta_f H^\circ(NH_3) - \Delta_f H^\circ(N_2) - 3 \Delta_f H^\circ(H_2) \\ &= 2(-46,210) \\ &= -92,420 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Réaction exothermique -

$$\begin{aligned} \Delta_r H^\circ(T_2) &= \Delta_r H^\circ(T_1) + \Delta C_p^\circ (T_2 - T_1) \\ &= -92,420 + (2 \times 28,05 - 3 \times 28,91 - 29,63)(770 - 298) \times 10^{-3} \\ &= -120,863 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Exercice 5.

Raisonnement très classique A SAVOIR REFAIRE.
Le point crucial est de bien définir les différents états.

a)
$$\text{CO(g)} + \frac{1}{2} \text{O}_2(\text{g}) (+ \text{N}_2(\text{g})) = \text{CO}_2(\text{g}) (+ \text{N}_2(\text{g}))$$

{	initial	n	$\frac{1}{2}n$	0	0
	final	$n - \xi_f$	$\frac{1}{2}n - \frac{\xi_f}{2}$	ξ_f	$\xi_f = n$
		0	0	0	0

b)
$$\left\{ \begin{array}{l} \text{initial} \\ \text{final} \end{array} \right. \begin{array}{l} n \\ 0 \end{array} \begin{array}{l} \frac{m}{L} \\ 0 \end{array} \begin{array}{l} 4 \times \frac{m}{L} = 2m \\ 2m \end{array} \begin{array}{l} 0 \\ m \end{array}$$

c)
$$\left\{ \begin{array}{l} \text{initial} \\ \text{final} \end{array} \right. \begin{array}{l} n \\ n - \xi_f = 0 \end{array} \begin{array}{l} m^* \\ m - \frac{\xi_f}{2} = \frac{m}{2} \end{array} \begin{array}{l} 4m^* \\ 4m \end{array} \begin{array}{l} 0 \\ m \end{array}$$

*
$$m_{\text{CO, initial}} = \frac{P}{RT} V_{\text{CO}}$$

$$m_{\text{CO, int}} + m_{\text{O}_2, \text{int}} = 4 m_{\text{CO, int}} + m_{\text{O}_2, \text{int}}$$

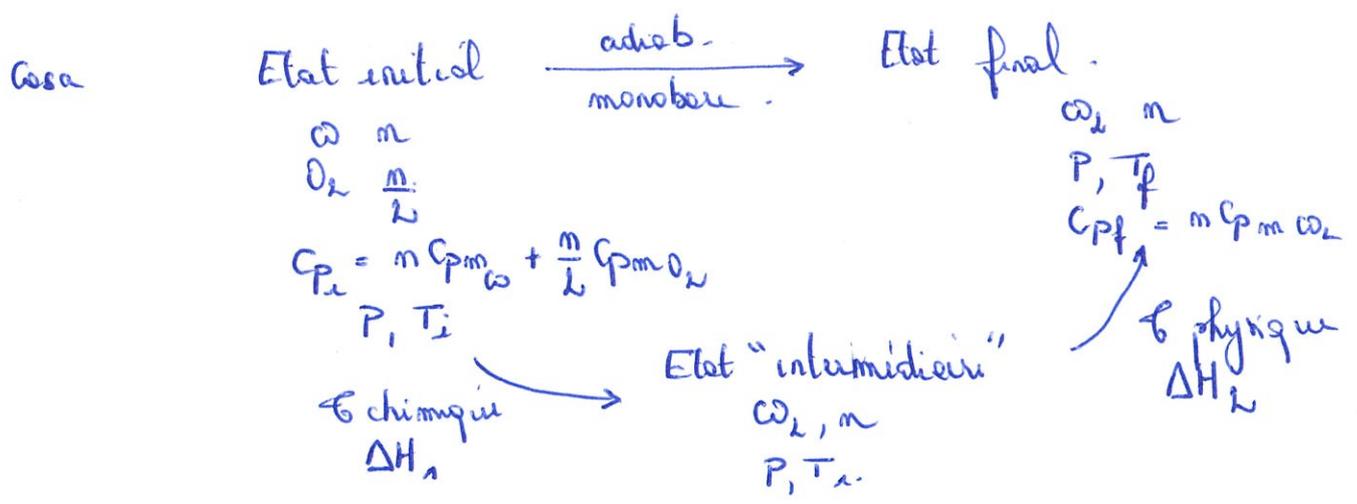
$$= 5 m_{\text{CO, int}}$$

$$= \frac{P}{RT} V_{\text{air}}$$

$$= \frac{P}{RT} 5 V_{\text{CO}}$$

$$= 5 m_{\text{CO, int}}$$

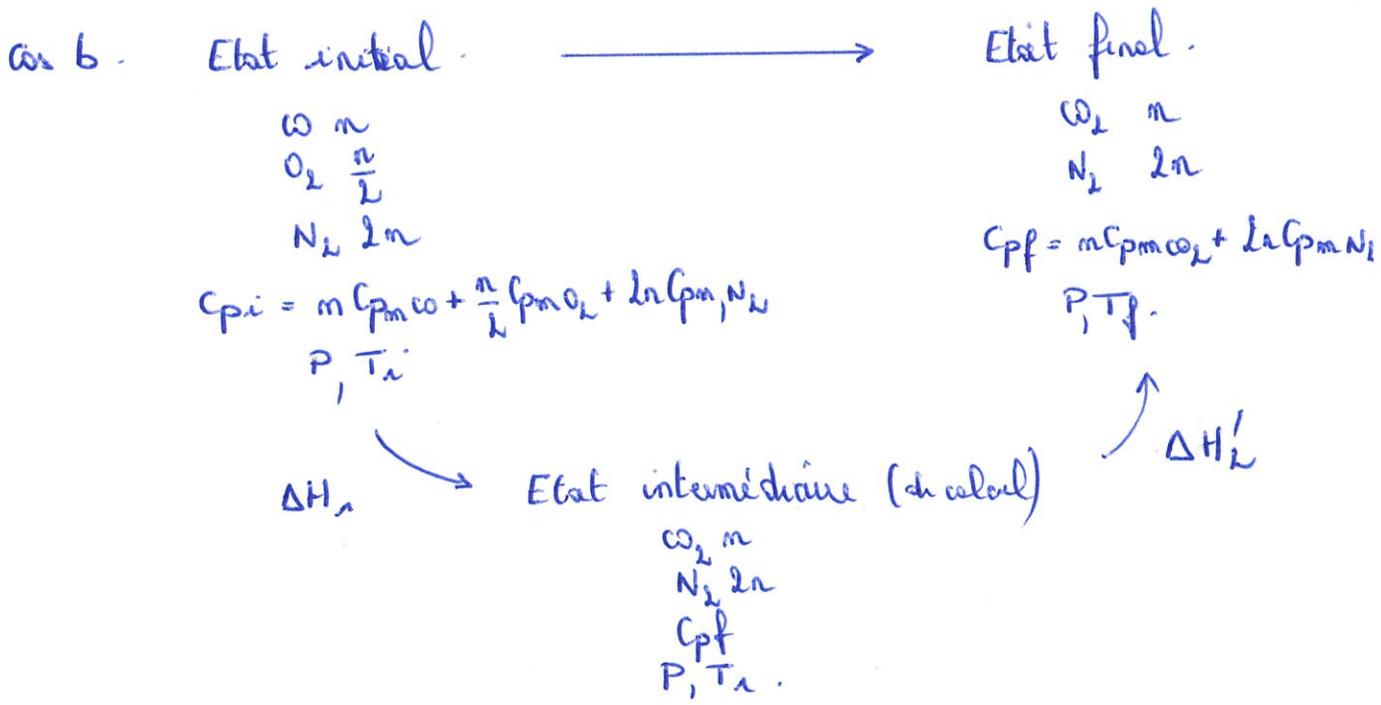
Donc $m_{\text{O}_2, \text{int}} = m_{\text{CO, int}}$.



$$\begin{aligned}
\Delta H &= Q_p \quad (\text{isobare}) \\
&= 0 \quad (\text{adiabatique}) \\
&= \Delta H_1 + \Delta H_2 \quad \text{car } H \text{ est une fonction d'etat.} \\
&= \sum_f \Delta_r H(T_i) + C_{pf} (T_f - T_i) \\
&= n \Delta H^\circ(T_i) + n C_{pm} \omega_L (T_f - T_i)
\end{aligned}$$

Donc
$$T_f = T_i - \frac{\Delta_r H^\circ(T_i)}{C_{pm} \omega_L}$$

AN
$$T_f = 25 + \frac{283 \cdot 10^3}{37,13} = 7647^\circ\text{C.}$$



Seul change C_{pf} et $\Delta H_2'$

$$T_f = T_i - \frac{\Delta_r H^\circ(T_i)}{C_{pm} \omega_2 + 2C_{pm} N_2}$$

AN
$$T_f = 25 + \frac{283 \cdot 10^3}{37,13 + 2 \times 29,12} = 2992^\circ\text{C.}$$

Cas c

Etat initial -

ω m
 O_2 n
 N_2 4m

$$C_{pi} = m C_{pm \omega} + n C_{pm O_2} + 4m C_{pm N_2}$$

P, T_i

Etat final

O_2 $\frac{m}{2}$
 N_2 4m
 ω_2 m

$$C_{pf} = \frac{m}{2} C_{pm O_2} + 4m C_{pm N_2} + m C_{pm \omega}$$

P, T_f

ΔH_1 ↘

Etat intermédiaire de calcul

O_2 $\frac{m}{2}$
 N_2 4m
 ω_2 m

P, T_i

↗ $\Delta H_2''$

Seul C_p change -

$$T_f = T_i - \frac{\Delta_r H^\circ(T_i)}{\frac{1}{2} C_{pm O_2} + 4 C_{pm N_2} + C_{pm \omega}}$$

$$AN \quad T_f = 25 + \frac{283 \cdot 10^3}{37,13 + 4 \cdot 29,12 + \frac{1}{2} 29,36} = 1707 \text{ } ^\circ\text{C}$$

Exercice 6

Etat initial -

P_i, V, T_i
 $\left\{ \begin{array}{l} CH_3OH \quad n = \frac{m}{M} \\ O_2 \quad \text{exc} \end{array} \right.$

P, V

Transformation physique
 ΔU_1

↳ adiabatique rochere -

Etat final -

P_f, V, T_f
 ω_2 m
 H_2O 2m
 O_2 exc.

Etat "intermédiaire" (de calcul)

V, T_f
 $\left\{ \begin{array}{l} CH_3OH \quad n \\ O_2 \quad \text{exc} \end{array} \right.$

Transformation chimique à T_f
 ΔU_2

Transformation isochore - $Q = Q_V = \Delta U = 0$.

Or $\Delta U = \Delta U_1 + \Delta U_2$ car U est une fonction d'état.

$$\Delta U_1 = P_V (T_f - T_i) \quad (\text{évolution "physique" à composition constante})$$

$$\Delta U_2 = \int_{S_i=0}^{S_f=n} \left(\frac{\partial U}{\partial S} \right)_{T,V} dS.$$

Or pour les systèmes étudiés U ne dépend que de T

$$\left(\frac{\partial U}{\partial S} \right)_{T,V} = \left(\frac{\partial U}{\partial S} \right)_T = \Delta_r U = \Delta_r U^\circ$$

$$\Delta U_2 = n \Delta_r U^\circ$$

$$\text{Or } \Delta_r H^\circ = \Delta_r U^\circ + \sum_{\text{gaz}} \nu_i RT = \Delta_r U^\circ + \left(1 - \frac{3}{2}\right) RT$$

$$\text{Donc } \Delta_r U^\circ = \Delta_r H^\circ + \frac{1}{2} RT.$$

$$\text{Ainsi } 0 = P_V (T_f - T_i) + n \left(\Delta_r H^\circ(T_f) + \frac{1}{2} RT_f \right)$$

$$\begin{aligned} \text{Donc } \Delta_r H^\circ(T_f) &= - \frac{P_V}{n} (T_f - T_i) - \frac{RT_f}{2} \\ &= - \frac{5,58 \cdot 10^3}{\frac{0,4867}{32,04}} (25,54 - 23,56) - \frac{8,314 (25,54 + 273)}{2} \\ &= - 728,6 \cdot 10^3 \text{ J mol}^{-1}. \end{aligned}$$
