TH 406

$$P(V-nb) = nRT \exp - \frac{na}{RTV}$$

<u>Point critique</u> = point d'inflexion à tangente horizontale en coord. de Clapeyron.

- $\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0 \Rightarrow \boxed{\frac{na}{RTV^2} = \frac{1}{V-nb}}.$

car $\left(\frac{\partial P}{\partial V}\right)_T = \frac{nRT}{V-nb} e^{-na/RTV}\left[-\frac{1}{V-nb} + \frac{na}{RTV^2}\right] = P\left[\frac{na}{RTV^2} - \frac{1}{V-nb}\right]$

- $\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0 = P\left[-\frac{2na}{RTV^3} + \frac{1}{(V-nb)^2}\right] + \underbrace{\left(\frac{\partial P}{\partial V}\right)_T}_{=0 \text{ en } T=T_c} \left[\frac{na}{RTV^2} - \frac{1}{V-nb}\right].$

$$\Rightarrow \boxed{\frac{1}{(V-nb)^2} = \frac{2na}{RTV^3}}$$

on a donc : $\boxed{V_c = 2nb}$.

$$\boxed{T_c = \frac{a}{Rb}}.$$

$$\boxed{P_c = \frac{a}{2e^2b^2}}$$

Corrigé Planche n° 19.



TH 101

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$$P = \frac{rT}{V-b} e^{-a/rTV} \qquad f(P,V,T) = \frac{rT}{V-b} e^{-a/rTV} - P = 0.$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{V} \frac{(\partial f/\partial T)_{P,V}}{(\partial f/\partial V)_{T,P}}$$

$$\left(\frac{\partial f}{\partial T}\right)_{P,V} = \left(\frac{r}{V-b} + \frac{a}{r T^2 V}\cdot\frac{rT}{V-b}\right) e^{-a/rTV} = \frac{r}{V-b}\left(1+\frac{a}{rTV}\right) e^{-a/rTV}.$$

$$\left(\frac{\partial f}{\partial V}\right)_{T,P} = \left(-\frac{rT}{(V-b)^2} + \frac{rT}{V-b}\cdot\frac{a}{rTV^2}\right) e^{-a/rTV} = \frac{rT}{V-b}\left(\frac{a}{rTV^2} - \frac{1}{V-b}\right) e^{-a/rTV}$$

$$\Rightarrow \quad \alpha = \frac{1}{TV} \frac{\left(1+\frac{a}{rTV}\right)}{\frac{a}{rTV^2} - \frac{1}{V-b}.} = \frac{1+\frac{a}{rTV}}{\frac{a}{rTV} - \frac{V}{V-b}.} \frac{1}{T}$$

D'où $\boxed{\alpha = \frac{f(T,V)}{T} \quad \text{avec} \quad f(T,V) = \frac{1+\frac{a}{rTV}}{\frac{a}{rTV} - \frac{V}{V-b}.}}$

$$f(T,V) = \frac{1+\frac{a}{rTV}}{\frac{-1}{1-\frac{b}{V}} + \frac{a}{rTV}} = \frac{1+\frac{a}{rTV}}{\frac{a}{rTV} - \left(1+\frac{b}{V}\right)} = \left(1+\frac{a}{rTV}\right)\left(1+\frac{b}{V} - \frac{a}{rTV}\right)$$

$$= -\left(1+\frac{a}{rTV} + \frac{b}{V} - \frac{a}{rTV}\right) \quad \text{au 1er ordre en } \frac{1}{V}$$

$$\Rightarrow \quad f(T,V) = -\left(1+\frac{b}{V}\right)$$

D'où $\boxed{\alpha \# -\frac{1+\frac{b}{V}}{T}}$

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Faibles pressions, volumes élevés $V \gg b$ et $\frac{a}{rTV} \ll 1.$

$$\Rightarrow \quad P = \frac{rT}{V}\left(1-\frac{b}{V}\right)^{-1}\left(1-\frac{a}{rTV} + \frac{a^2}{2r^2T^2V^2}\cdots\right)$$

$$= \frac{rT}{V}\left[\left(1+\frac{b}{V}+2\frac{b^2}{V^2}\right)\left(1-\frac{a}{rTV} + \frac{a^2}{2r^2T^2V^2}\right)\right] = \frac{rT}{V}\left[1+\frac{1}{V}\left(b-\frac{a}{rT}\right)+\frac{1}{V^2}\left(\frac{2b^2}{V^2} - \right.\right.$$

$$\frac{ab}{rT} + \frac{a^2}{2r^2T^2}\Big)\Big] \Rightarrow \quad pV = RT\left(1 + \frac{B}{V} + \frac{C}{V^2}\right)$$

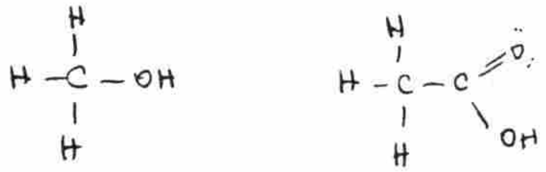
avec $\boxed{\begin{array}{l} B = b - \dfrac{a}{rT} \\ C = 2\dfrac{b^2}{V^2} - \dfrac{ab}{rT} + \dfrac{a^2}{2r^2T^2} \end{array}}$

# Corrigé planche chimie n° 1.

**THC 101.**

$$CH_3OH\,(g) + CO\,(g) \rightleftharpoons CH_3CO_2H\,(g)$$

1°



2°

$$C\,(graph) + 2\,H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \xrightarrow{\Delta_f H^\circ} CH_3OH\,(g)$$

$$\downarrow \Delta H_{subl.}(C)$$

$$C\,(g) + 2H_2\,(g) + \tfrac{1}{2}\,O_2\,(g)$$

$$\downarrow 2E_{H-H} + \tfrac{1}{2}E_{O=O}$$

$$C(g) + 4\,H(g) + O\,(g) \xrightarrow{-3E_{C-H} - E_{C-O} - E_{O-H}} CH_3OH\,(g)$$

$$\Rightarrow \Delta_f H^\circ = \Delta H_{subl}\,(C) + 2\,E_{H-H} + \tfrac{1}{2}\,E_{O=O} - 3E_{C-H} - E_{C-O} - E_{O-H}$$

$$= 717 + 2\times 436 + 0{,}5\times 498 - 3\times 415 - 356 - 463$$

$$\underline{\Delta_f H^\circ\,(CH_3OH) = -226\ kJ.mol^{-1}}$$

$$2\,C(graph) + 2\,H_2(g) + O_2(g) \xrightarrow{\Delta_f H^\circ} CH_3CO_2H\,(g)$$

$$\downarrow 2\,\Delta H_{subl}$$

$$2\,C(g) + 2\,H_2(g) + O_2\,(g)$$

$$\downarrow 2E_{H-H} + E_{O=O}$$

$$2\,C(g) + 4\,H(g) + 2O(g) \xrightarrow{-3\,E_{C-H} - E_{C-C} - E_{C=O} - E_{C-O} - E_{OH}} CH_3CO_2H\,(g)$$

$$\Delta_f H^\circ = 2\,\Delta H_{subl} + 2\,E_{HH} + E_{O=O} - 3\,E_{CH} - E_{CC} - E_{C=O} - E_{C-O} - E_{OH}$$

$$= 2\times 717 + 2\times 436 + 498 - 3\times 415 - 345 - 743 - 356 - 463.$$

$$\Rightarrow \underline{\Delta_f H^\circ(CH_3CO_2H) = -348\ kJ.mol^{-1}}$$

(2°) $\Delta_r H^\circ = \Delta_f H^\circ(CH_3CO_2H) - \Delta_f H^\circ(CO) - \Delta_f H^\circ(CH_3OH)$.

$\underline{\Delta_r H^\circ = -12 \text{ kJ.mol}^{-1}}$

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$\boxed{\text{THC } 102}$ . ancien exercice hors programme: n'est plus dans la planche

(1°)

$$\begin{tikzcd}
x\,M(s) + \frac{y}{2}O_2(g) \arrow[rr, "\Delta_f H^\circ(M_xO_y)"] \arrow[d, "x\Delta H_{subl}(M)"'] & & M_xO_y(s) \\
x\,M(g) + \frac{y}{2}O_2(g) \arrow[d, "\frac{y}{2}E_{O=O}"'] & & \\
x\,M(g) + y\,O(g) \arrow[rr, "x\,E_i(M) + y\,E_{ae}"'] & & y\,O^{2-} + x\,M^{\frac{2y}{x}\oplus} \arrow[uu, "-E_{ret}(M_xO_y)"']
\end{tikzcd}$$

$$\Rightarrow \boxed{\Delta_f H^\circ(M_xO_y) = x\,\Delta H_{subl}(M) + \frac{y}{2}E_{O=O} + x\,E_i(M) + y\,E_{ae} - E_{ret}(M_xO_y)}$$

(2°) Pour $Na_2O$ : $y = 1$ $x = 2$

$E_{ret}(Na_2O) = +415{,}9 + 2\times 107{,}5 + 0{,}5\times 498 + 2\times 492 + 710$

$\underline{E_{ret}(Na_2O) = 2574 \text{ kJ.mol}^{-1}}$

Pour $MgO$ : $y = x = 1$.

$E_{ret}(MgO) = 601{,}6 + 147{,}1 + 0{,}5 . 498 + 2188 + 710$

$\underline{E_{ret}(MgO) = 3896 \text{ kJ.mol}^{-1}}$

Pour $Al_2O_3$ : $y = 3$ $x = 2$.

$E_{ret}(Al_2O_3) = 1676 + 2\times 330 + 1{,}5\times 498 + 2\times 5139 + 3\times 710$

$\underline{E_{ret}(Al_2O_3) = 15\,491 \text{ kJ.mol}^{-1}}$

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$\boxed{\text{THC } 103}$ $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$.

(1°) $\Delta_r H^\circ = 179 \text{ kJ.mol}^{-1}$

$\Delta_r S^\circ = 164 \text{ J.K}^{-1}.\text{mol}^{-1}$

$\Delta_r G^\circ = \Delta H^\circ - T\,\Delta_r S^\circ = 130$ $\text{kJ.mol}^{-1}$

2°) $$\frac{d(\Delta_r H^\circ)}{dT} = \Delta_r C_p^\circ = -17 \ J.K^{-1}.mol^{-1}$$

$$\Rightarrow \Delta_r H^\circ(T) = \Delta_r H^\circ(298) + \Delta_r C_p^\circ (T-298)$$

$$\Rightarrow \boxed{\Delta_r H^\circ(T) = 184 - 17.10^{-3}\,T \quad (kJ.mol^{-1})}$$

$$\frac{d(\Delta_r S^\circ)}{dT} = \frac{\Delta_r C_p^\circ}{T}$$

$$\Rightarrow \Delta_r S^\circ = \Delta_r S^\circ(298) + \Delta_r C_p^\circ \ln\frac{T}{298}$$

$$\Rightarrow \boxed{\Delta_r S^\circ(T) = 261 - 17\ln T \quad (J.K^{-1}.mol^{-1})}$$

$$\boxed{\Delta_r G^\circ = \Delta_r H^\circ - T\,\Delta_r S^\circ = 184 - 0{,}278\,T + 17\,T\ln T.10^{-3} \quad (kJ.mol^{-1})}$$

3°) $\Delta_r G^\circ(T_i) = 0$ pour $T_i = 1165\ K$.

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THC 104 — Réaction de combustion :

$$\frac{3n+1}{2} O_2 + C_nH_{2n+2} \xrightarrow[\Delta H^\circ_{comb}]{} n\,CO_2 + (n+1)\,H_2O\ liq.$$

$$\Delta H^\circ_{comb} = (n+1)\,\Delta_f H^\circ(H_2O\,liq) + n\,\Delta_f H^\circ(CO_2) - \underbrace{\Delta_f H^\circ(C_nH_{2n+2})}_{\text{à calculer}}$$

$$\begin{tikzcd}
C_nH_{2n+2} & & n\,C(graph) + (n+1)\,H_2(g) \arrow[ll, "\Delta_f H^\circ"'] \arrow[d, "n\,\Delta H^\circ_{subl}(C)"] \\
 & & n\,C(g) + (n+1)\,H_2(g) \arrow[d, "(n+1)\,E_{H-H}"] \\
 & & n\,C(g) + 2(n+1)\,H(g) \arrow[uull, "-\left[(n-1)E_{C-C} + (2n+2)E_{C-H}\right]"]
\end{tikzcd}$$

$$\Rightarrow +\Delta_f H^\circ = n\,\Delta H^\circ_{subl}(C) + (n+1)\,E_{H-H} - \left[(n-1)E_{C-C} + (2n+2)E_{C-H}\right].$$

$$\Delta_f H^\circ = -23n - 44 \quad (kJ/mol).$$

D'où $$\Delta H^\circ_{comb.}(n) = 23n + 44 + (n+1)(-285{,}85) - 393{,}51.n$$

$$\Rightarrow \boxed{\Delta H^\circ_{comb}(n) = -656{,}36\,n - 241{,}85 \quad (kJ.mol^{-1})} \text{ à } 298\ K.$$

THC 105.

$$\begin{tikzcd}
H_2 + \frac{1}{2}O_2 \ (T_0 = 298\,K,\ 1\,bar) \arrow[rr, "\Delta H = 0"] \arrow[dr, "\Delta_f H^\circ(H_2O_v)"'] & & H_2O\ vap\ (T,\ 1\,bar) \\
& H_2O\ vap\ (298\,K,\ 1\,bar) \arrow[ur, "\Delta H_1"'] &
\end{tikzcd}$$

$$\Delta H_1 = \int_{T_0}^{T} C_p^\circ(H_2O)\, dT = 30{,}1\,(T-298) + \frac{9{,}6}{2}.10^{-3}\,(T^2 - 298^2)$$

$$= -9396{,}1 + 30{,}1\,T + 4{,}8.10^{-3}\,T^2$$

$$\Rightarrow \Delta H = 0 = -251\,396 + 30{,}1\,T + 4{,}8.10^{-3}\,T^2$$

$$\Rightarrow \boxed{T = 4752\,K}$$

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THC 106.

1°) Plus la différence d'électronégativité $|\chi_A - \chi_B|$ augmente, plus $E_{AB}$ augmente $\Rightarrow$ molécule AB + stable que A–A et B–B

2°)

$$\begin{tikzcd}
\frac{1}{2}X_2(g) + \frac{1}{2}Y_2(g) \arrow[rr, "\Delta_f H^\circ(XY)"] \arrow[dr, "\frac{1}{2}(E_{XX} + E_{YY})"'] & & XY(g) \\
& X(g) + Y(g) \arrow[ur, "-E_{XY}"'] &
\end{tikzcd}$$

$$\Rightarrow \Delta_r H^\circ(XY) = \frac{1}{2}\left[E_{XX} + E_{YY}\right] - E_{XY}$$

or $E_{XY} = \sqrt{E_{XX}E_{YY}} - k^2\,(X_X - X_Y)^2$

$$\Rightarrow \boxed{\Delta_r H^\circ(XY) = \frac{1}{2}\left(\sqrt{E_{XX}} - \sqrt{E_{YY}}\right)^2 - k^2\,(X_X - X_Y)^2}$$

$$\boxed{X_X - X_Y = \frac{\left(-\Delta_r H^\circ(XY) + \frac{1}{2}\left[\sqrt{E_{XX}} - \sqrt{E_{YY}}\right]^2\right)^{1/2}}{k}}$$

$\Rightarrow$

$X_F = 3{,}98$
$X_{Cl} = 3{,}49$
$X_{Br} = 3{,}04$
$X_I = 2{,}83$

3° Assez bonne corrélation entre valeurs calculées par les 2 méthodes.

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THC 107

1° $Zn + \frac{1}{2} O_2 \longrightarrow ZnO\ (s)$

on effectue l'approximation d'Ellingham dans les 3 domaines de t° : $T < T_f$ ; $T_f < T < T_v$ ; $T > T_v$.

Domaine 1 : $T \leq T_f$ : Zn solide

$\Delta_r G^0_1 = \Delta_r H^0_1 - T \Delta_r S^0_1$ $\left\{ \begin{array}{l} \Delta_r H^0_1 = -347,65 \text{ kJ.mol}^{-1} \\ \Delta_r S^0_1 = -99,8 \text{ J.K}^{-1}\text{.mol}^{-1} \end{array} \right.$

Domaine 2 : $T_f \leq T \leq T_v$ : Zn liq.

$$\Delta_r G^0_2 = \Delta_r H^0_2 - T\ \Delta_r S^0_2 .$$

$$\left\{ \begin{array}{l} \Delta_r H^0_2 = \Delta_f H^0 (ZnO) - \Delta_f H^0 (Zn_{liq}) = \Delta_r H^0_1 - \Delta H^0_F = X . \\ \Delta_r S^0_2 = \Delta_r S^0_1 - \dfrac{\Delta H^0_F}{T_F} \end{array} \right.$$

A 700°C : $\Delta_r G^0_2 = X - 973\ \Delta_r S^0_1 + \dfrac{973}{T_F} \Delta H^0_F$

d'où les deux équations :

$$\left\{ \begin{array}{l} X + \Delta H^0_F = -347,65 . \\ X + 1,405\ \Delta H^0_F = -344,60 \end{array} \right. \Rightarrow \left\{ \begin{array}{l} \underline{\Delta H^0_F = 7,53 \text{ kJ.mol}^{-1}} \\ \underline{X = -355,18 \text{ kJ.mol}^{-1}} \end{array} \right.$$

---

2° Domaine 3 : $T \geq T_v$.

$\Delta_r G^0_3 = \Delta_r H^0_3 - T\ \Delta_r S^0_3$ .

$\Delta_r H^0_3 = \Delta_r H^0_2 - \Delta H^0_V = \boxed{-469,96 \text{ kJ.mol}^{-1} = Z}$

$\Delta_r S^0_3 = \Delta_r S^0_2 - \dfrac{\Delta H^0_V}{T_V} = -99,8 - \dfrac{7530}{692,65} - \dfrac{114\,780}{1180,15} = -207,93 \text{ J.K}^{-1}\text{.mol}^{-1}$

D'où $Y = \Delta_r G^0_3 (1000°C) = -469,96 + 207,93 \times 1,273$

$\Rightarrow \boxed{Y = -205,26 \text{ kJ.mol}^{-1}}$

THC 108

1° $$\Delta_r U = \left(\frac{\partial U}{\partial \xi}\right)_{T,V}.$$

$$\Rightarrow \quad U(\xi) = U(0) + \Delta_r U \cdot \xi .$$

$$\Rightarrow \quad \boxed{\Delta U(\xi) = \xi \cdot \Delta_r U} \quad \text{à } T, V \text{ ctes}$$

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2° a) $$Al + \frac{3}{4} O_2 \longrightarrow \frac{1}{2} Al_2O_3$$

b)

$$\begin{tikzcd}
0{,}02 \text{ mol } Al + O_2(g) \text{ à } T \arrow[rr, "\Delta U_1 = Q_V = 0"] \arrow[dr, "\Delta U = 0{,}02\,\Delta_r U"'] & & 0{,}01 \text{ mol } Al_2O_3 \\
& 0{,}01 \text{ mol de } Al_2O_3 \text{ à } T \arrow[ur, "\substack{\text{à } T' = T + 3{,}8 \\ \Delta U' = C\Delta T}"'] &
\end{tikzcd}$$

$$\Rightarrow \quad \Delta U + C\,\Delta T = 0$$

D'où $\quad C\Delta T = -0{,}02\,\Delta_r U = -\Delta U$.

D'où $\boxed{\Delta U = -1669{,}4\ J}$

$\boxed{\Delta_r U = -\ 83{,}47\ kJ.mol^{-1}}$ pour la combustion d'1 mole de Al.

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3° $$\Delta_r H^\circ = \Delta_r U^\circ + \Delta\nu_g RT = \Delta_r U^\circ - 0{,}75\,RT$$

$$\Rightarrow \quad \Delta_r H^\circ = -85{,}33\ kJ.mol^{-1} = \frac{1}{2}\Delta_f H^\circ(Al_2O_3).$$

D'où $\boxed{\Delta_f H^\circ(Al_2O_3) = -\ 170{,}66\ kJ.mol^{-1}}$