19 g/L

28 g.mol^{-1}

$n = \frac{m}{M} = 0,65$

Chapitre 4

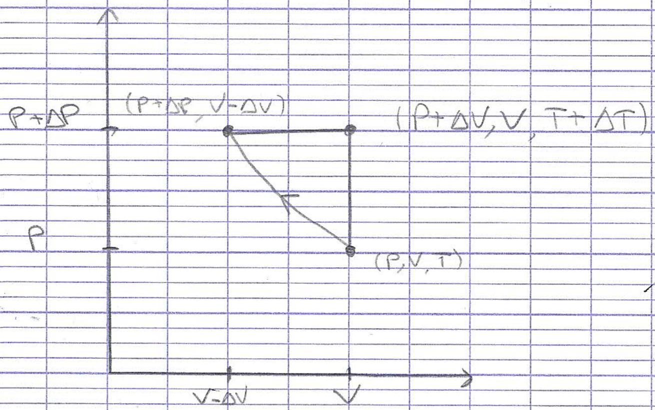
Exercice 15

(1) $\chi_T = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ $\qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

$\beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$

$PV = nRT \iff V = \frac{nRT}{P}$

$\chi_T = -\frac{1}{V}\left(-\frac{nRT}{P^2}\right) = \frac{1}{P}$



$\alpha = \frac{1}{T} \qquad \beta = \frac{1}{T}$

(2) $\boxed{\frac{\alpha}{\beta \chi_T} = P}$

(3) On applique une surpression ΔP (à T=cte donc avec des parois ~~adiabatiques~~ diathermanes) et on mesure ΔV

On chauffe le gaz avec le piston libre ($\Rightarrow P = cte$) (paroi adiabatique) ainsi le volume va augmenter

On rend les parois diathermanes, on bloque le piston

Exercice 11

$m = 0{,}01$ mol $\qquad T_0 = 250\,K$

$P_0 = 0{,}211$ Bar

$V = 8L \quad , \quad S = 0{,}05\ m^2$

(1) $P_0V_0 = nRT_0 \Rightarrow V_0 = \frac{nRT_0}{P_0} = 1L = 10^{-3}\ m^3$

(2) (a) $C_v = \frac{5}{2} nR$

(b) $C_p - C_v = Rn \qquad C_p = \frac{7}{2} nR$

(c) $\gamma = C_p/C_v = 7/5 = 1{,}4$

(d) $\frac{C_p}{C_v} - 1 = \frac{nR}{C_v} = \gamma - 1$

$C_v = \frac{nR}{\gamma - 1}$

(3) P_g , T_g , $V_g = V$

(a) $dU = \delta W + \delta Q$

$\Delta U = W_{ext} + Q_{ext}$

(b) $Q = 0$

(c) $\delta W = -P_{ext}\, dV$

P_{ext} = pression contre laquelle lutte le système

donc $P_{ext} = 0$

(d) $\Delta U = 0$

$\Delta U = C_v \Delta T$

$\Rightarrow \Delta T = 0 \Rightarrow T_g = T_0$

4) a) $\vec{F_R} = k x_g \vec{e_x}$

$\vec{F_G} = -P_g S \vec{e_x}$

b) À l'équilibre $\sum \vec{F} = \vec{0}$

$k x_g = P_g S$

$P_g = \frac{k x_g}{S}$

5) a) $W_G = -W_R$

$\Delta U = -W_R = -\frac{1}{2} k x_g^2$

b) $\Delta U = C_v \Delta T = -\frac{1}{2} k x_g^2$

c) $\frac{mR}{\gamma - 1} (T_g - T_0) = -\frac{1}{2} k x_g^2$

$T_g = T_0 - \frac{(\gamma - 1)}{2mR} k x_g^2$

6) $\gamma = 1,4407$

γ^{exp} proche de γ^{th} (à $\simeq 3\%$)

$P_g V_g = mRT_g$

$V_g = S x_g + V_0$

P_g $T_g = \frac{P_g V_g}{mR} = \frac{\frac{k x_g}{S}(V_0 + S x_g)}{mR}$

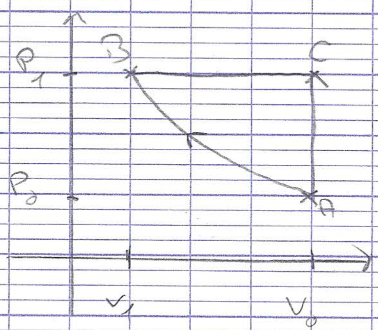
Exercice 17

(1) $n = n_1 + n_2 = \frac{P_1V_1}{RT_1} + \frac{P_2V_2}{RT_2} = 0,12$ mol

(2) $P_0 = nRT_0 / V_0 = 64450$ Pa $= 0,6445$ bar

(3) $P_1 = 2$ bar $\quad V_1 = \frac{nRT_0}{P_1} = 1,61$ L

$T_1 = T_0$



(4) $V_1 = 1,61$ L

$T_2 = 1002$ K

W_1 $(0 \to 1)$

$\delta W = -P_{ext} dV$

$= -P_{int} dV$

$= -\frac{nRT_0}{V} dV$

$W_1 = \int \delta W = nRT_0 \ln\left[\frac{V_0}{V_1}\right]$

$= 365,2$ J

W_2 $(1 \to 2)$

$\delta W = -P_{ext} dV = -P_1 dV$

$W_2 = \int dW = \int_{V_1}^{V_0} -P_1 dV$

$= -P_1 \Delta V = -678$ J

W_3 $(2 \to 0) = 0$

$\delta W = -P_{ext} dV = 0$

(6) $\Delta U = W + Q$

$\Delta U = \frac{5}{2} nR\Delta T$

- $Q_1 = -365,2$ J
- $Q_2 = 1694,3 + 678 = 2372,3$ J
- $Q_3 = -1694,3$ J

(7) $W = \Sigma_i W_i = -315,8\ J$

$Q = \Sigma Q_i = 315,8\ J$

$\Delta U = 0$ (cycle)

(8) $\gamma = C_p / C_v = 7/5$

(9) $0 \to 1'$ adiabatique

V_1' et T_1', $P_1' = P_1$

Par loi de Laplace

$PV^\gamma = c^{te}$

$P_0 V_0^\gamma = P_1 (V_1')^\gamma$

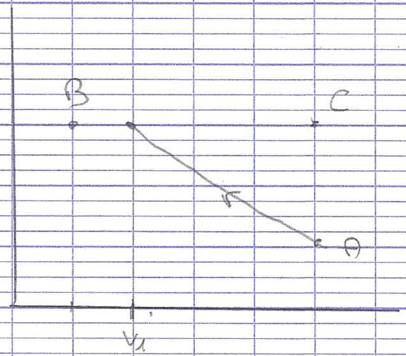
$(V_1')^\gamma = \frac{P_0}{P_1} V_0^\gamma$

$V_1' = \left(\frac{P_0}{P_1}\right)^{\frac{1}{\gamma}} V_0 = 8,83\ L$

$T_1' = \frac{P_1 V_1'}{nR} = 446,4\ K$

$c^{te} = P_0 V_0^{\gamma} = P_1 (V_1')^\gamma$

(10)



(11) W_1'

$\delta W = -P_{ext}\, dV$

$= -P_{int}\, dV$

$= \frac{nRT}{V} dV$ ⚠

$= -\frac{c^{te}}{V^\gamma} dV$

$= -c^{te} \left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V_0}^{V_1'}$

$= \frac{1}{\gamma - 1} \left[P_1 V_1' - P_0 V_0\right]$

$W = 309,3\ J$

(12) W_1' directement

$\Delta U_1 = W_1' + Q_1' = W_1$ car adiabatique

$= 5/2\, nR\, (T_1' - T_0)$

$= 307,8\ J$

(13) $W_1' = 307,8\ J$

$W_2' = \cancel{W_2} - P_1 \Delta V = -554\ J$ $\quad W_3' = 0$ $\quad W' = \cancel{-246\ J}$

Exercice 18

1) $T, V_m = \frac{V}{m}$

$$\delta P = \frac{R}{V_m - b}\, dT - \left(\frac{RT}{(V_m-b)^2} - \frac{2a}{V_m^3} \right) dV_m$$

On va montrer que $\delta P = dP$

$$\frac{\partial}{\partial V_m}\left(\frac{R}{V_m - b}\right) = \frac{\partial}{\partial T}\left(\frac{RT}{(V_m-b)^2} + \frac{2a}{V_m^3}\right)$$

$$\Leftrightarrow -\frac{R}{(V_m-b)^2} = -\frac{R}{(V_m-b)^2}$$

donc $\delta P = dP = \left(\frac{\partial P}{\partial T}\right)_{V_m} dT + \left(\frac{\partial P}{\partial V_m}\right)_T dV_m$

2)
$$\begin{cases} \dfrac{\partial P}{\partial T} = \dfrac{R}{V_m - b} & (1) \\[2ex] \dfrac{\partial P}{\partial V_m} = -\dfrac{RT}{(V_m-b)^2} + \dfrac{2a}{V_m^3} & (2) \end{cases}$$

(1) $\Leftrightarrow$ $P(T, V_m) = \frac{RT}{V_m - b} + f(V_m)$

$$\frac{\partial P}{\partial V_m} = -\frac{RT}{(V_m-b)^2} + \frac{df}{dV_m}$$

$$= -\frac{RT}{(V_m-b)^2} + \frac{2a}{V_m^3}$$

donc $\frac{df}{dV_m} = \frac{2a}{V_m^3} \Rightarrow f(V_m) = -\frac{a}{V_m^2} + cte$

$$\Rightarrow P(T, V_m) = \frac{RT}{V_m - b} - \frac{a}{V_m^2} + cte$$

Si $V_m \to \infty$ (à $T = cte$), $P \to 0 \Rightarrow c^{te} = 0$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

3) $V_m = \frac{V}{n}$

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$\Leftrightarrow \left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$ Van der Waals

4) β, χ_T, α $\qquad \frac{\alpha}{\beta \chi_T} = P$

$$\beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$$

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

- $\beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)$ $\qquad \frac{\partial P}{\partial T} = \frac{nR}{V - nb}$, $P = \frac{nRTV^2 - n^2 a (V - nb)}{V^2 (V - nb)}$

$$\Rightarrow \beta = \frac{V^2 (V - nb)}{nRTV^2 - n^2 a (V - nb)} \times \frac{nR}{V - nb}$$

$$= \frac{RV^2}{RTV^2 - na(V - nb)}$$

$$\rightarrow \frac{1}{T}$$

- $\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(-\frac{nRT}{(V - nb)^2} + \frac{2n^2 a}{V^3}\right)^{-1}$

$$= -\frac{1}{V}\left(\frac{2n^2 a (V - nb)^2 - nRTV^3}{V^3 (V - nb)^2}\right)^{-1}$$

$$= \frac{V^2 (V - nb)^2}{2n^2 a (V - nb)^2 - nRTV^3}$$

si $a = b \Rightarrow 0$

$\chi_T \rightarrow \dfrac{V^4}{mRTV^3} = \dfrac{V}{mRT} = \dfrac{1}{P}$

$\dfrac{\alpha}{\beta \chi_T} = P \Leftrightarrow \alpha = P\beta\chi_T = \dfrac{\partial P}{\partial T} \chi_T$

$= \dfrac{mR}{V-mb} \dfrac{V^2(V-mb)^2}{mRTV^3 - 2m^2a(V-mb)^2}$

$= \dfrac{RV^2(V-mb)}{RTV^3 - 2ma(V-mb)^2}$

si $a = b \rightarrow 0$

$\alpha = \dfrac{1}{T}$

5) $\cancel{d}\ U(T,V)$

$dU = \left(\dfrac{\partial U}{\partial T}\right)_V dT + \left(\dfrac{\partial U}{\partial V}\right)_T dV$

à $T = c^{te}$

$dU = \left(\dfrac{\partial U}{\partial V}\right)_T dV$

Or $dU = -pdV + TdS + \cancel{\mu dN}$

$\Leftrightarrow \left(\dfrac{\partial U}{\partial V}\right)_T d\cancel{V} = -pdV + TdS$

$\Leftrightarrow \left(\dfrac{\partial U}{\partial V}\right)_T = -p + T\dfrac{dS}{dV}$

$= -p + T\left(\dfrac{\partial S}{\partial V}\right)_T = P - p$

$dU = \left(\dfrac{\partial U}{\partial T}\right)_V dT + \cancel{\left(\dfrac{\partial U}{\partial V}\right)_T dV}$

~~à T~~

6) $F = U - TS$ (énergie libre)

$dF = d(U - TS)$

$= dU - d(TS)$

$= dU - TdS - SdT$

$= -pdV + TdS - TdS - SdT$

$= -pdV - SdT$

Théorème de Schwarz : $\frac{\partial(-p)}{\partial T} = \frac{\partial(-S)}{\partial V} = \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

$\Rightarrow \ell = T\left(\frac{\partial S}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V = T\,\frac{mR}{V - mb} = P + \frac{m^2 a}{V^2}$

$\Rightarrow \ell = p + \frac{m^2 a}{V^2}$

$\Rightarrow \ell = p + \frac{a}{V_m^2}$

7) $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

$\left(\frac{\partial U}{\partial T}\right)_V = C_V$ par déf

$\left(\frac{\partial U}{\partial V}\right)_T = \ell - p \Rightarrow dU = C_V dT + (\ell - p)\, dV$

$C_V = C_V(T)$

$dU = C_V dT + (\ell - p) dV$

Théo de Schwarz : $\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial(\ell - p)}{\partial T}\right)_V$

$\Rightarrow \frac{\partial}{\partial T}\left(\frac{m^2 a}{V^2}\right) = 0 \Rightarrow \frac{\partial C_V}{V} = 0 \Rightarrow C_V(T)$

8) $dU = C_V(T)\, dT + (\ell - p)\, dV$

$= C_V(T)\, dT + \frac{m^2 a}{V^2}\, dV$

$$\begin{cases} \frac{\partial U}{\partial T} = C_V \\ \frac{\partial U}{\partial V} = \frac{m^2 a}{V^2} \end{cases}$$

$\Rightarrow U = C_V T + g(V)$

$\frac{\partial U}{\partial V} = \frac{dg}{dV} = \frac{m^2 a}{V^2}$

$\Leftrightarrow g(V) = -\frac{m^2 a}{V} + cte$

$$U = C_v T - \frac{m^2 a}{V} + cte$$

Quand $T \to 0$ et $V \to \infty$ $E_c \to 0$ $E_p \to 0$ $\Rightarrow U \to 0$

$\Rightarrow U \to 0$

$\Rightarrow c^{te} = 0$

$$\boxed{U(T,V) = C_v T - \frac{m^2 a}{V}}$$

Exercice 19

Partie 1

1) $dW = -P_{ext}\, dV$

$\delta W = \delta W_1 + \delta W_2$

$= -P_{ext}\, dV = -P_1 dV$

$W_1 = \int_{i \to 8} -P_1\, dV = -P_1 \Delta V = -P_1 (V_8 - V_i)$

$= P_1 V_1$

$W_2 = -P_2 \Delta V = -P_2 V_2$

$W = P_1 V_1 - P_2 V_2$

2) $\Delta H = 0$

$H = U + PV$

$H_i = U_i + P_1 V_1$

$H_8 = U_8 + P_2 V_2$

$\Delta H = H_8 - H_i = U_8 - U_i + P_2 V_2 - P_1 V_1$

$= \Delta U + P_2 V_2 - P_1 V_1$

$= W + P_2 V_2 - P_1 V_1 = 0$

$Q = 0$

$H = C_p T \quad \Leftrightarrow \quad \Delta H = C_p \Delta T$

$\Delta H = 0 \Rightarrow \Delta T = 0 \Rightarrow T = cte$

$\Delta U = C_v \Delta T = 0$

$= W + Q = W = 0$

$\Leftrightarrow \quad P_1 V_1 = P_2 V_2$

3) $dH = 0$

$H = U + PV$

$dH = dU + PdV + VdP$

$= -pdV + TdS + \mu dN + PdV + VdP$

$= TdS + VdP = 0$

$\Leftrightarrow ds = -\frac{V}{T} dP$ or S est une variable d'état

donc $dS = -\frac{nR}{P} dP$

$\Delta S = nR \ln\left(\frac{P_1}{P_2}\right) > 0$

ou

$dU = -pdV + TdS$

$dS = \frac{P}{T} dV$

$= \frac{nR}{V} dV$

$S = nR \ln\left(\frac{V_2}{V_1}\right) = nR \ln\left(\frac{P_1}{P_2}\right) > 0$

Partie 2

1) $PV \simeq nRT + npb - \frac{n^2 a}{V}$

$V \simeq \frac{nRT}{P}$

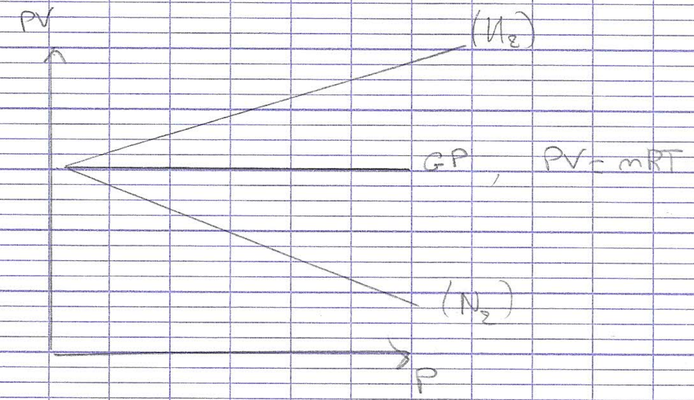
$PV = nRT + np\left(b - \frac{a}{RT}\right)$

$PV = nRT$ si $T = T_M$

$\Leftrightarrow b - \dfrac{a}{RT} = 0$

$$\boxed{T_M = \frac{a}{bR}}$$

5)



$PV = nRT + nPb - nP\dfrac{a}{RT}$

$= n\left(b - \dfrac{a}{RT}\right)P + nRT$

$T = cte$: $n\left(b - \dfrac{a}{RT}\right) = \alpha$

$PV = \alpha P + cte$

Si $T > T_M \Rightarrow T > \dfrac{a}{bR} \Leftrightarrow b > \dfrac{a}{RT} \Leftrightarrow \alpha > 0$

Si $T < T_M$, $\alpha < 0$

6) $U(T,V) = C_v T - \dfrac{n^2 a}{V}$

$H = U + PV$

$= C_v T - \dfrac{n^2 a}{V} + nRT + nP\left(b - \dfrac{a}{RT}\right)$

7) $H = C_v T + mRT - \frac{m^2 a}{V} + mPb - \frac{maP}{RT}$

$= C_v T + mRT + mPb - \frac{m^2 a}{V} - \frac{maP}{RT}$

$V \simeq \frac{mRT}{P}$

$H = C_v T + mRT + mPb - \frac{m^2 aP}{mRT} - \frac{maP}{RT}$

$= C_v T + mRT + mPb - \frac{2maP}{RT}$

8) $dH = C_v dT + mRdT$

$= \frac{\partial H}{\partial T} dT + \frac{\partial H}{\partial P} dP$

$= \left(C_v + mR + \frac{2maP}{RT^2}\right) dT + \left(mb - \frac{2ma}{RT}\right) dP$

$= (C_v + mR)\, dT + \left(mb - \frac{2ma}{RT}\right) dP$

$dH \simeq C_p dT + m\left(b - \frac{2a}{RT}\right) dP$

9) $\beta_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$

$H = cste$, $dH = 0$

$\Leftrightarrow C_p\, dT + m\left(b - \frac{2a}{RT}\right) dP = 0$

$\Leftrightarrow \frac{dT}{dP} = \frac{-m\left(b - \frac{2a}{RT}\right)}{C_p}$

10) $H = C_p T + mp\left(b - \frac{2a}{RT}\right)$

Si $H = C_p T \Leftrightarrow b - \frac{2a}{RT}$

$\Leftrightarrow \quad T = T_i = \dfrac{2a}{bR} = 2\,T_M$

11) Si $T < T_i$

$\Leftrightarrow T < \dfrac{2a}{bR} \Leftrightarrow b < \dfrac{2a}{RT}$

$b - \dfrac{2a}{RT} < 0 \Leftrightarrow \beta_{JT} > 0$

$\Leftrightarrow \cancel{\beta_{JT} = \left(\dfrac{\partial T}{\partial\right.}}$

come $\beta_{JT} = \left(\dfrac{\partial T}{\partial P}\right)$

Si $\beta > 0$ alors les variations de T et P sont de même signe. Donc T ↘ si P ↘

donc il se refroidit