

Chapitre 4

Exercice 15

$$19 \text{ g/L} \quad \checkmark$$
$$28 \text{ g/mol}$$

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

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

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

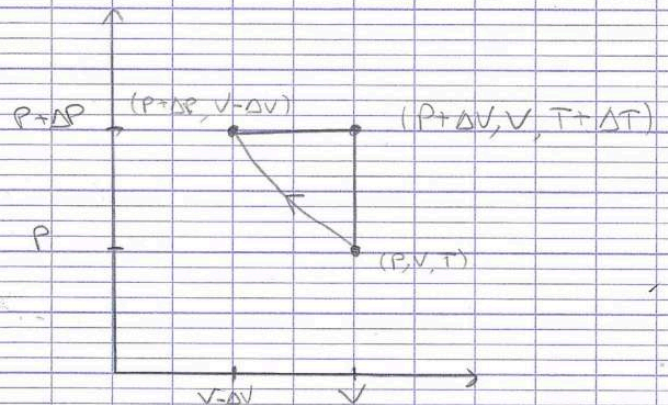
$$\beta = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_V$$

$$PV = nRT \quad \Leftrightarrow \quad V = \frac{nRT}{P}$$

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

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

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



(2) On applique une surpression ΔP (à $T = \text{cte}$ donc avec des parois ~~adiabatiques~~ diathermes) et on mesure ΔV .

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

On rend les parois diathermes, on bloque le piston.

Exercice 11

$$m = 0,01 \text{ mol}$$

$$T_0 = 250 \text{ K}$$

$$P_0 = 0,211 \text{ bar}$$

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

$$(1) P_0 V_0 = n R T_0 \Rightarrow V_0 = \frac{n R T_0}{P_0} = 1 \text{ L} = 10^{-3} \text{ m}^3$$

$$(2) (a) C_V = \frac{5}{2} n R$$

$$(b) C_P - C_V = R n$$

$$C_P = \frac{7}{2} n R$$

$$(c) \gamma = C_P / C_V = 7/5 = 1,4$$

$$(d) \frac{C_P}{C_V} - 1 = \frac{n R}{C_V} = \gamma - 1$$

$$C_V = \frac{n R}{\gamma - 1}$$

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

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

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

$$(b) Q = 0$$

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

P_{ext} = pression contre laquelle agit le système
donc $P_{\text{ext}} = 0$

$$(d) \Delta U = 0$$

$$\Delta U = C_V \Delta T$$

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

4) a)

$$\vec{F}_p = k x_g \vec{e}_x$$

$$\vec{F}_g = -P_g S \vec{e}_x$$

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

$$k x_g = P_g S$$

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

5) a)

$$W_G = -W_R$$

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

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

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

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

6)

$$\gamma = 1,409$$

γ^{exp} proche de γ^{th} ($\alpha \approx 3\%$)

$$P_g V_g = n R T_g$$

$$V_g = S x_g + V_0$$

$$P_g T_g = \frac{P_g V_g}{nR}$$

$$= \frac{\frac{k x_g}{S} (V_0 + S x_g)}{nR}$$

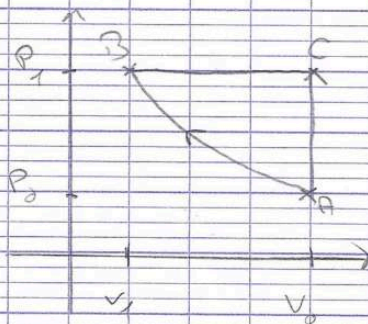
Exercice 17

$$(1) \quad n = n_1 + n_2 = \frac{P_1 V_1}{RT_1} + \frac{P_2 V_2}{RT_2} = 0,18 \text{ mol}$$

$$(2) \quad P_0 = nRT_0 / V_0 = 64450 \text{ Pa} = 0,6445 \text{ bar}$$

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

$$T_1 = T_0$$



$$(4) \quad V_1 = 1,61 \text{ L}$$

$$T_2 = 1002 \text{ K}$$

$$W_1 (0 \rightarrow 1)$$

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

$$= -P_{\text{int}} dV$$

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

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

$$= 365,2 \text{ J}$$

$$W_2 (1 \rightarrow 2)$$

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

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

$$= -P_1 \Delta V = -678 \text{ J}$$

$$W_3 (2 \rightarrow 0) = 0$$

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

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

$$\Delta U = \frac{f}{2} n R \Delta T$$

$$Q_1 = 0 - 365,2 \text{ J}$$

$$Q_2 = 1694,3 \text{ J} + 678 \text{ J} = 2372,3 \text{ J}$$

$$Q_3 = -1694,3 \text{ J}$$

$$(7) W = \sum W_i = -315,8 \text{ J}$$

$$Q = \sum Q_i = 315,8 \text{ J}$$

$$\Delta U = 0 \quad (\text{cycle})$$

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

$$(9) 0 \rightarrow 1' \quad \text{adiabatique}$$

$$V_1' \text{ et } T_1', \quad P_1' = P_1$$

Par la loi de Laplace

$$PV^\gamma = c$$

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

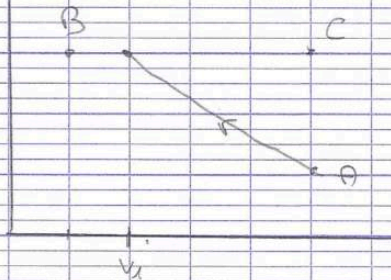
$$(V_1')^\gamma = \frac{P_0}{P_1'} V_0^\gamma$$

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

$$T_1' = \frac{P_1' V_1'}{nR} = 446,1 \text{ K}$$

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

(10)



$$(11) W_1'$$

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

$$= -P_1' dV$$

$$= -\frac{nRT}{V} dV \quad \Delta$$

$$= -\frac{c_k}{V^\gamma} dV$$

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

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

$$(12) W_1' \text{ directement}$$

$$\Delta U_1 = W_1' + Q_1' = W_1' \text{ car}$$

adiabatique

$$= \frac{5}{2} nR (T_1' - T_0)$$

$$= 303,8 \text{ J}$$

$$W = 303,8 \text{ J}$$

$$(13) W_1' = 303,8 \text{ J}$$

$$W_2' = \cancel{W_2} - P_1' \Delta V = -554 \text{ J}$$

$$W_2' = 0$$

$$W_2' = 246 \text{ J}$$

Exercice 18

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

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

On va montrer que $\delta P = dP$

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

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

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

2)

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

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

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

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

$$\text{donc } \frac{dg}{dV_m} = \frac{2a}{V_m^3} \Rightarrow g(V_m) = - \frac{a}{V_m^2} + c_1$$

$$\Rightarrow P(T, V_m) = \frac{RT}{V_m - b} - \frac{a}{V_m^2} + c_1$$

$$\text{Si } V_m \rightarrow \infty \text{ (à } T = c_1 \text{)}, P \rightarrow 0 \Rightarrow c_1 = 0$$

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

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

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

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

$$4) \quad \beta, \chi_T, \alpha$$

$$\beta \frac{\alpha}{\chi_T} = P$$

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

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

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

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

$$\frac{\partial P}{\partial T} = \frac{nR}{V - nb}, \quad P = \frac{nRTV^2 - n^2 a (V - nb)}{V^2 (V - nb)}$$

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

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

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

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

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

$$21' \quad a = b \Rightarrow 0$$

$$\beta_T \rightarrow \frac{V^2}{mRTV^3} = \frac{V}{mRT} = \frac{1}{P}$$

$$\beta \frac{\alpha}{\beta_T} = P \Rightarrow \alpha = P \beta_T = \frac{\partial P}{\partial T} \beta_T$$

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

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

$$21' \quad a = b \Rightarrow 0$$

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

5)

$U(T, V)$

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

$$2 \quad T = \text{cte}$$

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

$$\text{CA} \quad dU = -pdV + TdS + \cancel{pdW}$$

$$\Rightarrow \left(\frac{\partial U}{\partial V} \right)_T dV = -pdV + TdS$$

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

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

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

$$2 \quad T$$

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

$$\Rightarrow P = T \left(\frac{\partial S}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V = T \frac{nR}{V-nb} = P + \frac{n^2 a}{V^2}$$

7) $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \Rightarrow P = P + \frac{n^2 a}{V^2}$

$$\left[\left(\frac{\partial U}{\partial T}\right)_V = C_V \text{ par def} \Rightarrow P = P + \frac{a}{V^2}\right]$$

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

$$C_V = C_V(T)$$

$$dU = C_V dT + (P - P) dV$$

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

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

8) $dU = C_V(T) dT + (P - P) dV$
 $= C_V(T) dT + \frac{n^2 a}{V^2} dV$

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

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

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

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

$$U = C_V T + \frac{m^2 c^2}{V} + \text{cte}$$

Quand $T \rightarrow 0$ et $V \rightarrow \infty$

$$\begin{aligned} E_c &\rightarrow 0 \\ E_p &\rightarrow 0 \end{aligned} \Rightarrow U \rightarrow 0$$

$$\Rightarrow U \rightarrow 0$$

$$\Rightarrow C^{\text{re}} = 0$$

$$U(T, V) = C_V T + \frac{m^2 c^2}{V}$$

Exercice 19

Partie 1

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

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

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

$$W_1 = \int_{i \rightarrow g} -P_1 dV = -P_1 \Delta V = -P_1 (V_g - V_i)$$

$$= P_1 V_1$$

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

$$W = P_1 V_1 - P_2 V_2$$

2) $\Delta H = 0$

$$H = U + PV$$

$$H_i = U_i + P_1 V_1$$

$$H_g = U_g + P_2 V_2$$

$$\Delta H = H_g - H_i = U_g - U_i + P_2 V_2 - P_1 V_1$$

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

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

$Q = 0$

$$H = C_p T \Rightarrow \Delta H = C_p \Delta T$$

$$\Delta H = 0 \Rightarrow \Delta T = 0 \Rightarrow T = \text{cte}$$

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

$$= W + Q = W = 0$$

$$\Rightarrow P_1 V_1 = P_2 V_2$$

$$3) \quad dH = 0$$

$$H = U + PV$$

$$dH = dU + P dV + V dP$$

$$= -p dV + T dS + \mu dN + P dV + V dP$$

$$= T dS + V dP = 0$$

$$\Rightarrow dS = -\frac{V}{T} dP$$

or S est une variable d'état

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

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

ou

$$dU = -p dV + T dS$$

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

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

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

Partie 2

$$1) \quad PV \approx nRT + n_p b - \frac{n^2 a}{V}$$

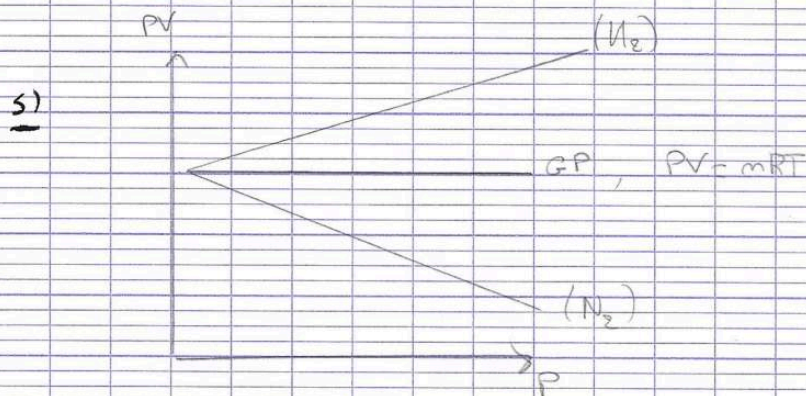
$$V \approx \frac{nRT}{P}$$

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

$$PV = nRT \quad \text{si } T = T_m$$

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

$$T_m = \frac{a}{bR}$$



$$PV = nRT + nPb - n^2P \frac{a}{RT}$$

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

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

$$PV = \alpha P + nRT$$

$$\text{Si } T > T_m \Rightarrow T > \frac{a}{bR} \Leftrightarrow b > \frac{a}{RT} \Leftrightarrow \alpha > 0$$

$$\text{Si } T < T_m, \alpha < 0$$

$$6) \quad U(T, V) = C_V T - \frac{n^2 a}{V}$$

$$H = U + PV$$

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

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

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

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

$$H = C_V T + mRT + mPb - \frac{m^2 a P}{mRT} - \frac{maP}{RT}$$

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

$$8) dH = C_V dT + mRdT$$

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

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

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

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

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

$$H = \text{const} \quad , \quad dH = 0$$

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

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

$$1a) H = C_P T + mp \left(b - \frac{2a}{RT} \right)$$

$$S: H = C_P T \quad \Leftrightarrow \quad b - \frac{2a}{RT} = 0$$

$$\Leftrightarrow T = T_i = \frac{2a}{bR} = 2 T_m$$

11) Si $T < T_i$

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

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

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

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

Si $\beta > 0$ alors les variations de T et P sont de même signe. Donc $T \nearrow$ si $P \nearrow$
donc P se refroidit