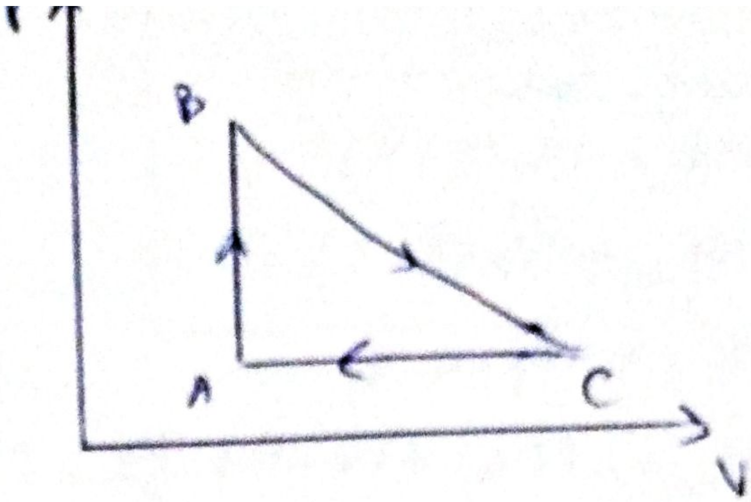
Exercice 1 :



1) $W, \Delta U, Q, \Delta H$ et ΔS

* $A \to B$: Isochore

$W = -\int P\,dV$

$\boxed{W = 0}$

$\Delta U = Q + \cancel{W}^{0} \Rightarrow \Delta U = Q = n C_v \Delta T = n C_v (T_B - T_A)$

$\boxed{\Delta U_{A\to B} = Q_{A\to B} = n C_v (T_B - T_A)}$

$\Delta H = n C_p \Delta T = n C_p (T_B - T_A)$

$\boxed{\Delta H_{A\to B} = n C_p (T_B - T_A)}$

$\boxed{\Delta S_{A\to B} = \int_{T_A}^{T_B} \frac{\delta Q}{T} = \int_{T_A}^{T_B} \frac{n C_v\, dT}{T} = n C_v \ln \frac{T_B}{T_A}}$

* $B \to C$: Isotherme

A $T = \text{cste}$, $\boxed{\Delta U = 0 \quad \text{et} \quad \Delta H = 0}$

$\Rightarrow \Delta U = Q + W = 0 \Rightarrow Q = -W$

$W = -\int_{V_B}^{V_C} P\,dV = -\int_{V_B}^{V_C} \frac{nRT}{V}\,dV = -nRT \ln \frac{V_C}{V_B}$

$\boxed{W_{B\to C} = -nRT \ln \frac{P_B}{P_C}}$

$\boxed{Q_{B\to C} = nRT \ln \frac{P_B}{P_C}}$

$\Delta S = \int_B^C \frac{\delta Q}{T} = \frac{1}{T} \int_{V_B} P\,dV = \frac{1}{T} \int_{V_B}^{V} \frac{nRT}{V}\,dV = nR \int_{V_B}^{V_C} \frac{dV}{V} \Rightarrow$

$\boxed{\Delta S_{B\to C} = nR \ln \frac{V_C}{V_B} = nR \ln \frac{P_B}{P_C}}$

* $C \to A$: Isobare

$$\Delta U_{C\to A} = nC_V (T_A - T_C)$$

$$\Delta H_{C\to A} = nC_p (T_A - T_C)$$

$$Q_{C\to A} = nC_p (T_A - T_C)$$

$$W_{C\to A} = -P(V_A - V_C) = -P\left(\frac{nRT_A}{P} - \frac{nRT_C}{P}\right) \Rightarrow \boxed{W_{C\to A} = -nR(T_A - T_C)}$$

$$\Delta S_{C\to A} = \int \frac{\delta Q}{T} = \int_{T_C}^{T_A} \frac{nC_p\, dT}{T} = nC_p \ln\frac{T_A}{T_C} \Rightarrow \boxed{\Delta S_{C\to A} = nC_p \ln\frac{T_A}{T_C}}$$

2) On a $C_p - C_V = R$ et $T_B = T_C = T$

$$Q_{cycle} = nC_V (T_B - T_A) + nC_p (T_A - T_C) + nRT \ln\frac{P_B}{P_C} \Rightarrow$$

$$Q_{cycle} = nR(T_A - T_C) + nRT \ln\frac{P_B}{P_C}$$

$$W_{cycle} = -nR(T_A - T_C) - nRT\ln\frac{P_B}{P_C}$$

$\Rightarrow \boxed{W_{cycle} = -Q_{cycle}}$ Principe d'équivalence vérifié

$$\Delta U_{cycle} = nC_V(T_A - T_C) + 0 + nC_V(T_B - T_A) \qquad (\text{Avec } T_B = T_C)$$

$$\Rightarrow \boxed{\Delta U_{cycle} = 0}$$

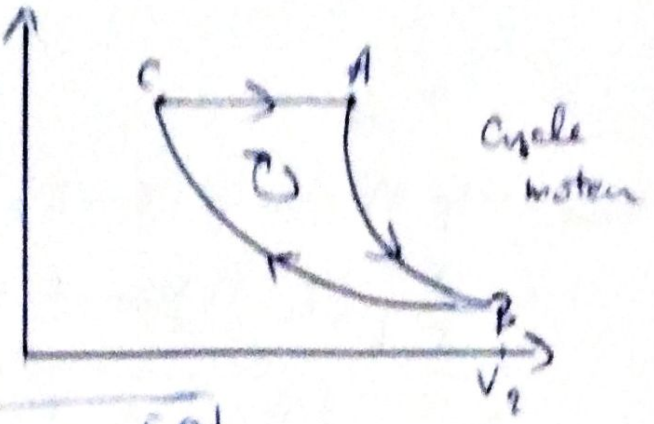
$$\Delta H_{cycle} = nC_p (T_B - T_A) + nC_p (T_A - T_C) \Rightarrow \boxed{\Delta H = 0}$$

$$\Delta S_{cycle} = nC_V \ln\frac{T_B}{T_A} + nR\ln\frac{P_B}{P_C} + nC_p \ln\frac{T_A}{T_C} \qquad \left(\begin{array}{l}\text{avec } T_C = T_B \\ \text{et } C_p - C_V = R\end{array}\right)$$

$$\Delta S_{cycle} = nC_V \ln\frac{T_B}{T_A} + nR\ln\frac{P_B}{P_C} - nC_p \ln\frac{T_B}{T_A}$$

$$\boxed{\Delta S_{cycle} = -nR\ln\frac{T_B}{T_A} + nR\ln\frac{P_B}{P_C}}$$

Exercice 2 :



1) Calcul de P_1 et T_2 :

$P_1 = P_A$

$P_1 V_1 = nRT_1 \Rightarrow$

$$\boxed{P_1 = \frac{nRT_1}{V_1} = \frac{1 \cdot 8{,}31 \cdot 423}{1 \cdot 10^{3}} = 35{,}15 \cdot 10^5 \text{ Pa}}$$

$T_2 = ?$

$TV^{\gamma-1} = \text{cte}$

$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$$\boxed{T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1} \Rightarrow T_2 = 423 \left(\frac{1}{10}\right)^{1{,}33-1} = 423 \cdot (0{,}1)^{0{,}33} = 197{,}85 \text{ K}}$$

3) Q :

- $A \to B$: adiabatique $Q_{A\to B} = 0$
- $B \to C$: isotherme $\Delta U = Q + W = 0 \Rightarrow Q = -W = \int_{V_B}^{V_C} P\,dV$

$\Rightarrow Q_{B\to C} = nRT_2 \ln \frac{P_2}{P_3} = nRT_2 \ln \frac{V_3}{V_2}$

$(P_C = P_A)$

$Q_{B\to C} = nRT_2 \ln \frac{P_2}{P_1}$

On a aussi : $A \to B$ $\quad \frac{P_A}{P_B} = \left(\frac{V_2}{V_1}\right)^{\gamma} \Rightarrow \frac{P_B}{P_A} = \left(\frac{V_1}{V_2}\right)^{\gamma}$

$\Rightarrow Q_{B\to C} = nRT_2 \ln \left(\frac{V_1}{V_2}\right)^{\gamma} = n\gamma RT_2 \ln \frac{V_1}{V_2}$

$$\boxed{Q_{B\to C} = 1 \cdot 1{,}33 \cdot 8{,}31 \cdot 197{,}85 \ln 0{,}1 = -5035{,}057 \text{ J}}$$

• $C \to A$: $P = cst$

$$Q_{CA} = n C_p \Delta T = n C_p (T_A - T_C) = n C_p (T_1 - T_2)$$

$$= \frac{n \gamma R}{\gamma - 1}(T_1 - T_2) = \frac{1 \cdot 1{,}33 \cdot 8{,}31}{1{,}33 - 1}(423 - 197{,}85)$$

$$\Rightarrow \boxed{Q_{CA} = 7540{,}68 \ J}$$

Pour le cycle : $\Delta U = 0 \Rightarrow Q_{cycle} = - W_{cycle}$

$$Q_{cycle} = Q_{AB} + Q_{BC} + Q_{CA} = 0 - 5035{,}057 + 7540{,}68$$

$$= 2505{,}623 \ J$$

$$\boxed{Q_{cycle} = 2505{,}623 \ J} \qquad \boxed{W_{cycle} = -2505{,}623 \ J}$$

$W_{cycle} < 0 \Rightarrow$ Cycle moteur.

5) Rendement :

$$\rho = \frac{|W_{cycle}|}{Q_{reçue}} \cdot 100 = \frac{-W_{cycle}}{Q_{reçue}} \cdot 100 \Rightarrow$$

$$\rho = \frac{2505{,}623}{7540{,}68} \cdot 100 = 33{,}22 \%$$

$$\boxed{\rho = 33{,}22 \%}$$

Exercice 3 :

1) $A \rightarrow B$ $V = cst$.

$W = 0$.

$Q_{A-B} = n c_v (T_B - T_A)$ $Q_{A-B} > 0$

$Q_{A-B} = \frac{nR}{\gamma - 1}(T_B - T_A)$.

2) $W_{cycle} = \cancel{W_{A-B}}^{0} + W_{B-C} + \cancel{W_{C-D}}^{0} + W_{D-A}$

$\Rightarrow W_{cycle} = W_{B-C} + W_{D-A}$

$B - C$. $Q = 0$. $\Rightarrow W = \Delta U = n c_v \Delta T$

$W_{B-C} = n c_v (T_C - T_B)$.

$D - A$ $Q = 0$ $\rightarrow W = \Delta U = n c_v \Delta T$.

$W_{D-A} = n c_v (T_A - T_D)$.

$W_{cycle} = n c_v (T_C - T_B) + n c_v (T_A - T_D)$.

$W_{cycle} = n c_v (T_C - T_B + T_A - T_D) = -(Q_{ch} + Q_f) < 0$

3) le rendement du cycle.

$$\rho = -\frac{W_{cycle}}{Q_{reç}} = \frac{-W_{cycle}}{Q_{ch}} = \frac{Q_{ch} + Q_{fr}}{Q_{ch}}$$

$$\boxed{\rho = 1 + \frac{Q_{fr}}{Q_{ch}}}$$

$$\rho = 1 - \frac{n C_V (T_D - T_C)}{n C_V (T_B - T_A)} = 1 - \frac{T_D - T_C}{T_B - T_A}$$ en fct de T

• en fonction de a et γ.

On a. $T_D = T_A \left(\frac{V_A}{V_D}\right)^{\gamma - 1}$ — (1)

$T_B = T_C \left(\frac{V_C}{V_B}\right)^{\gamma - 1}$ — (2)

$$\boxed{\frac{V_D}{V_A} = \frac{V_C}{V_B}}$$

$$\frac{(2)}{(1)} \Longrightarrow \frac{T_B}{T_A} = \frac{T_C}{T_D}$$

$$\Rightarrow \rho = 1 - \frac{T_D}{T_A} \left(\frac{1 - \frac{T_C}{T_D}}{\frac{T_B}{T_A} - 1} \right)$$

$$\Rightarrow \boxed{\rho = 1 - \frac{T_D}{T_A}}$$

$$(1) \rightarrow \frac{T_D}{T_A} = \left(\frac{V_A}{V_D}\right)^{\gamma - 1} = \left(\frac{1}{a}\right)^{\gamma - 1}$$

$$\Rightarrow \rho = 1 - a^{1-\gamma} = 1 - 9^{1 - 1,4}$$

$$\boxed{\rho = 0,58 = 58\%}$$

Calcul de l'entropie :

$B - C$ et $D - A$, $\Delta S = \int \frac{\cancel{\delta Q}^{0}}{T} = 0$,

$A - B$ $V = cst$,

$\Rightarrow \Delta S = n c_v \ln \frac{T_B}{T_A}$

$C - D$

$\Delta S = n . C_v \ln \frac{T_D}{T_C}$

$\Delta S_{cycle} = \Delta S_{A-B} + \Delta S_{B-C} + \Delta S_{C-D} + \Delta S_{D-A}$

$\Delta S_{cycle} = n c_v \ln \frac{T_B}{T_A} + n c_V \ln \frac{T_D}{T_C}$

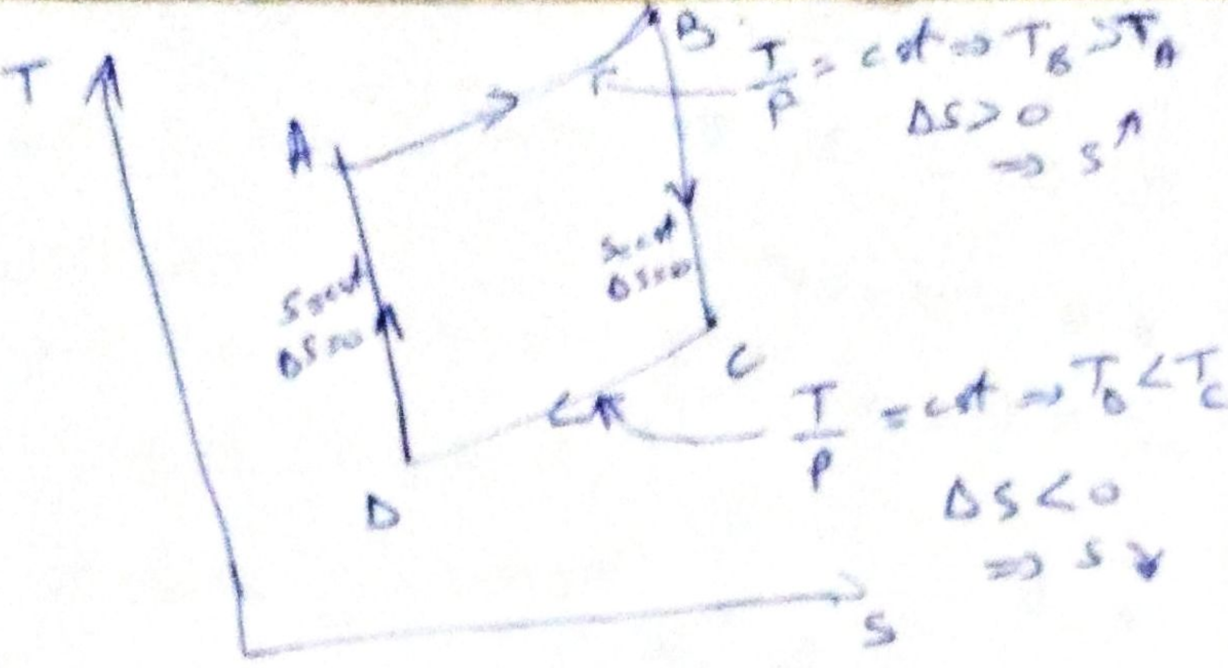
$\Delta S_{cycle} = n c_V \ln \frac{\cancel{T_B} T_D}{\cancel{T_A} \cancel{T_C}}$ $\quad \frac{T_B}{T_A} = \frac{T_C}{T_D}$

$\Rightarrow \Delta S_{cycle} = n c_V \ln 1 = 0 \, J . K^{-1}$

diagramme TS .

Transformation AB et DC . $\Leftrightarrow$ $V = cst$.

$\frac{T}{P} = cst \Rightarrow P^{\nearrow} T^{\nearrow}$


T
S
A
B
C
D
S = cst
ΔS = 0
S = cst
ΔS = 0
$\frac{T}{P} = cst \Rightarrow T_B > T_A$
ΔS > 0
⇒ S ↑
$\frac{T}{P} = cst \Rightarrow T_D < T_C$
ΔS < 0
⇒ S ↓

Exercice 4 :

$m = 100\,g$ de Al , $T_1 = 10°C$, $T_2 = 20°C$

1) $\Delta S_{sys} = \Delta S_{créée} + \Delta S_{éch}$

ΔS est fonction d'état $\Rightarrow \Delta S_{irr} = \Delta S_{rev}$

$$\Delta S_{sys} = \int \frac{\delta Q}{T} = \int_{T_i}^{T_f} \frac{m C_p\, dT}{T} = m C_p \ln \frac{T_f}{T_i}$$

$$\Delta S_{sys} = 100.10^{-3}.896 \ln \frac{293}{283} = 3{,}11\ J.K^{-1}$$

2) $\Delta S_{air} = \int \frac{\delta Q}{T} = \frac{1}{T} \int \delta Q = \frac{Q_{air}}{T_2}$, $Q_{air} = -Q_{Al}$

$T_f = T_2 = T_{air}$

$$\Rightarrow \Delta S_{air} = \frac{-Q_{Al}}{T_{air}} = -m\, C_{Al} (T_f - T_i)$$

$$\Rightarrow \Delta S_{air} = -\frac{100.10^{-3}.896\,(293-283)}{293} = -3{,}06\ J.K^{-1}$$

3) $\Delta S_{Al+air} = \Delta S_{Al} + \Delta S_{air} = 3{,}11 - 3{,}06 = 0{,}05\ J.K^{-1}$

$\Delta S > 0$ Augmentation d'entropie pour un système isolé

$\Delta S_{éch} = 0$ pour un système isolé

$$\Delta S_{créée} \geq 0 : \begin{cases} \Delta S > 0 & irr \\ \Delta S = 0 & rev \end{cases}$$

L'augmentation de l'entropie de l'univers est conforme au second principe :

$\Delta S_{sys\ isolé\ et\ irr} > 0$

Exercice 5 :

1) La différentielle de U : dU

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

2) L'expression de dS :

$$dQ = dU - \delta W \quad \text{et} \quad \delta W = P\,dV = -\frac{nRT}{V}\,dV$$

$$dS = \frac{\delta Q}{T} = \frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right) + \frac{nRT}{TV}\,dV$$

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + \frac{nR}{V}\,dV$$

$$= \frac{1}{T}\left(\frac{\partial U}{\partial T}\right) dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + \frac{nR}{V}\right] dV \,. \qquad \left(\frac{nR}{V} = \frac{P}{T}\right)$$

3) $\Delta F \geq W$

on a $F = U - TS$

$\Delta U = Q + W$

$\Delta S \geq \frac{Q}{T}$ inégalité de Clausius second principe.

$$\Delta F = \Delta U - T\Delta S = Q + W - T\Delta S$$

On a $\Delta S \geq \frac{Q}{T} \Rightarrow T\Delta S \geq Q$

$\Delta F = Q + W - T\Delta S \Rightarrow$

$Q = \Delta F - W + \cancel{T\Delta S} \leq \cancel{T\Delta S}$

$\Delta F - W \leq 0 \Rightarrow \boxed{\Delta F \leq W}$

4) $dU = n\,C_v\,dT$, $\boxed{U = nC_vT}$

$C_v = \alpha R$

$$dS = \frac{\delta Q}{T} = \frac{\delta U - \delta W}{T} = \frac{nC_v\,dT - P\,dV}{T}$$

$$\Delta S = S - S_0 = \int \frac{nC_v}{T}\,dT - \int \frac{P}{T}\,dV \qquad \left(\text{avec } \frac{P}{T} = \frac{nR}{V}\right)$$

$$\Rightarrow \boxed{S = nC_v \ln T - nR \ln V + S_0}$$

- Pression P : $PV = nRT \Rightarrow P = \frac{nRT}{V}$

- F :

$F = U - TS \Rightarrow U = nC_v T$

$dF = dU - TdS - SdT \Rightarrow dF = TdS - PdV - TdS - SdT$

$dF = -PdV - SdT$

$\Rightarrow S = \left(-\frac{\partial F}{\partial T}\right)_V$

$P = \left(-\frac{\partial F}{\partial V}\right)_T = \frac{nRT}{V}$

Exercice 6 :

1) $\left(\frac{\partial G}{\partial P}\right)_{T,n} = V = \frac{nRT}{P}$

Après intégration, $G(P,T,n) = \overset{\circ}{G}(\overset{\circ}{P},T,n) + nRT \ln \frac{P}{P_0}$

$\mu = \frac{G}{n}$

$\Rightarrow \mu(P,T) = \mu(\overset{\circ}{P},T) + RT \ln \frac{P}{P^\circ}$ (gaz parfait)

Cas de mélange

$\mu_i = \mu_i^\circ + RT \ln \frac{P_i}{P^\circ}$ (gaz parfait)

$\mu_i = \mu_i^\circ + RT \ln \frac{x_i P}{P^\circ}$

2) Pour un gaz réel

$\mu = \mu^\circ + RT \ln \frac{f}{f^\circ}$ $\qquad f^\circ \rightarrow P^\circ$

$\mu_i = \mu_i^\circ + RT \ln \frac{f_i}{f^\circ}$

3) Pour un gaz réel, $a = 0$

$\Rightarrow P(V_m - b) = RT$

$\Rightarrow V_m = \frac{RT}{P} + b$

$\Rightarrow \left(\frac{\partial G}{\partial P}\right)_{T,n} = V$

$d\mu = \int V dP = \int \left(\frac{RT}{P} + b\right) dP$

$\mu = \mu^\circ + b(P - P^\circ) + RT \ln \frac{P}{P^\circ}$ (Van der waals

La fonction est donc :

$\mu = \mu^\circ + RT \ln \frac{f}{P^\circ}$ (général)

$\Rightarrow \ln \frac{f}{P^\circ} = \frac{\mu - \mu^\circ}{RT} = \frac{b}{RT}(P - P^\circ) + \ln \frac{P}{P^\circ}$

$\Rightarrow \quad f = P_{ext}\left[\frac{b}{RT}(P - P^{\circ})\right]$

4) $\Delta\Gamma = RT \ln \frac{P_i}{P^{\circ}} = 8{,}31 \cdot 303 \cdot \ln \frac{32}{252}$

$$\boxed{\Delta\Gamma = -2537{,}16 \text{ J mol}^{-1}}$$

5) . Eau liquide :

$\Delta\Gamma = \int_{P_1}^{P_2} V_m \, dP = V_m (P_2 - P_1)$

$\Delta\Gamma = 18 \cdot 10^{-6} (10^6 - 10^5) = 16{,}2 \text{ J mol}^{-1}$

. Eau gaz :

$\Delta\Gamma = \int_{P_1}^{P_2} V_m^2 \, dP = \int_{P_1}^{P_2} \frac{RT}{P} dP = RT \ln \frac{P_2}{P_1}$

$\Delta\Gamma = 8{,}31 \cdot 298 \ln 10 = 5707 \text{ J mol}^{-1}$

L'eau est une phase condensée, elle est peu compressible, donc la variation de son potentiel chimique est faible comparée à celle du gaz.

Exercice 7 :

I - 1) $\mu = \mu^0 + RT \ln \frac{P}{P^0}$

2) $\mu_i = \mu_i^0 + RT \ln \frac{x_i P}{P^0}$

3) $\left(\frac{\partial G}{\partial T}\right)_{P,n} \Leftrightarrow \left(\frac{\partial \mu}{\partial T}\right)_P = -S_m$

Relation de Gibbs

$\sum n_i d\mu_i = 0 \Rightarrow n_A d\mu_A + n_B d\mu_B = 0$

$G = \sum n_i \mu_i$

$dG = \sum n_i d\mu_i + \sum \mu_i dn_i \ \cdots (1)$

On a $dG = VdP - SdT + \sum \mu_i dn_i - (2)$

$(1) = (2)$

$\sum n_i d\mu_i + \cancel{\sum \mu_i dn_i} = VdP - SdT + \cancel{\sum \mu_i dn_i}$

$\Rightarrow \sum n_i d\mu_i = VdP - SdT$, à T et P = cst $\Rightarrow$

$\sum n_i d\mu_i = 0 \Rightarrow d\mu_B = \frac{-n_A}{n_B} d\mu_A$

II - T = 300K , CO et CO_2 dans un balon

1 - μ de chaque gaz

$\mu_i = \mu_i^0 + RT \ln \frac{P_i}{P^0} = \underline{\mu_i + RT \ln \frac{P}{P^0} + RT \ln x_i}$

$PV = nRT \Rightarrow P_{CO} = \frac{n_{CO} RT}{V_{tot}} = \frac{10^{-2} * 8,31 \cdot 300}{1 \cdot 10^{-3}} = 24930 \, Pa$

$P_{CO} = 0,249 \, atm$

$\mu_{CO} = -169 \cdot 10^{3} + \left[8,31 \times 300 \ln \frac{0,246}{1}\right] = -1,7249 \cdot 10^5 \, J\,mol^{-1}$

$$\Gamma_{CO_2} = \Gamma^{\circ}_{CO_2} + RT \ln \frac{P_{CO_2}}{P_0}$$

$$\begin{cases} P_{CO_2} = \frac{RT}{V_{tot}} \cdot n_{CO_2} \\ = 0{,}738 \text{ atm} \end{cases}$$

$$= -458 \cdot 10^3 + 8{,}31 \cdot 300 \ln \frac{0{,}738}{1}$$

$$\Rightarrow \Gamma_{CO_2} = -4{,}587 \cdot 10^5 \text{ J mol}^{-1}$$

Calcul de G :

$$G = \sum n_i \Gamma_i = n_{CO}\Gamma_{CO} + n_{CO_2}\Gamma_{CO_2}$$

$$= 10^{-2}(-1{,}7249 \cdot 10^5) + 3 \cdot 10^{-2}(-4{,}587 \cdot 10^5) = \boxed{-15486 \text{ J}}$$

Exercice 8:

1) $\Delta\Gamma = \Gamma_{gR} - \Gamma_{gP} = RT \ln \phi = RT \ln \frac{f}{P} = -960 \ J\ mol^{-1}$

$f = 2,83 . 10^5 \ Pa$, $P = 4 \ atm = 4 . 10^5 \ Pa$

$\Delta\Gamma = RT \ln \frac{f}{P} \Rightarrow \boxed{T = \frac{\Delta\Gamma}{R \ln \frac{f}{P}}} = \frac{-960}{8,31 \ln \frac{(2,83 . 10^5)}{(4 . 10^5)}} = \boxed{333,81 K}$

2) $\Delta\Gamma = \Gamma_{gR} - \Gamma_{gP} = RT \ln \phi = 8,31 . 200 \ln 0,72 = \boxed{-545,97 \ J\ mol^{-1}}$

3) $\Delta\Gamma = \Gamma_{gR} - \Gamma_{gP} = RT \ln \phi = RT \int (Z-1) \frac{dP}{P}$

$\Delta\Gamma = \int \left(1 + \left(\frac{B}{RT}\right) - 1\right) \frac{dP}{P}$

$\ln \phi = \int \frac{B}{RT} dP = \frac{B}{RT} [P_a - P^{\circ}] = \frac{-261 . 10^{-6}}{8,31 . 300} (50 - 1) . 10^5$

$\ln \phi = -0,51 \Rightarrow \boxed{\phi = e^{-0,51} = 0,59}$

calcul de f : $\phi = \frac{f}{P} \Rightarrow f = \phi P$

$\boxed{f = 0,59 . 50 = 29,5 \ bars}$

4)

a. $\Gamma - \Gamma^{\circ} = b(P - P^{\circ}) + RT \ln \frac{P}{P^{\circ}}$ (voir questi-3 exo6)

On a : $\Gamma - \Gamma^{\circ} = RT \ln \frac{f}{P^{\circ}}$

$RT \ln \frac{f}{P^{\circ}} = b(P - P^{\circ}) + RT \ln \frac{P}{P_o} \Rightarrow$

$RT \ln \frac{f}{P} = \frac{b(P - P^{\circ})}{RT} \Rightarrow f = P \exp\left(\frac{b(P-P^{\circ})}{RT}\right) \Rightarrow$

$\phi = \exp\left(\frac{b(P-P^{\circ})}{RT}\right)$

P	1	5	50	1000
ϕ	1	1,00497	1,0627	3,46
f	1	5,02	53,1	3460

Conclusion :

A basse pression $\phi \simeq 1 \Rightarrow$ le GR $\rightarrow$ GP

A forte pression $\phi \nearrow \Rightarrow$ Ecart aux GP