$\boxed{1}$ En un sistema aïllat $\Delta S \geq 0$

En un sistema a S, V ct. $\Delta U \leq 0$

$\boxed{2}$ $d'Q$ no és una diferencial exacta, de manera que no és esperable el compliment de la condició de Schwarz de derivades segones.

De fet c_V és constant (o funció de T exclusivament) $\rightarrow \left(\frac{\partial c_V}{\partial V}\right)_T = 0$ mentre que

$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \neq 0$

$\boxed{3}$ $dH = T\left(\frac{\partial S}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial V}\right)_P dV + VdP \rightarrow \left(\frac{\partial H}{\partial V}\right)_P = T\left(\frac{\partial S}{\partial V}\right)_P = \underbrace{T\left(\frac{\partial S}{\partial T}\right)_P}_{c_P}\left(\frac{\partial T}{\partial V}\right)_P = c_P \frac{P}{R}$

alternativament

$dH = \underbrace{\left(\frac{\partial H}{\partial T}\right)_P}_{c_P} dT + \underbrace{\left(\frac{\partial H}{\partial P}\right)_T}_{0\,(GI)} dP = c_P \left(\frac{\partial T}{\partial P}\right)_V dP + c_P\left(\frac{\partial T}{\partial V}\right)_P dV \rightarrow \left(\frac{\partial H}{\partial V}\right)_P = c_P\left(\frac{\partial T}{\partial V}\right)_P = c_P \frac{P}{R}$

$\boxed{4}$ $G = ng \rightarrow G_2 - G_1 = \Delta G = n(g_2 - g_1)$; $g = g^\circ(T) + RT \ln f$ per el cas de gas real

$\rightarrow \Delta G = n\, RT \ln f_2/f_1$

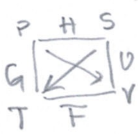
$\boxed{5}$ $g = g^\circ(T) + RT \ln P + RT \ln \gamma \rightarrow \ln \gamma = \frac{A+BP}{RT}$, però $\ln \gamma = \int_0^P \frac{(z-1)}{P} dP$

$\rightarrow \frac{\partial}{\partial P}\left(\frac{A+BP}{RT}\right) = \frac{z-1}{P} \Rightarrow \frac{B}{RT} = \frac{z-1}{P} \rightarrow z = 1 + \frac{BP}{RT}$

Alternativament: $dg = s\,dT + v\,dP \rightarrow v = \left(\frac{\partial g}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(g^\circ(T) + RT \ln P + A + BP\right)\Big|_T =$

$\rightarrow v = \frac{RT}{P} + B$; $z = \frac{v}{v_{id}} = \frac{\frac{RT}{P} + B}{\frac{RT}{P}} = 1 + \frac{BP}{RT}$

$\boxed{6}$ $dU = TdS - PdV = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV - PdV \rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$



$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \rightarrow \left(\frac{\partial U}{\partial V}\right)_T + P = T\left(\frac{\partial P}{\partial T}\right)_V$; GI : $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} = \frac{P}{T}$

$\rightarrow \left(\frac{\partial U}{\partial V}\right)_T + \cancel{P} = \cancel{P} \rightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0$

$\boxed{7}$ a) $V = \sum_i n_i \frac{RT}{P} = n\frac{RT}{P} \rightarrow \left(\frac{\partial V}{\partial n_i}\right)_{TPn_j} = \frac{RT}{P}$; $\left(\frac{\partial V}{\partial n}\right)_{PT} = \frac{RT}{P}$

b) $G = \sum \mu_i n_i$; $dG_{PT} = \sum \mu_i dn_i$ perquè $\left(\sum n_i\, d\mu_i\right)_{PT} = 0$, eq Gibbs-Duhem

$\Rightarrow \left(\frac{\partial G}{\partial n_i}\right)_{TPn_j} = \mu_i$; però en $\left(\frac{\partial G}{\partial n}\right)_{TP}$ hi ha moltes formes d'afegir o eliminar dn.

Per exemple, mantenint la composició constant i.e. $dx_i = 0\ \forall i \Rightarrow dn_i = x_i\, dn$

En tal cas, $dG_{PT} = \left(\sum \mu_i x_i\right) dn \rightarrow \left(\frac{\partial G}{\partial n}\right)_{PTx} = \sum \mu_i x_i \neq \mu_i$

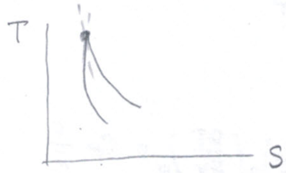
En general doncs no podem identificar entalpia lliure molar amb molar parcial

$\boxed{8}$

$$\left.\begin{array}{l} dG = -SdT + VdP \\ dF = -SdT - PdV \end{array}\right| \xrightarrow{T\,ct} \begin{array}{l} dG_T = VdP \\ dF_T = -PdV \end{array} \; ; \quad GI: \text{ si } T = ct \quad d(PV) = PdV + VdP = 0$$

$$\rightarrow PdV = -VdP \rightarrow dG_T = dF_T$$

$\boxed{9}$



$$\left.\begin{array}{l} \left(\frac{\partial T}{\partial S}\right)_P \Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{T\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{d'Q}{dT}\right)_P = \frac{C_P}{T} \\ \left(\frac{\partial T}{\partial S}\right)_V \Rightarrow \left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{T\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{d'Q}{dT}\right)_V = \frac{C_V}{T} \end{array}\right\} \cdot \frac{\left(\frac{\partial T}{\partial S}\right)_P}{\left(\frac{\partial T}{\partial S}\right)_V} = \frac{C_V}{C_P}$$

alternativament:

$$\left.\begin{array}{l} dU_V = d'Q_V = C_V dT = T\,dS_V \rightarrow C_V = T\left(\frac{\partial S}{\partial T}\right)_V \\ dH_P = d'Q_P = C_P dT = T\,dS_P \rightarrow C_P = T\left(\frac{\partial S}{\partial T}\right)_P \end{array}\right\} \frac{C_V}{C_P} = \frac{(\partial S/\partial T)_P}{(\partial S/\partial T)_V}$$

$\boxed{10}$

$$\left.\begin{array}{l} dG = -SdT + VdP + \mu dn \\ dG = n\,d\mu + \mu\,dn \end{array}\right\} \frac{n}{n}d\mu = -\frac{S}{n}dT + \frac{V}{n}dP \Rightarrow d\mu = -s\,dT + v\,dP$$