Resumen #3 termodinámica

- coef. expansión térmica: $\boxed{\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}$
- factor compresibilidad: $\boxed{K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}$
- $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{K} > 0$ (relación entre α y K)
- Expresiones para dS:
  (i) $dS = \frac{C_v}{T}\,dT + \frac{\alpha}{K}\,dV$
  (ii) $dS = \frac{C_p}{T}\,dT + V^{\alpha}\,dP$
- (i) $\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{K}$; (ii) $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} = \frac{1}{T}\left(\frac{\partial T}{\partial T}\right)_P$ (iii) $\left(\frac{\partial S}{\partial P}\right)_T = -V^{\alpha}$
- $\Delta S_T^{\circ} = \Delta S_{T_0}^{\circ} + \int_{T_0}^{T} \frac{\Delta C_p^{\circ}}{T}\,dT$; para $T = 0\,K$, en un cristal perfecto $\Rightarrow S_0 = 0$
(p cte)

Energía libre y criterios de espontaneidad:

- $A = U - TS$
- $G = H - TS$
- Ecs. fundamentales de la termodinámica:
  1) $dU = TdS - PdV$
  2) $dH = TdS + VdP$
  3) $dA = -SdT - PdV$
  4) $dG = -SdT + VdP$
- Ecs. de Maxwell:
  1) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
  3) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
  2) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
  4) $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

• 2° principio, criterios de espontaneidad:

$$\boxed{TdS > dE + PdV} \quad (*) \quad \begin{cases} \cdot\ dS > dQ/T \\ \cdot\ dQ = dE + PdV \end{cases}$$

obs: válida para procesos reales (irreversibles)

1) S y V ctes

• $dS = dV = 0$; en $(*)$: $\quad 0 > dE_{S,V} + 0$

$\Rightarrow \boxed{\Delta E_{S,V} < 0}$

2) E, V ctes

• $dE = dV = 0$; en $(*)$:

$\Rightarrow TdS_{E,V} > 0 + 0 \quad / T°[K] > 0$

$\therefore \boxed{\Delta S_{E,V} > 0}$

3) P, T ctes

• $G = H - TS = (E + PV) - TS$

$\Rightarrow dG = dE + PdV + V\cancel{dP}^{\,0} - TdS - S\cancel{dT}^{\,0} \quad / dP = dT = 0$

$\Rightarrow dG = dE + PdV - TdS \quad (**)$

• de $(*) \Rightarrow TdS > dE + PdV$

$\Rightarrow dE + PdV - TdS < 0 \quad (***)$

$(***)$ en $(**)$
$\Rightarrow \quad dG_{P,T} < 0$

$\therefore \boxed{\Delta G_{P,T} < 0}$

4) V, T ctes

• $A = E - TS \quad / dV = dT = 0$

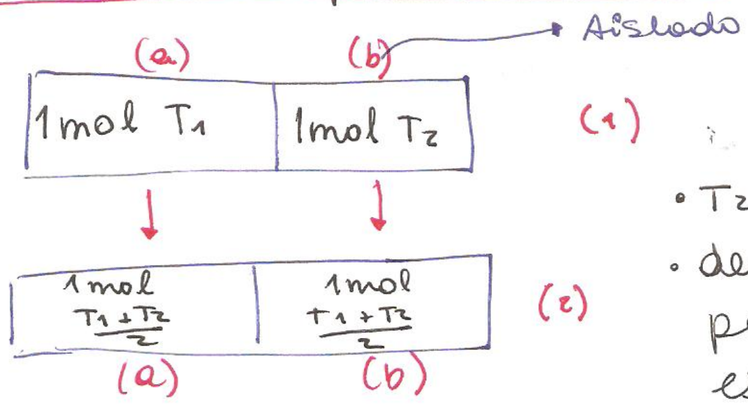
$\Rightarrow dA = dE - TdS - S\cancel{dT}^{\,0}$

$\Rightarrow dA = dE - TdS$

• de $(*) \Rightarrow TdS > dE + P\cancel{dV}^{\,0} \Rightarrow dE - TdS < 0$

• Así $\Rightarrow dA_{V,T} < 0 \Rightarrow \therefore \Delta A_{V,T}$

- Ejercicio espontaneidad



- $T_2 > T_1$, C_p cte
- demostrar que el proceso (1) → (2) es espontáneo.

- $S_1 = S_{a1} + S_{b1}$
- $S_2 = S_{a2} + S_{b2}$

- $\Delta S = (S_2 - S_1) = (S_{a2} + S_{b2}) - (S_{a1} + S_{b1})$

$$\Delta S = (S_{a2} - S_{a1}) + (S_{b2} - S_{b1})$$

$$\Delta S = \Delta S_a + \Delta S_b$$

- $\Delta S_a = \int_{T_1}^{\frac{T_1+T_2}{2}} \frac{C_p}{T}\, dT = C_p \cdot \ln\left(\frac{\frac{T_1+T_2}{2}}{T_1}\right)$

- $\Delta S_b = \int_{T_2}^{\frac{T_1+T_2}{2}} \frac{C_p}{T}\, dT = C_p \cdot \ln\left(\frac{\frac{T_1+T_2}{2}}{T_2}\right)$

$\Rightarrow \Delta S = \Delta S_a + \Delta S_b = C_p \ln\left(\frac{\frac{T_1+T_2}{2}}{T_1}\right) + C_p \ln\left(\frac{\frac{T_1+T_2}{2}}{T_2}\right)$

$\Rightarrow \Delta S = C_p \cdot \ln\left(\frac{(T_1+T_2)^2}{4T_1T_2}\right)$

- Vemos el signo de $\ln(\cdot/.)$

$\Rightarrow$ asumamos que $\frac{(T_1+T_2)^2}{4T_1T_2} > 1$

$\Rightarrow T_1^2 + T_2^2 + 2T_1T_2 > 4T_1T_2$

$\Rightarrow T_1^2 + T_2^2 - T_1T_2 > 0$

$\Rightarrow (T_1 - T_2)^2 > 0$ ✓ $\therefore \frac{(T_1+T_2)^2}{4T_1T_2} > 1$ //

Así, $\boxed{\Delta S > 0}$ $\Rightarrow$ V cte y E cte

$\Rightarrow$ espontáneo ✓