P1)

(a)

(i) $\underline{a \to b}$: adiabático

- $Q_{ab} = 0$
- $\Delta E_{ab} = nC_v(T_b - T_a)$
- 1º ley $\Rightarrow$ $W_{ab} = -\Delta E_{ab} = nC_v(T_a - T_b)$

(ii) $\underline{b \to c}$: isobárico

- $Q_p = nC_p\Delta T \Rightarrow Q_{bc} = nC_p(T_c - T_b)$
- $\Delta E_{bc} = nC_v(T_c - T_b)$
- 1º ley $\Rightarrow$ $W_{bc} = Q_{bc} - \Delta E_{bc} = n(C_p - C_v)(T_c - T_b)$
  $= nR(T_c - T_b)$

(iii) $\underline{c \to d}$: adiabático

- $Q_{cd} = 0$
- $\Delta E_{cd} = nC_v(T_d - T_c)$
- $W_{cd} = -\Delta E_{cd} = nC_v(T_c - T_d)$

(iv) $\underline{d \to a}$: isobárico

- $Q_{da} = nC_p(T_a - T_d)$
- $\Delta E_{da} = nC_v(T_a - T_d)$
- 1º ley $\to$ $W_{da} = n(C_p - C_v)(T_a - T_d)$
  $= nR(T_a - T_d)$

(b) $\eta_b = \dfrac{|W_{neto}|}{Q_{abs}}$; $Q_{abs} > 0$

· tenemos 2 Q en el proceso: $Q_{bc} = nC_p(T_c - T_b) < 0$ ×

$Q_{da} = nC_p(T_a - T_d) > 0$ ✓

· 1° ley en todo el ciclo cerrado $\Rightarrow \Delta \cancel{E_t}^{0} = Q_t - W_t$

$\Rightarrow Q_t = W_t$

$$\Rightarrow \eta_b = \frac{Q_t}{Q_{abs}} = \frac{\cancel{nC_p}(T_c - T_b) + \cancel{nC_p}(T_a - T_d)}{\cancel{nC_p}(T_a - T_d)} = \frac{T_a - T_d - T_b + T_c}{T_a - T_d}$$

$$= 1 - \left(\frac{T_b - T_c}{T_a - T_d}\right)$$

· Debemos dejar T_i en función de P_i:

· a→b y c→d adiabáticos $\Rightarrow T^{\gamma} \cdot P^{1-\gamma} = cte$

$$\Rightarrow T_a^{\gamma} \cdot P_a^{1-\gamma} = T_b^{\gamma} \cdot P_b^{1-\gamma} = K_1$$

$$T_c^{\gamma} \cdot P_c^{1-\gamma} = T_d^{\gamma} \cdot P_d^{1-\gamma} = K_2$$

$$\Rightarrow \eta_b = 1 - \left[\frac{\left(\frac{K_1}{P_b^{1-\gamma}}\right)^{1/\gamma} - \left(\frac{K_2}{P_c^{1-\gamma}}\right)^{1/\gamma}}{\left(\frac{K_1}{P_a^{1-\gamma}}\right)^{1/\gamma} - \left(\frac{K_2}{P_d^{1-\gamma}}\right)^{1/\gamma}}\right] \quad ; \text{ Pero } \begin{array}{l} P_a = P_d \\ P_b = P_c \end{array}$$

$$\Rightarrow \eta_b = 1 - \left[\frac{\left(\frac{K_1}{P_b^{1-\gamma}}\right)^{1/\gamma} - \left(\frac{K_2}{P_b^{1-\gamma}}\right)^{1/\gamma}}{\left(\frac{K_1}{P_a^{1-\gamma}}\right)^{1/\gamma} - \left(\frac{K_2}{P_a^{1-\gamma}}\right)^{1/\gamma}}\right] = 1 - \left(\frac{P_a}{P_b}\right)^{\frac{1-\gamma}{\gamma}} \cdot \frac{\cancel{(K_1 - K_2)}}{\cancel{(K_1 - K_2)}}$$

$$* \left.\begin{array}{l} \gamma = C_p/C_v \\ C_p - C_v = R \end{array}\right\} \frac{1-\gamma}{\gamma} = \frac{\frac{C_v - C_p}{\cancel{C_v}}}{\frac{C_p}{\cancel{C_v}}} = -\frac{R}{C_p} \Rightarrow \eta_b = 1 - \left(\frac{P_a}{P_b}\right)^{-R/C_p}$$

$$= 1 - (P_b/P_a)^{R/C_p}$$

P2) pdq: $U = \bar{C}_V T - \frac{a}{V} + cte$; $n = 1$ mol
gas. van der Waals
$\bar{C}_p, \bar{C}_V$ ctes.

• Ec. estado $\rightarrow \left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$ / $n=1 \Rightarrow V = \bar{V}$

• 1° ley : $dE = dQ - dW = dQ - PdV$ / $dS = \frac{dQ}{T}$

$\Rightarrow dE = TdS - PdV$

• enunciado $S(V,T)$:

$dS = \left(\frac{\partial S}{\partial T}\right)_V \cdot dT + \left(\frac{\partial S}{\partial V}\right)_T dV$ / • $\left(\frac{\partial S}{\partial T}\right)_V \overset{\text{def.}}{=} \frac{1}{T}\left(\frac{\partial Q}{\partial T}\right)_V = \frac{1}{T} C_V$; $C_V = \left(\frac{\partial Q}{\partial T}\right)_V$

/ • maxwell: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$\Rightarrow dS = \frac{1}{T} C_V dT + \left(\frac{\partial P}{\partial T}\right)_V dV \Rightarrow TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$

• ec. de estado $\Rightarrow P = \frac{RT}{(V-b)} - \frac{a}{V^2} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{T}\left(P + \frac{a}{V^2}\right)$

$\Rightarrow TdS = C_V dT + \cancel{T} \cdot \frac{1}{\cancel{T}}\left(P + \frac{a}{V^2}\right) dV = C_V dT + \left(P + \frac{a}{V^2}\right) dV$

• 1° ley $\Rightarrow dE = \left(C_V dT + \left(P + \frac{a}{V^2}\right) dV\right) - PdV = C_V dT + \cancel{PdV} + \frac{a}{V^2} dV - \cancel{PdV}$

$\Rightarrow dE = C_V dT + \frac{a}{V^2} dV$ / $\int$ $\Rightarrow \Delta E = C_V \Delta T - \frac{a}{\Delta V} + cte$ //

P3 (a)

$$\alpha_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$$

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

• Regla cadena: $\left(\frac{\partial V}{\partial T}\right)_S = -\left(\frac{\partial S}{\partial P}\right)_V = -\left(\frac{\partial S}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial P}\right)_V$

$\star$ $C_V = \left(\frac{\partial Q}{\partial T}\right)_V \overset{\text{def}}{=} T\left(\frac{\partial S}{\partial T}\right)_V \Rightarrow \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V}{T}\cdot\left(\frac{\partial T}{\partial P}\right)_V$$

• en derivadas parciales:

$$\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V = -1 \Rightarrow \left(\frac{\partial T}{\partial P}\right)_V = \frac{-1}{\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P} = \frac{-\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_P}$$

$$= \frac{-(-KV)}{\alpha V} = \frac{K}{\alpha}$$

$$\therefore \alpha_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S = -\frac{1}{V}\frac{C_V}{T}\left(\frac{\partial T}{\partial P}\right)_V = -\frac{1}{V}\frac{C_V}{T}\cdot\frac{K}{\alpha} = -\frac{C_V\cdot K}{TV\cdot\alpha} \;//$$

(b) g.i $\rightarrow PV = nRT$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial(nRT/P)}{\partial T}\right)_P = \frac{nR}{PV}\left(\frac{\partial T}{\partial T}\right)_P = \frac{nR}{PV} = \frac{1}{T}$$

$$k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial(nRT/P)}{\partial P}\right)_T = -\frac{nRT}{V}\left(\frac{\partial(1/P)}{\partial P}\right)_T = -\frac{nRT}{V}\left(-\frac{1}{P^2}\right) = \frac{P}{P^2} = \frac{1}{P}$$

$$\Rightarrow \alpha_S = -\frac{C_V\cdot(1/P)}{\cancel{T}\cdot V\cdot\cancel{(1/T)}} = -\frac{C_V}{PV} = -\frac{C_V}{nRT} \;//$$

$$\cdot \; \alpha_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S \underset{\substack{\uparrow \\ \text{g.i.}}}{=} -\frac{C_v}{mRT}$$

$$\Rightarrow \quad \frac{\partial V_s}{V} = -\left(\frac{C_v}{m}\right)\cdot\frac{\partial T_s}{T}\cdot\frac{1}{R} \quad \Big/ \quad \frac{\bar{C}_v}{R} = \bar{C_v} \; ; \; dS = \frac{\delta Q}{T} \Rightarrow S \text{ cte}$$

$\Rightarrow Q = 0$

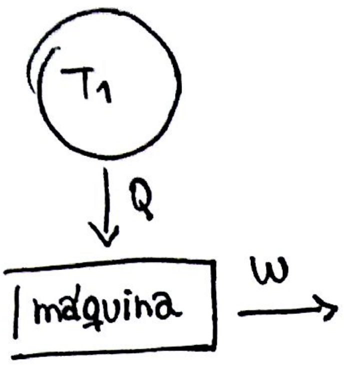
(adiabática

$$\Rightarrow \quad \frac{dV}{V} = -\left(\frac{\bar{C}_v}{R}\right)\cdot\frac{dT}{T} \Rightarrow d\ln V = -\left(\frac{\bar{C}_v}{R}\right)\cdot d\ln T \quad \Big/ \int$$

$$\Rightarrow \ln V = -\left(\frac{\bar{C}_v}{R}\right)\cdot \ln T + K \Rightarrow \ln V + \left(\frac{\bar{C}_v}{R}\right)\ln T = K$$

$$\therefore \; V T^{\bar{c}_v/R} = \text{cte}$$

T4



· máquina : ciclo cerrado

$$\Delta S_t = \Delta S_{fuente} + \Delta S_{máquina} + \Delta S_{entorno}$$

· $\Delta S_{fuente} = \dfrac{Q_{fuente}}{T_{fuente}}$ | · asumimos T cte.
· cede calor ⇒ $Q < 0$

⇒ $\Delta S_{fuente} < 0$

· $\Delta S_{máquina} = 0$ (ciclo cerrado ; función de estado)

· $\Delta S_{entorno} = \dfrac{\cancelto{0}{Q_{entorno}}}{T_{entorno}}$ (no recibe ni cede calor)

$$\therefore \Delta S_t = \underbrace{\Delta S_F}_{<0} + \underbrace{\Delta S_M}_{=0} + \underbrace{\Delta S_e}_{=0} < 0 \quad \rightarrow\leftarrow$$

∴ no es posible