

Problema 1:  $S(T) = \frac{\alpha}{T}$

(a) Capacidad calorífica molar:  $dQ = C dT$

Veamos que  $ds = -\frac{\alpha}{T^2} dT \rightarrow T ds = -\frac{\alpha}{T} dT$

2º ley:  $dQ = T ds \rightarrow C = -\frac{\alpha}{T}$

$$(b) \quad Q = \int_{T_1}^{T_2} C dT = \int_{T_1}^{T_2} \left(-\frac{\alpha}{T}\right) dT = -\alpha \int_{T_1}^{T_2} \frac{dT}{T} = -\alpha \ln\left(\frac{T_2}{T_1}\right)$$

$$\rightarrow Q = \alpha \ln\left(\frac{T_1}{T_2}\right)$$

$$(c) \quad Q = \Delta U + W \rightarrow W = Q - \Delta U$$

con  $\Delta U = C_V \Delta T = C_V (T_2 - T_1)$ , tenemos que

$$W = \alpha \ln\left(\frac{T_1}{T_2}\right) + C_V (T_1 - T_2)$$



## Problema 2

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

$C_V$ : calor específica a volumen constante

$U$ : Energía interna por mol

$V$ : Volumen molar,

$$\rightarrow \left( \frac{\partial C_V}{\partial V} \right)_T = \frac{\partial^2 U}{\partial V \partial T} = \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right)_T \quad (*)$$

\* Notemos que  $dU = TdS - PdV = T \left( \frac{\partial S}{\partial T} \right)_V dT + \left\{ T \left( \frac{\partial S}{\partial V} \right)_T - P \right\} dV$

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

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

Ahora,  $\left( \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial T} \right)_V \right)_T = \left( \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right)_T \right)_V$

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

$$\Rightarrow \boxed{\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V}$$

$$\rightarrow \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$$

$$\therefore \left( \frac{\partial C_V}{\partial V} \right)_T = \frac{\partial}{\partial T} \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] = \cancel{\left( \frac{\partial P}{\partial T} \right)_V} + \left( \frac{\partial^2 P}{\partial T^2} \right)_V - \left( \frac{\partial P}{\partial T} \right)_V$$

$$\Rightarrow \left( \frac{\partial C_V}{\partial V} \right)_T = \left( \frac{\partial^2 P}{\partial T^2} \right)_V$$

Para el gas de van der Waals:  $P = \frac{RT}{V-b} - \frac{a}{V^2}$

$$\rightarrow \left( \frac{\partial^2 P}{\partial T^2} \right)_V = 0 \Rightarrow \boxed{\frac{\partial C_V}{\partial V} = 0} \Rightarrow C_V \text{ no depende de } V.$$



Energía interna: Tenemos

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

$$dU = C_V dT + \frac{a}{V^2} dV$$

$$\Rightarrow U - U_0 = \int_{T_0}^T C_V dT - \frac{a}{V} + \frac{a}{V_0} \quad \begin{array}{l} U_0 : \text{cte.} \\ V_0 : \text{cte.} \end{array}$$

Entropía: Tenemos que  $TdS = dU + PdV$

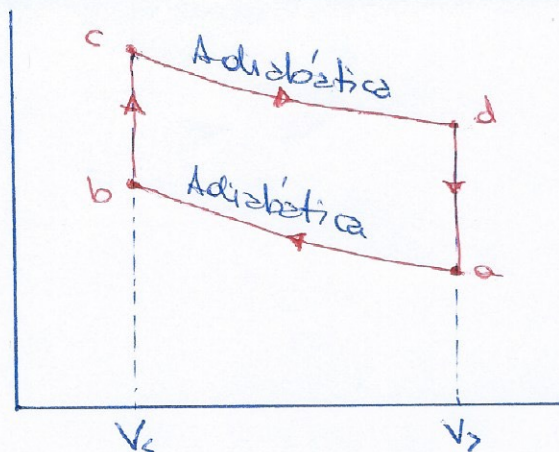
$$= C_V dT + \frac{a}{V^2} dV + \frac{RT}{V-b} dV - \frac{a}{V^2} dV$$

$$\Rightarrow dS = \frac{C_V}{T} dT + \frac{R}{V-b} dV$$

$$\Rightarrow S - S_0 = \int_{T_0}^T \frac{C_V}{T} dT + R \ln \left( \frac{V-b}{V_0-b} \right)$$



### Problema 3 :



• Trabajo neto entregado por el sistema  $W = W_2 + W_1$

$W_2$ : trabajo realizado por el gas ;  $W_1$ : trabajo realizado sobre el gas.

$$Q_{ab} = 0 = \Delta U_{ab} + W_1 \Rightarrow W_1 = -\Delta U_{ab} = -C_v(T_b - T_a)$$

$$Q_{cd} = 0 = \Delta U_{cd} + W_2 \Rightarrow W_2 = -\Delta U_{cd} = -C_v(T_d - T_c) = C_v(T_c - T_d)$$

$$\Rightarrow W = C_v(T_c - T_d) - C_v(T_b - T_a) = C_v(T_a + T_c - T_b - T_d)$$

Por otro lado, el gas recibe calor en el proceso bc

$$Q = C_v(T_c - T_b)$$

Así, la eficiencia es  $\eta = \frac{W}{Q} = \frac{T_a + T_c - T_b - T_d}{T_c - T_b} = 1 - \frac{T_d - T_a}{T_c - T_b}$

En procesos adiabáticos:  $TV^{\gamma-1} = \text{cte}$

$$\therefore T_a V_c^{\gamma-1} = T_b V_g^{\gamma-1} \quad \wedge \quad T_d V_g^{\gamma-1} = T_c V_c^{\gamma-1}$$

$$\Rightarrow \frac{T_a}{T_b} = \frac{T_d}{T_c} = \left(\frac{V_c}{V_g}\right)^{\gamma-1} = \frac{T_d - T_a}{T_c - T_b}$$

$$\Rightarrow \eta = 1 - \left(\frac{V_c}{V_g}\right)^{\gamma-1}$$

$$V_g = 10 V_c ; \text{ Para nitrógeno: } \gamma = \frac{7}{5}$$

$$\eta = 1 - 10^{-2/5} = 1 - 0,398 =$$

$$\eta = 0,602$$



Problema 4: Combinando el primer y segundo principio:

$$TdS = dU + PdV$$

$$\rightarrow dS = \frac{1}{T} dU + \frac{P}{T} dV$$

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

Ya que  $dS$  es diferencial exacta

$$\left\{ \frac{\partial}{\partial T} \left[ \frac{1}{T} \left( \frac{\partial U}{\partial V} \right)_T + \frac{P}{T} \right] \right\}_V = \left\{ \frac{\partial}{\partial V} \left[ \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V \right] \right\}_T$$

$$* \left( \frac{\partial U}{\partial V} \right)_T = \frac{BT^m}{V} ; * \frac{P}{T} = \frac{AT^2}{V}$$

$$\rightarrow \frac{\partial}{\partial T} \left[ \frac{1}{T} \left( \frac{\partial U}{\partial V} \right)_T + \frac{P}{T} \right] = \frac{\partial}{\partial T} \left[ \frac{BT^{m-1}}{V} + \frac{AT^2}{V} \right] = \frac{(m-1)BT^{m-2} + 2AT}{V}$$

$$* \left( \frac{\partial U}{\partial T} \right)_V = mBT^{m-1} \ln\left(\frac{V}{V_0}\right) + f'(T) \rightarrow \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V = mBT^{m-2} \ln\left(\frac{V}{V_0}\right) + \frac{f'(T)}{T}$$

$$\frac{\partial}{\partial V} \left[ \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V \right]_T = \frac{mBT^{m-2}}{V}$$

Luego,  $(m-1)BT^{m-2} + 2AT = mBT^{m-2}$

$$2AT = BT^{m-2}$$

$$\Rightarrow B = 2A$$

$$m = 3$$