Gabarito – Físico-Química I – EC4

1

$$\left(\frac{\partial V}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_P = -1 \quad \therefore \quad \left(\frac{\partial V}{\partial P}\right)_S = \frac{\left(\frac{\partial V}{\partial S}\right)_P}{-\left(\frac{\partial P}{\partial S}\right)_V}$$

$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S \qquad \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_V = -1$$

gás ideal:

$$P = nRT/V$$

$$\left(\frac{\partial P}{\partial T}\right)_V = nR/V$$

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

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

$$dS_V = \frac{1}{T} \cdot dQ_V = \frac{1}{T} \cdot dU$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V = \frac{C_V}{T}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{-nR/V}{C_V/T} = \frac{-nRT}{V \cdot C_V}$$

$$\boxed{-\left(\frac{\partial P}{\partial S}\right)_V = \frac{-nRT}{V \cdot C_V}}$$

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \qquad \left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -1$$

gás ideal

$$V = nRT/P$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{-\left(\partial S/\partial P\right)_T}{\left(\partial S/\partial T\right)_P} \qquad -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$dS_P = \frac{dQ_P}{T} \quad \therefore \quad \frac{1}{T}\left(\frac{\partial Q_P}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \boxed{\left(\frac{\partial V}{\partial S}\right)_P = \frac{nR/P}{C_P/T} = \frac{nRT}{P \cdot C_P}}$$

$$\left(\frac{\partial V}{\partial P}\right)_S = \frac{nRT/P \cdot C_P}{-nRT/V \cdot C_V} = -\frac{\cancel{nRT}}{P \cdot C_P} \cdot \frac{V \cdot C_V}{\cancel{nRT}} = -\frac{V}{P} \cdot \frac{C_V}{C_P}$$

$$P \cdot \gamma \cdot \kappa_S = \cancel{P} \cdot \frac{\cancel{C_P}}{\cancel{C_V}} \cdot \left(\frac{-1}{\cancel{V}}\right) \cdot \left(\frac{-\cancel{V}}{\cancel{P}}\right) \cdot \frac{\cancel{C_V}}{\cancel{C_P}} = 1 \quad //$$

2 $\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$; dado: $H = U + PV$

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

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial (U+PV)}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + P + V\left(\frac{\partial P}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial P}\right)_T$$

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

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1 \quad \therefore \quad \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad (2)$$

Substituindo (2) em (1):

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V \quad //$$

③ $\mu_J = \left(\frac{\partial T}{\partial V}\right)_U$

$$\underbrace{\left(\frac{\partial T}{\partial V}\right)_U}_{\mu_J} \left(\frac{\partial V}{\partial U}\right)_T \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} = -1 \quad \therefore \quad \mu_J C_V = -\left(\frac{\partial U}{\partial V}\right)_T$$

$$dU = T\,dS - P\,dV \quad \therefore \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

Rel. Maxwell: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \therefore \quad -\left(\frac{\partial U}{\partial V}\right)_T = P - T\left(\frac{\partial P}{\partial T}\right)_V$

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1 \quad ; \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \ \text{e} \ K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{(\partial V/\partial T)_P}{-(\partial V/\partial P)_T} = \frac{\alpha \cdot \cancel{V}}{K_T \cdot \cancel{V}} = \frac{\alpha}{K_T} \Rightarrow$$

$$\Rightarrow -\left(\frac{\partial U}{\partial V}\right)_T = P - T \cdot \left(\frac{\alpha}{K_T}\right)$$

$$\Rightarrow \mu_J C_V = P - \left(\frac{\alpha T}{K_T}\right)$$

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