Joule-Thomson & TD Relations for Real Gases

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Previously: Maxwell & TD Relations, Clapeyron Eq.

$$du = T\,ds - P\,dv \qquad da = -s\,dT - P\,dv$$

$$dh = T\,ds + v\,dP \qquad dg = -s\,dT + v\,dP$$

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \qquad \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P \qquad \left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

$$\boxed{\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{T\left(v_g - v_f\right)}}$$

$$\ln\left(\frac{P_2}{P_1}\right)_{\text{sat}} \cong \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)_{\text{sat}}$$

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v\,dT + \int_{v_1}^{v_2}\left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]dv$$

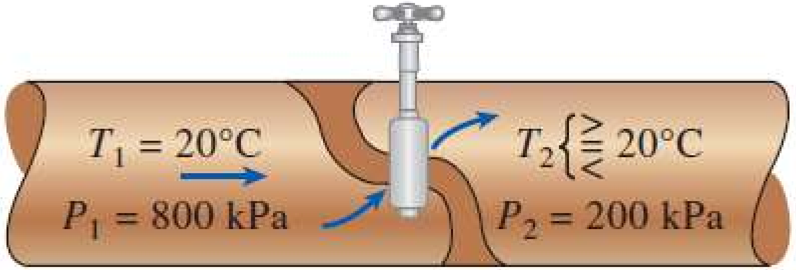
$$h_2 - h_1 = \int_{T_1}^{T_2} c_p\,dT + \int_{P_1}^{P_2}\left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]dP$$

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p}{T}\,dT - \int_{P_1}^{P_2}\left(\frac{\partial v}{\partial T}\right)_P dP$$

$$c_p - c_v = T\left(\frac{\partial v}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_v$$

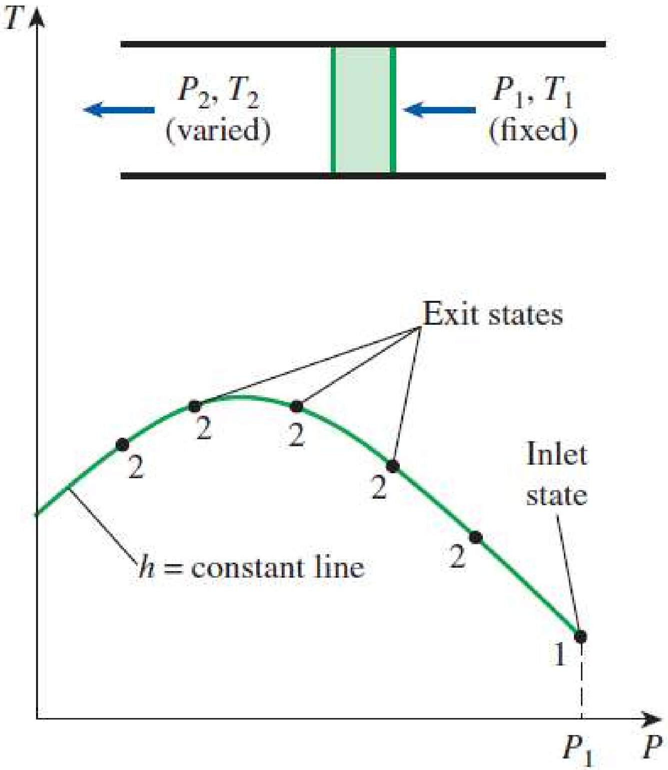
$$c_p - c_v = \frac{vT\beta^2}{\alpha}$$

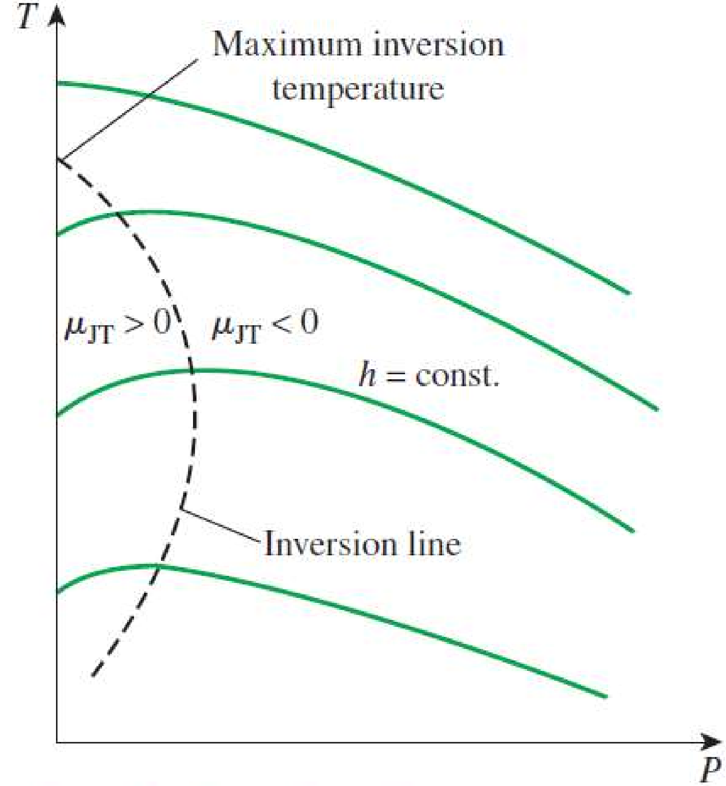
Joule-Thomson Coefficient in IsoEnthalpic throttling



$$\mu = \left(\frac{\partial T}{\partial P}\right)_h$$

$$\mu_{JT} \begin{cases} < 0 & \text{temperature increases} \\ = 0 & \text{temperature remains constant} \\ > 0 & \text{temperature decreases} \end{cases}$$





$$dh = c_p\, dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP$$

$$-\frac{1}{c_p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] = \left(\frac{\partial T}{\partial P}\right)_h = \mu_{JT}$$

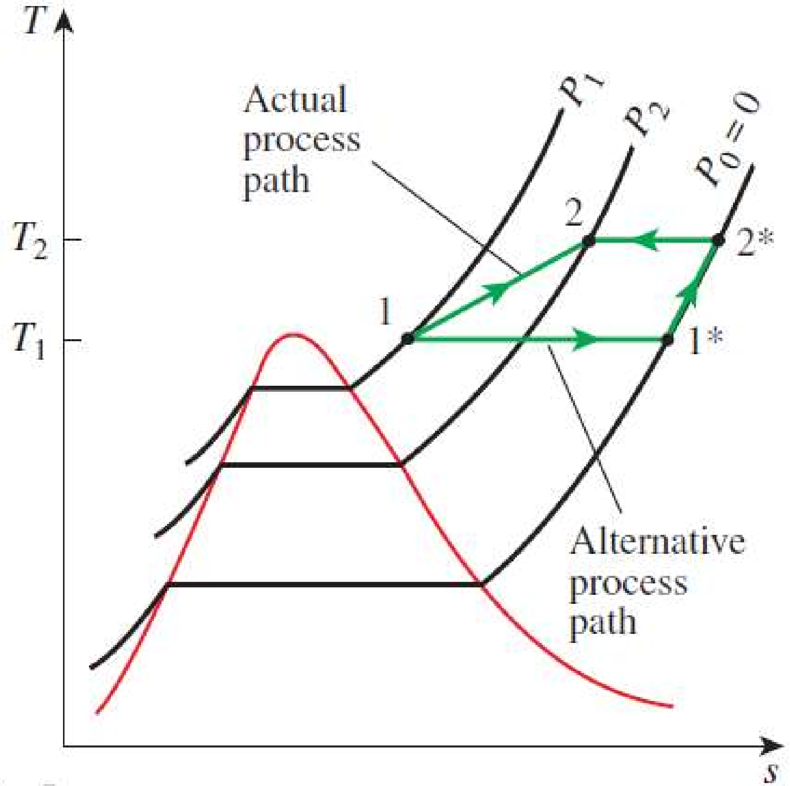
Figs: TD-Cengel & Boles

ΔH *in Real Gases*

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p \, dT + \int_{P_1}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right] dP$$

$$h_2 - h_1 = (h_2 - h_2^*) + (h_2^* - h_1^*) + (h_1^* - h_1)$$

Pv = ZRT



$$h_2 - h_2^* = 0 + \int_{P_2^*}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right]_{T=T_2} dP = \int_{P_0}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right]_{T=T_2} dP$$

$$h_2^* - h_1^* = \int_{T_1}^{T_2} c_p \, dT + 0 = \int_{T_1}^{T_2} c_{p0}(T) \, dT$$

$$h_1^* - h_1 = 0 + \int_{P_1}^{P_1^*} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right]_{T=T_1} dP = -\int_{P_0}^{P_1} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right]_{T=T_1} dP$$

$$(h^* - h)_T = -RT^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

Figs: TD-Cengel & Boles

Enthalpy Departure in Real Gases

$$T = T_{\rm cr}T_R \quad \text{and} \quad P = P_{\rm cr}P_R$$

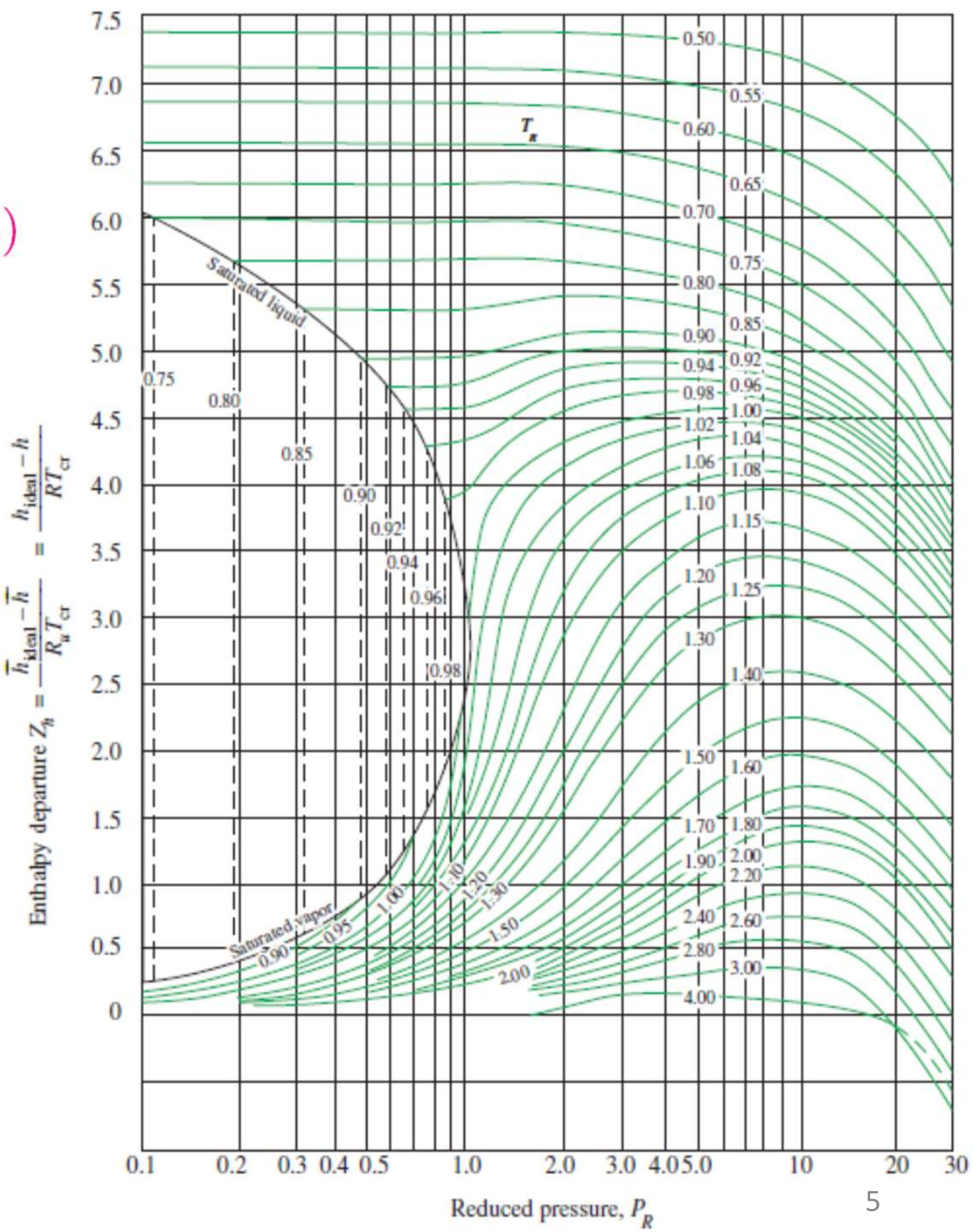
$$Z_h = \frac{(\bar{h}^* - \bar{h})_T}{R_u T_{\rm cr}} = T_R^2 \int_0^{P_R} \left(\frac{\partial Z}{\partial T_R}\right)_{P_R} d(\ln P_R)$$

$$h_2 - h_1 = (h_2 - h_2^*) + (h_2^* - h_1^*) + (h_1^* - h_1)$$

$$\bar{h}_2 - \bar{h}_1 = (\bar{h}_2 - \bar{h}_1)_{\rm ideal} - R_u T_{\rm cr}(Z_{h_2} - Z_{h_1})$$

$$\bar{h} = \bar{u} + P\bar{v} = \bar{u} + ZR_uT:$$

$$\bar{u}_2 - \bar{u}_1 = (\bar{h}_2 - \bar{h}_1) - R_u(Z_2T_2 - Z_1T_1)$$



Figs: TD-Cengel & Boles

ΔS in Real Gases

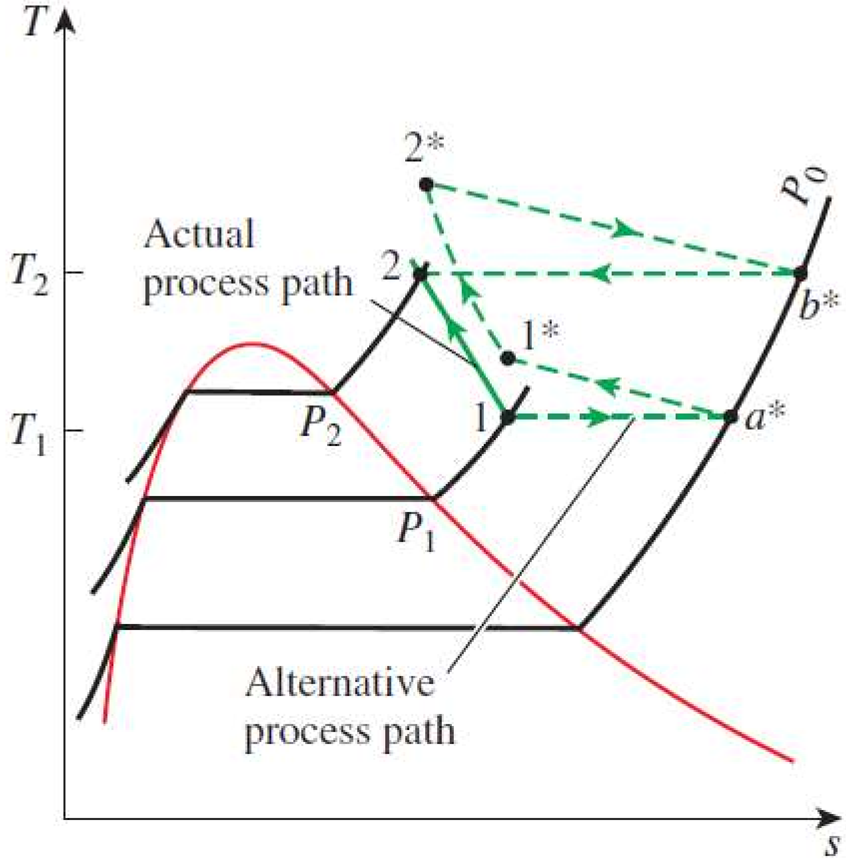
$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p}{T}\, dT - \int_{P_1}^{P_2} \left(\frac{\partial v}{\partial T}\right)_P dP$$

$$s_2 - s_1 = (s_2 - s_b^*) + (s_b^* - s_2^*) + (s_2^* - s_1^*) + (s_1^* - s_a^*) + (s_a^* - s_1)$$

$$(s_P - s_P^*)_T = (s_P - s_0^*)_T + (s_0^* - s_P^*)_T = -\int_0^P \left(\frac{\partial v}{\partial T}\right)_P dP - \int_P^0 \left(\frac{\partial v^*}{\partial T}\right)_P dP$$

$$v = ZRT/P \qquad v^* = v_{\text{ideal}} = RT/P$$

$$(s_P - s_P^*)_T = \int_0^P \left[\frac{(1-Z)R}{P} - \frac{RT}{P}\left(\frac{\partial Z r}{\partial T}\right)_P\right] dP$$



Figs: TD-Cengel & Boles

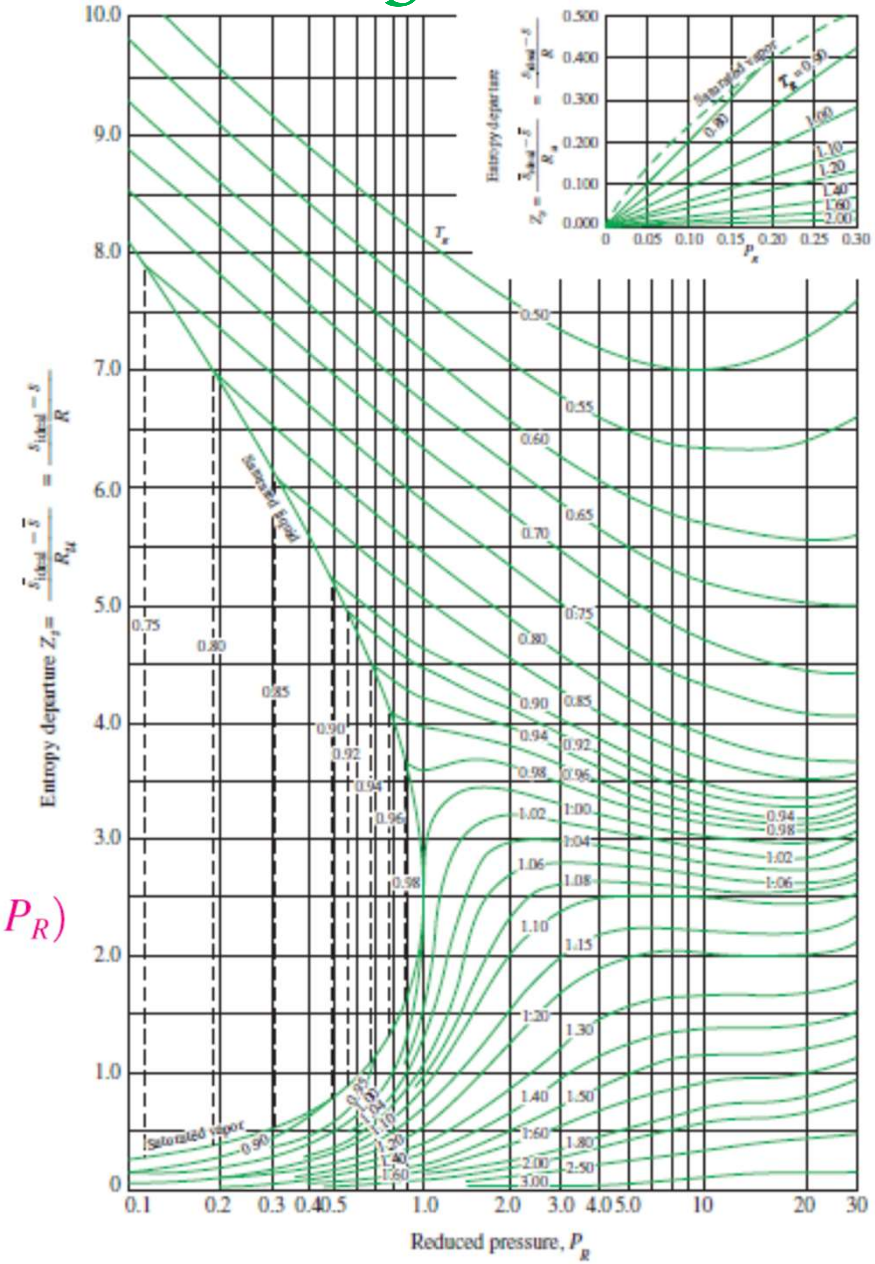
Entropy departure in Real Gases

$$(s_P - s_P^{*})_T = \int_0^P \left[\frac{(1-Z)R}{P} - \frac{RT}{P}\left(\frac{\partial Zr}{\partial T}\right)_P\right] dP$$

$$T = T_{cr}T_R \text{ and } P = P_{cr}P_R$$

$$Z_s = \frac{(\bar{s}^* - \bar{s})_{T,P}}{R_u} = \int_0^{P_R}\left[Z - 1 + T_R\left(\frac{\partial Z}{\partial T_R}\right)_{P_R}\right] d(\ln P_R)$$

$$\bar{s}_2 - \bar{s}_1 = (\bar{s}_2 - \bar{s}_1)_{\text{ideal}} - R_u(Z_{s_2} - Z_{s_1})$$



Figs: TD-Cengel & Boles

What's next?

- TD of chemical reactions