Sharif University of Technology

School of Mechanical Engineering

Center of Excellence in Energy Conversion

Advanced Thermodynamics

Lecture 23

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Ø   Fugacity is pseudo pressure and has a dimension as pressure

$$dg = -s\ dT + v\ dP$$

$$T = const. \rightarrow dg = v\ dP$$

Ideal gas: $v = \dfrac{RT}{P} \rightarrow dg = RT\ d\ln P$ Eq. (1)

Real gas: $v = \dfrac{ZRT}{P} \rightarrow dg = ZRT\ d\ln P = RT\ d\ln f$ Eq. (2)
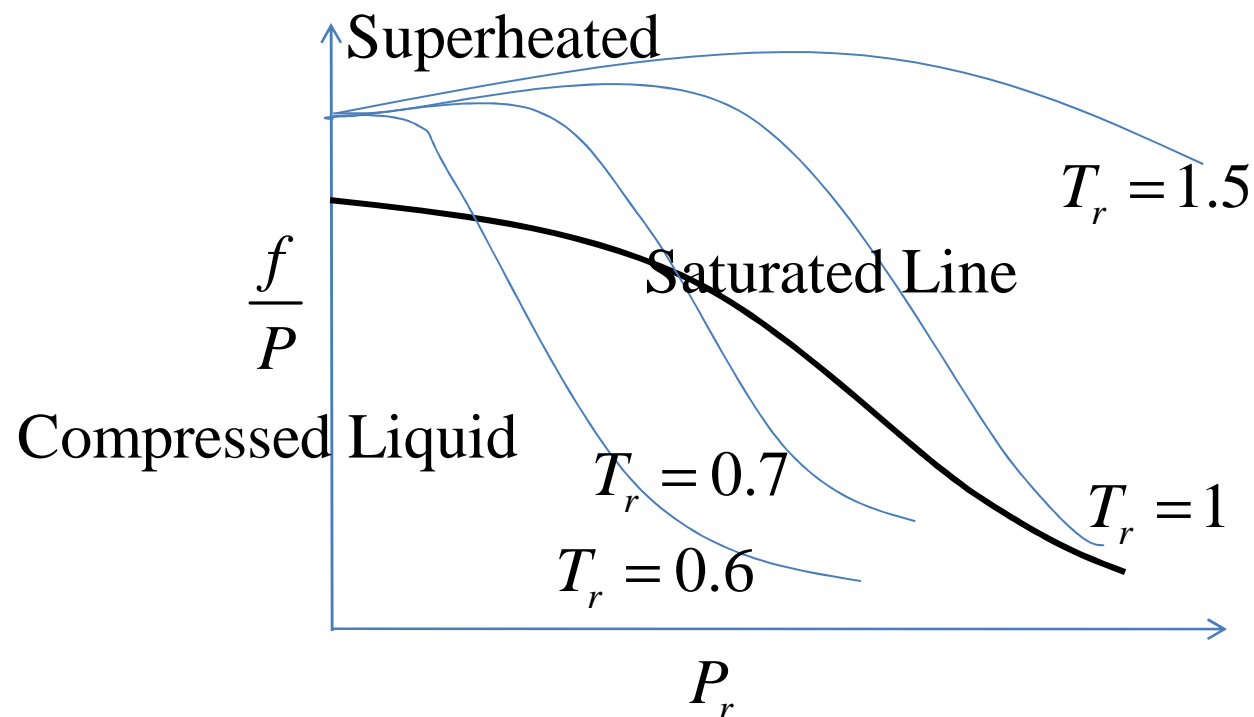
$$f \equiv \text{Fugacity}$$

$$\lim_{P \to 0} \frac{f}{P} = 1$$

Eqs. (1) & (2) $\rightarrow \displaystyle\int_{\ln\left(\frac{f}{P}\right)=0}^{\ln\left(\frac{f}{P}\right)} RT d\ln\left(\frac{f}{P}\right) = \int_{P^* \to 0}^{P}\left(v - \frac{RT}{P}\right)dP$

$$\rightarrow RTd\ln\left(\frac{f}{P}\right)=\int_0^P\left(v-\frac{RT}{P}\right)dP$$

Ø R.H.S. may be substituted by generalized compressibility factor Eq.

$$\boxed{\ln\left(\frac{f}{P}\right)=\int_0^{P_r}(Z-1)\,d\ln P_r}$$ Generalized Fugacity Equation

$$s = s(T,\ P) \rightarrow ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$$

$$ds_T = \left(\frac{\partial s}{\partial P}\right)_T dP = -\left(\frac{\partial v}{\partial T}\right)_P dP_T$$

For real gas $(Pv = ZRT) \Rightarrow \left(s_P - s_0^*\right)_T = -\int_{P^*=0}^{P} \left(\frac{\partial v}{\partial T}\right)_P dP_T$

For ideal gas $(Pv = RT) \Rightarrow \left(s_P^* - s_0^*\right)_T = -\int_{P^*=0}^{P^*} \left(\frac{\partial v}{\partial T}\right)_P dP_T$

$$\Rightarrow \left(s_P^* - s_P\right)_T = -\int_{P=0}^{P} \left[\frac{R}{P} - \left(\frac{\partial v}{\partial T}\right)_P\right] dP_T$$

$$\Rightarrow \left(\bar{s}_P^* - \bar{s}_P\right)_T = -\int_{P=0}^{P} \left[\frac{\bar{R}}{P} - \frac{2\bar{R}}{P} - \frac{\bar{R}T}{P}\left(\frac{\partial Z}{\partial T}\right)_P\right] dP_T$$

$$\left(\overline{s}_P^* - \overline{s}_P\right)_T = -\int_{P=0}^{P}\left[\frac{\overline{R}}{P} - \frac{2\overline{R}}{P} - \frac{\overline{R}T}{P}\left(\frac{\partial Z}{\partial T}\right)_P\right]dP_T$$

$$\text{Generalization} \rightarrow \left(\overline{s}_P^* - \overline{s}_P\right)_{T_r} = \overline{R}\int_{P=0}^{P}(Z-1)\frac{dP_r}{P_r} + \overline{R}T_r\int_{P=0}^{P}\left(\frac{\partial Z}{\partial T_r}\right)_{P_r}\frac{dP_r}{P_r}$$
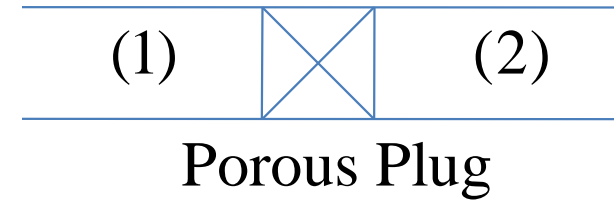
$$\left(\overline{s}_P^* - \overline{s}_P\right)_{T_r} = \overline{R}\ln\frac{f}{P} + \frac{\overline{h}^* - \overline{h}}{T_C T_r}$$

Ø Alternatively:

$$\left.\begin{array}{l} ds = \dfrac{c_P}{T}dT - \left(\dfrac{\partial v}{\partial T}\right)_P dP \\[3mm] \left(\overline{g}^* - \overline{g}\right) = \left(\overline{h}^* - \overline{h}\right) - T\left(\overline{s}^* - \overline{s}\right) \end{array}\right\} \rightarrow \left(\overline{s}_P^* - \overline{s}_P\right)_{T_r} = \frac{\overline{h}^* - \overline{h}}{T_C T_r} - \frac{\overline{g}^* - \overline{g}}{T_C T_r}$$

$$dg = RTd\ln f \rightarrow \left(\overline{s}_P^* - \overline{s}_P\right)_{T_r} = \overline{R}\ln\frac{f}{P} + \frac{\overline{h}^* - \overline{h}}{T_C T_r}$$

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

(1) (2)

Porous Plug

$$\text{Steady and Adiabatic} \rightarrow h_1 + \frac{v_1^2}{2} = h_2 + \frac{v_2^2}{2} \Rightarrow h_1 = h_2$$

Inversion Point

Max. Inversion Temp.

2_d

2_c

2_b

2_a

T

$m_j > 0$

$m_j < 0$

1

Cooling Zone

Heating Zone

P

Joule-Thomson Inversion Curve
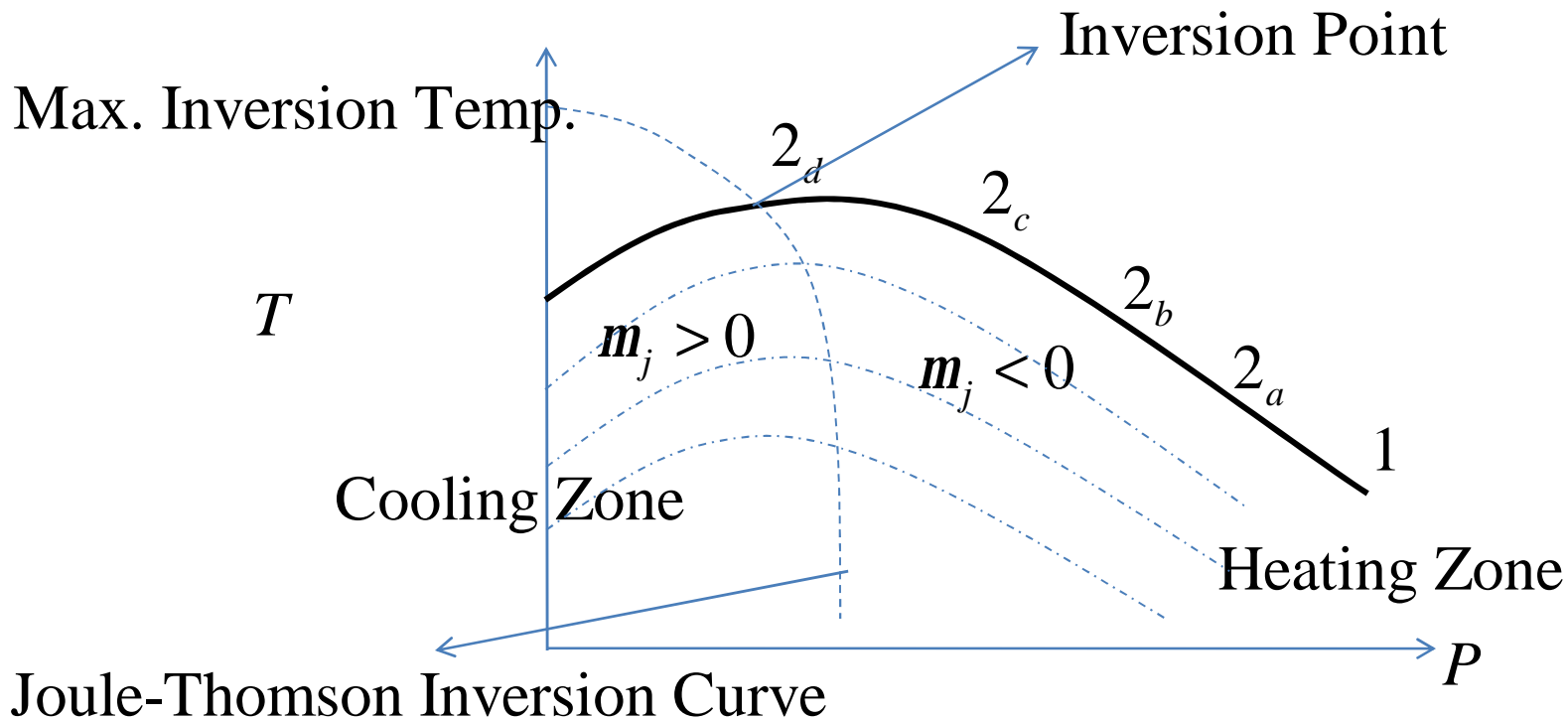
Ø   It is possible to have only heating zone.

Ø   If the initial temperature of Joule-Thomson expansion is over maximum inversion temperature, the cooling is impossible.

$$dh = c_P dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right] dP \rightarrow dT = \frac{dh}{c_P} + \frac{1}{c_P}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v \right] dP$$

$$\boxed{m_j = \left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{c_P}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v \right]}$$

$$\text{For real gas} \rightarrow \boxed{m_j = \frac{RT^2\left(\frac{\partial Z}{\partial T}\right)_P}{P c_P}}$$

Ø   If we set $m_j = 0$, the inversion curve will be obtained.

$$g = h - T\,s \text{ and } F = v - T\,s$$

$$dF = dv - T\,ds - s\,dT = -s\,dT - P\,dv$$

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

Ø   For an isotherm, reversible process:

$$dF = -P\,dv \rightarrow F_f - F_i = -\int_i^f P\,dv$$

Ø   For an isotherm, reversible process with constant volume:

$$dF = 0 \rightarrow F = cte$$

Ø   For an isotherm, reversible process with constant pressure:

$$dg = 0 \rightarrow g = cte$$

Ø   For vaporization, fusion, and sublimation

$$g' = g'' = g'''$$