

化工熱力學

# Ch.6

## Calculation of the Properties of Pure Fluids



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# Outline

**1. Describing Thermodynamic Properties**

**2. EOS (PVT relationships) of Matters**

**3. The Corresponding State Theorem**

**4. Calculation of Property Changes**

# Thermodynamic Properties: What we know

- We have applied balance analysis to solve the energy issue of all kinds of process.
  - System definition.
  - Process description.
  - Mass balance.
  - Energy balance.
  - Entropy balance.
  - Find **thermodynamic properties of matters** in the process.
  - Solve the energy issue of the process.
- These confirm that  $U$ ,  $H$ ,  $A$ ,  $G$ ,  $S$  are all important thermodynamic properties.
- How can we obtain all these thermodynamic properties of different matters?

# 1. Describing Thermodynamic Properties

- Need to calculate  $\underline{U}$ ,  $\underline{H}$ ,  $\underline{S}$ , ....., which are appeared in energy and entropy balance equations
  - The thermodynamic properties are usually expressed in terms of easily measurable variables,  $f(T, P)$  or  $f(T, \underline{V})$ .
  - Estimate the properties from Tables, Charts, or thermodynamic models (CSP, EOS)
- 
- Thermodynamic state variables:  $P, T, \underline{V}, \underline{S}, \underline{U}, \underline{H}, \underline{A}, \underline{G}$
  - For a single-component and one phase system, there are two independent intensive variables and remaining six variables are dependent variables.
  - e.g.,  $T$ , and  $\underline{V}$  are independent variables, thus
  - $\underline{U} = f(T, \underline{V}), \underline{H} = f(T, \underline{V}), \underline{A} = f(T, \underline{V}), \underline{G} = f(T, \underline{V}), \underline{S} = f(T, \underline{V}),$
  - $P = f(T, \underline{V}) \Leftarrow$  Equation of State

# Thermodynamic Properties

- The importance of partial derivative,  $\left(\frac{\partial X}{\partial Y}\right)_Z$
- Tools while using mathematics,

$$\left(\frac{\partial X}{\partial Y}\right)_X = 0 \quad \left(\frac{\partial X}{\partial X}\right)_Z = 1 \quad \left(\frac{\partial X}{\partial Y}\right)_Z = \frac{1}{\left(\frac{\partial Y}{\partial X}\right)_Z}$$

- Extensive and Intensive properties:

$$\left(\frac{\partial X}{\partial Y}\right)_{Z,N} = \left(\frac{\partial(NX)}{\partial Y}\right)_{Z,N} = N \left(\frac{\partial X}{\partial Y}\right)_Z$$

→

$$\left(\frac{\partial U}{\partial T}\right)_{V,N} = N \left(\frac{\partial U}{\partial T}\right)_V = NC_V$$

$$\left(\frac{\partial X}{\partial Y}\right)_{Z,N} = \left(\frac{\partial(NX)}{\partial(NY)}\right)_{Z,N} = \frac{N}{N} \left(\frac{\partial X}{\partial Y}\right)_Z = \left(\frac{\partial X}{\partial Y}\right)_Z$$

→

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

- Triple products rule:

$$\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial Y}{\partial Z}\right)_X = -1$$

→

$$\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Z}{\partial X}\right)_Y = - \left(\frac{\partial Z}{\partial Y}\right)_X$$

- Chain rule:

$$\left(\frac{\partial X}{\partial K}\right)_Z = \left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial K}\right)_Z$$

# Triple products rule

Differentiation of  $f(x, y)$  gives

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \quad (1.5)$$

Now since  $y$  is a function of  $x$  and  $z$ , it can be differentiated similarly:

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \quad (1.6)$$

Substituting Eq. (1.6) into Eq. (1.5) gives

$$df = \left[ \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \right] dx + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz$$

However, when  $f$  is expressed as a function of  $x$  and  $z$  and differentiated, the result is

$$df = \left(\frac{\partial f}{\partial x}\right)_z dx + \left(\frac{\partial f}{\partial z}\right)_x dz$$

If we now equate the coefficients of  $dz$  in these two equations, we find

$$\left(\frac{\partial f}{\partial z}\right)_x = \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x \quad \left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

# Thermodynamic Properties

- By correlations,

- an open system during a reversible process without  $W_S$

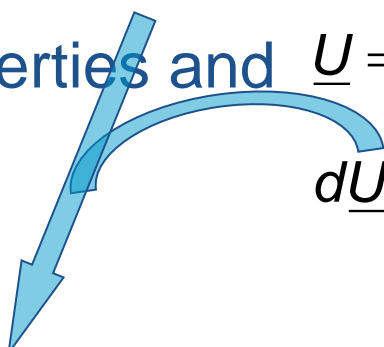
$$dU = TdS - PdV + \hat{G}dM \quad \text{or} \quad d\underline{U} = Td\underline{S} - Pd\underline{V} + \underline{G}dN \quad (4.2-13a)$$

- a closed system during a reversible process without  $W_S$ ,

$$dU = TdS - PdV \quad \text{or} \quad d\underline{U} = Td\underline{S} - Pd\underline{V}$$

- While  $\underline{U}$  is a state properties and  $\underline{U} = \underline{U}(\underline{S}, \underline{V})$

$$d\underline{U} = \left( \frac{\partial \underline{U}}{\partial \underline{S}} \right)_{\underline{V}} d\underline{S} + \left( \frac{\partial \underline{U}}{\partial \underline{V}} \right)_{\underline{S}} d\underline{V}$$


$$\therefore \left( \frac{\partial \underline{U}}{\partial \underline{S}} \right)_{\underline{V}} = T \quad \text{and} \quad \left( \frac{\partial \underline{U}}{\partial \underline{V}} \right)_{\underline{S}} = -P$$

# Evaluation of Thermodynamic Partial Derivatives

- ❖ **Special definitions for some partial derivatives:**

$$\left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} \equiv C_V ; \left(\frac{\partial \underline{H}}{\partial T}\right)_P \equiv C_P$$

$$\frac{1}{\underline{V}} \left(\frac{\partial \underline{V}}{\partial T}\right)_P = \alpha \text{ (coeff. of thermal expansion)}$$

$$\frac{-1}{\underline{V}} \left(\frac{\partial \underline{V}}{\partial P}\right)_T = \kappa_T \text{ (isothermal compressibility)}$$

- ❖ **For an open system (extensive properties)**

$$d\underline{U} = T d\underline{S} - P d\underline{V} + \underline{G} d\underline{N} \Rightarrow d\underline{S} = \frac{d\underline{U}}{T} + \frac{P d\underline{V}}{T} - \frac{\underline{G} d\underline{N}}{T}$$

- ❖ **For a closed system (intensive properties)**

$$d\underline{U} = T d\underline{S} - P d\underline{V} \Rightarrow d\underline{S} = \frac{d\underline{U}}{T} + \frac{P d\underline{V}}{T}$$

$$\underline{H} = \underline{U} + P\underline{V} \Rightarrow d\underline{H} = d\underline{U} + P d\underline{V} + \underline{V} dP \Rightarrow$$

$$d\underline{H} = T d\underline{S} + \underline{V} dP \text{ \& } dH = T dS + V dP + \underline{G} dN$$

$$\underline{A} = \underline{U} - T\underline{S} \Rightarrow d\underline{A} = d\underline{U} - T d\underline{S} - \underline{S} dT \Rightarrow$$

$$d\underline{A} = -P d\underline{V} - \underline{S} dT \text{ \& } dA = -P dV - S dT + \underline{G} dN$$

$$\underline{G} = \underline{H} - T\underline{S} \Rightarrow d\underline{G} = d\underline{H} - T d\underline{S} - \underline{S} dT \Rightarrow$$

$$d\underline{G} = \underline{V} dP - \underline{S} dT \text{ \& } dG = V dP - S dT + \underline{G} dN$$



$$\diamond dU = T dS - P dV + G dN$$

$$\diamond U = f(S, V, N)$$

$$\Rightarrow dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{V,S} dN$$

$\therefore$

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = \left(\frac{\partial U}{\partial S}\right)_V = T$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = \left(\frac{\partial U}{\partial V}\right)_S = -P$$

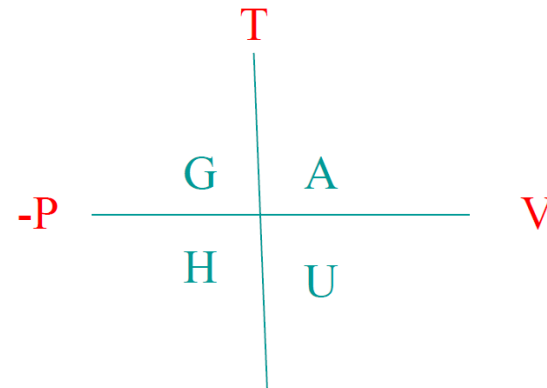
$$\left(\frac{\partial U}{\partial N}\right)_{V,S} = G$$

- $\diamond$  **Maxwell's relations (From the commutative property of the mixed second derivatives)**

$$\frac{\partial}{\partial V} \Big|_S \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial}{\partial S} \Big|_V \left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

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

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



# Entropy change

## ❖ Entropy Change

- ❖  $\underline{S} = f(\underline{U}, \underline{V}) \Rightarrow \underline{S} = f(T, \underline{V})$  or  $f(T, P)$ 
  - ❖ Let  $\underline{S} = f(T, \underline{V})$

$$d\underline{S} = \left( \frac{\partial \underline{S}}{\partial T} \right)_{\underline{V}} dT + \left( \frac{\partial \underline{S}}{\partial \underline{V}} \right)_T d\underline{V}$$

$$\left( \frac{\partial \underline{S}}{\partial T} \right)_{\underline{V}} = \left( \frac{\partial \underline{S}}{\partial \underline{U}} \right)_{\underline{V}} \left( \frac{\partial \underline{U}}{\partial T} \right)_{\underline{V}} = \left[ \left( \frac{\partial \underline{U}}{\partial \underline{S}} \right)_{\underline{V}} \right]^{-1} \left( \frac{\partial \underline{U}}{\partial T} \right)_{\underline{V}} = \frac{C_V}{T}$$

$$\left( \frac{\partial \underline{S}}{\partial \underline{V}} \right)_T = \left( \frac{\partial P}{\partial T} \right)_{\underline{V}} \text{ from Maxwell's relation}$$

$$\Rightarrow d\underline{S} = \frac{C_V}{T} dT + \left( \frac{\partial P}{\partial T} \right)_{\underline{V}} d\underline{V}$$

Similarly,

$$\Rightarrow d\underline{S} = \frac{C_P}{T} dT - \left( \frac{\partial \underline{V}}{\partial T} \right)_P dP$$

# Internal Energy Change & Enthalpy Change

## ❖ Internal Energy Change & Enthalpy Change

$$\begin{aligned}d\underline{U} &= T d\underline{S} - P d\underline{V} = T \left[ \frac{C_V}{T} dT + \left( \frac{\partial P}{\partial T} \right)_V d\underline{V} \right] - P d\underline{V} \\ &= C_V dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] d\underline{V} = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T d\underline{V}\end{aligned}$$

$$\text{For an ideal gas} \Rightarrow \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P = T \frac{R}{V} - P = P - P = 0$$

$$d\underline{H} = C_P dT + \left[ \underline{V} - T \left( \frac{\partial \underline{V}}{\partial T} \right)_P \right] dP = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP$$

$$\text{For an ideal gas} \Rightarrow \left( \frac{\partial H}{\partial P} \right)_T = \underline{V} - T \left( \frac{\partial \underline{V}}{\partial T} \right)_P = \underline{V} - T \frac{R}{P} = \underline{V} - \underline{V} = 0$$

## ❖ Express thermodynamic properties in terms of

$$T, P, \underline{V}, C_P \text{ or } C_V \text{ \& } \left( \frac{\partial}{\partial P} \right), \left( \frac{\partial}{\partial V} \right), \left( \frac{\partial}{\partial T} \right), \dots$$

## ❖ If EOS, $C_P$ or $C_V$ are given, thermodynamic properties can be calculated.

# Useful definitions & thermodynamic identities

$$\frac{\partial}{\partial \underline{V}} \Big|_T \left( \frac{\partial \underline{U}}{\partial T} \right)_{\underline{V}} = \left( \frac{\partial C_V}{\partial \underline{V}} \right)_T = \frac{\partial}{\partial T} \Big|_{\underline{V}} \left( \frac{\partial \underline{U}}{\partial \underline{V}} \right)_T = \left\{ \frac{\partial}{\partial T} \left[ T \left( \frac{\partial P}{\partial T} \right)_{\underline{V}} - P \right] \right\}_{\underline{V}} = T \left( \frac{\partial^2 P}{\partial T^2} \right)_{\underline{V}}$$

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

Similarly,

$$\Rightarrow \left( \frac{\partial C_P}{\partial P} \right)_T = -T \left( \frac{\partial^2 \underline{V}}{\partial T^2} \right)_P$$

$$\Rightarrow C_P = C_V + \frac{TV\alpha^2}{\kappa_T}$$

❖ Table 6.2-1

❖ Useful definitions & thermodynamic identities

# Summary: Thermodynamic Properties

- Ex.

**Table 6.2-1** Some Useful Definitions and Thermodynamic Identities

*Definitions*

$$\text{Constant-volume heat capacity} = C_V = \left( \frac{\partial U}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V$$

$$\text{Constant-pressure heat capacity} = C_P = \left( \frac{\partial H}{\partial T} \right)_P = T \left( \frac{\partial S}{\partial T} \right)_P$$

$$\text{Isothermal compressibility} = \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

$$\text{Coefficient of thermal expansion} = \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

$$\text{Joule-Thomson coefficient} = \mu = -\frac{\left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right]}{C_P}$$

*Maxwell relations*

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

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

*Thermodynamic identities*

$$\left( \frac{\partial H}{\partial S} \right)_P = \left( \frac{\partial U}{\partial S} \right)_V = T \quad \left( \frac{\partial G}{\partial P} \right)_T = \left( \frac{\partial H}{\partial P} \right)_S = V$$

$$\left( \frac{\partial U}{\partial V} \right)_S = \left( \frac{\partial A}{\partial V} \right)_T = -P \quad \left( \frac{\partial A}{\partial T} \right)_V = \left( \frac{\partial G}{\partial T} \right)_P = -S$$

*Thermodynamic functions*

$$dU = T dS - P dV = C_V dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV$$

$$dH = T dS + V dP = C_P dT + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP$$

$$dA = -P dV - S dT$$

$$dG = V dP - S dT$$

*Miscellaneous*

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P = \frac{T\alpha}{\kappa_T} - P \quad \frac{\partial}{\partial T} \Big|_P \left( \frac{G}{T} \right) = -\frac{H}{T^2} \quad \frac{\partial}{\partial T} \Big|_P \left( \frac{G}{T} \right) = H$$

$$\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P = V(1 - T\alpha) \quad \frac{\partial}{\partial T} \Big|_V \left( \frac{A}{T} \right) = -\frac{U}{T^2} \quad \frac{\partial}{\partial T} \Big|_V \left( \frac{A}{T} \right) = U$$

$$\bar{G} = \left( \frac{\partial G}{\partial N} \right)_{T,P} = \left( \frac{\partial A}{\partial N} \right)_{T,V} = \left( \frac{\partial H}{\partial N} \right)_{P,S} = \left( \frac{\partial U}{\partial N} \right)_{S,V} = -T \left( \frac{\partial S}{\partial N} \right)_{U,V}$$

### Ex. 6.2.3

Develop expressions of (i) thermal expansion coefficient, (ii) isothermal compressibility, (iii) Joule-Thompson coefficient, and (iv)  $C_P - C_V$ . Apply (a) ideal gas and (b) van der Waal gas into these expressions.

<sol>

(a) Ideal gas  $\Rightarrow PV = RT$

$$\textcircled{1} \alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \stackrel{\text{EOS}}{=} \frac{1}{V} \left[ \frac{\partial}{\partial T} \left( \frac{RT}{P} \right) \right]_P$$

$$= \frac{1}{V} \frac{R}{P} = \frac{1}{T}$$

$$\textcircled{2} \kappa_T \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \stackrel{\text{EOS}}{=} -\frac{1}{V} \left[ \frac{\partial}{\partial P} \left( \frac{RT}{P} \right) \right]_T$$

$$= -\frac{1}{V} RT (-1) \frac{1}{P^2} = \frac{1}{P}$$

$$\textcircled{3} \mu \equiv \left( \frac{\partial T}{\partial P} \right)_H$$

Eq (6.2-22)  $dH = C_p dT + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP$

For constant H,  $dH = 0$

$$\therefore 0 = C_p dT|_H + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP|_H$$

$$\Rightarrow \alpha \equiv \left( \frac{\partial T}{\partial P} \right)_H = \frac{- \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right]}{C_p} \quad \leftarrow \text{EOS}$$

$$= - \frac{V}{C_p} \left[ 1 - \frac{T}{V} \left( \frac{\partial V}{\partial T} \right)_P \right]$$

$$= - \frac{V}{C_p} (1 - T \alpha) = - \frac{V}{C_p} \left( 1 - T \cdot \frac{1}{T} \right) = 0 \quad \ast$$

$$\textcircled{3} \quad C_p = T \left( \frac{\partial S}{\partial T} \right)_P$$

Eq. (4.2-19)  $dS = \frac{C_v}{T} dT + \left( \frac{\partial P}{\partial T} \right)_V dV$

$$\therefore \left( \frac{\partial S}{\partial T} \right)_P = \frac{C_v}{T} \left( \frac{\partial T}{\partial T} \right)_P + \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P$$

$$= \frac{C_v}{T} + \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P$$

$$= \frac{C_p}{T} \quad \leftarrow \text{EOS}$$

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

For ideal gases

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{\partial}{\partial T} \left( \frac{RT}{V} \right)_V = \frac{R}{V}$$

$$\left( \frac{\partial V}{\partial T} \right)_P = \frac{\partial}{\partial T} \left( \frac{RT}{P} \right)_P = \frac{R}{P}$$

$$\therefore (C_p^* - C_v^*) = T \cdot \frac{R}{V} \cdot \frac{R}{P} = R \quad \ast$$

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT$$

$\langle \rangle$  vdW EOS

$$T = \frac{PV}{R} - \frac{Pb}{R} + \frac{a}{VR} - \frac{ab}{RV^2}$$

$$\textcircled{1} \quad \alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \frac{1}{\left( \frac{\partial T}{\partial V} \right)_P}$$

$$= \frac{1}{V} \frac{1}{\frac{\partial}{\partial V} \left[ \frac{PV}{R} - \frac{Pb}{R} + \frac{a}{VR} - \frac{ab}{RV^2} \right]_P}$$

$$= \left( \frac{PV}{R} - \frac{a}{VR} + \frac{2ab}{RV^2} \right)^{-1}$$

vdW

$$\frac{PV}{R} = \frac{TV}{(V-b)} - \frac{a}{RV} = \left[ \frac{TV}{V-b} - \frac{2a}{RV^2} (V-b) \right]^{-1} \quad \ast$$

$$\textcircled{2} \quad \kappa_T \equiv - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = - \frac{1}{V} \frac{1}{\left( \frac{\partial P}{\partial V} \right)_T}$$

vdW EOS:  $P = \frac{RT}{V-b} - \frac{a}{V^2}$

$$\left( \frac{\partial P}{\partial V} \right)_T = \frac{\partial}{\partial V} \left( \frac{RT}{V-b} - \frac{a}{V^2} \right)_T$$

$$= \frac{-RT}{(V-b)^2} + \frac{2a}{V^3}$$

$$\therefore \kappa_T = \left[ \frac{RTV}{(V-b)^2} - \frac{2a}{V^2} \right]^{-1} \quad \ast$$

$$\textcircled{3} \quad \mu \equiv \left( \frac{\partial T}{\partial P} \right)_H = - \frac{[V - T \left( \frac{\partial V}{\partial T} \right)_P]}{C_p}$$

$$= - \frac{[V - T \left( \frac{\partial T}{\partial V} \right)_P^{-1}]}{C_p}$$

vdW EOS

$$\left( \frac{\partial T}{\partial V} \right)_P = \frac{P}{R} - \frac{a}{RV^2} + \frac{2ab}{RV^3}$$

$$\uparrow$$

$$\frac{T}{V-b} - \frac{a}{RV^2}$$

$$\therefore \mu^{vdW} = - \frac{V}{C_p} \left[ 1 - \frac{1}{\frac{V}{V-b} - \frac{2a}{RT} \left( \frac{V-b}{V^2} \right)} \right] \quad *$$

$$\textcircled{4} \quad C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P$$

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

vdW EOS

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{\partial}{\partial T} \left[ \frac{RT}{V-b} - \frac{a}{V^2} \right] \Big|_V = \frac{R}{V-b}$$

$$\left( \frac{\partial T}{\partial V} \right)_P = \frac{T}{V-b} - \frac{2a}{RV^2} + \frac{2ab}{RV^3}$$

$$\therefore (C_p - C_v)^{vdW} = \frac{R}{1 - \frac{2a}{RT} \frac{(V-b)^2}{V^3}} \quad *$$



# Evaluation of changes in thermodynamic properties of real substance accompanying a change of state

- Evaluate the changes of U, H, S, ...for real fluids from Charts or Tables.
- Calculate changes of U, H, S,....for real fluids from equations with parameters that have been fitted to experimental data.

## ❖ Volumetric Equations of State (P-V-T)

## ❖ Cubic equations of state (EOS)

### ❖ General form

$$\underline{V}^3 + a_1 \underline{V}^2 + a_2 \underline{V} + a_3 = 0 \quad \text{or}$$

$$Z^3 + \alpha Z^2 + \beta Z + \gamma = 0 \quad \text{where } Z = \frac{P\underline{V}}{RT}$$

### ❖ General form of some simple cubic EOS (Table 6.4-2)

$$P = \frac{RT}{\underline{V} - b} - \frac{(\underline{V} - \eta)\theta}{(\underline{V} - b)(\underline{V}^2 + \delta\underline{V} + \varepsilon)}$$

# Cubic equation of state (EOS)

- ❖ van der Waals EOS (1873)

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2}$$

where  $a$  and  $b$  are parameters of the equation which are substance-specified constants. They can be estimated from critical point data (Sec. 6.6)

$$\left( \frac{\partial P}{\partial \underline{V}} \right)_T \Big|_{at T_c, P_c, V_c} = 0 \quad \& \quad \left( \frac{\partial^2 P}{\partial \underline{V}^2} \right)_T \Big|_{at T_c, P_c, V_c} = 0$$

$$\Rightarrow a = f(\text{critical point data}) \quad \& \quad b = f(\text{critical point data})$$

- ❖ Redlich-Kwong (RK) EOS (1949)

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{T^{1/2} \underline{V}(\underline{V} + b)}$$

- ❖ Soave (SRK) EOS (1972)

$$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b)}$$

- ❖ Peng-Robinson (PR) EOS (1976)

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)}$$

- Cubic EOS are generally applicable to both vapor and liquid regions for hydrocarbons, of the vapor region only for many other pure fluids.

# Cubic Equation of State

- The general form of Cubic EOS (in the P-explicit format),

$$P = \frac{RT}{\underline{V} - b} - \frac{(\underline{V} - \eta)\theta}{(\underline{V} - b)(\underline{V}^2 + \delta\underline{V} + \varepsilon)}$$

**Table 6.4-2** Parameters for Cubic Equations of State  $P = \frac{RT}{\underline{V} - b} - \Delta$

Author	Year	$\theta$	$\eta$	$\delta$	$\varepsilon$	$\Delta$
van der Waals	1873	$a$	$b$	0	0	$\frac{a}{\underline{V}^2}$
Clausius	1880	$a/T$	$b$	$2c$	$c^2$	$\frac{a/T}{(\underline{V} + c)^2}$
Berthelot	1899	$a/T$	$b$	0	0	$\frac{a/T}{\underline{V}^2}$
Redlich-Kwong	1949	$a/\sqrt{T}$	$b$	$b$	0	$\frac{a/\sqrt{T}}{\underline{V}(\underline{V} + b)}$
Soave	1972	$\theta_S(T)$	$b$	$b$	0	$\frac{\theta_S(T)}{\underline{V}(\underline{V} + b)}$
Lee-Erbar-Edmister	1973	$\theta_L(T)$	$\eta(T)$	$b$	0	$\frac{\theta_L(T)[\underline{V} - \eta(T)]}{(\underline{V} - b)(\underline{V} + b)}$
Peng-Robinson	1976	$\theta_{PR}(T)$	$b$	$2b$	$-b^2$	$\frac{\theta_{PR}(T)}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)}$
Patel-Teja	1981	$\theta_{PT}(T)$	$b$	$b + c$	$-cb$	$\frac{\theta_{PT}(T)}{\underline{V}(\underline{V} + b) + c(\underline{V} - b)}$

Note: If  $\eta = b$ , Eq. 6.4-3 reduces to

$$P = \frac{RT}{\underline{V} - b} - \frac{\theta}{\underline{V}^2 + \delta\underline{V} + \varepsilon}$$

# Virial equation

## ❖ Virial equation (Onnes, 1901)

$$\frac{PV}{RT} = 1 + \frac{B(T)}{\underline{V}} + \frac{C(T)}{\underline{V}^2} + \dots$$

where  $B$  and  $C$  are the second virial and the third virial coefficients, respectively.

- virial equation can be derived from statistical mechanics.
- virial coefficients can be evaluated if the potential function between molecules is given.
- virial equation with sufficient number of coefficients is good for vapor-phase prediction, but not for liquid phase.
  - ◆ Two-term virial equation

$$\frac{PV}{RT} = 1 + \frac{B(T)}{\underline{V}}$$

useful only  $P < 10$  bar (low density region)

# Virial-type equations of state

## ❖ BWR equation (Benedict, Webb & Rubin, 1940)

$$\frac{P\underline{V}}{RT} = 1 + \left( B - \frac{A}{RT} - \frac{C}{RT^3} \right) \frac{1}{\underline{V}} + \left( b - \frac{a}{RT} \right) \frac{1}{\underline{V}^2} + \frac{a\alpha}{RT\underline{V}^5} + \frac{\beta}{RT^3\underline{V}} \left( 1 + \frac{\gamma}{\underline{V}^2} \right) \exp\left( \frac{-\gamma}{\underline{V}^2} \right)$$

eight parameters:  $a$ ,  $b$ ,  $A$ ,  $B$ ,  $C$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  are specific to each fluid, which were determined from experimental data: vapor pressures and/or density data

## ❖ Bender equation (1970)- 20 parameters

$$P = \frac{T}{\underline{V}} \left[ R + \frac{B}{\underline{V}} + \frac{C}{\underline{V}^2} + \frac{D}{\underline{V}^3} + \frac{E}{\underline{V}^4} + \frac{F}{\underline{V}^5} + \left( G + \frac{H}{\underline{V}^2} \right) \frac{1}{\underline{V}^2} \exp\left( \frac{-a_{20}}{\underline{V}^2} \right) \right]$$

where  $B$ ,  $C$ ,  $D$ ,  $E$ ,  $F$ ,  $G$  &  $H$  are functions of  $T$ .

- Coefficients of these equations known only for light hydrocarbons and a few other substances.

## ❖ Evaluation of $\Delta H$ , $\Delta U$ , and $\Delta S$

$$\Delta H = H(T_2, P_2) - H(T_1, P_1) = \int_{T_1, P_1}^{T_2, P_2} dH$$

State function  $\Delta H_{12} = \Delta H_a + \Delta H_b + \Delta H_c$

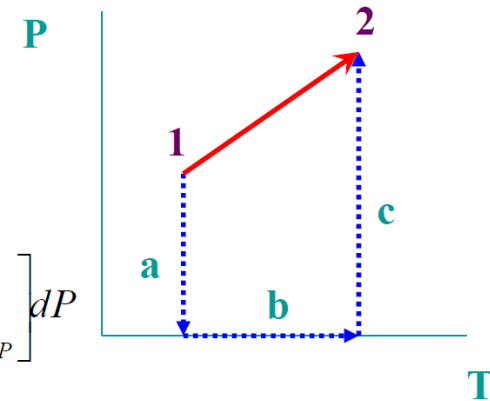
$$\Delta H = \int_{P_1, T_1}^{P=0, T_1} \left[ \underline{V} - T \left( \frac{\partial \underline{V}}{\partial T} \right)_P \right] dP + \int_{T_1, P=0}^{T_2, P=0} C_P^* dT + \int_{P=0, T_2}^{P_2, T_2} \left[ \underline{V} - T \left( \frac{\partial \underline{V}}{\partial T} \right)_P \right] dP$$

Similarly,

$$\Delta S = - \int_{P_1, T_1}^{P=0, T_1} \left( \frac{\partial \underline{V}}{\partial T} \right)_P dP + \int_{T_1, P=0}^{T_2, P=0} \frac{C_P^*}{T} dT - \int_{P=0, T_2}^{P_2, T_2} \left( \frac{\partial \underline{V}}{\partial T} \right)_P dP$$

$$\Delta S = \int_{V_1, T_1}^{V=\infty, T_1} \left( \frac{\partial P}{\partial T} \right)_V dV + \int_{T_1, V=\infty}^{T_2, V=\infty} \frac{C_V^*}{T} dT + \int_{V=\infty, T_2}^{V_2, T_2} \left( \frac{\partial P}{\partial T} \right)_V dV$$

$$\Delta U = \int_{V_1, T_1}^{V=\infty, T_1} \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV + \int_{T_1, V=\infty}^{T_2, V=\infty} C_V^* dT + \int_{V=\infty, T_2}^{V_2, T_2} \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV$$



- Given  $C_P^*$ ,  $C_V^*$  data and volumetric EOS, it is possible to calculate  $\Delta H$ ,  $\Delta U$ ,  $\Delta S$  for any two states of fluids

# Ideal gas: change of state

$$d\underline{H} = C_P dT + \left[ \underline{V} - T \left( \frac{\partial \underline{V}}{\partial T} \right)_P \right] dP$$

For an ideal gas  $\Rightarrow \left( \frac{\partial \underline{H}}{\partial P} \right)_T = \underline{V} - T \left( \frac{\partial \underline{V}}{\partial T} \right)_P = \underline{V} - T \frac{R}{P} = \underline{V} - \underline{V} = 0$

$$\underline{H}^{IG}(T_2, P_2) - \underline{H}^{IG}(T_1, P_1) = \int_{T_1, P=0}^{T_2, P=0} C_P^* dT$$

$$d\underline{S} = \frac{C_P}{T} dT - \left( \frac{\partial \underline{V}}{\partial T} \right)_P dP$$

For ideal gas  $\Rightarrow d\underline{S} = \frac{C_P^*}{T} dT - \left( \frac{R}{P} \right) dP$

$$\underline{S}^{IG}(T_2, P_2) - \underline{S}^{IG}(T_1, P_1) = - \int_{T_1, P_1}^{T_1, P=0} \left( \frac{R}{P} \right) dP + \int_{T_1}^{T_2} \frac{C_P^*}{T} dT - \int_{T_2, P=0}^{T_2, P_2} \left( \frac{R}{P} \right) dP = \int_{T_1}^{T_2} \frac{C_P^*}{T} dT - R \ln \frac{P_2}{P_1}$$

$$\underline{S}^{IG}(T_2, \underline{V}_2) - \underline{S}^{IG}(T_1, \underline{V}_1) = \int_{T_1, \underline{V}_1}^{T_1, \underline{V}=\infty} \left( \frac{R}{\underline{V}} \right) d\underline{V} + \int_{T_1}^{T_2} \frac{C_V^*}{T} dT + \int_{T_2, \underline{V}=\infty}^{T_2, \underline{V}_2} \left( \frac{R}{\underline{V}} \right) d\underline{V} = \int_{T_1}^{T_2} \frac{C_V^*}{T} dT + R \ln \frac{\underline{V}_2}{\underline{V}_1}$$

# Departure functions

$$\begin{aligned}\Delta \underline{H} &= \underline{H}(T_2, P_2) - \underline{H}(T_1, P_1) = \int_{P_1, T_1}^{P=0, T_1} \left[ \underline{V} - T \left( \frac{\partial \underline{V}}{\partial T} \right)_P \right] dP + \underline{H}^{IG}(T_2, P_2) - \underline{H}^{IG}(T_1, P_1) + \int_{P=0, T_2}^{P_2, T_2} \left[ \underline{V} - T \left( \frac{\partial \underline{V}}{\partial T} \right)_P \right] dP \\ &= -(\underline{H} - \underline{H}^{IG})_{T_1, P_1} + \underline{H}^{IG}(T_2, P_2) - \underline{H}^{IG}(T_1, P_1) + (\underline{H} - \underline{H}^{IG})_{T_2, P_2}\end{aligned}$$

Similarly,

$$\begin{aligned}\Delta \underline{S} &= \underline{S}(T_2, P_2) - \underline{S}(T_1, P_1) = -\int_{P_1, T_1}^{P=0, T_1} \left[ \left( \frac{\partial \underline{V}}{\partial T} \right)_P \right] dP + \int_{T_1}^{T_2} \frac{C_P^*}{T} dT - \int_{P=0, T_2}^{P_2, T_2} \left[ \left( \frac{\partial \underline{V}}{\partial T} \right)_P \right] dP \\ &= -\int_{P_1, T_1}^{P=0, T_1} \left[ \left( \frac{\partial \underline{V}}{\partial T} \right)_P \right] dP + \underline{S}^{IG}(T_2, P_2) - \underline{S}^{IG}(T_1, P_1) + \int_{P_1, T_1}^{P=0, T_1} \left[ \frac{R}{P} \right] dP + \int_{P=0, T_2}^{P_2, T_2} \left[ \frac{R}{P} \right] dP - \int_{P=0, T_2}^{P_2, T_2} \left[ \left( \frac{\partial \underline{V}}{\partial T} \right)_P \right] dP \\ &= -\int_{P_1, T_1}^{P=0, T_1} \left[ \left( \frac{\partial \underline{V}}{\partial T} \right)_P - \frac{R}{P} \right] dP + \underline{S}^{IG}(T_2, P_2) - \underline{S}^{IG}(T_1, P_1) - \int_{P=0, T_2}^{P_2, T_2} \left[ \left( \frac{\partial \underline{V}}{\partial T} \right)_P - \frac{R}{P} \right] dP \\ &= -(\underline{S} - \underline{S}^{IG})_{T_1, P_1} + \underline{S}^{IG}(T_2, P_2) - \underline{S}^{IG}(T_1, P_1) + (\underline{S} - \underline{S}^{IG})_{T_2, P_2}\end{aligned}$$

$$\begin{aligned}\Delta \underline{S} &= \underline{S}(T_2, V_2) - \underline{S}(T_1, V_1) = \int_{V_1, T_1}^{V=\infty, T_1} \left[ \left( \frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV + \underline{S}^{IG}(T_2, V_2) - \underline{S}^{IG}(T_1, V_1) + \int_{V=\infty, T_2}^{V_2, T_2} \left[ \left( \frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV \\ &= -(\underline{S} - \underline{S}^{IG})_{T_1, V_1} + \underline{S}^{IG}(T_2, V_2) - \underline{S}^{IG}(T_1, V_1) + (\underline{S} - \underline{S}^{IG})_{T_2, V_2}\end{aligned}$$

## ■ Departure H and Departure S

$$(\underline{H} - \underline{H}^{IG})_{T, P} = \int_{T, P=0}^{T, P} \left[ \underline{V} - T \left( \frac{\partial \underline{V}}{\partial T} \right)_P \right] dP$$

$$(\underline{S} - \underline{S}^{IG})_{T, P} = -\int_{T, P=0}^{T, P} \left[ \left( \frac{\partial \underline{V}}{\partial T} \right)_P - \frac{R}{P} \right] dP$$

$$(\underline{S} - \underline{S}^{IG})_{T, V} = \int_{T, V=\infty}^{T, V} \left[ \left( \frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV$$

**EOS**  $P = f(T, V)$



# Evaluate departure H & S from EOS

Express  $\left(\frac{\partial \underline{V}}{\partial T}\right)_P$  in terms of  $\left(\frac{\partial P}{\partial T}\right)_V$  or  $\left(\frac{\partial P}{\partial \underline{V}}\right)_T$

$$d(P\underline{V}) = P d\underline{V} + \underline{V} dP \Rightarrow dP \equiv \frac{1}{\underline{V}} d(P\underline{V}) - \frac{P}{\underline{V}} d\underline{V}$$

From triple product rule,  $\left(\frac{\partial \underline{V}}{\partial T}\right)_P \left(\frac{\partial P}{\partial \underline{V}}\right)_T \left(\frac{\partial T}{\partial P}\right)_V = -1 \Rightarrow \left(\frac{\partial \underline{V}}{\partial T}\right)_P dP \Big|_T = -\left(\frac{\partial P}{\partial T}\right)_V d\underline{V} \Big|_T$

$$\therefore \left[ \underline{V} - T \left(\frac{\partial \underline{V}}{\partial T}\right)_P \right] dP = \underline{V} dP - T \left[ \left(\frac{\partial \underline{V}}{\partial T}\right)_P dP \right] = \underline{V} \left[ \frac{1}{\underline{V}} d(P\underline{V}) - \frac{P}{\underline{V}} d\underline{V} \right] + T \left[ \left(\frac{\partial P}{\partial T}\right)_V d\underline{V} \right] = d(P\underline{V}) + \left[ T \left(\frac{\partial P}{\partial T}\right)_V - P \right] d\underline{V}$$

$$\left( \underline{H} - \underline{H}^{IG} \right)_{T,P} = \int_{P\underline{V}=RT}^{P\underline{V}} d(P\underline{V}) + \int_{\underline{V}=\infty}^{\underline{V}} \left[ T \left(\frac{\partial P}{\partial T}\right)_V - P \right] d\underline{V} = RT(Z-1) + \int_{\underline{V}=\infty}^{\underline{V}} \left[ T \left(\frac{\partial P}{\partial T}\right)_V - P \right] d\underline{V}$$

Similarly,

$$\frac{R}{P} dP \equiv R \frac{d(P\underline{V})}{P\underline{V}} - R \frac{d\underline{V}}{\underline{V}} = R d \ln(P\underline{V}) - \frac{R}{\underline{V}} d\underline{V}$$

$$\int_{P=0}^P \left[ \frac{R}{P} - \left(\frac{\partial \underline{V}}{\partial T}\right)_P \right] dP = R \int_{P\underline{V}=RT}^{P\underline{V}} d \ln(P\underline{V}) - R \int_{\underline{V}=\infty}^{\underline{V}} \frac{d\underline{V}}{\underline{V}} + \int_{\underline{V}=\infty}^{\underline{V}} \left(\frac{\partial P}{\partial T}\right)_V d\underline{V}$$

$$\left( \underline{S} - \underline{S}^{IG} \right)_{T,P} = R \ln Z + \int_{\underline{V}=\infty}^{\underline{V}} \left[ \left(\frac{\partial P}{\partial T}\right)_V - \frac{R}{\underline{V}} \right] d\underline{V}$$

# Calculate departure H & S from PR EOS

$$\text{Peng - Robinson EOS : } P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)}$$

Eq. (6.4-29)

$$\left(\underline{H} - \underline{H}^{IG}\right)_{T,P} = RT(Z - 1) + \int_{\underline{V}=\infty}^{\underline{V}} \left[ T \left( \frac{\partial P}{\partial T} \right)_{\underline{V}} - P \right] d\underline{V} = RT(Z - 1) + \frac{T \left( \frac{da}{dT} \right) - a}{2\sqrt{2}b} \ln \left[ \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right]$$

$$\left(\underline{S} - \underline{S}^{IG}\right)_{T,P} = R \ln Z + \int_{\underline{V}=\infty}^{\underline{V}} \left[ \left( \frac{\partial P}{\partial T} \right)_{\underline{V}} - \frac{R}{\underline{V}} \right] d\underline{V} = R \ln(Z - B) + \frac{\left( \frac{da}{dT} \right)}{2\sqrt{2}b} \ln \left[ \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right]$$

where  $Z = P\underline{V} / (RT)$  &  $B = Pb / (RT)$

Eq. (6.4-30)

## Illustration 6.4.1: Construction of Thermodynamic Properties Charts

$O_2$ ,  $-100^\circ C \sim 150^\circ C$ ,  $1 \sim 100 \text{ bar}$

(1) Calculate  $z$ ,  $v$ ,  $H$ ,  $S = f(T, P)$

(2)  $p - v$  chart

(3)  $p - H$  chart

(4)  $T - S$  chart

Assumptions: \*  $O_2$  follows PR EOS

$$* C_p^* \left( \frac{J}{\text{mol K}} \right) = 25.46 + 1.519 \times 10^{-2} T - 0.7151 \times 10^{-5} T^2 + 1.311 \times 10^{-9} T^3$$

Reference states:

$$H^{ig}(25^\circ C, 1 \text{ bar}) = 0$$

$$S^{ig}(25^\circ C, 1 \text{ bar}) = 0$$

PR EOS

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)}$$

$$a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T) = a_c \alpha(T)$$

$$b = 0.0778 \frac{RT_c}{P_c}$$

$$\alpha(T) = \left\{ 1 + 0.4069 \left[ 1 - \sqrt{T/T_c} \right] \right\}^2$$

$$O_2: T_c = 154.6 \text{ K}, P_c = 5.046 \text{ MPa}$$

<Sol>

(1) \* Find  $Z$  and  $V$  at given  $T$  &  $P$

In a single phase region (e.g.  $T > T_c$ )

Procedure:

① given  $T_c, P_c \rightarrow b$  and  $a_c$

② given  $T \rightarrow \alpha(T)$  then  $a(T)$

③ given  $P \rightarrow$  solve

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}$$

$$\Downarrow \\ \frac{P}{RT} V, \text{ then } Z = \frac{PV}{RT}$$

or

Solve

$$Z^3 + (B-1)Z^2 + (A-3B^2-2B)Z + (B^3+B^2-AB) = 0$$

where

$$B = \frac{bP}{RT}$$

$$A = \frac{aP}{(RT)^2}$$

$$Z = \frac{PV}{RT}$$

Cubic  
in  $Z$

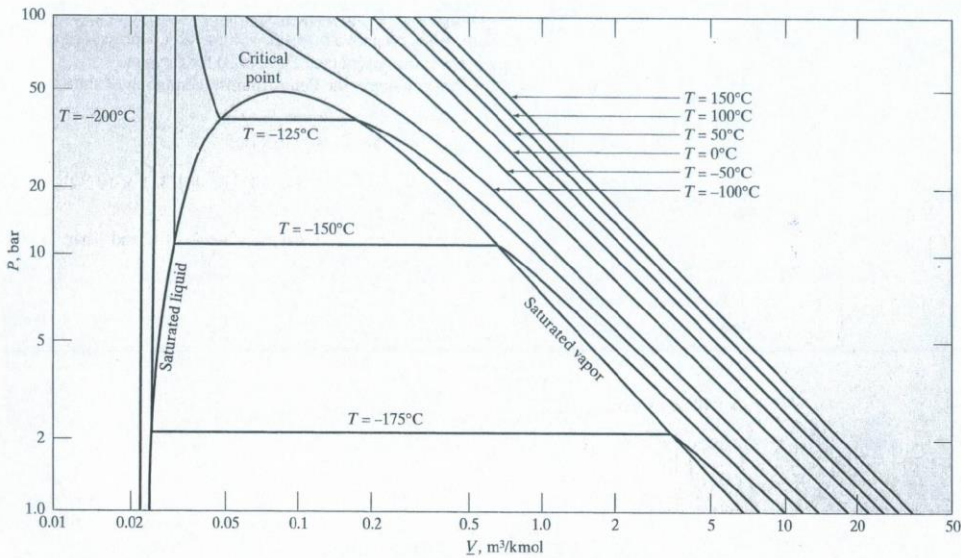
$$\Downarrow \\ Z, \text{ then } \underline{V} = \frac{ZRT}{P}$$

Change  $T$  and  $P \rightarrow V$  and  $Z$  (Table 6.4-4)

(2)  $p$  vs.  $\underline{V}$  chart (Fig. 6.4-3)  $\ln P$  vs.  $\ln \underline{V}$

\* For ideal gases,  $P = \frac{RT}{V}$  or  $\uparrow$

$$\underline{\ln P} = \underline{\ln(RT)} - \underline{\ln V} \text{ a straight line}$$



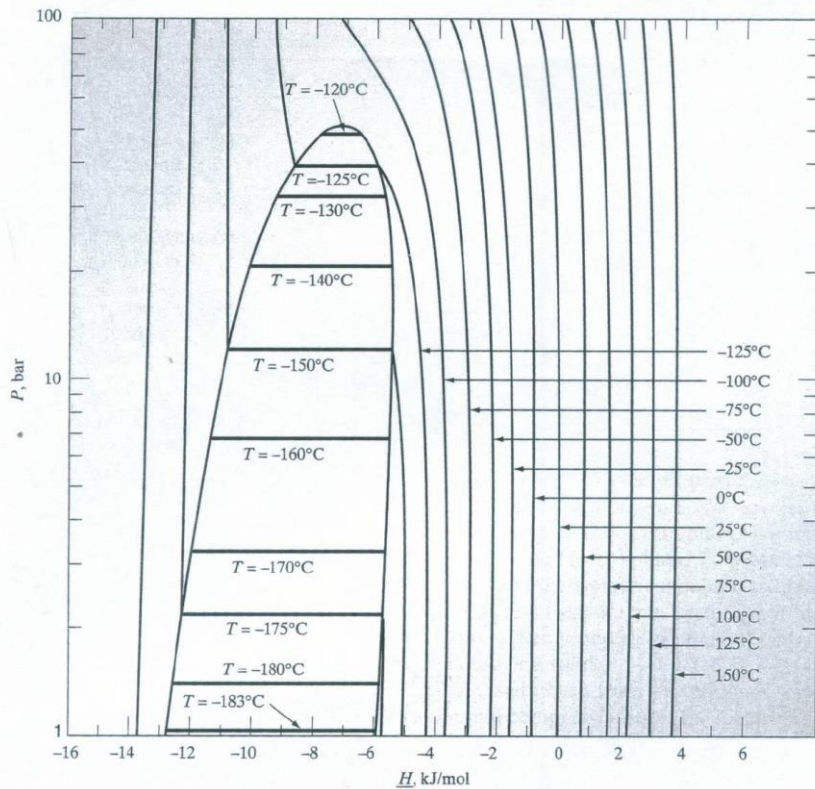
Pressure-volume diagram for oxygen calculated using the Peng-Robinson equation of state.

### (3) Enthalpy

$$\begin{aligned}
 \underline{H}(T, P) - \underline{H}^{\text{IG}}(25^\circ\text{C}, 1\text{bar}) &= \underline{H}(T, P) \\
 &= [\underline{H}(T, P) - \underline{H}^{\text{IG}}(T, P)] + [\underline{H}^{\text{IG}}(T, P) - \underline{H}^{\text{IG}}(25^\circ\text{C}, 1\text{bar})] \\
 &= \underbrace{(\underline{H} - \underline{H}^{\text{IG}})_{T, P}}_{\text{departure } \underline{H}} + \int_{T=298.15}^T C_p^* dT \\
 &\quad \text{Eq. (6.4-29) for PR EOS} \\
 &= (\underline{H} - \underline{H}^{\text{IG}})_{T, P} + 25.46 (T - 298.15) + \frac{1.519 \times 10^{-2}}{2} \\
 &\quad (T^2 - 298.15^2) - \frac{0.711 \times 10^{-5}}{3} (T^3 - 298.15^3) \\
 &\quad + \frac{1.311 \times 10^{-9}}{4} (T^4 - 298.15^4) \quad \sim (*a)
 \end{aligned}$$

Algorithm:

- ① given  $T_c, P_c \rightarrow b, a_c$
- ② given  $T \rightarrow \alpha(T)$  then  $a(T)$
- ③ given  $P \rightarrow$  solve PR EOS to find  $V, Z, B = \frac{Pb}{RT}$
- ④ Calc.  $(\underline{H} - \underline{H}^{\text{IG}})_{T, P}$  from Eq. (6.4-29)
- ⑤ Calc.  $\underline{H}(T, P)$  from Eq. (\*a)
- ⑥  $\underline{H} = f(T, P) \rightarrow$  Table 6.4-4
- ⑦  $p-H$  diagram  $\rightarrow$  Fig. 6.4-4



e.g.  $T = 25^\circ\text{C}$ ,  $p = 1\text{ bar}$

$\Rightarrow z = 0.9991$  ( $\text{O}_2$  is not an ideal gas)

$$\Rightarrow (\underline{H} - \underline{H}^{\text{IG}})_{T=25^\circ\text{C}, p=1\text{ bar}} = -9.44 \text{ J/mol.}$$

#### (4) Entropy

$$\underline{S}(T, P) - \underline{S}^{\text{IG}}(25^\circ\text{C}, 1\text{ bar}) = \underline{S}(T, P)$$

$$= (\underline{S} - \underline{S}^{\text{IG}})_{T, P} + [\underline{S}^{\text{IG}}(T, P) - \underline{S}^{\text{IG}}(25^\circ\text{C}, 1\text{ bar})]$$

$$= \underbrace{(\underline{S} - \underline{S}^{\text{IG}})_{T, P}}_{\text{departure } \underline{S}} + \int_{298.15}^T \frac{C_p^*}{T} dT - R \ln\left(\frac{P}{1\text{ bar}}\right)$$

departure  $\underline{S}$

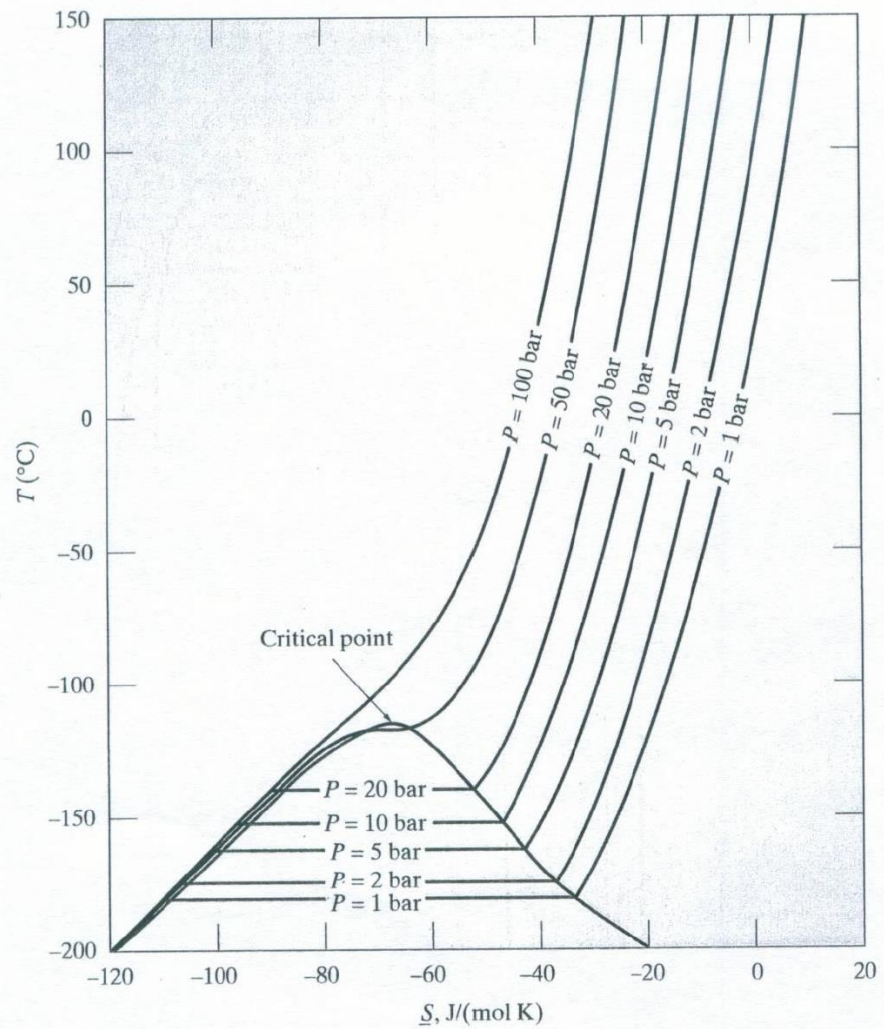
Eq (4.4-30) for PR EOS

The calculation procedure is similar to that describes in (3)

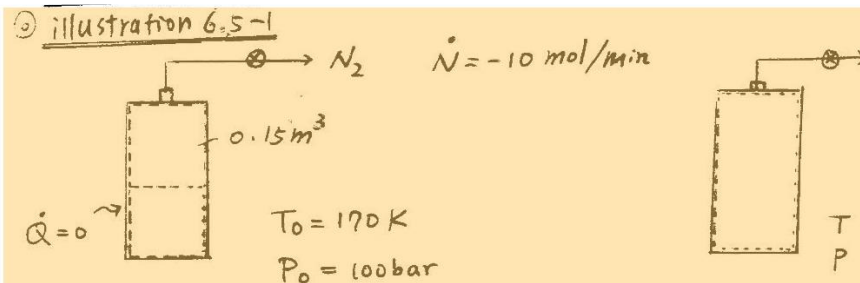
$$\underline{S} = f(T, P) \rightarrow \underline{\text{Table 6.4-4}}$$

⊙ T-s diagram  $\rightarrow$  Fig. 6.4-5





# Illustration 6.5-1



- (1) How many moles of gas will be in the cylinder at any time?
- (2) What will be the  $T$  and  $P$  of the gas in the cylinder after 50 min.?
  - (a) Assume that  $N_2$  is an ideal gas
  - (b) Use the  $N_2$  data in Fig. 3.3-3
  - (c) Assume that  $N_2$  is a van der Waals fluid.

Data:

$$c_p^* \text{ (J/molK)} = 27.2 + 4.2 \times 10^{-3} T \text{ (K)}$$



<sol>

(1) Calculation of  $N(t)$

System: the gas in the cylinder (open system)

Mass balance:  $\frac{dN}{dt} = \dot{N}$

integrate  $\Rightarrow N(t) = N_0 + \dot{N}t$

where

$N_0 = N|_{t=0} = \frac{V_{cylinder}}{V_0}$

(a) ideal gas

$V_0 = \frac{RT_0}{P_0} = 1.4134 \times 10^{-4} \text{ m}^3/\text{mol}$

$N_0 = \frac{0.15}{1.4134 \times 10^{-4}} = 1061.3 \text{ mol}$

$\therefore N(t) = 1061.3 - 10t$

(b) Using Fig. 3.3-3

$\hat{V}_0(170K, 100\text{bar}) \equiv \hat{V}_0(170K, 10\text{MPa})$   
 $\approx 0.0035 \text{ m}^3/\text{kg}$

$\therefore V_0 = (MW)\hat{V}_0 = 9.8 \times 10^{-5} \text{ m}^3/\text{mol}$

$N_0 = \frac{0.15}{9.8 \times 10^{-5}} = 1529.8 \text{ mol}$

$\Rightarrow N(t) = 1529.8 - 10t$

(c) Using Van der Waals Eos

$P = \frac{RT}{V-b} - \frac{a}{V^2}$

From Table 6.4-1, we have  $a_{N_2} = 0.1368$ ,

$b_{N_2} = 3.864 \times 10^{-5}$

$\Rightarrow 100 \text{ bar} = 1 \times 10^7 \text{ Pa} = \frac{8.314 \times 170}{V_0 - 3.864 \times 10^{-5}} - \frac{0.1368}{V_0^2}$

$\Downarrow$

$V_0 = 9.435 \times 10^{-5} \text{ m}^3/\text{mol}$

$N_0 = \frac{0.15}{9.435 \times 10^{-5}} = 1589.9 \text{ mol}$

$\therefore N(t) = 1589.9 - 10t$

(2) Calculate T and P at  $t = 50 \text{ min}$ , i.e.  $T_2, P_2$ .

To calculate  $T_2$  and  $P_2$ , we need an additional balance equation.

System: the portion of the gas that always in the cylinder

(closed system)

Entropy balance:

$\frac{ds}{dt} = 0$  (adiabatic & reversible expansion)

$S_0 = S(t)$

(a) ideal gas

$$\text{Eq (4.4-1)} \quad dS = C_V^* \frac{dT}{T} + R \frac{dV}{V}$$

$$C_V^* = C_P^* - R = 18.9 + 4.2 \times 10^{-3} T \quad (\text{J/mol}\cdot\text{K})$$

$$\Delta S = S_0 - S_{t=50\text{min}} = 0$$

$$\int_{S_0}^{S_{t=50\text{min}}} dS = \int_{T_0=170}^{T_2} \frac{(18.9 + 4.2 \times 10^{-3} T)}{T} dT$$

$$+ 8.314 \int_{V_0}^{V_2} \frac{dV}{V} = 0$$

$$\begin{cases} V_0 = 1.413 \times 10^{-4} \text{ m}^3/\text{mol} \\ V_2 = \frac{0.15}{1061.3 - 10 \times 50} = 2.672 \times 10^{-4} \text{ m}^3/\text{mol} \end{cases}$$

$$\therefore 18.9 \ln \frac{T_2}{170} + 4.2 \times 10^{-3} (T_2 - 170) + 8.314 \ln \left( \frac{2.672}{1.413} \right)$$

$$= 0$$

$$\Rightarrow \underline{T_2 = 130.3 \text{ K}} \quad \checkmark$$

$$\underline{P_2 = \frac{RT_2}{V_2} = 40.5 \text{ bar}} \quad \checkmark$$

(b) Using Fig. 3.3-3

$$v_2 = \frac{0.15}{1529.8 - 10 \times 50} = 1.0457 \times 10^{-4} \text{ m}^3/\text{mol}$$

$$\therefore \hat{v}_2 = \frac{v_2}{M} = 5.20 \times 10^{-3} \text{ m}^3/\text{kg}$$

\*1 Find the initial pt. ( $T = 170 \text{ K}$ ,  
 $P = 10 \text{ MPa}$ )

\*2 Follow the constant- $S$  curve down to  
the intersection with a curve of  
constant- $\hat{v}$  through  $\hat{v} = 5.2 \times 10^{-3} \text{ m}^3/\text{kg}$

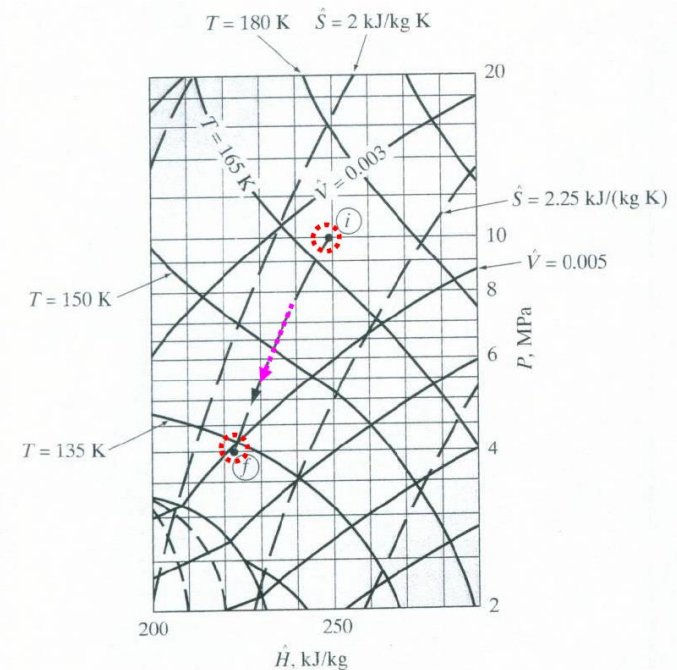
\*3 This intersection gives  $T_2$  and  $P_2$

$$\Rightarrow \begin{array}{l} T_2 = 133 \text{ K} \\ P_2 \approx 3.9 \text{ MPa} = 39 \text{ bar} \end{array}$$

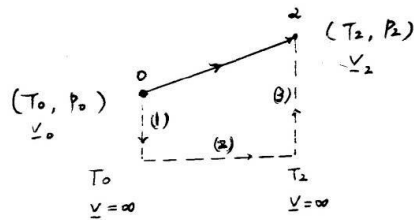
(c) Using vdW EOS

$$\text{Eq (6.2-19)} \Rightarrow dS = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

$$\text{vdW EOS} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b}$$



$$\int_{s_0}^{s_2} d\underline{s} = \int_{T_0}^{T_2} \frac{C_V^*}{T} dT + \int_{V_0}^{V_2} \frac{R}{V-b} dV = 0$$



$$0 = R \int_{V_0}^{V_2} \frac{dV}{V-b} + \int_{T_0=170\text{K}}^{T_2} \frac{C_V^*}{T} dT + \int_{V_0}^{V_2} \frac{dV}{V-b}$$

$$= R \int_{V_0}^{V_2} \frac{dV}{V-b} + \int_{170}^{T_2} \frac{C_V^*}{T} dT$$

$$\begin{cases} \frac{V_2}{V_0} = \frac{0.15}{1589.5 - 10 \times 50} = 1.377 \times 10^{-4} \text{ m}^3/\text{mol} \\ V_0 = 9.437 \times 10^{-5} \text{ m}^3/\text{mol} \end{cases}$$

$$\Rightarrow 0 = 8.314 \ln \left[ \frac{(1.377 - 3.864) \times 10^{-5}}{(9.437 - 3.864) \times 10^{-5}} \right] + 18.9 \ln \left( \frac{T_2}{170} \right)$$

$$+ 4.2 \times 10^{-3} (T_2 - 170)$$

$$\Rightarrow \boxed{T_2 = 133.1 \text{ K}}$$

$$\boxed{P_2 = \frac{RT_2}{V_2 - b} = \frac{a}{V_2^2} = 39.5 \text{ bar}}$$

\* The most convenient method  $\Rightarrow$  method (b).

# The Principles of corresponding states

## Ideal gas heat capacity:

- ❖ Intramolecular structure (e.g., bond length, vibration frequencies, configuration of constituent atoms, ...)
- ❖ Internal energy

## Volumetric EOS:

- ❖ intermolecular forces (interactions of each molecule with its neighbors)
- ❖ External energy
- ❖ Intermolecular interactions depend on the nature of the molecules:
  - ❖ Spherical molecules (e.g., Ar, CH<sub>4</sub>, .....
  - ❖ Nonspherical molecules (e.g., n-C<sub>10</sub>, n-C<sub>16</sub>, ...)
  - ❖ Molecules with permanent dipole moment (e.g., water, methanol, acetone, ...)
  - ❖ Molecules with permanent quadrupolar moment (e.g., CO<sub>2</sub>, N<sub>2</sub>, ..)
- ❖ Any one class molecular interactions are similar =>
- ❖ Volumetric EOS fits the volumetric data for one member of a class =>
- ❖ The same EOS is likely to fit the data for other molecules in the same class.

# The Corresponding State EOS

- By analyzing van der Waal EOS (read pp.237-240), it is suggested that all fluids can obey the same EOS in terms of reduced T ( $T_r = T/T_C$ ), reduced P ( $P_r = P/P_C$ ), reduced  $\underline{V}$  ( $\underline{V}_r = \underline{V}/\underline{V}_C$ ). This is called the corresponding state theorem.
- Experiments verify the existence of such a possibility.

# The Corresponding State EOS

- By defining  $Z = PV / RT$ 
  - Two-parameter corresponding state is
$$Z = Z(P_r, T_r)$$
  - Three-parameter corresponding state is
$$Z = Z(P_r, T_r, \omega)$$
where  $\omega = -1 - \log_{10}[P^{vap}(T_r = 0.7) / P_C]$ , the acentric factor.
- Typically, the plot of  $Z$  vs  $P_r$  is used (the following pages).

# The first generalized correction: the vdW EOS

## ❖ Critical point:

- ❖ The point of the highest temperature at which a liquid can exist.
- ❖ An inflection point on an isotherm in the P-V plane.

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \quad \& \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \quad \text{at } P_c \text{ and } V_c$$

Also, the first non-zero derivative should be odd and negative.

At critical point,

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \Rightarrow 0 = \frac{-RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \Rightarrow 0 = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4}$$

$$a = \frac{9V_c RT_c}{8} \quad \& \quad b = \frac{V_c}{3} \quad \text{when } V_c = 3b, \quad T_c = \frac{8a}{27bR}, \quad P_c = \frac{a}{27b^2}$$

or

$$P_c = \frac{RT_c}{V_c - (V_c/3)} - \frac{9V_c RT_c}{8V_c^2} = \frac{3}{8} \frac{RT_c}{V_c} \quad \& \quad Z_c = \frac{RT_c}{P_c V_c} = \frac{3}{8} = 0.375 \quad \text{or} \quad V_c = \frac{8}{3} \frac{RT_c}{P_c}$$



$$a, b = f(T_c, P_c) \Rightarrow a = \frac{9V_c RT_c}{8} = \frac{27R^2 T_c^2}{64P_c} \quad \& \quad b = \frac{V_c}{3} = \frac{RT_c}{8P_c}$$

vdW EOS :

$$\left[ P + \frac{27R^2 T_c^2 / (64P_c)}{V^2} \right] \left( V - \frac{V_c}{3} \right) = RT \Rightarrow$$

$$\left[ \frac{P}{P_c} + 3 \left( \frac{V_c}{V} \right)^2 \right] \left[ 3 \left( \frac{V}{V_c} \right) - 1 \right] = 8 \frac{T}{T_c} \Rightarrow$$

$$\left( P_r + \frac{3}{V_r^2} \right) (3V_r - 1) = 8T_r \quad \text{where } T_r = T/T_c, P_r = P/P_c, V_r = V/V_c$$

$T_r, P_r$  &  $V_r$  are reduced properties (dimensionless)

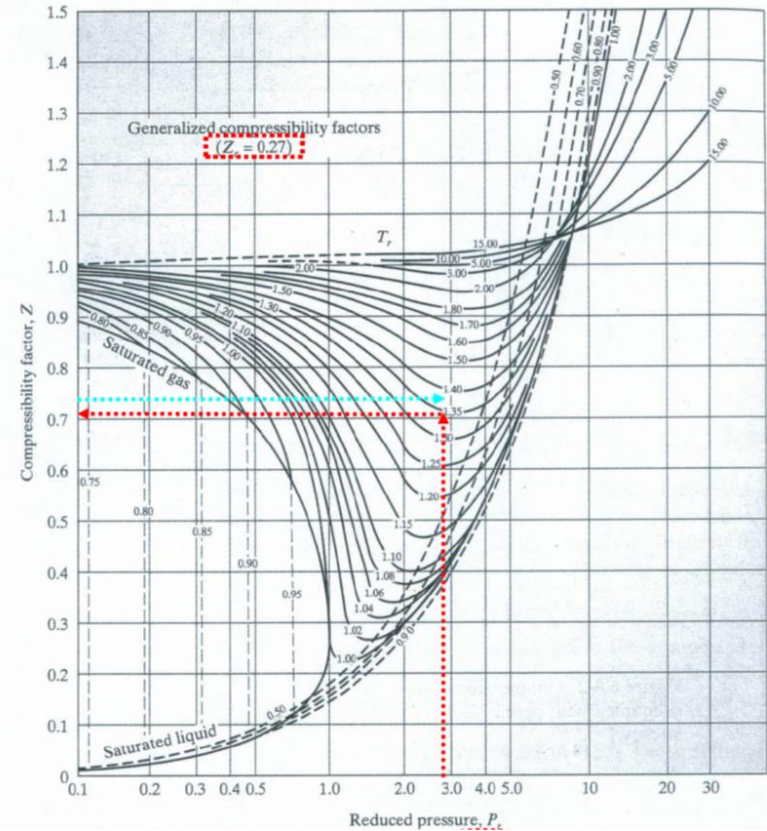
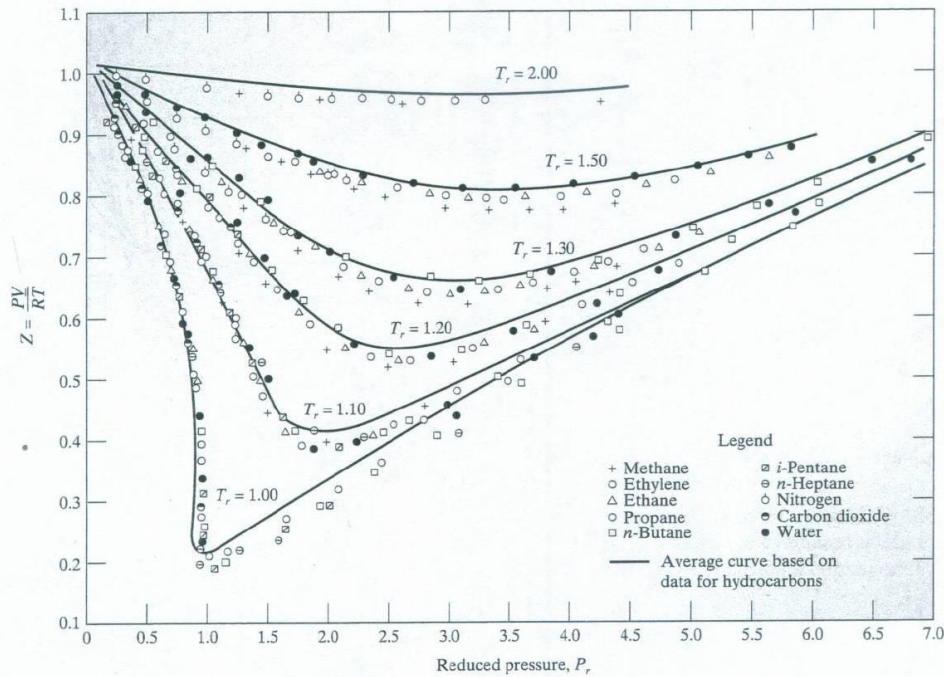
- ❖ **Two fluids, which have the same values of reduced T and P, have the same reduced volume (at the corresponding state)**
- ❖ **Two-parameter corresponding-states principle:**

$$Z = \frac{PV}{RT} = Z(T_r, P_r)$$

- ❖ **The function Z is determined by experimental data or Fig. 6.6-2**

# The generalized chart of compressibility factor

❖ Fig. 6.6-2



# Three parameters CSP

- ❖ vdW EOS => Two-parameter CSP => All vdW fluids have the same  $Z_C = 3/8 = 0.375$
- ❖ Table 6.6-1 shows  $Z_C$  for most real fluids ranges from 0.23 to 0.31
- ❖ Two-parameter CSP is failed => Three-parameter CSP

$$Z = Z(T_r, P_r, Z_C) \quad [\text{Fig. 6.6-3, } Z = f(T_r, P_r) \text{ at } Z_C = 0.27]$$

or

$$Z = Z(T_r, P_r, \omega) \leftarrow \text{Pitzer (1955)}$$

$$Z = Z^{(0)}(T_r, P_r) + \omega Z^{(1)}(T_r, P_r)$$

$$Z = Z^{(r1)}(T_r, P_r) + \frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}} [Z^{(r2)}(T_r, P_r) - Z^{(r1)}(T_r, P_r)]$$

$$\text{If } \omega^{(r1)} = 0 \Rightarrow Z = Z^{(r1)}(T_r, P_r) + \frac{\omega}{\omega^{(r2)}} [Z^{(r2)}(T_r, P_r) - Z^{(r1)}(T_r, P_r)] \Rightarrow$$

$$Z^{(0)} = Z^{(r1)} \ \& \ Z^{(1)} = \frac{1}{\omega^{(r2)}} [Z^{(r2)}(T_r, P_r) - Z^{(r1)}(T_r, P_r)]$$

where  $\omega$ : acentric factor (account for molecular structure)

$$\omega = -1.0 - \log_{10} \left( \frac{P^{vap}}{P_C} \right)_{T_r=0.7}$$

- ❖ This CSP can not be expected to be applicable to fluids with permanent dipoles and quadrupoles.

# Departure functions from CSP

$$\underline{H}(T, P) - \underline{H}^{IG}(T, P) = \int_{P=0, T}^{P, T} \left[ \underline{V} - T \left( \frac{\partial \underline{V}}{\partial T} \right)_P \right] dP \Rightarrow \text{expressed it in terms of } P_r \text{ \& } T_r$$

Based on the two - parameter CSP,  $\underline{V} = \frac{RT}{P} Z(T_r, P_r) \Rightarrow \underline{V} - T \left( \frac{\partial \underline{V}}{\partial T} \right)_P = \frac{-RT^2}{P} \left( \frac{\partial Z}{\partial T} \right)_P$

$$\underline{H}(T, P) - \underline{H}^{IG}(T, P) = - \int_{P=0, T}^{P, T} \left[ \frac{RT^2}{P} \left( \frac{\partial Z}{\partial T} \right)_P \right] dP = -RT_C \int_{P_r=0, T_r}^{P_r, T_r} \frac{T_r^2}{P_r} \left( \frac{\partial Z}{\partial T_r} \right)_{P_r} dP_r \text{ or}$$

$$\frac{\underline{H}(T, P) - \underline{H}^{IG}(T, P)}{T_C} = -RT_r^2 \int_{P_r=0, T_r}^{P_r, T_r} \frac{T_r^2}{P_r} \left( \frac{\partial Z}{\partial T_r} \right)_{P_r} dP_r \quad \leftarrow \text{Fig. 6.6-4 for } Z_C = 0.27$$

$$\begin{aligned} \underline{H}(T_2, P_2) - \underline{H}(T_1, P_1) &= \left[ \underline{H}^{IG}(T_1, P_1) - \underline{H}(T_1, P_1) \right] + \left[ \underline{H}^{IG}(T_2, P_2) - \underline{H}^{IG}(T_1, P_1) \right] + \left[ \underline{H}(T_2, P_2) - \underline{H}^{IG}(T_2, P_2) \right] \\ &= -T_C \left[ \frac{\underline{H}(T, P) - \underline{H}^{IG}(T, P)}{T_C} \right]_{T_{r1}, P_{r1}} + \int_{T_1}^{T_2} C_P^* dT + T_C \left[ \frac{\underline{H}(T, P) - \underline{H}^{IG}(T, P)}{T_C} \right]_{T_{r2}, P_{r2}} \end{aligned}$$

Similarly for  $\Delta \underline{S}$  calculation,

$$\underline{S}(T_2, P_2) - \underline{S}(T_1, P_1) = \int_{T_1}^{T_2} \frac{C_P^*}{T} dT - R \int_{P_1}^{P_2} \frac{dP}{P} + \left\{ \left[ \underline{S} - \underline{S}^{IG} \right]_{T_{r2}, P_{r2}} - \left[ \underline{S} - \underline{S}^{IG} \right]_{T_{r1}, P_{r1}} \right\}$$

❖ If  $\underline{H}$  &  $\underline{S}$  are calculated, then

$$\underline{U} = \underline{H} - P\underline{V}, \underline{A} = \underline{U} - T\underline{S}, \underline{G} = \underline{H} - T\underline{S}$$

❖ Fig. 6.6-5 for  $Z_C = 0.27$

# Pitzer's three parameter CSP

$$Z = Z^{(0)} + \omega Z^{(1)}$$

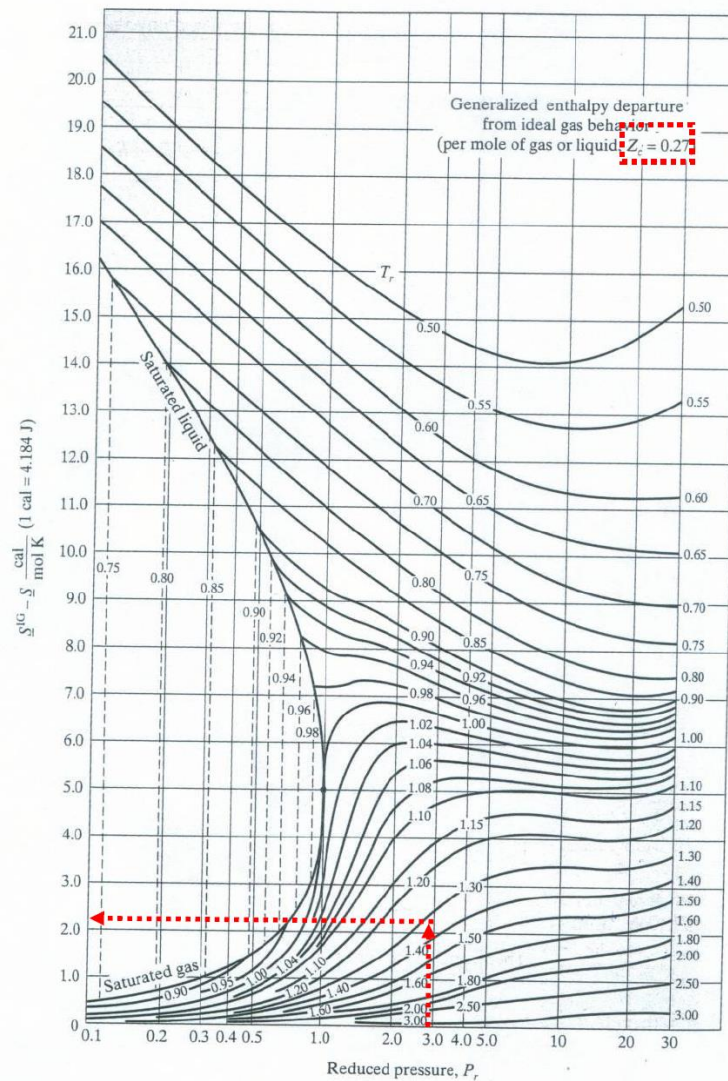
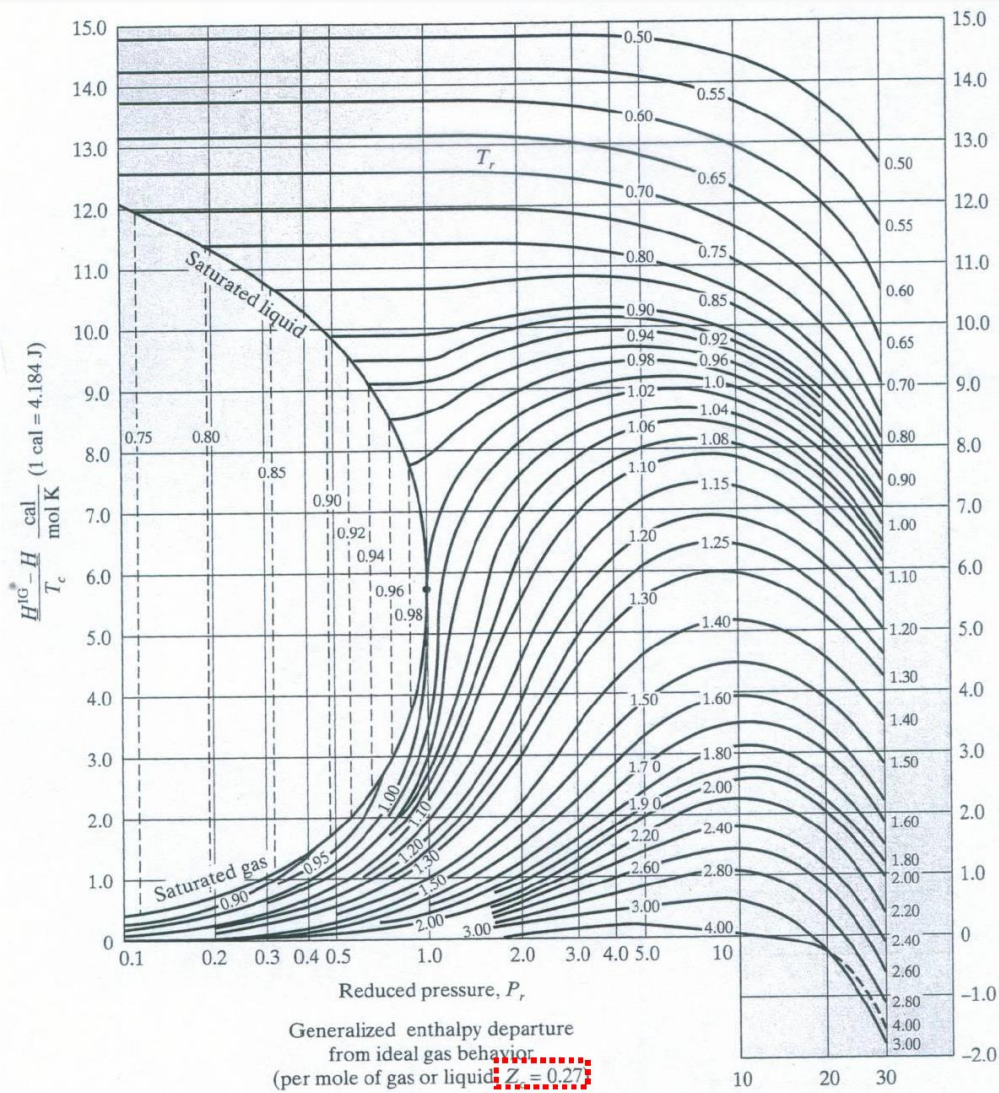
$$\frac{\underline{H}(T, P) - \underline{H}^{IG}(T, P)}{RT_C} = \left[ \frac{\underline{H}(T_r, P_r) - \underline{H}^{IG}(T_r, P_r)}{RT_C} \right]^{(0)} + \omega \left[ \frac{\underline{H}(T_r, P_r) - \underline{H}^{IG}(T_r, P_r)}{RT_C} \right]^{(1)}$$

Similarly,

$$\frac{\underline{S}(T, P) - \underline{S}^{IG}(T, P)}{R} = \left[ \frac{\underline{S}(T_r, P_r) - \underline{S}^{IG}(T_r, P_r)}{R} \right]^{(0)} + \omega \left[ \frac{\underline{S}(T_r, P_r) - \underline{S}^{IG}(T_r, P_r)}{R} \right]^{(1)}$$

❖ From Tables or Charts





# Illustration 6.5-1: Use of Generalized chat (CSP)

Solve illustration 6.5-1 by using Figs. 6.6-3 ~ 6.6-5.

Data:  $N_2$ :  $T_c = 126.2 \text{ K}$ ,  $P_c = 33.94 \text{ bar}$

$Z_c = 0.29$

<sol>

Initial condition:  $\begin{cases} T_{r_0} = 170/126.2 = 1.347 \\ P_{r_0} = 100/33.94 = 2.946 \end{cases}$

Fig. 6.6-3

From Fig. 6.6-3  $\Rightarrow Z_0 = 0.741$

$$\therefore \underline{V}_0 = \frac{Z_0 R T_0}{P_0} = Z_0 V_0^{IG} = 1.047 \times 10^{-4} \text{ m}^3/\text{mol}$$

$$N_0 = \frac{0.15}{1.047 \times 10^{-4}} = 1432.7 \text{ mol.}$$

$$\therefore \underline{N}(t) = 1432.7 - 10t$$

Final state:

$$\begin{cases} \underline{V}_2 = \frac{0.15}{1432.7 - 10 \times 50} = 1.6082 \times 10^{-4} \text{ m}^3/\text{mol} \\ \underline{S}_2 = \underline{S}_0 \text{ (isentropic expansion)} \end{cases}$$

$$\text{Let } \underline{S}_0 = \underline{S}^{IG}(T_0, \underline{V}_0) + (\underline{S} - \underline{S}^{IG})_0$$

$$\underline{S}_2 = \underline{S}^{IG}(T_2, \underline{V}_2) + (\underline{S} - \underline{S}^{IG})_2$$

$$\begin{aligned} S_2 - S_0 &= S^{ig}(T_2, V_2) - S^{ig}(T_0, V_0) + (S - S^{ig})_2 \\ - (S - S^{ig})_0 &= S^{ig}(T_2, P_2) - S^{ig}(T_0, P_0) + (S - S^{ig})_2 - (S - S^{ig})_0 \quad (*a) \end{aligned}$$

ideal gas part:

$$\begin{aligned} S^{ig}(T_2, P_2) - S^{ig}(T_0, P_0) &= -8.314 \ln\left(\frac{P_2}{100}\right) \\ &+ 27.2 \ln\left(\frac{T_2}{170}\right) + 4.2 \times 10^{-3} (T_2 - 170) \end{aligned}$$

where  $T_0 = 170 \text{ K}$ ,  $V_0 = 1.047 \times 10^{-4} \text{ m}^3/\text{mol}$   
 $P_0 = 100 \text{ bar}$

$$(S - S^{ig})_0 = ?$$

$$\begin{aligned} T_0 = 1.347 \quad P_0 = 2.946 \quad \xrightarrow{\text{Fig. 6.6-5}} (S - S^{ig})_0 &= -2.08 \frac{\text{cal}}{\text{mol K}} \\ &= -8.70 \frac{\text{J}}{\text{mol K}} \end{aligned}$$

$$(S - S^{ig})_2 = ?$$

$$\begin{cases} T_2 = ? \\ P_2 = ? \end{cases} \rightarrow \begin{cases} T_{r2} = ? \\ P_{r2} = ? \end{cases}$$

$$\begin{aligned} \text{Eq. (*a)} \Rightarrow 0 &= -8.314 \ln\left(\frac{P_2}{100}\right) + 27.2 \ln\left(\frac{T_2}{170}\right) \\ &+ 4.2 \times 10^{-3} (T_2 - 170) + (S - S^{ig})_2 + 8.70 \end{aligned}$$

$\uparrow$  Find  $T_2$  and  $P_2$  by trial & errors  $f(T_2, P_2)$   $L(*b)$



⊙ Algorithm:

(1) Assume  $(\underline{s} - \underline{s}^{ig})_2 = 0$ .

Solve Eq (\*b)  $\Rightarrow T_2^{(1)}$

**Guess  $T_2^{(1)}$  from ideal gas assumption**

$$(2) \underline{p}_2 = \frac{RT_2}{\underline{v}_2} \underbrace{z(T_2, \underline{p}_2)}_{\text{Fig. 6.6-3}}$$

Compute  $\underline{p}_2^{(1)}$  by trial and errors

$$(3) \begin{matrix} T_2^{(1)} \\ \underline{p}_2^{(1)} \end{matrix} \xrightarrow{\text{Fig. 6.6-5}} (\underline{s} - \underline{s}^{ig})_2^{(1)}$$

(4) Use Eq (\*b) to solve new  $T_2^{(2)}$ .

(5) Check  $T_2^{(2)} \approx T_2^{(1)}$

(6) If not converge, back to step (2) with  $T_2^{(2)}$

Solution:

$$\begin{matrix} T_2 = 136 \text{ K} \\ \underline{p}_2 = 41 \text{ bar} \end{matrix}$$

# Generalized EOS

❖ **van der Waals EOS**  $P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2}$

**From critical point analysis, we have**

$$a = \frac{27R^2T_c^2}{64P_c} \quad \& \quad b = \frac{RT_c}{8P_c}$$

**If  $T_c$  and  $P_c$  of the fluids are known, the PVT behavior can be calculated, just like a two-parameter CSP.**

❖ **More useful EOS =>**

**Peng-Robinson (PR) EOS is applicable for hydrocarbons, inorganic gases such as  $N_2$ ,  $O_2$ ,  $H_2S$ , ....**

$$P = \frac{RT}{\underline{V}-b} - \frac{a(T)}{\underline{V}(\underline{V}+b)+b(\underline{V}-b)}$$

*Applying critical conditions, we have*

$$a(T_c) = 0.45724 \frac{R^2T_c^2}{P_c} \quad \& \quad b = 0.0778 \frac{RT_c}{P_c}$$

$$\text{Let } a(T) = a(T_c) \times \alpha(T) = a(T_c) \times [1 + k(1 - T_r^{0.5})]^2$$

*Fit "k" to vapor pressure data for some fluids of interest =>*

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

**PR EOS => ( $T_c$ ,  $P_c$ ,  $\omega$ ) <= three-parameter EOS**

# Departure functions from PR EOS

- ❖ Departure H and S from the PR EOS [eqs. (6.4-29) & (6.4-30)]

$$\left(\underline{H} - \underline{H}^{IG}\right)_{T,P} = RT(Z-1) + \int_{V=\infty}^V \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV = RT(Z-1) + \frac{T \left( \frac{da}{dT} \right) - a}{2\sqrt{2}b} \ln \left[ \frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B} \right]$$

$$\left(\underline{S} - \underline{S}^{IG}\right)_{T,P} = R \ln Z - \left\{ \int_{V=\infty}^V \left[ \left( \frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV \right\} = R \ln(Z-B) + \frac{\left( \frac{da}{dT} \right)}{2\sqrt{2}b} \ln \left[ \frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B} \right]$$

- ❖ Calculation procedure (in a single phase region)
  - ❖  $T_C$ ,  $P_C$  and  $\omega$  of the fluid are known  $\Rightarrow$  calculate  $b$ ,  $\kappa$ ,  $a(T_C)$
  - ❖ Given  $T \Rightarrow$  calculate  $\alpha(T)$  and then  $a(T)$
  - ❖ At given  $T$  &  $P$ , solve  $\underline{V}$  from the PR EOS or solve  $Z$  from
    - ❖  $Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0$   
where  $B = Pb/RT$  and  $A = aP/R^2T^2$
  - ❖ Calculate  $da/dT$
  - ❖ Calculate departure  $\underline{H}$  &  $\underline{S}$
- ❖ Advantages over two-parameter CSP
  - ❖ Analytic computation
  - ❖ Three-parameter model
  - ❖ Easy to recode the program if other EOS are to be used.

# Illustration 6.7-1

Rework illustration 6.5-1 by using PREOS

<sol>

$$\begin{array}{l} T_0 = 170\text{K} \\ P_0 = 100\text{bar} \end{array} \xrightarrow[\text{(Tc, Pc, w)}]{\text{PREOS}} Z_0 = 0.6769$$

$$V_0 = \frac{Z_0 R T_0}{P_0} = Z_0 V_0^{\text{IG}} = 0.9567 \times 10^{-4} \text{ m}^3/\text{mol}$$

$$N_0 = \frac{0.15}{0.9567 \times 10^{-4}} = 1567.9 \text{ mol}$$

$$\therefore \underline{N(t) = 1567.9 - 10t} \quad \ast$$

$$(\underline{S - S^{\text{IG}}})_0 = ?$$

$$\xrightarrow[\text{Eq. 6.4-30}]{} -9.18 \text{ J/mol.}$$

$$N_2 = 1567.9 - 10 \times 50 = 1067.9 \text{ mol}$$

$$V_2 = \frac{0.15}{1067.9} = 1.4046 \times 10^{-4} \text{ m}^3/\text{mol}$$

Find  $T_2$  and  $P_2$  by iteration.

⊙ Algorithm:

- (1) Guess  $T_2^{(1)}$  from ideal gas assumption
- (2) Compute  $P_2^{(1)}$  from the PR EoS with  $T_2^{(1)}$  and  $V_2$
- (3) Calculate  $(\underline{S} - \underline{S}^{IG})_2^{(1)}$  at  $T_2^{(1)}, P_2^{(1)}$   
 $\uparrow$   
 Eq. (6.4-30)
- (4) Solve  $\underline{S}_2 - \underline{S}_0 = 0$  to find new  $T_2^{(2)}$   
 $\hookrightarrow$  Eq. (6.4-30) in illustration 6.6-2.
- (5) Check  $T_2^{(2)} \approx T_2^{(1)}$
- (6) If not converge, back to step (2) with  $T_2^{(2)}$

Solution:

$$T_2 = 134.66 \text{ K}$$

$$P_2 = 40.56 \text{ bar}$$

$$(\underline{S} - \underline{S}^{IG})_2 = -10.19 \text{ J/mol K}$$

Comparison

	$V_2$ ( $\text{m}^3/\text{mol}$ )	$T_2$ (K)	$P_2$ (bar)
Ideal gas	$2.672 \times 10^{-4}$	129.6	40.3
Fig. 3.3-3	$1.457 \times 10^{-4}$	133	39.0
VdW	$1.376 \times 10^{-4}$	133.1	39.5
CS P	$1.608 \times 10^{-4}$	136	41.0
<u>PR</u>	<u><math>1.405 \times 10^{-4}</math></u>	<u>134.7</u>	<u>40.6</u>

# Estimation methods for critical and other properties

- ❖ To use either the generalized EOS or the method of corresponding states, we need information on the critical and other properties of interest.
  - ❖ Find the properties from literature, if available.
  - ❖ Estimate the properties from predictive models.
- ❖ Group contribution method => Estimate the properties of a compound from its molecular structure.
- ❖ Product Engineering: creating a compound or mixture of compounds with certain desired properties.
- ❖ Estimation of the critical properties from a group contribution method- Joback model

$$T_c(K) = \frac{T_b(K)}{0.584 + 0.965 \sum_i v_i \Delta T_{c,i} - \left( \sum_i v_i \Delta T_{c,i} \right)^2} \quad P_c(\text{bar}) = \frac{1}{\left( 0.113 + 0.0032 \cdot n + \sum_i v_i \Delta P_{c,i} \right)^2}$$

$$\underline{V}_c \left( \frac{\text{cm}^3}{\text{mol}} \right) = 17.5 + \sum_i v_i \Delta V_{c,i} \quad T_b(K) = 198 + \sum_i v_i \Delta T_{b,i} \quad T_f(K) = 122 + \sum_i v_i \Delta T_{f,i}$$

***n*: number of atoms in the molecule**

$$\omega = -\log \frac{P^{\text{vap}}(T = 0.7T_c)}{P_c} - 1 \quad \text{or} \quad \omega = \frac{3}{7} \frac{T_{br}}{1 - T_{br}} \log P_c - 1 \quad \text{where } T_{br} = T_b / T_c ; \log P^{\text{vap}} = A + (B / T)$$

# Joback Group Parameters

Table 6.9-1 Joback Group Contributions to Pure Component Properties

Group	$\Delta T_b$	$\Delta P_v$	$\Delta V_c$	$\Delta T_m$	$\Delta T_f$
-CH <sub>3</sub> nonring	0.0141	-0.0012	65	23.58	-5.1
\CH <sub>3</sub> nonring	0.0189	0.0000	56	22.88	11.27
-CH <sub>2</sub> - ring	0.0100	0.0025	48	27.15	7.75
\CH- nonring	0.0164	0.0020	41	21.74	12.64
\CH- ring	0.0122	0.0004	38	21.78	19.88
\C< nonring	0.0067	0.0043	27	18.25	46.43
\C< ring	0.0042	0.0061	27	21.32	60.15
=CH <sub>2</sub> nonring	0.0113	-0.0028	56	18.18	-4.32
=CH- nonring	0.0129	-0.0006	46	24.96	8.73
=CH- ring	0.0082	0.0011	41	26.73	8.13
=C< nonring	0.0117	0.0011	38	24.14	11.14
=C< ring	0.0143	0.0008	32	31.01	37.02
=C= nonring	0.0026	0.0028	36	26.15	17.78
≡CH nonring	0.0027	-0.0008	46	9.2	-11.18
≡C- nonring	0.0020	0.0016	37	27.38	64.32
-F all	0.0111	-0.0057	27	-0.03	-15.78
-Cl all	0.0105	-0.0049	58	38.13	13.55
-Br all	0.0133	0.0057	71	66.86	43.43
-I all	0.0068	-0.0034	97	93.84	41.69
-OH alcohol	0.0741	0.0112	28	92.88	44.45
-OH phenol	0.0240	0.0184	-25	76.34	82.85
-O- nonring	0.0168	0.0015	18	22.42	22.23
-O- ring	0.0098	0.0048	13	31.22	23.05
\C=O nonring	0.0380	0.0031	62	76.75	61.2
\C=O ring	0.0284	0.0028	55	94.97	75.97
O=CH- aldehyde	0.0379	0.003	82	72.24	36.9
-COOH acid	0.0791	0.0077	89	169.09	155.5
-COO- nonring	0.0481	0.0005	82	81.1	53.6
=O other	0.0143	0.0101	36	-10.5	2.08
-NH <sub>2</sub> all	0.0243	0.0109	38	-10.5	2.08
\NH nonring	0.0295	0.0077	35	50.17	52.66
\NH ring	0.0130	0.0114	29	52.82	101.51
\N- nonring	0.0169	0.0074	9	11.74	48.84
-N= nonring	0.0255	-0.0099	0	74.6	0
-N= ring	0.0085	0.0076	34	57.55	68.4
-CN all	0.0496	-0.0101	91	125.66	59.89
-NO <sub>2</sub> all	0.0437	0.0064	91	152.54	127.24
-SH all	0.0031	0.0084	63	63.56	20.09
-S- nonring	0.0119	0.0049	54	68.78	34.4
-S- ring	0.0019	0.0051	38	52.1	79.93

# Illustration 6.9-1 Group contribution

□ Use the methods described above to estimate the properties of n-octane that has a boiling point of 398.8 K and ethylene glycol (1,2-diethanediol) that has a boiling point of 470.5 K. Also compare the estimates of using and not using the measured boiling points.

<sol>

The results for n-octane,  $(\text{CH}_3)-(\text{CH}_2)_6-(\text{CH}_3)$

	Expt'l	Using $T_b$	Not using $T_b$
$T_b$ (K)	398.8	398.8	382.4
$T_f$ (K)	216.4	179.4	179.4
$T_c$ (K)	568.8	569.2	545.9
$P_c$ (bar)	24.9	25.35	25.35
$V_c$ (cc/mol)	492	483.5	483.5
$\omega$	0.392	0.402	0.402



□ The results for ethylene glycol, OH-(CH<sub>2</sub>)-(CH<sub>2</sub>)-OH

	Expt'l	Using T <sub>b</sub>	Not using T <sub>b</sub>
T <sub>b</sub> (K)	470.5	470.5	429.5
T <sub>f</sub> (K)	260.2	233.4	233.4
T <sub>c</sub> (K)	645.0	645.5	589.3
P <sub>c</sub> (bar)	77.0	66.5	66.5
V <sub>c</sub> (cc/mol)	?	185.5	185.5
ω	?	1.094	1.094

# The 3<sup>rd</sup> Law of Thermodynamics

- The 1<sup>st</sup> Law of Thermodynamics: the conservation of energy.
- The 2<sup>nd</sup> Law of Thermodynamics: the positive-definite nature of entropy generation.
- The 3<sup>rd</sup> Law of Thermodynamics:  
The entropy of all substance in the perfect crystalline state (for solids) or the perfect liquid state (for liquids, e.g., He) is zero at the absolute zero of temperature
  - $\Delta S = 0$  for any chemical reaction at 0 K.
  - It is impossible to obtain a temperature of absolute zero.