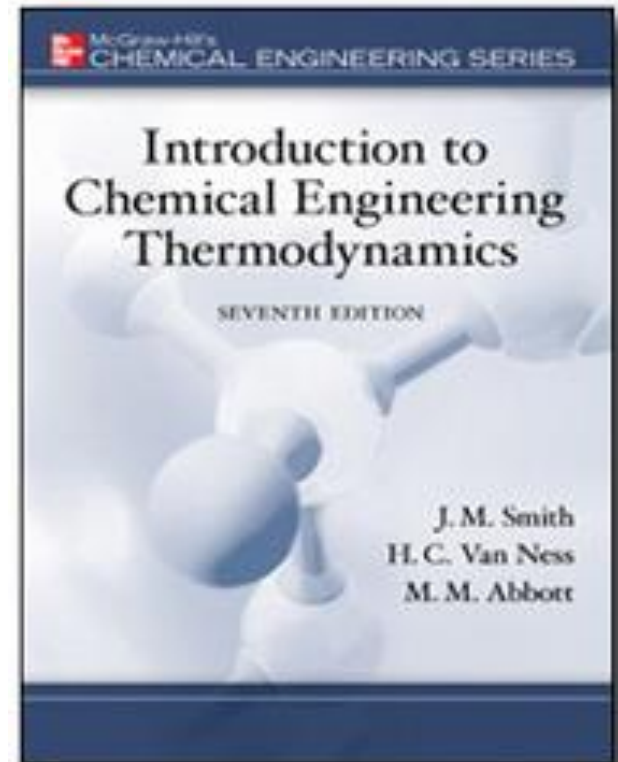# *Chapter 6. Thermodynamic Properties of Fluids*

Introduction

❑ **Numerical values of thermodynamic properties are most important for heat and work calculations**

- **Enthalpy, Internal Energy, Entropy, …..**

- **Measurable Quantities : PVT data and heat capacity**

- **Properties relations are important to calculate one properties from the other.**

- **Generalized correlations are used when experimental values are not available.**

6.1 Properties Relations for Homogeneous Phases

❑ **From the 1ˢᵗ law and 2ⁿᵈ law of Thermodynamics,**

$$d(nU) = dW_{rev} + dW_{rev}$$

$$dW_{rev} = -Pd(nV)$$

$$dQ_{rev} = Td(nS)$$

$$\boxed{d(nU) = Td(nS) - Pd(nV)}$$

Although this eqn. has been derived for the special case of **reversible process**, it only contain **state properties** of the system.

Can be applied to any process from one equilibrium state to another

The only requirements are that the system be closed and that the change occur between equilibrium states.

❑ **When the equations are written in molar units;**

$$dU = TdS - PdV$$

$$H \equiv U + PV$$

$$A \equiv U - TS$$

$$G \equiv H - TS$$

$$dH = dU + d(PV) = TdS - PdV + PdV + VdP \longrightarrow dH = TdS + VdP$$

$$dA = dU - d(TS) = TdS - PdV - TdS - SdT \longrightarrow dA = -PdV - SdT$$

$$dG = dH - d(TS) = TdS + VdP - TdS - SdT \longrightarrow dG = VdP - SdT$$

6.1 Properties Relations for Homogeneous Phases

❑ **Fundamental Properties Relations**

$$dU(S, V) = TdS - PdV$$

$$dH(S, P) = TdS + VdP$$

$$dA(V, T) = -PdV - SdT$$

$$dG(T, P) = VdP - SdT$$

> **These fundamental properties relations are general equation for homogeneous fluid of constant composition**

❑ **Exact Differential Equation**

- ● **If a function F is a property (not depending on the path)**

$$F = F(x, y)$$

- ● **The total differentiation**

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$$

$$dF = M\,dx + N\,dy$$

$$M = \left(\frac{\partial F}{\partial x}\right)_y , \; N = \left(\frac{\partial F}{\partial y}\right)_x$$

❑ **Exact Differential Equation**

- ● **Condition for exactness**

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$$

$$dF = M dx + N dy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 F}{\partial x \partial y} \qquad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 F}{\partial x \partial y}$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

6.1 Properties Relations for Homogeneous Phases

❑ **Maxwell's Relation**

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$dU(S, V) = TdS - PdV \longrightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$dH(S, P) = TdS + VdP \longrightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$dA(V, T) = -PdV - SdT \longrightarrow \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$dG(T, P) = VdP - SdT \longrightarrow \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

Maxwell Relation

S   H   P

U   G

V   A   T

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -PdV - SdT$$

$$dG = VdP - SdT$$

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

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

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

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

Enthalpy as a Function of T and P

❏ *T* and *P* : **easily measurable**

$$dH(S,P) = TdS + VdP \longrightarrow dH(T,P) = ?dT + ?dP$$

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

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

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

Entropy as a Function of T and P

❑ *T* and *P* : **easily measurable**

$$dS(T,P) = ?\,dT + ?\,dP$$

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \qquad dH(S,P) = TdS + VdP$$

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

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

Internal Energy as a Function of T and P

❑ *T* and *P* : **easily measurable**

$$dU(T,P) = ?\,dT + ?\,dP$$

$$U = H - PV$$

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

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

Ideal-Gas State

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

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

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

$$dH = C_P dT$$

$$dS = C_P \frac{dT}{T} - R \frac{dP}{P}$$

Alternative Form for Liquid

❑ **For liquids,**

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

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

$$\left(\frac{\partial V}{\partial T} \right)_P = \beta V$$

$$dH = C_P dT + \left[1 - \beta T \right] V dP$$

$$dS = C_P \frac{dT}{T} - \beta V dP$$

Internal Energy as a Function of T and V

❑ **Sometimes *T* and *V* are more useful than *T* and *P***

   ● **Equation of States are expressed as *P = F(V,T)***

$$dU(S, V) = TdS - PdV \longrightarrow dU(T, V) = ?\,dT + ?\,dV$$

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

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

Entropy as a Function of T and V

❑ **Sometimes *T* and *V* are more useful than *T* and *P***

● **Equation of States are expressed as *P = F(V,T)***

$$dU(S, V) = TdS - PdV \qquad \longrightarrow \qquad dS(T, V) = ?\, dT + ?\, dV$$

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

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

Gibbs Free Energy as a Generating Function

❑ *G = G(T,P)*

- **T, P → Canonical Variables for Gibbs energy**
- **Conforms to a general rule that is both simple and clear**

$$dG(T,P) = VdP - SdT$$

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT}dG - \frac{G}{RT^2}dT$$

$$= \frac{1}{RT}\left[VdP - SdT\right] - \frac{1}{RT^2}\left[H - TS\right]dT$$

$$= \frac{V}{RT}dP - \frac{S}{RT}dT - \frac{H}{RT^2}dT + \frac{S}{RT}dT$$

$$= \frac{V}{RT}dP - \frac{H}{RT^2}dT$$

Gibbs Free Energy as a Generating Function

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{RT^2}dT$$

➡ **Fundamental Properties Relationship**

$$\frac{V}{RT} = \left[\frac{\partial(G/RT)}{\partial P}\right]_T \qquad\qquad \frac{H}{RT} = -T\left[\frac{\partial(G/RT)}{\partial T}\right]_P$$

Gibbs energy, when given as a function of *T* and *P*, serves as a *generating function* for other thermodynamic properties, and implicitly represents complete property information

Example 6.1

Determine the enthalpy and entropy changes of liquid water for a change of state from 1 bar and 25 °C to 1,000 bar and 50 °C. Data for water are given in the following table.

T (°C)	P (bar)	C_p (J/mol·K)	V (cm³/mol)	β (K⁻¹)
25	1	75.305	18.071	256×10^{-6}
25	1,000	……	10.012	366×10^{-6}
50	1	75.314	18.234	458×10^{-6}
50	1,000	……	18.174	568×10^{-6}

Example 6.1

Use mean averaged values from Table

$$dH = C_P dT + \left[1 - \beta T\right] V dP \quad\longrightarrow\quad \Delta H = \langle C_P \rangle (T_2 - T_1) + (1 - \beta T_2)\langle V \rangle (P_2 - P_1)$$

$$dS = C_P \frac{dT}{T} - \beta V dP \quad\longrightarrow\quad \Delta S = \langle C_P \rangle \ln \frac{T_2}{T_1} - \langle \beta \rangle \langle V \rangle (P_2 - P_1)$$
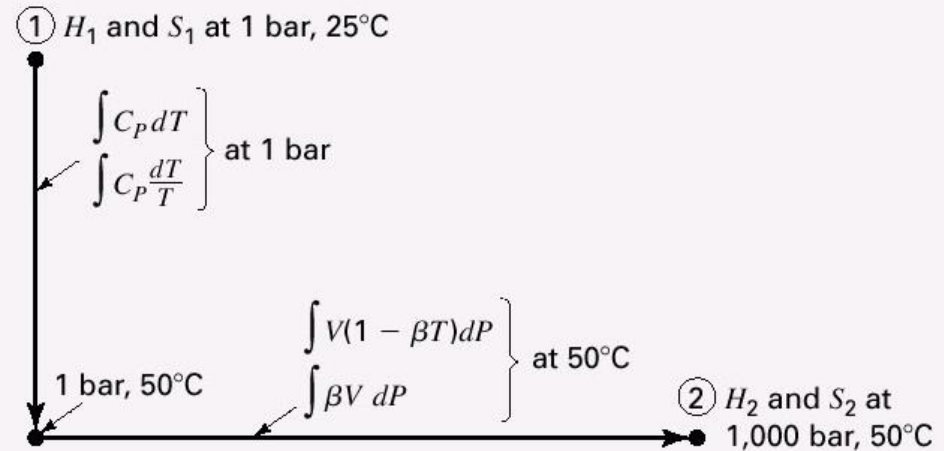
For P = 1 bar,

$$\langle C_P \rangle = \frac{75.305 + 75.314}{2} = 75.310 \text{J} / \text{mol} \cdot \text{K}$$

For T = 50 ⁰C,

$$\langle V \rangle = \frac{18.234 + 18.174}{2} = 18.204 \text{cm}^3 / \text{mol}$$

$$\langle \beta \rangle = \frac{458 + 568}{2} \times 10^{-6} = 513 \times 10^{-6} \text{K}^{-1}$$

① H_1 and S_1 at 1 bar, 25°C

$$\left. \begin{array}{l} \int C_P dT \\ \int C_P \frac{dT}{T} \end{array} \right\} \text{at 1 bar}$$

1 bar, 50°C

$$\left. \begin{array}{l} \int V(1 - \beta T) dP \\ \int \beta V \, dP \end{array} \right\} \text{at 50°C}$$

② H_2 and S_2 at 1,000 bar, 50°C

$$\Delta H = \langle C_P \rangle (T_2 - T_1) + (1 - \beta T_2)\langle V \rangle (P_2 - P_1) = 3{,}400 \text{J} / \text{mol}$$

$$\Delta S = \langle C_P \rangle \ln \frac{T_2}{T_1} - \langle \beta \rangle \langle V \rangle (P_2 - P_1) = 5.13 \text{J} / \text{mol} \cdot \text{K}$$

6.2 *Residual Properties*

❑ **No experimental method to measure *G* as a function of *T* and *P***

❑ **Residual Property**

● **Departure function from ideal gas value**

$$M^R = M - M^{id}$$

● *M* **is any molar property :** *V, U, H, S, A* **or** *G*

$$V^R = V - V^{id} = V - \frac{RT}{P} = \frac{RT}{P}(Z-1) \quad \left(V = \frac{ZRT}{P}\right)$$

$$G^R = G - G^{id}$$

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{RT^2}dT \quad \Longrightarrow \quad d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}dP - \frac{H^R}{RT^2}dT$$

6.2 Residual Properties

❑ **Fundamental residual-property relation**

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}dP - \frac{H^R}{RT^2}dT$$

➡ $$\frac{V^R}{RT} = \left[\frac{\partial\left(G^R/RT\right)}{\partial P}\right]_T \qquad \frac{H^R}{RT} = -T\left[\frac{\partial\left(G^R/RT\right)}{\partial T}\right]_P$$

$$\frac{G^R}{RT} = \left(\frac{G^R}{RT}\right)_{P=0} + \int_0^P \frac{V^R}{RT}dP = J + \int_0^P (Z-1)\frac{dP}{P} \qquad \text{(const T)}$$

➡ $$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \qquad \text{(const T)}$$

$$\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P} \qquad \text{(const T)}$$

Derive yourself!
(Page 209 – 210)

Residual Properties as P → 0

❑ **A gas become ideal as P → 0**

- ● **Then, all residual properties are zero???**

  - Not generally true…

$$\lim_{P \to 0} U^R = 0, \quad \text{as} \lim_{P \to 0} U = U^{ig}$$

$$\lim_{P \to 0} H^R = \lim_{P \to 0} U^R + \lim_{P \to 0} (PV^R) = 0$$

$$\lim_{P \to 0} V^R = RT \lim_{P \to 0} \left(\frac{Z-1}{P} \right) = RT \lim_{P \to 0} \left(\frac{\partial Z}{\partial P} \right)_T$$

See Figure 3.9 (Page 87)

$$\frac{H^R}{RT} = -T \left[\frac{\partial (G^R / RT)}{\partial T} \right]_P \quad \Rightarrow \quad \lim_{P \to 0} \frac{G^R}{RT} = \left(\frac{G^R}{RT} \right)_{P=0} = J$$
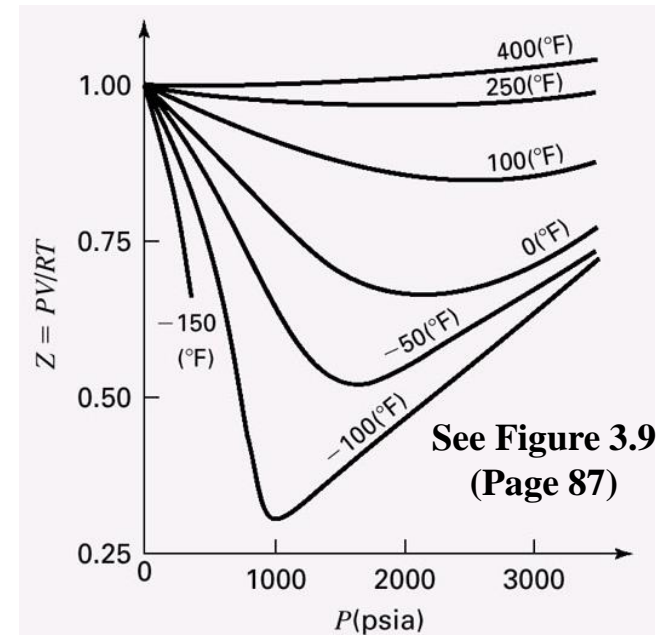
Enthalpy and Entropy from Residual Properties

$$H = H^{ig} + H^R$$

$$S = S^{ig} + S^R$$

$$H^{ig} = H_0^{ig} + \int_{T_0}^{T} C_P^{ig} dT$$

$$S^{ig} = S_0^{ig} + \int_{T_0}^{T} C_P^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0}$$

$$H = H_0^{ig} + \int_{T_0}^{T} C_P^{ig} dT + H^R$$
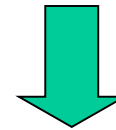
$$S = S_0^{ig} + \int_{T_0}^{T} C_P^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0} + S^R$$

Residual Properties

❑ **Advantages of using Residual Properties**

- **Generating Function ➔ Normally function of T, P**

- **Ideal Gas Property**

  - P = RT/V

  - $C_p = C_p(T) = dH/dT$, $C_v = C_v(T) = dU/dT$, Function of T only

- **If we can use other method to evaluate residual properties, we can calculate all the other properties**

  - Equation of State

  - Generalized Correlation

Example 6.3

Calculate the enthalpy and entropy of saturated isobutane vapor at 360 K from the following information.

1. Table 6.1 gives compressibility-factor data (Z) for isobutane vapor.

2. The vapor pressure of isobutane vapor at 360 K is 15.41 bar.

3. Set $H_0^{ig} = 18{,}115 J/mol$ and $S_0^{ig} = 295.976 J/mol \cdot K$ for the ideal-gas reference state at 300 K and 1 bar.

4. The ideal gas heat capacity of isobutene vapor is $\dfrac{C_p}{R} = 1.7765 + 33.037 \times 10^{-3} T$ (T in Kelvin)

Table 6.1: Compressibility Factors Z for Isobutane

P/bar	340 K	350 K	360 K	370 K	380 K
0.10	0.99700	0.99719	0.99737	0.99753	0.99767
0.50	0.98745	0.98830	0.98907	0.98977	0.99040
2	0.95895	0.96206	0.96483	0.96730	0.96953
4	0.92422	0.93069	0.93635	0.94132	0.94574
6	0.88742	0.89816	0.90734	0.91529	0.92223
8	0.84575	0.86218	0.87586	0.88745	0.89743
10	0.79659	0.82117	0.84077	0.85695	0.87061
12	······	0.77310	0.80103	0.82315	0.84134
14	······	······	0.75506	0.78531	0.80923
15.41	······	······	0.71727		

Example 6.3

$$H = H_0^{ig} + \int_{T_0}^{T} C_P^{ig}\,dT + H^R \qquad\qquad S = S_0^{ig} + \int_{T_0}^{T} C_P^{ig}\,\frac{dT}{T} - R\ln\frac{P}{P_0} + S^R$$

$$\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P} \qquad\qquad \frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

$$\Rightarrow \text{Need to evalute } \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \text{ and } \int_0^P (Z-1)\frac{dP}{P}$$

From the data in Table 6.1,
Fit the data Z vs. T at different P…

$$\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} = 26.37 \times 10^{-4}\,\text{K}^{-1}$$

$$\int_0^P (Z-1)\frac{dP}{P} = -0.2596$$

Then, you can perform the rest of

calculation!

Table 6.2: Values of the Integrands Required in Ex. 6.3
Values in parentheses are by extrapolation.

P/bar	$[(\partial Z/\partial T)_P/P] \times 10^4/\text{K}^{-1}\,\text{bar}^{-1}$	$[-(Z-1)/P] \times 10^2/\text{bar}^{-1}$
0	(1.780)	(2.590)
0.10	1.700	2.470
0.50	1.514	2.186
2	1.293	1.759
4	1.290	1.591
6	1.395	1.544
8	1.560	1.552
10	1.777	1.592
12	2.073	1.658
14	2.432	1.750
15.41	(2.720)	(1.835)

6.3 Residual Properties by Equations of State

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \qquad \frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P} \qquad \textbf{(const T)}$$

❑ **To evaluate above expression, equation of state is to be expressed as a**
function of P at const T.

- **Volume explicit: Z (or V) = f(P)** $\qquad Z = 1 + B'P + C'P^2 + \cdots$

- **Pressure explicit: Z (or V) = f(P)** $\qquad Z = 1 + \dfrac{B}{V} + \dfrac{C}{V^2} + \cdots$

- **However, many cases are pressure explicit!**

6.3 Residual Properties by Equations of State

❑ **For two-term virial equation,** $\quad Z = 1 + \dfrac{BP}{RT}$

$$\frac{G^R}{RT} = \int_0^P (Z-1)\frac{dP}{P} = \frac{BP}{RT}$$

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} = \frac{P}{R}\left(\frac{1}{T}\frac{dB}{dT} - \frac{B}{T^2}\right)$$

$$\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P} = -\frac{P}{R}\frac{dB}{dT}$$

6.3 *Residual Properties by Equations of State*

❑ **Pressure-explicit EOS**

● **In general, EOS can be expressed as Z = PV/RT**

● **By replacing V by ρ (molar density) → P = ZρRT**

● **Differentiation gives**

$$dP = RT(Zd\rho + \rho dZ) \quad \Rightarrow \quad \frac{dP}{P} = \frac{d\rho}{\rho} + \frac{dZ}{Z}$$

$$\frac{G^R}{RT} = \int_0^P (Z-1)\frac{dP}{P} = \int_0^\rho (Z-1)\frac{d\rho}{\rho} + Z - 1 - \ln Z$$

$$\frac{H^R}{RT} = -T\int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} + Z - 1$$

$$\frac{S^R}{R} = \ln Z - T\int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - \int_0^\rho (Z-1)\frac{d\rho}{\rho}$$

Residual Properties as a function of T and P

❑ **From the supplement, we can also derive the following alternative expression.**

$$H^R(T,P) = H(T,P) - H^{ig}(T,P) = \int_0^P \left[V - T\left(\frac{\partial V}{\partial T}\right)_P \right] dP = -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

$$S^R(T,P) = S(T,P) - S^{ig}(T,P) = -\int_0^P \left[\left(\frac{\partial V}{\partial T}\right)_P - \frac{R}{P} \right] dP = -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P}$$

$$G^R(T,P) = G(T,P) - G^{ig}(T,P) = \int_0^P \left[V - \frac{RT}{V} \right] dP = \int_0^P (Z-1)\frac{dP}{P}$$

Residual Properties as a function of T,V

❑ **However, the application of the previous expression is not straightforward, especially for complicate E.O.S.**

❑ **From the supplement, we derived the alternative expressions, which is much more useful to use for any pressure explicit E.O.S.**

$$H(T,V) = \int_{\infty}^{V}\left[T\left(\frac{\partial P}{\partial T}\right)_{V} - P\right]dV + RT(Z-1) + H^{ig}(T,P^{0})$$

$$S(T,V) = \int_{\infty}^{V}\left[\left(\frac{\partial P}{\partial T}\right)_{V} - \frac{R}{V}\right]dV + R\ln Z - R\ln\frac{P}{P^{0}} + S^{ig}(T,P^{0})$$

$$G(T,V) = H(T,V) - T \times S(T,V)$$

$$= -\int_{\infty}^{V}\left[P - \frac{RT}{V}\right]dV - RT\ln Z + RT(Z-1) + RT\ln\frac{P}{P^{0}} + G^{ig}(T,P^{0})$$

6.4 Two-Phase Systems

❑ **Vapor-Liquid Transition**

- ● **Specific Volume : large change**

- ● **U, H, S : also large change**

- ● **G ?**

$$dG(T,P) = VdP - SdT$$

- ● **At constant T and P**

$$d(nG) = 0$$

$$G^{\alpha} = G^{\beta}$$

P

Vapor-Liquid Boundary

Solid Phase

Liquid Phase

P_c

triple point

Gas

Vapor Phase

T_c

T
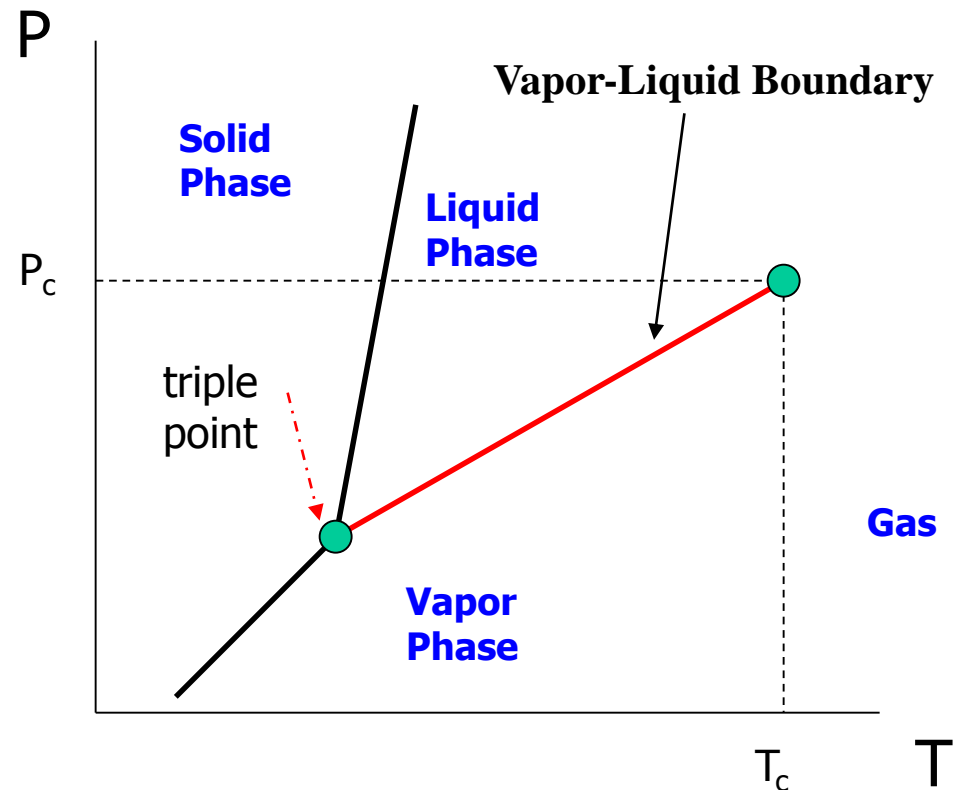
6.4 Two-Phase Systems

❑ **Derivation of Clapeyron Equation**

● **Phase Transition $\alpha \rightarrow \beta$**

$$dG^{\alpha} = dG^{\beta}$$

$$dG(T, P) = VdP - SdT$$

$$V^{\alpha}dP^{sat} - S^{\alpha}dT = V^{\beta}dP^{sat} - S^{\beta}dT$$

$$\frac{dP^{sat}}{dT} = \frac{S^{\beta} - S^{\alpha}}{V^{\beta} - V^{\alpha}} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}}$$

$$\Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta}$$

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}$$

6.4 Two-Phase Systems

❑ **Derivation of Clapeyron Equation**

● **Especially for vapor→ liquid transition**

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{vl}}{T \Delta V^{vl}}$$

$$\Delta V^{vl} = \frac{RT}{P^{sat}} \Delta Z^{vl}$$

$$\frac{d \ln P^{sat}}{dT} = \frac{\Delta H^{vl}}{RT^2 \Delta Z^{vl}}$$

$$\frac{d \ln P^{sat}}{d(1/T)} = -\frac{\Delta H^{vl}}{R \Delta Z^{vl}}$$

Relation between Vapor pressure and heat of vaporization

Example 6.5

The Clapeyron equation for vaporization may be simplified by introduction of reasonable approximations, namely, that the vapor phase is an ideal gas and that the molar volume of the liquid is negligible compared with the molar volume of the vapor. How do these assumptions alter the Clapeyron equation?

From the assumption,

$$\Delta V^{vl} = V^{v} = \frac{RT}{P^{sat}} \quad \text{or} \quad \Delta Z^{lv} = 1$$

The Clapeyron equation becomes

$$\frac{d \ln P^{sat}}{d(1/T)} = -\frac{\Delta H^{vl}}{R \Delta Z^{vl}} \quad \longrightarrow \quad \Delta H^{vl} = -R \frac{d \ln P^{sat}}{d(1/T)}$$

the Calusius/Calpeyron equation

$$\Rightarrow \quad \ln P^{sat} = A - \frac{B}{T}$$

6.4 Two-Phase Systems

❑ **Temperature Dependence of Vapor Pressure**

● Empirical equation for P vs. T

$$\frac{d \ln P^{sat}}{d(1/T)} = -\frac{\Delta H^{vl}}{R \Delta Z^{vl}}$$

Simple Expression

$$\ln P^{sat} = A - \frac{B}{T}$$

Antoine Equation
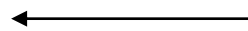
$$\ln P^{sat} = A - \frac{B}{T + C}$$ ⟵ **Specific Temperature Range**

Wagner Equation

$$\ln P^{sat} = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1 - \tau} \qquad \tau = 1 - T_r$$

6.4 Two-Phase Systems

❑ **Two phase Liquid/Vapor System**

● When system consist of saturated liquid and saturated vapor

$$nV = n^l V^l + n^v V^v$$

$$V = x^l V^l + x^v V^v$$

$$V = (1 - x^v) V^l + x^v V^v$$

● Other extensive thermodynamic properties, M (M=U, H, S, A, G,..)

$$M = (1 - x^v) M^l + x^v M^v$$

$$M = M^l + x^v \Delta M^{lv}$$

6.5 Thermodynamic Diagrams

❑ **Graph showing for a particular substance a set of properties (T, P, V, H, S,…)**

- **TS Diagram**

- **PH Diagram (ln P vs. H)**

- **HS Diagram (Mollier Diagram)**
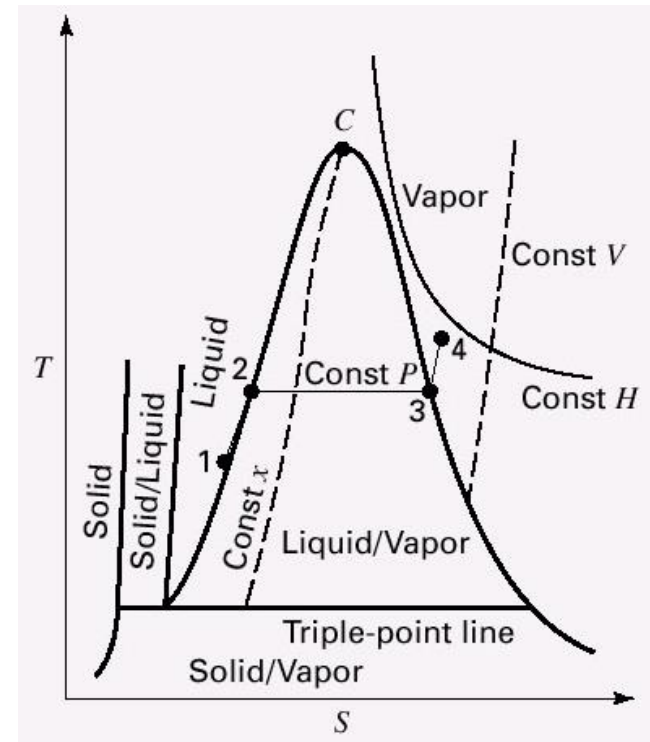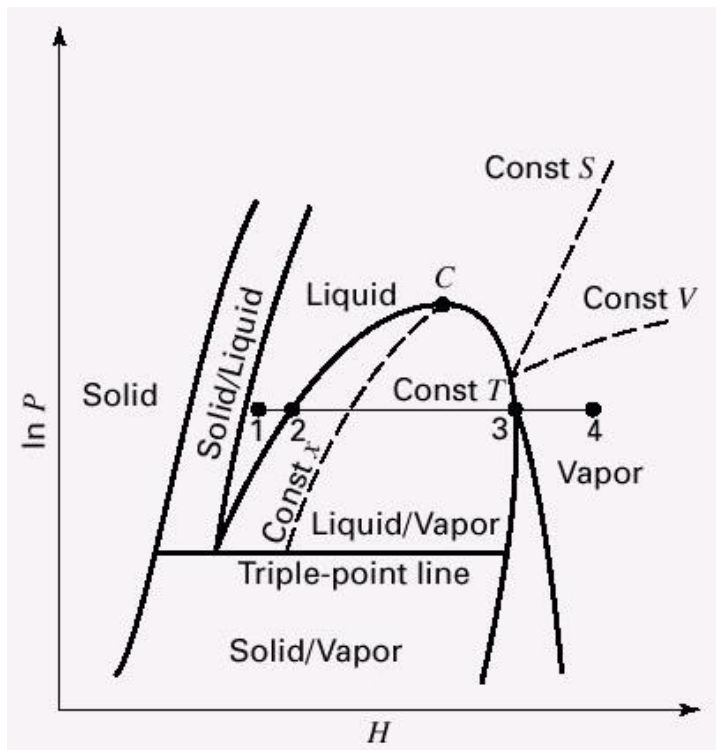
6.6 Tables of Thermodynamic Properties

❑ *U, H, S, V,…* → **Thermodynamic function**

❑ **Tables of Thermodynamic Data**

- **Tabulation of values of thermodynamic functions (*U, H, V*,..) at various condition (*T* and *P*)**

- **It is impossible to know the absolute values of *U* , *H* for process materials → Only changes are important (*ΔU, ΔH*,…)**

- Reference state

  - Choose a *T* and *P* as a reference state and measure changes of *U* and *H* from this reference state → tabulation

Steam Tables

❑ Compilation of physical properties of water (H, U, V)

❑ Reference state: liquid water at triple point (0.01 °C, 0.00611 bar)

Properties of Superheated Steam

P/kPa (t^{sat}/°C)		sat. liq.	sat. vap.	TEMPERATURE: t°C (TEMPERATURE: T kelvins)							
				75 (348.15)	100 (373.15)	125 (398.15)	150 (423.15)	175 (448.15)	200 (473.15)	225 (498.15)	250 (523.15)
1 (6.98)	V	1.000	129200.	160640.	172180.	183720.	195270.	206810.	218350.	229890.	241430.
	U	29.334	2385.2	2480.8	2516.4	2552.3	2588.5	2624.9	2661.7	2698.8	2736.3
	H	29.335	2514.4	2641.5	2688.6	2736.0	2783.7	2831.7	2880.1	2928.7	2977.7
	S	0.1060	8.9767	9.3828	9.5136	9.6365	9.7527	9.8629	9.9679	10.0681	10.1641
10 (45.83)	V	1.010	14670.	16030.	17190.	18350.	19510.	20660.	21820.	22980.	24130.
	U	191.822	2438.0	2479.7	2515.6	2551.6	2588.0	2624.5	2661.4	2698.6	2736.1
	H	191.832	2584.8	2640.0	2687.5	2735.2	2783.1	2831.2	2879.6	2928.4	2977.4
	S	0.6493	8.1511	8.3168	8.4486	8.5722	8.6888	8.7994	8.9045	9.0049	9.1010
20 (60.09)	V	1.017	7649.8	8000.0	8584.7	9167.1	9748.0	10320.	10900.	11480.	12060.
	U	251.432	2456.9	2478.4	2514.6	2550.9	2587.4	2624.1	2661.0	2698.3	2735.8
	H	251.453	2609.9	2638.4	2686.3	2734.2	2782.3	2830.6	2879.2	2928.0	2977.1
	S	0.8321	7.9094	7.9933	8.1261	8.2504	8.3676	8.4785	8.5839	8.6844	8.7806
30 (69.12)	V	1.022	5229.3	5322.0	5714.4	6104.6	6493.2	6880.8	7267.5	7653.8	8039.7
	U	289.271	2468.6	2477.1	2513.6	2550.2	2586.8	2623.6	2660.7	2698.0	2735.6
	H	289.302	2625.4	2636.8	2685.1	2733.3	2781.6	2830.0	2878.7	2927.6	2976.8
	S	0.9441	7.7695	7.8024	7.9363	8.0614	8.1791	8.2903	8.3960	8.4967	8.5930
40 (75.89)	V	1.027	3993.4	....	4279.2	4573.3	4865.8	5157.2	5447.8	5738.0	6027.7
	U	317.609	2477.1	....	2512.6	2549.4	2586.2	2623.2	2660.3	2697.7	2735.4
	H	317.650	2636.9	....	2683.8	2732.3	2780.9	2829.5	2878.2	2927.2	2976.5
	S	1.0261	7.6709	....	7.8009	7.9268	8.0450	8.1566	8.2624	8.3633	8.4598
50 (81.35)	V	1.030	3240.2	....	3418.1	3654.5	3889.3	4123.0	4356.0	4588.5	4820.5
	U	340.513	2484.0	....	2511.7	2548.6	2585.6	2622.7	2659.9	2697.4	2735.1
	H	340.564	2646.0	....	2682.6	2731.4	2780.1	2828.9	2877.7	2926.8	2976.1
	S	1.0912	7.5947	....	7.6953	7.8219	7.9406	8.0526	8.1587	8.2598	8.3564
75 (91.79)	V	1.037	2216.9	....	2269.8	2429.4	2587.3	2744.2	2900.2	3055.8	3210.9
	U	384.374	2496.7	....	2509.2	2546.7	2584.2	2621.6	2659.0	2696.7	2734.5
	H	384.451	2663.0	....	2679.4	2728.9	2778.2	2827.4	2876.6	2925.8	2975.3
	S	1.2131	7.4570	....	7.5014	7.6300	7.7500	7.8629	7.9697	8.0712	8.1681
100 (99.63)	V	1.043	1693.7	....	1695.5	1816.7	1936.3	2054.7	2172.3	2289.4	2406.1
	U	417.406	2506.1	....	2506.6	2544.8	2582.7	2620.4	2658.1	2695.9	2733.9
	H	417.511	2675.4	....	2676.2	2726.5	2776.3	2825.9	2875.4	2924.9	2974.5
	S	1.3027	7.3598	....	7.3618	7.4923	7.6137	7.7275	7.8349	7.9369	8.0342

Example 6.7

Superheated steam originally at P_1 and T_1 expands through a nozzle to an exhaust pressure P_2. Assuming the process is reversible and adiabatic, determine the downstream state of the steam and ΔH for the following condition.

$$P_1 = 1,000 \text{ kPa}, T_1 = 250 \text{ °C, and } P_2 = 200 \text{ kPa}$$

Solution

Since it is adiabatic process, $\Delta S = 0 \rightarrow S_1 = S_2$

To calculate ΔH, find H_1 and H_2.

At the initial state, find the H_1 and S_1 at $P_1 = 1,000$ kPa and $T_1 = 250$ °C

$\rightarrow$ From steam table, interpolation between 240 and 260 °C gives

$$H_1 = 2942 \text{ kJ/kg}, \quad S_1 = 6.9252 \text{ kJ/kg·K} = S_2 \qquad \text{From page 731}$$

Since the entropy of saturated vapor at 200 kPa is greater than S_2, the final state is the two phase liquid/vapor region!

Steam Table (page 731)

		sat. liq.	sat. vap.	175 (448.15)	200 (473.15)	220 (493.15)	240 (513.15)	260 (533.15)	280 (553.15)	300 (573.15)	325 (598.15)
950 (177.67)	V	1.124	204.03	....	217.48	228.96	240.05	250.86	261.46	271.91	284.81
	U	751.754	2580.4	....	2623.2	2659.5	2694.6	2728.7	2762.1	2795.1	2836.0
	H	752.822	2774.2	....	2829.8	2877.0	2922.6	2967.0	3010.5	3053.4	3106.6
	S	2.1166	6.6005	....	6.7209	6.8187	6.9093	6.9941	7.0742	7.1505	7.2413
975 (178.79)	V	1.126	199.04	....	211.55	222.79	233.64	244.20	254.56	264.76	277.35
	U	756.663	2581.1	....	2622.0	2658.6	2693.8	2728.0	2761.5	2794.6	2835.6
	H	757.761	2775.2	....	2828.3	2875.8	2921.6	2966.1	3009.7	3052.8	3106.1
	S	2.1275	6.5916	....	6.7064	6.8048	6.8958	6.9809	7.0612	7.1377	7.2286
1000 (179.88)	V	1.127	194.29	....	205.92	216.93	227.55	237.89	248.01	257.98	270.27
	U	761.478	2581.9	....	2620.9	2657.7	2693.0	2727.4	2761.0	2794.2	2835.2
	H	762.605	2776.2	....	2826.8	2874.6	2920.6	2965.2	3009.0	3052.1	3105.5
	S	2.1382	6.5828	....	6.6922	6.7911	6.8825	6.9680	7.0485	7.1251	7.2163
1050 (182.02)	V	1.130	185.45	....	195.45	206.04	216.24	226.15	235.84	245.37	257.12
	U	770.843	2583.3	....	2618.5	2655.8	2691.5	2726.1	2759.9	2793.2	2834.4
	H	772.029	2778.0	....	2823.8	2872.1	2918.5	2963.5	3007.5	3050.8	3104.4
	S	2.1588	6.5659	....	6.6645	6.7647	6.8569	6.9430	7.0240	7.1009	7.1924
1100 (184.07)	V	1.133	177.38	....	185.92	196.14	205.96	215.47	224.77	233.91	245.16
	U	779.878	2584.5	....	2616.2	2653.9	2689.9	2724.7	2758.8	2792.2	2833.6
	H	781.124	2779.7	....	2820.7	2869.6	2916.4	2961.8	3006.0	3049.6	3103.3
	S	2.1786	6.5497	....	6.6379	6.7392	6.8323	6.9190	7.0005	7.0778	7.1695
1150 (186.05)	V	1.136	169.99	....	177.22	187.10	196.56	205.73	214.67	223.44	234.25
	U	788.611	2585.8	....	2613.8	2651.9	2688.3	2723.4	2757.7	2791.3	2832.8
	H	789.917	2781.3	....	2817.6	2867.1	2914.4	2960.0	3004.5	3048.2	3102.2
	S	2.1977	6.5342	....	6.6122	6.7147	6.8086	6.8959	6.9779	7.0556	7.1476
1200 (187.96)	V	1.139	163.20	....	169.23	178.80	187.95	196.79	205.40	213.85	224.24
	U	797.064	2586.9	....	2611.3	2650.0	2686.7	2722.1	2756.5	2790.3	2832.0
	H	798.430	2782.7	....	2814.4	2864.5	2912.2	2958.2	3003.0	3046.9	3101.0
	S	2.2161	6.5194	....	6.5872	6.6909	6.7858	6.8738	6.9562	7.0342	7.1266
1250 (189.81)	V	1.141	156.93	....	161.88	171.17	180.02	188.56	196.88	205.02	215.03
	U	805.259	2588.0	....	2608.9	2648.0	2685.1	2720.8	2755.4	2789.3	2831.1
	H	806.685	2784.1	....	2811.2	2861.9	2910.1	2956.5	3001.5	3045.6	3099.9
	S	2.2338	6.5050	....	6.5630	6.6680	6.7637	6.8523	6.9353	7.0136	7.1064
1300 (191.61)	V	1.144	151.13	....	155.09	164.11	172.70	180.97	189.01	196.87	206.53
	U	813.213	2589.0	....	2606.4	2646.0	2683.5	2719.4	2754.3	2788.4	2830.3
	H	814.700	2785.4	....	2808.0	2859.3	2908.0	2954.7	3000.0	3044.3	3098.8
	S	2.2510	6.4913	....	6.5394	6.6457	6.7424	6.8316	6.9151	6.9938	7.0869

Steam Table (page 725)

		sat. liq.	sat. vap.	300 (573.15)	350 (623.15)	400 (673.15)	450 (723.15)	500 (773.15)	550 (823.15)	600 (873.15)	650 (923.15)
101.325 (100.00)	V	1.044	1673.0	2604.2	2833.2	3061.9	3290.3	3518.7	3746.9	3975.0	4203.1
	U	418.959	2506.5	2810.6	2888.5	2968.0	3048.9	3131.6	3215.9	3302.0	3389.8
	H	419.064	2676.0	3074.4	3175.6	3278.2	3382.3	3488.1	3595.6	3704.8	3815.7
	S	1.3069	7.3554	8.2105	8.3797	8.5381	8.6873	8.8287	8.9634	9.0922	9.2156
125 (105.99)	V	1.049	1374.6	2109.7	2295.6	2481.2	2666.5	2851.7	3036.8	3221.8	3406.7
	U	444.224	2513.4	2810.2	2888.2	2967.7	3048.7	3131.4	3215.8	3301.9	3389.7
	H	444.356	2685.2	3073.9	3175.2	3277.8	3382.0	3487.9	3595.4	3704.6	3815.5
	S	1.3740	7.2847	8.1129	8.2823	8.4408	8.5901	8.7316	8.8663	8.9951	9.1186
150 (111.37)	V	1.053	1159.0	1757.0	1912.2	2066.9	2221.5	2375.9	2530.2	2684.5	2838.6
	U	466.968	2519.5	2809.7	2887.9	2967.4	3048.5	3131.2	3215.6	3301.7	3389.5
	H	467.126	2693.4	3073.3	3174.7	3277.5	3381.7	3487.6	3595.1	3704.4	3815.3
	S	1.4336	7.2234	8.0280	8.1976	8.3562	8.5056	8.6472	8.7819	8.9108	9.0343
175 (116.06)	V	1.057	1003.34	1505.1	1638.3	1771.1	1903.7	2036.1	2168.4	2300.7	2432.9
	U	486.815	2524.7	2809.3	2887.5	2967.1	3048.3	3131.0	3215.4	3301.6	3389.4
	H	487.000	2700.3	3072.7	3174.2	3277.1	3381.4	3487.3	3594.9	3704.2	3815.1
	S	1.4849	7.1716	7.9561	8.1259	8.2847	8.4341	8.5758	8.7106	8.8394	8.9630
200 (120.23)	V	1.061	885.44	1316.2	1432.8	1549.2	1665.3	1781.2	1897.1	2012.9	2128.6
	U	504.489	2529.2	2808.8	2887.2	2966.9	3048.0	3130.8	3215.3	3301.4	3389.2
	H	504.701	2706.3	3072.1	3173.8	3276.7	3381.1	3487.0	3594.7	3704.0	3815.0
	S	1.5301	7.1268	7.8937	8.0638	8.2226	8.3722	8.5139	8.6487	8.7776	8.9012
225 (123.99)	V	1.064	792.97	1169.2	1273.1	1376.6	1479.9	1583.0	1686.0	1789.0	1891.9
	U	520.465	2533.2	2808.4	2886.9	2966.6	3047.8	3130.6	3215.1	3301.2	3389.1
	H	520.705	2711.6	3071.5	3173.3	3276.3	3380.8	3486.8	3594.4	3703.8	3814.8
	S	1.5705	7.0873	7.8385	8.0088	8.1679	8.3175	8.4593	8.5942	8.7231	8.8467
250 (127.43)	V	1.068	718.44	1051.6	1145.2	1238.5	1331.5	1424.4	1517.2	1609.9	1702.5
	U	535.077	2536.8	2808.0	2886.5	2966.3	3047.6	3130.4	3214.9	3301.1	3389.0
	H	535.343	2716.4	3070.9	3172.8	3275.9	3380.4	3486.5	3594.2	3703.6	3814.6
	S	1.6071	7.0520	7.7891	7.9597	8.1188	8.2686	8.4104	8.5453	8.6743	8.7980
275 (130.60)	V	1.071	657.04	955.45	1040.7	1125.5	1210.2	1294.7	1379.0	1463.3	1547.6
	U	548.564	2540.0	2807.5	2886.2	2966.0	3047.3	3130.2	3214.7	3300.9	3388.8
	H	548.858	2720.7	3070.3	3172.4	3275.5	3380.1	3486.2	3594.0	3703.4	3814.4
	S	1.6407	7.0201	7.7444	7.9151	8.0744	8.2243	8.3661	8.5011	8.6301	8.7538
300 (133.54)	V	1.073	605.56	875.29	953.52	1031.4	1109.0	1186.5	1263.9	1341.2	1418.5
	U	561.107	2543.0	2807.1	2885.8	2965.8	3047.1	3130.0	3214.5	3300.8	3388.7
	H	561.429	2724.7	3069.7	3171.9	3275.2	3379.8	3486.0	3593.7	3703.2	3814.2
	S	1.6716	6.9909	7.7034	7.8744	8.0338	8.1838	8.3257	8.4608	8.5898	8.7135

Example 6.7

Since the entropy of saturated vapor at 200 kPa is greater than S_2, the final state is the two phase liquid/vapor region!

From the steam table (page 725), the final T_2 is the saturation temperature at 200 kPa,

$$\rightarrow T_2 = 120.23 \,^{\circ}C$$

At $T_2 = 120.23 \,^{\circ}C$, $S_2^l = 1.5301 \, kJ/kg \cdot K, S_2^v = 7.1268 \, kJ/kg \cdot K$

$$H_2^l = 504.7 \, kJ/kg, H_2^v = 2,706.3 \, kJ/kg$$

From page 725

From $S = (1-x^v)S^l + x^v S^v$,

$$6.9252 = (1-x^v)1.5301 + x^v 7.1268$$

$$\Rightarrow x^v = 0.9640$$

$$H_2 = (1-x^v)H_2^l + x^v H_2^v = (1-0.9640) \times 504.7 + 0.9640 \times 2,706.3 = 2,627.0 kJ/kg$$

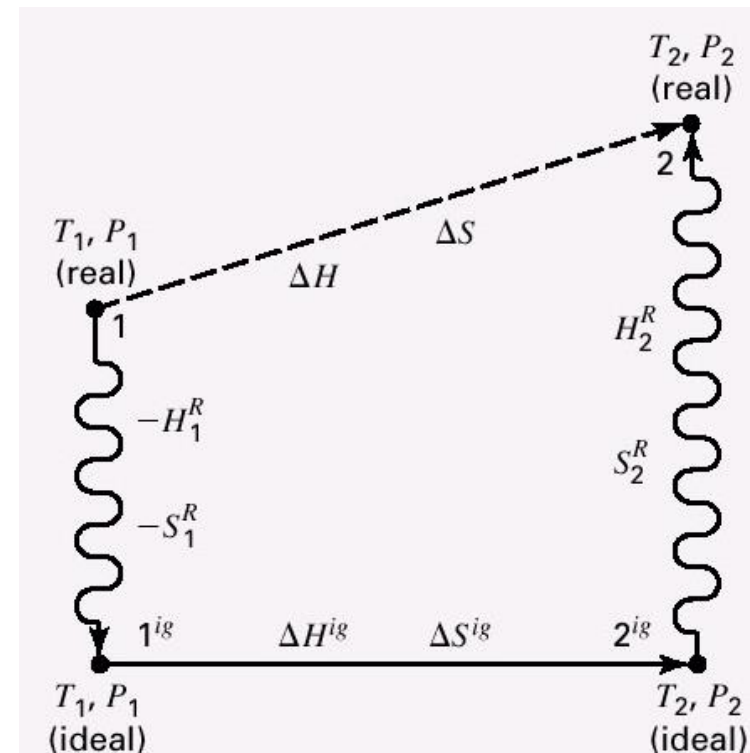$$\Delta H = H_2 - H_1 = 2,627.0 - 2,942.9 = -315.9 kJ/kg$$

Calculation of Enthalpy and Entropy for Real Fluids

❑ **Using residual properties, H^R and S^R, and ideal gas heat capacities, we can now calculate the enthalpy and entropy for real fluids at any T and P!**

❑ **For a change from state 1 to state 2,**

$$H_1 = H_0^{ig} + \int_{T_0}^{T} C_P^{ig} dT + H_1^R \qquad\qquad H_2 = H_0^{ig} + \int_{T_0}^{T} C_P^{ig} dT + H_2^R$$

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} C_P^{ig} dT + H_2^R - H_1^R$$

$$\Delta S = \int_{T_1}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_1} + S_2^R - S_1^R$$

Calculation of Enthalpy and Entropy for Real Fluids

❏ **Step 1 → 1ig**

$$H_1^{ig} - H_1 = -H_1^R \qquad S_1^{ig} - S_1 = -S_1^R$$

❏ **Step 1ig → 2ig**

$$\Delta H^{ig} = H_2^{ig} - H_1^{ig} = \int_{T_1}^{T_2} C_P^{ig} dT$$

$$\Delta S^{ig} = S_2^{ig} - S_1^{ig} = \int_{T_1}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_1}$$

❏ **Step 2ig → 2**

$$H_2 - H_2^{ig} = H_2^R \qquad S_2 - S_2^{ig} = S_2^R$$
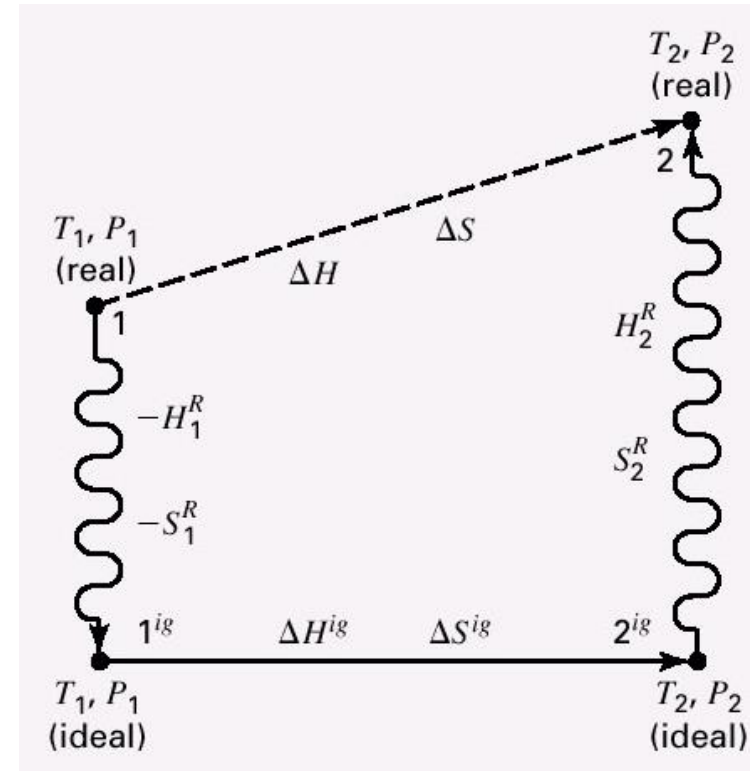
Homework

❑ Problems

- **6.3, 6.11, 6.23, 6.48, 6.54, 6.74**

- **For 6.54**

    - use the heat capacity of n-butane from Table C.1.

    - For H^R and S^R, use Pitzer correlations for the Compressibility factor (Z).

- **Due:**

❑ Recommend Problems

- **6.2, 6.4, 6.9, 6.12, 6.17, 6.30, 6.31, 6.49, 6.57, 6.58, 6.71, 6.72, 6.76, 6.80, 6.92, 6.93, 6.94**

Homework – from Supplement

❑ **Derive the following expressions**

$$H(T,P) = \int_0^P \left[V - T\left(\frac{\partial V}{\partial T} \right)_P \right] dP + H^{ig}(T,P)$$

$$S(T,P) = -\int_0^P \left[\left(\frac{\partial V}{\partial T} \right)_P - \frac{R}{P} \right] dP + S^{ig}(T,P^0) - R\ln\frac{P}{P^o}$$

$$G(T,P) = \int_0^P \left[V - \frac{RT}{P} \right] dP + H^{ig}(T,P) - TS^{ig}(T,P^0) + RT\ln\frac{P}{P^0}$$

$$H(T,V) = \int_\infty^V \left[T\left(\frac{\partial P}{\partial T} \right)_V - P \right] dV + RT(Z-1) + H^{ig}(T,P^0)$$

$$S(T,V) = \int_\infty^V \left[\left(\frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV + R\ln Z - R\ln\frac{P}{P^0} + S^{ig}(T,P^0)$$

$$G(T,V) = H(T,V) - T \times S(T,V)$$

$$= -\int_\infty^V \left[P - \frac{RT}{V} \right] dV - RT\ln Z + RT(Z-1) + RT\ln\frac{P}{P^0} + G^{ig}(T,P^0)$$