Thermodynamics II

Thermodynamic Properties of Fluids

Chapter 6

Property relations for homogeneous phases

- First law for a closed system: $\boxed{d(nU)=dQ+dW}$

a special reversible process

$$\boxed{d(nU)=dQ_{rev}+dW_{rev}}$$

$$\boxed{dW_{rev}=-Pd(nV)} \qquad \boxed{dQ_{rev}=Td(nS)}$$

Second law for a closed system

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

Note that only properties (state function) of system are involved:

- It can be applied to any process in a closed system (not necessarily reversible processes).

- The change occurs between equilibrium states.

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

The primary thermodynamic properties: $\boxed{P, V, T, U, and\ S}$

The enthalpy: $\boxed{H \equiv U + PV}$

The Helmholtz energy: $\boxed{A \equiv U - TS}$

The Gibbs energy: $\boxed{G \equiv H - TS}$

For one mol of homogeneous fluid of constant composition (intensive properties):

$$\boxed{dU = TdS - PdV}$$

$$\boxed{dH = TdS + VdP}$$

$$\boxed{dA = -PdV - SdT}$$

$$\boxed{dG = VdP - SdT}$$

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

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

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

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

→ Maxwell's equations

How to derive Maxwell’s equations?

By application of the criterion of exactness for a differential expression. If $F = F(x, y)$, then the total differential of F is defined as:

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

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

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

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

The order of differentiation in mixed second derivatives is immaterial, Thus:

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

Example. Prove that: $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

$$U = U(S,V)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV = TdS - PdV$$

$$\left.\begin{array}{l} \left(\frac{\partial U}{\partial S}\right)_V = T \Rightarrow \frac{\partial^2 U}{\partial S \partial V} = \left(\frac{\partial T}{\partial V}\right)_S \\ \left(\frac{\partial U}{\partial V}\right)_S = -P \Rightarrow \frac{\partial^2 U}{\partial V \partial S} = -\left(\frac{\partial P}{\partial S}\right)_V \end{array}\right\} \frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S} \Rightarrow \boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

Exercise. Try to verify the other Maxwell's equations (ME's)

Enthalpy, entropy and internal energy change calculations *f (P,T)*

$$\boxed{H = H(T,P)}$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

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

$$dH = TdS + VdP$$

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

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

$$dH = C_P dT + \left(T\left(\frac{\partial S}{\partial P}\right)_T + V\right) dP$$

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

ME

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

$$\boxed{S = S(T,P)}$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

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

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

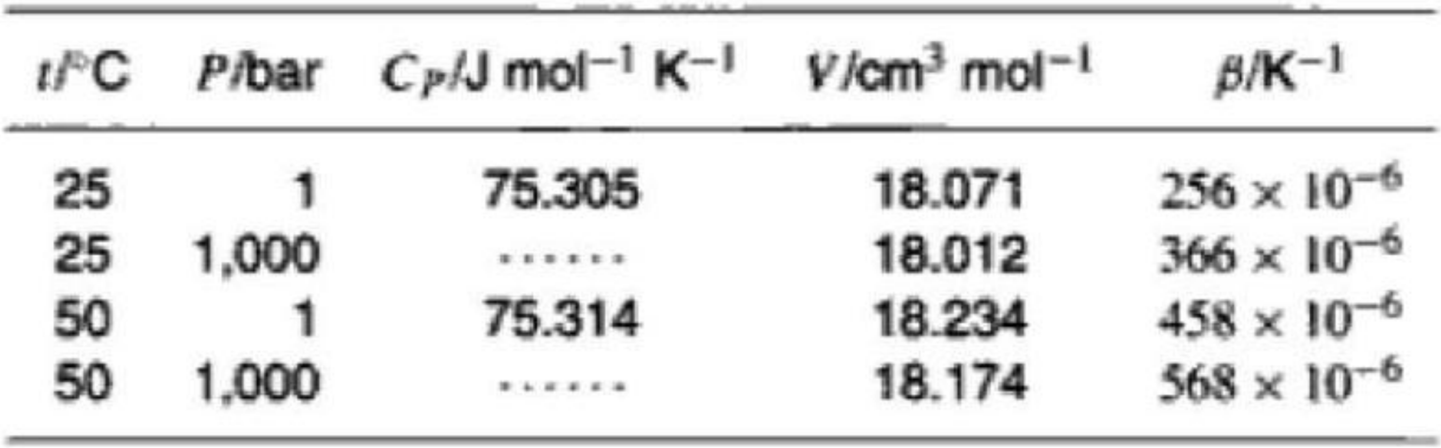
$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$H \equiv U + PV$$

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

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

Example 6.1. Determine the enthalpy and entropy changes of liquid water for a change of state from 1 bar and 25°C to 1000 bar and 50°C. The data for water are given.



t/°C	P/bar	C_P/J mol^{-1} K^{-1}	V/cm^3 mol^{-1}	β/K^{-1}
25	1	75.305	18.071	256×10^{-6}
25	1,000	....	18.012	366×10^{-6}
50	1	75.314	18.234	458×10^{-6}
50	1,000	....	18.174	568×10^{-6}

H_1 and S_1 at 1 bar, 25°C

H_2 and S_2 at 1 bar, 50°C

Calculation path:
isobaric followed by isothermal

H_3 and S_3 at
1000 bar, 50°C

$$\Delta H = (H_2 - H_1)\big|_{isobaric} + (H_3 - H_2)\big|_{isothermal}$$

$$\Delta S = (S_2 - S_1)\big|_{isobaric} + (S_3 - S_2)\big|_{isothermal}$$

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

volume expansivity

$$dH = C_P dT + \left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right)dP \longrightarrow dH = C_P dT + (1 - \beta T)V dP$$

$$dH = C_P dT + (1 - \beta T) V dP$$

$$dH = dH\big|_{isobaric} + dH\big|_{isothermal}$$

$\langle\ \rangle$: average value

$$\Delta H = \langle C_P \rangle (T_2 - T_1) + (1 - \langle \beta \rangle T_2) \langle V \rangle (P_2 - P_1)$$

$$\Delta H = 75.310(323.15 - 298.15) + \frac{(1 - (513\times10^{-6})(323.15))(18.204)(1000-1)}{10} = 3400\, J/mol$$

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

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

volume expansivity

$$dS = dS\big|_{isobaric} + dS\big|_{isothermal}$$

$$\Delta S = \langle C_P \rangle \ln\frac{T_2}{T_1} - \langle \beta \rangle \langle V \rangle (P_2 - P_1)$$

$$\Delta S = 75.310 \ln\frac{323.15}{298.15} - \frac{(513\times10^{-6})(18.204)(1000-1)}{10} = 5.13\, J/mol$$

Internal energy and entropy change calculations *f (V,T)*

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

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

$$dU = TdS - PdV$$

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

$$dU = C_V dT + \left(T\left(\frac{\partial S}{\partial V}\right)_T - P\right) dV$$

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

ME

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

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$dU = TdS - PdV$$

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

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

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

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

Gibbs energy $G = G(P,T)$

$$\boxed{dG = VdP - SdT}$$

Thermodynamic property of great potential utility

$$\begin{tikzcd}
\boxed{d\left(\frac{G}{RT}\right) \equiv \frac{1}{RT}dG - \frac{G}{RT^2}dT} \arrow[d, swap, "\boxed{G \equiv H - TS}"] \arrow[d, "\boxed{dG = VdP - SdT}"] & \\
\boxed{d\left(\frac{G}{RT}\right) \equiv \frac{V}{RT}dP - \frac{H}{RT^2}dT} \arrow[r, leftrightarrow] & \boxed{d\left(\frac{G}{RT}\right) = \left(\frac{\partial(G/RT)}{\partial P}\right)_T dP + \left(\frac{\partial(G/RT)}{\partial T}\right)_P dT}
\end{tikzcd}$$

$$\boxed{\frac{V}{RT} = \left(\frac{\partial(G/RT)}{\partial P}\right)_T}$$

$$\boxed{\frac{H}{RT} = -T\left(\frac{\partial(G/RT)}{\partial T}\right)_P}$$

$$G/RT = g(P,T)$$

The Gibbs energy serves as a generating function for the other thermodynamic properties.

Residual properties

- The definition for the generic residual property:

$$\boxed{M^R \equiv M - M^{ig}}$$

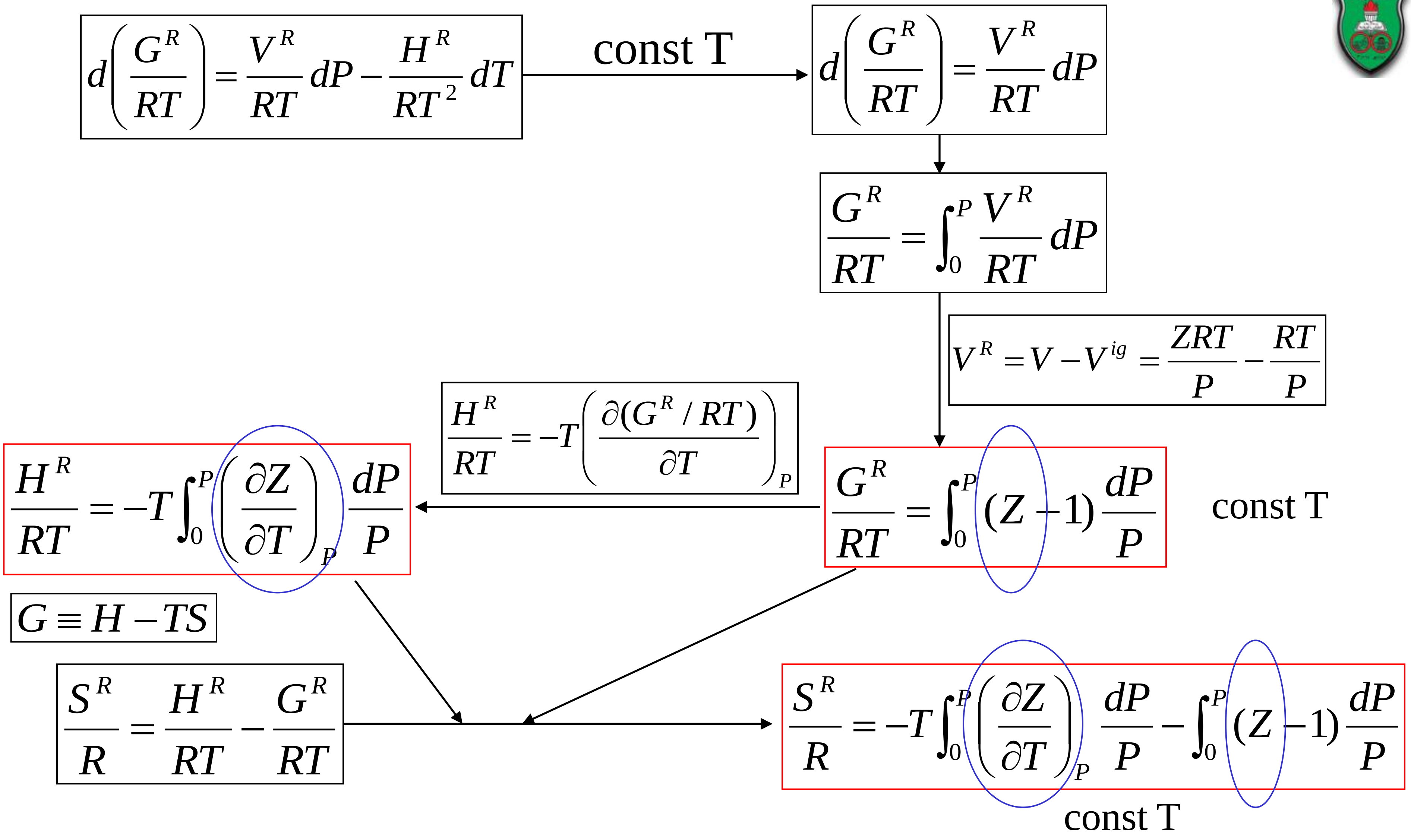
  - M and M^{ig} are the actual and ideal-gas properties, respectively.
  - M is the molar value of any extensive thermodynamic properties, e.g., V, U, H, S, or G.

- The residual molar volume is:

$$\boxed{V^R \equiv V - V^{ig} = \frac{ZRT}{P} - \frac{RT}{P} = \frac{RT}{P}(Z-1)}$$

- The residual Gibbs energy serves as a generating function for the other residual properties:

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



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

const T

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

$$\frac{G^R}{RT} = \int_0^P \frac{V^R}{RT}dP$$

$$V^R = V - V^{ig} = \frac{ZRT}{P} - \frac{RT}{P}$$

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

const T

$$\frac{H^R}{RT} = -T\left(\frac{\partial(G^R/RT)}{\partial T}\right)_P$$

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

$$G \equiv H - TS$$

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT}$$

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

const T

Z = PV/RT: experimental measurement .Given PVT data or an appropriate EOS, we can evaluate H^R and S^R and hence all other residual properties.

Residual properties

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

$$\boxed{dH^{ig} = C_P^{\ ig} dT}$$

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

$$\begin{aligned}
H = H^{ig} + H^R &= \left\{ H_0^{ig} + \int_{T_0}^{T} C_P^{ig} dT \right\} + \left\{ -RT^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \right\} \\
&= \left\{ H_0^{ig} + R \times ICPH(T_0, T; A, B, C, D) \right\} + \left\{ -RT^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \right\} \\
&= \left\{ H_0^{ig} + \left\langle C_P^{ig} \right\rangle_H (T - T_0) \right\} + \left\{ -RT^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \right\} \\
&= \left\{ H_0^{ig} + R \times MCPH(T_0, T; A, B, C, D)(T - T_0) \right\} + \left\{ -RT^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \right\}
\end{aligned}$$

The reference-state conditions T_o and P_o are selected for convenience

Residual properties

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

$$\boxed{\begin{aligned} & dS^{ig} = C_P{}^{ig} \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP = C_P{}^{ig} \frac{dT}{T} - \frac{R}{P} dP \\ & S^{ig} - S_0^{ig} = \int_{T_0}^{T} C_P^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0} \end{aligned}}$$

$$\boxed{\begin{aligned} S = S^{ig} + S^R &= \left\{ S_0^{ig} + \int_{T_0}^{T} C_P^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0} \right\} + R \left\{ -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1) \frac{dP}{P} \right\} \\ &= \left\{ S_0^{ig} + R \times ICPS(T_0, T; A, B, C, D) - R \ln \frac{P}{P_0} \right\} + R \left\{ -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1) \frac{dP}{P} \right\} \\ &= \left\{ S_0^{ig} + \left\langle C_P^{ig} \right\rangle_S \ln \frac{T}{T_0} - R \ln \frac{P}{P_0} \right\} + R \left\{ -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1) \frac{dP}{P} \right\} \\ &= \left\{ S_0^{ig} + R \times MCPS(T_0, T; A, B, C, D) \ln \frac{T}{T_0} - R \ln \frac{P}{P_0} \right\} + R \left\{ -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1) \frac{dP}{P} \right\} \end{aligned}}$$

Residual properties

D.I DEFINED FUNCTIONS

Mean Cp for enthalpy calculations :

$$\text{MCPH} \equiv \frac{\langle C_P \rangle_H}{R} = A + \frac{B}{2} T_0(\tau + 1) + \frac{C}{3} T_0^2(\tau^2 + \tau + 1) + \frac{D}{\tau T_0^2}$$

Integral of Cp/R for enthalpy calculations:

$$\text{ICPH} \equiv \int_{T_0}^{T} \frac{C_P}{R} dT = \text{MCPH} * (T - T_0)$$

Mean Cp for entropy calculations:

$$\text{MCPS} \equiv \frac{\langle C_P^{ig} \rangle_S}{R} = A + \left[BT_0 + \left(CT_0^2 + \frac{D}{\tau^2 T_0^2} \right) \left(\frac{\tau + 1}{2} \right) \right] \left(\frac{\tau - 1}{\ln \tau} \right)$$

Mean [Cp/(RT)] for entropy calculations:

$$\text{ICPS} \equiv \int_{T_0}^{T} \frac{C_P^{ig}}{R} \frac{dT}{T} = \text{MCPS} * \ln \tau$$

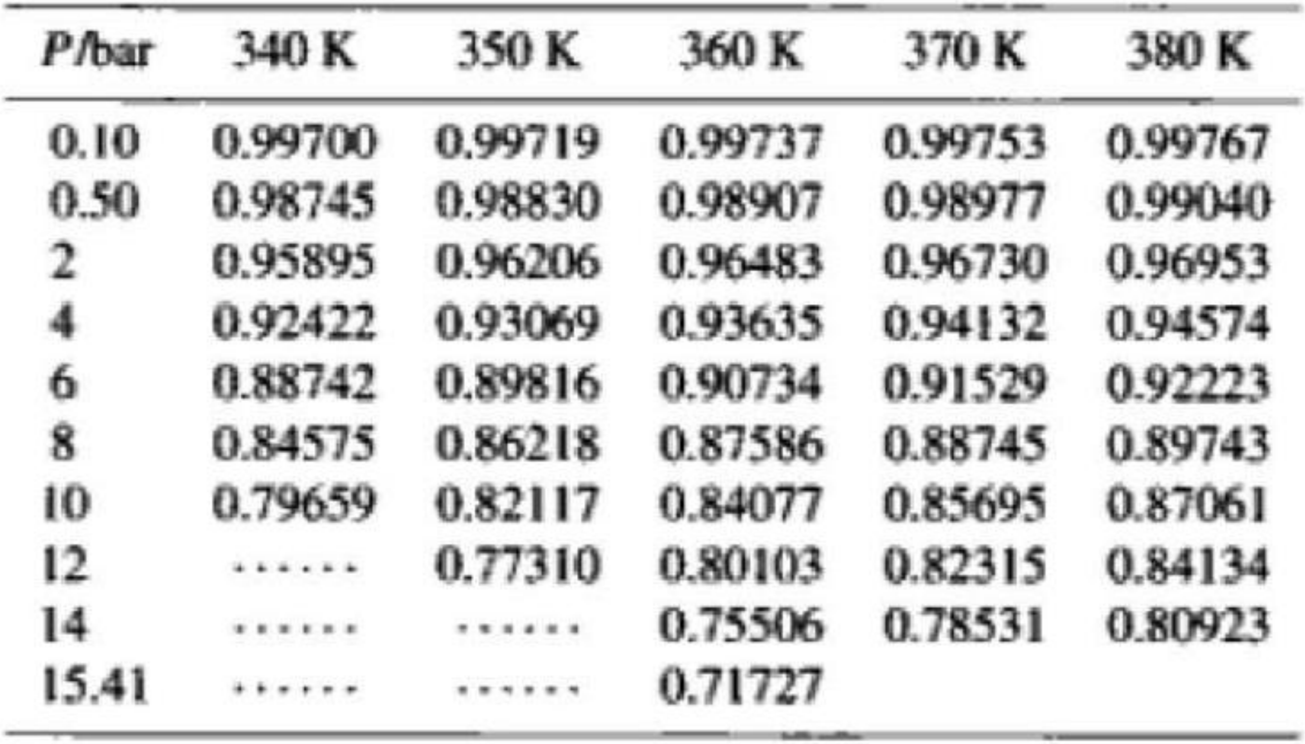
where

$$\tau \equiv \frac{T}{T_0}$$

Example 6.3

Calculate the enthalpy and entropy of saturated isobutane vapor at 360 K from the following information: (1) compressibility-factor for isobutane vapor; (2) the vapor pressure of isobutane at 360 K is 15.41 bar; (3) at 300K and 1 bar, $H_0^{ig} = 18115\ J/mol\ S_0^{ig} = 295.976\ J/mol \cdot K$ (4) the ideal-gas heat capacity of isobutane vapor: $C_P^{ig}/R = 1.7765 + 33.037 \times 10^{-3} T$

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

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

Graphical integration requires plots of $\left(\frac{\partial Z}{\partial T}\right)_P / P$ and (Z-1)/P vs. P.

$$\boxed{\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} = -(360)(26.37\times 10^{-4}) = -0.9493} \rightarrow \boxed{H^R = -2841.3 J/mol}$$

$$\boxed{\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P} = -0.9493 - (-0.02596) = -0.6897} \rightarrow \boxed{S^R = -5.734 J/mol\cdot K}$$

$$\boxed{H = \left\{H_0^{ig} + R\times ICPH(300,360;1.7765,33.037E-3,0.0,0.0)\right\} + H^R = 21598.5\frac{J}{mol}}$$

$$\boxed{S = \left\{S_0^{ig} + R\times ICPS(300,360;1.7765,33.037E-3,0.0,0.0)\right\} - R\ln\frac{15.41}{1} + S^R = 286.676\frac{J}{mol\cdot K}}$$

Example 6.3

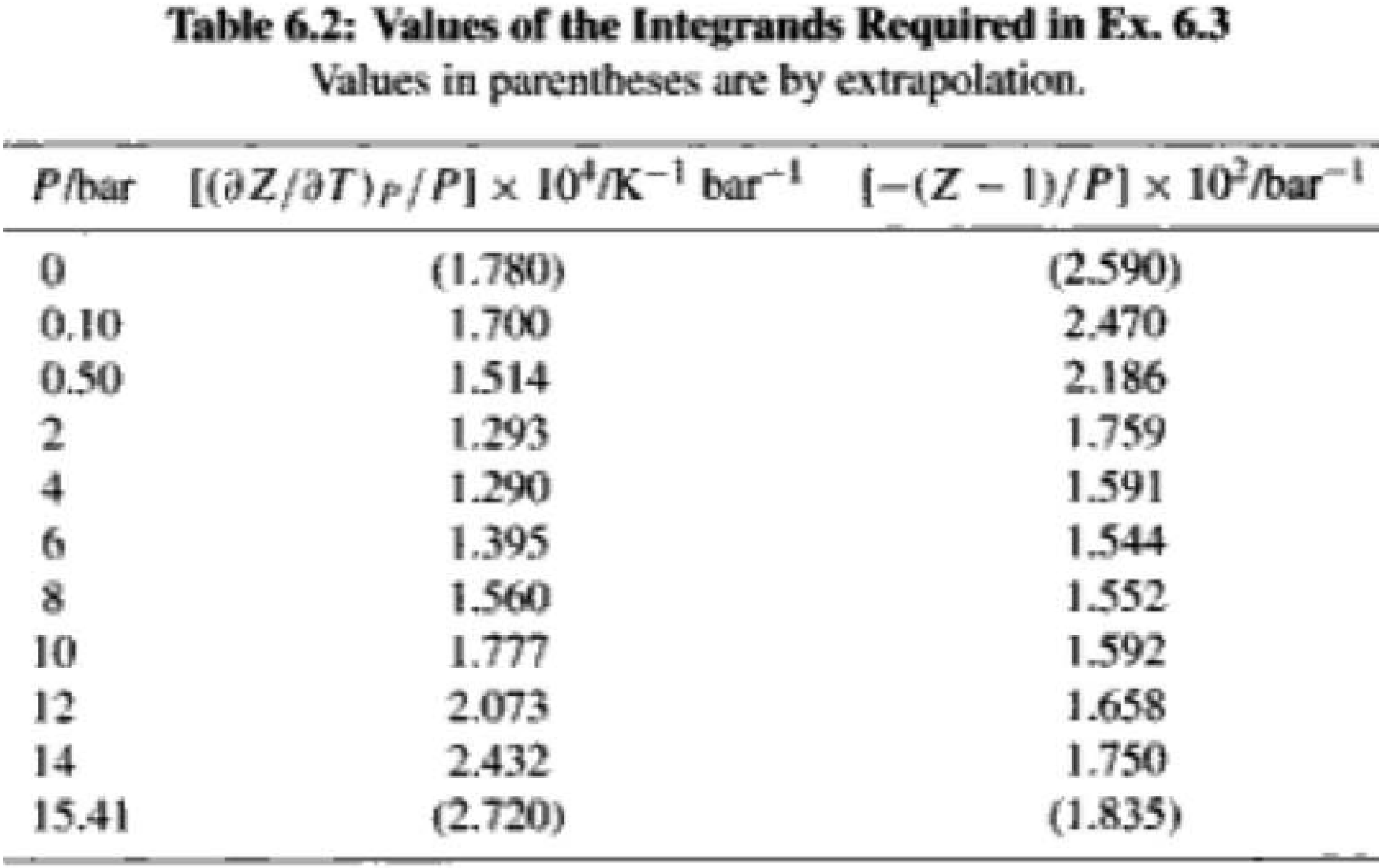


Table 6.2: Values of the Integrands Required in Ex. 6.3

Values in parentheses are by extrapolation.

P/bar	$[(\partial Z/\partial T)_P/P] \times 10^4/\mathrm{K}^{-1}\ \mathrm{bar}^{-1}$	$[-(Z-1)/P] \times 10^2/\mathrm{bar}^{-1}$
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)

Residual properties by virial cubic EOS

- If Z = f (P,T):

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

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

- Calculations of residual properties for gases and vapors through use of the virial equations and cubic equation of state.

Use of 2nd virial coefficient EOS (Pitzer correlations)

- For gases at low pressure .

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

$$\boxed{Z-1=\frac{BP}{RT}}$$

$$\boxed{\frac{H^R}{RT}=-T\int_0^P\left(\frac{\partial Z}{\partial T}\right)_P\frac{dP}{P}} \longrightarrow \boxed{\frac{H^R}{RT}=-T\int_0^P\left(\frac{\partial}{\partial T}(1+\frac{BP}{RT})\right)_P\frac{dP}{P}}$$

$$\downarrow$$

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

$$\downarrow$$

$$\boxed{\frac{H^R}{RT}=\frac{P}{R}\left(\frac{B}{T}-\frac{dB}{dT}\right)}$$

$$\boxed{\frac{S^R}{R}=\frac{H^R}{RT}-\frac{G^R}{RT}} \longrightarrow \boxed{\frac{S^R}{RT}=-\frac{P}{R}\frac{dB}{dT}}$$

Use of 2nd virial coefficient EOS (Pitzer correlations)

$$\frac{H^R}{RT} = \frac{P}{R}\left(\frac{B}{T} - \frac{dB}{dT}\right)$$

$$\hat{B} = \frac{BP_c}{RT_c} = \left(B^0 + \omega B^1\right)$$

$$\frac{d\hat{B}}{dT_r} = \frac{dB^0}{dT_r} + \omega\frac{dB^1}{dT_r}$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{\,1.6}}$$

$$\frac{dB^0}{dT_r} = \frac{0.675}{T_r^{\,2.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{\,4.2}}$$

$$\frac{dB^1}{dT_r} = \frac{0.722}{T_r^{\,5.2}}$$

Note that the B’s coefficients are function of temperature only

$$\frac{H^R}{RT_c} = P_r\left[B^0 - T_r\frac{dB^0}{dT_r} + \omega\left(B^1 - T_r\frac{dB^1}{dT_r}\right)\right]$$

Use of 2nd virial coefficient (Pitzer correlations)

$$\frac{S^R}{RT} = -\frac{P}{R}\frac{dB}{dT}$$

$$\hat{B} = \frac{BP_c}{RT_c} = \left(B^0 + \omega B^1\right)$$

$$\frac{d\hat{B}}{dT_r} = \frac{dB^0}{dT_r} + \omega\frac{dB^1}{dT_r}$$

Note that the B’s coefficients are function of temperature only

$$B^0 = 0.083 - \frac{0.422}{T_r^{\,1.6}}$$

$$\frac{dB^0}{dT_r} = \frac{0.675}{T_r^{\,2.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{\,4.2}}$$

$$\frac{dB^1}{dT_r} = \frac{0.722}{T_r^{\,5.2}}$$

$$\frac{S^R}{R} = -P_r\left(\frac{dB^0}{dT_r} + \omega\frac{dB^1}{dT_r}\right)$$

Use of cubic and 3rd virial coefficient EOS

- It is helpful to do the following:

$$\begin{tikzcd}
\boxed{P = Z\rho RT} \arrow[d, "\text{(Constant T)}"] \\
\boxed{dP = RTd(Z\rho) = RT(Zd\rho + \rho dz)} \arrow[d] \\
\boxed{\frac{dP}{P} = \frac{RT(Zd\rho + \rho dz)}{P} = \frac{RTZd\rho}{P} + \frac{RT\rho dZ}{P} = \frac{d\rho}{\rho} + \frac{dZ}{Z}} \arrow[d] \\
\boxed{\frac{G^R}{RT} = \int_0^P (Z-1)\frac{dP}{P} = \int_0^\rho (Z-1)\frac{d\rho}{\rho} + \int_1^Z (Z-1)\frac{dZ}{Z}} \arrow[d] \\
\boxed{\frac{G^R}{RT} = \int_0^\rho (Z-1)\frac{d\rho}{\rho} + Z - 1 - \ln Z}
\end{tikzcd}$$

Use of cubic and 3rd virial coefficient EOS

- It is helpful to do the following:

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

$$\boxed{\frac{H^R}{RT^2}=\frac{V^R}{RT}\left(\frac{\partial P}{\partial T}\right)_\rho-\left(\frac{\partial G^R/RT}{\partial T}\right)_\rho}$$

$$\boxed{P=Z\rho RT}$$

$$\boxed{V^R=RT(Z-1)/P}$$

$$\boxed{G^R/RT=\int_0^\rho (Z-1)\,d\rho/\rho+Z-1-\ln Z}$$

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

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

Use of 3rd virial coefficient EOS

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

$$Z-1=B\rho+C\rho^2$$

$$\frac{G^R}{RT}=2B\rho+\frac{3}{2}C\rho^2-\ln Z$$

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

$$Z-1=B\rho+C\rho^2$$

$$\frac{H^R}{RT}=T\left[\left(\frac{B}{T}-\frac{dB}{dT}\right)\rho+\left(\frac{C}{T}-\frac{1}{2}\frac{dC}{dT}\right)\rho^2\right]$$

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

$$Z-1=B\rho+C\rho^2$$

$$\frac{S^R}{R}=\ln Z-T\left[\left(\frac{B}{T}+\frac{dB}{dT}\right)\rho+\frac{1}{2}\left(\frac{C}{T}+\frac{dC}{dT}\right)\rho^2\right]$$

- ➢The above equation are applied for moderate pressure

Use of the cubic equation of state

- The generic cubic equation of state:

$$\boxed{q \equiv \frac{a(T)}{bRT}}$$

$$\boxed{P = \frac{RT}{V-b} - \frac{a(T)}{(V+\varepsilon b)(V+\sigma b)}} \longrightarrow \boxed{Z = \frac{1}{1-\rho b} - q\frac{\rho b}{(1+\varepsilon\rho b)(1+\sigma\rho b)}}$$

$$\boxed{Z-1 = \frac{\rho b}{1-\rho b} - q\frac{\rho b}{(1+\varepsilon\rho b)(1+\sigma\rho b)}}$$

$$\boxed{\beta \equiv \frac{bP}{RT} = \Omega\frac{P_r}{T_r}} \qquad \boxed{q \equiv \frac{a(T)}{bRT} = \frac{\Psi\alpha(T_r)}{\Omega T_r}}$$

$$\boxed{\int_0^\rho (Z-1)\frac{d\rho}{\rho} = -\ln(1-\rho b) - qI}$$

$$\boxed{\int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} = -\frac{dq}{dT}I}$$

Where $\boxed{I \equiv \int_0^\rho \frac{d(\rho b)}{(1+\varepsilon\rho b)(1+\sigma\rho b)} \quad const\ T}$

Let us evaluate the integral for following two cases:

Cases I: If $(\sigma = \varepsilon)$

Cases II: If $(\sigma \neq \varepsilon)$

Use of the cubic equation of state

Cases I: $(\sigma = \varepsilon)$

$$\boxed{I \equiv \int_0^{\rho} \frac{d(\rho b)}{(1+\varepsilon\rho b)(1+\sigma\rho b)} = \frac{\rho b}{1+\varepsilon\rho b} \quad const\ T}$$

$$\beta \equiv \frac{bP}{RT} = \frac{ZbP}{ZRT} = \frac{Zb}{V} = Z\rho b \rightarrow \boxed{\rho b = \frac{\beta}{Z}}$$

$$\boxed{I \equiv \frac{\beta}{Z+\varepsilon\beta} \quad const\ T}$$

For van der Waals EOS: $\boxed{\sigma = \varepsilon = 0 \rightarrow I \equiv \frac{\beta}{Z} = \rho b \quad vdw, const\ T}$

Use of the cubic equation of state

Cases II: $(\sigma \neq \varepsilon)$

$$\boxed{I \equiv \int_0^{\rho} \frac{d(\rho b)}{(1+\varepsilon\rho b)(1+\sigma\rho b)} = \frac{1}{\sigma-\varepsilon}\ln\left(\frac{1+\sigma\rho b}{1+\varepsilon\rho b}\right) \quad const\ T}$$

$$\boxed{\rho b = \frac{\beta}{Z}}$$

$$\downarrow$$

$$\boxed{I \equiv \frac{1}{\sigma-\varepsilon}\ln\left(\frac{Z+\sigma\beta}{Z+\varepsilon\beta}\right) \quad RK, SRK, PR\ at\ const\ T}$$

Use of the cubic equation of state

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

$$\rho b = \beta / Z$$

$$\int_0^\rho (Z-1)\frac{d\rho}{\rho} = -\ln(1-\rho b) - qI$$

$$\frac{G^R}{RT} = Z - 1 - \ln(Z-\beta) - qI$$

$$q = \frac{\Psi \alpha(T_r)}{\Omega T_r}$$

$$\ln q = \ln \Psi + \ln \alpha(T_r) - \ln \Omega - \ln T_r$$

$$d\ln q = d\ln \alpha(T_r) - d\ln T_r$$

$$\frac{d\ln q}{d\ln T_r} = \frac{d\ln \alpha(T_r)}{d\ln T_r} - 1$$

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

$$q \equiv \frac{a(T)}{bRT} = \frac{\Psi \alpha(T_r)}{\Omega T_r}$$

$$\int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} = -\frac{dq}{dT} I$$

$$\frac{H^R}{RT} = T_r \frac{dq}{dT_r} I + Z - 1$$

$$\frac{H^R}{RT} = q\frac{dq/q}{dT_r/T_r} I + Z - 1 = q\frac{d\ln q}{d\ln T_r} I + Z - 1$$

$$\frac{H^R}{RT} = Z - 1 + \left[\frac{d\ln \alpha(T_r)}{d\ln T_r} - 1\right] qI$$

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT}$$

$$\frac{S^R}{R} = \ln(Z-\beta) + \left[\frac{d\ln \alpha(T_r)}{d\ln T_r} - 1\right] qI$$

Example 6.4. Find values for the residual enthalpy H^R and the residual entropy S^R for n-butane gas at 500 K and 50 bar as given by Redlich/Kwong equation.

$$\boxed{T_r=\frac{500}{425.1}=1.176}\quad\boxed{P_r=\frac{50}{37.96}=1.317}\quad\boxed{\beta=\Omega\frac{P_r}{T_r}=0.09703}\quad\boxed{q=\frac{\Psi\alpha(T_r)}{\Omega T_r}=3.8689}$$

$$\boxed{Z=1+\beta-q\beta\frac{Z-\beta}{(Z+\varepsilon\beta)(Z+\sigma\beta)}}\xrightarrow[\sigma=1]{\varepsilon=0}\boxed{Z=0.685}$$

$$\boxed{I\equiv\int_0^{\rho}\frac{d(\rho b)}{(1+\varepsilon\rho b)(1+\sigma\rho b)}\qquad const\ T}\longrightarrow\boxed{I=\frac{1}{\sigma-\varepsilon}\ln\left(\frac{Z+\sigma\beta}{Z+\varepsilon\beta}\right)=0.13247}$$

Table 3.1 RK: $\alpha(T_r)=T_r^{-0.5}$

$$\boxed{\frac{H^R}{RT}=Z-1+\left[\frac{d\ln\alpha(T_r)}{d\ln T_r}-1\right]qI}\xrightarrow[\boxed{d\ln\alpha(T_r)/d\ln T_r=-0.5}]{\boxed{\ln\alpha(T_r)=-0.5\ln T_r}}\boxed{H^R=-4505\frac{J}{mol}}$$

$$\boxed{\frac{S^R}{R}=\ln\left(Z-\beta\right)+\left[\frac{d\ln\alpha(T_r)}{d\ln T_r}-1\right]qI}\longrightarrow\boxed{S^R=-6.546\frac{J}{mol\cdot K}}$$

Exercise. Repeat solving the example using van der Waal.

Two-phase systems

- Whenever a phase transition at **constant temperature and pressure** occurs,
  - The molar or specific volume, internal energy, enthalpy, and entropy changes abruptly.
  - The exception is the molar or specific Gibbs energy, which for a pure species does not change during a phase transition:

$$\begin{tikzcd}
\boxed{d(nG)=nVdP-nSdT=0} \arrow[d, "\boxed{dn=dn^{\alpha}+dn^{\beta}=0}\ \text{(closed system)}"] & \text{(Equilibrium; constant T and P)} \\
\boxed{ndG=0\rightarrow dG=0\rightarrow G=constant} \arrow[r] & \boxed{G^{\alpha}=G^{\beta}}
\end{tikzcd}$$

where G^{α} and G^{β} are the molar or specific Gibbs energies of the individual phases.

$$\boxed{G^{\alpha} = G^{\beta}} \longrightarrow \boxed{dG^{\alpha} = dG^{\beta}}$$

$$\boxed{dG = VdP - SdT}$$

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

constant temperature and pressure

$$\boxed{dH = TdS + VdP} \longrightarrow \boxed{\Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta}}$$

The latent heat of phase transition

The Clapeyron equation

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

Vapor/liquid system

$$\boxed{\alpha \equiv l;\ \beta \equiv v}$$

$$\boxed{\Delta V^{\alpha\beta} = V^{v} = \frac{RT}{P^{sat}}}$$

Ideal gas, and $V^{l} << V^{g}$

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

The Clausius/Clapeyron equation

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

- According to Clausius/Clapeyron equation, latent heat of vaporization is proportional to the slope of a plot of $\ln P^{sat}$ vs. $1/T$.
- Experimental data showed that $\ln P^{sat}$ vs. $1/T$ is linear for many substances:

$$\begin{tikzcd}
\boxed{\ln P^{sat} = A - \frac{B}{T}} \arrow[d] & \\
\boxed{B = -\frac{d\ln P^{sat}}{d(1/T)} = -\frac{\ln P^{sat}(T) - \ln P_c^{sat}}{1/T - 1/T_c}} \arrow[r, "\boxed{\ln P^{sat} = A - B/T}"] & \boxed{A = \ln P_c + \frac{B}{T_c}}
\end{tikzcd}$$

For the entire temperature range from the triple point to the critical point

- **Other empirical relations between P^{sat} and 1/*T*:**

  - The Antoine equation, for a specific temperature range

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

See Table B.2 of Appendix B for values of Antoine constants for selected substances .

  - The Wagner equation, over a wide temperature range:

$$\left\{ \begin{array}{l} \boxed{\ln P_r^{sat} = \dfrac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1 - \tau}} \\ \boxed{\tau = 1 - T_r} \end{array} \right.$$

Values of the constants A, B, C, and D are given by R.C. Reid, J. M. Prausnitz, and B. E. Poling, The Properties of Gases and Liquids, 4th ed., App. A, McGraw-Hill,.1987.

Estimation of latent heat of vaporization

- Empirical equation proposed by Riedel to estimate the latent heat of vaporization at normal boiling point (T_n):

$$\boxed{\frac{\Delta H_n^{lv}}{RT_n} = \frac{1.092\left(\ln Pc - 1.013\right)}{0.930 - T_{rn}} \quad ; T_{rn} = \frac{T_n}{T_c}}$$

(error rarely exceed 5%)

- Empirical equation proposed by Watson to estimate the latent heat of vaporization of pure liquid at any temperature:

$$\boxed{\frac{\Delta H^{lv}(T_2)}{\Delta H^{lv}(T_1)} = \left(\frac{1-T_{r2}}{1-T_{r1}}\right)^{0.38} \quad ; T_{r1} = \frac{T_1}{T_c}, T_{r2} = \frac{T_2}{T_c}}$$

(fairly accurate)

Two-phase liquid/vapor systems

- When a system consists of saturated-liquid and saturated-vapor phases coexisting in equilibrium, the total value of any extensive property of the two-phase system is the sum of the total properties of the phases:

$$\boxed{nM = n^l M^l + n^v M^v}$$

Dividing by n and using mole balance ($n = n^l + n^v$) gives

$$\boxed{M = (1 - x^v) M^l + x^v M^v}$$

Where $x^v = n^v / n$ is the quality.

  - M represents V, U, H, S, etc.
  - e.g., $V = (1 - x^v) V^v + x^v V^v$

Thermodynamic diagrams and tables (Thermodynamics (1) Course)

- A thermodynamic diagram represents the temperature, pressure, volume, enthalpy, and entropy of a substance on a single plot. Common diagrams are:
  - PT diagram
  - PV diagram
  - TS diagram
  - PH diagram (ln P vs. H); see Appendix G
  - HS diagram (Mollier diagram); See the back cover of the textbook.
- In many instances, thermodynamic properties are reported in tables. The steam tables are the most thorough compilation of properties for a single material (Appendix F).

Thermodynamic diagrams

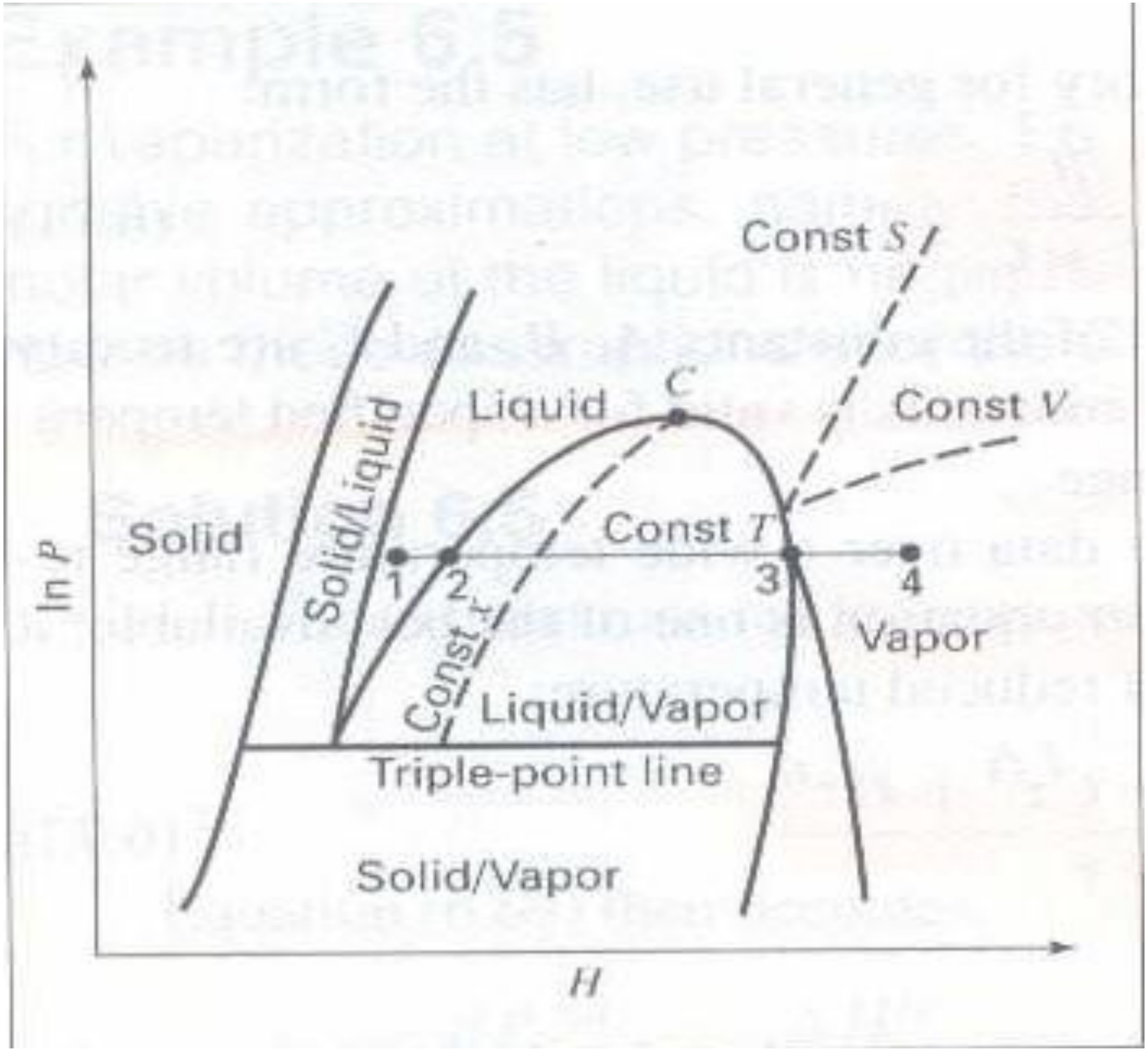


Fig. 6.2

Thermodynamic diagrams

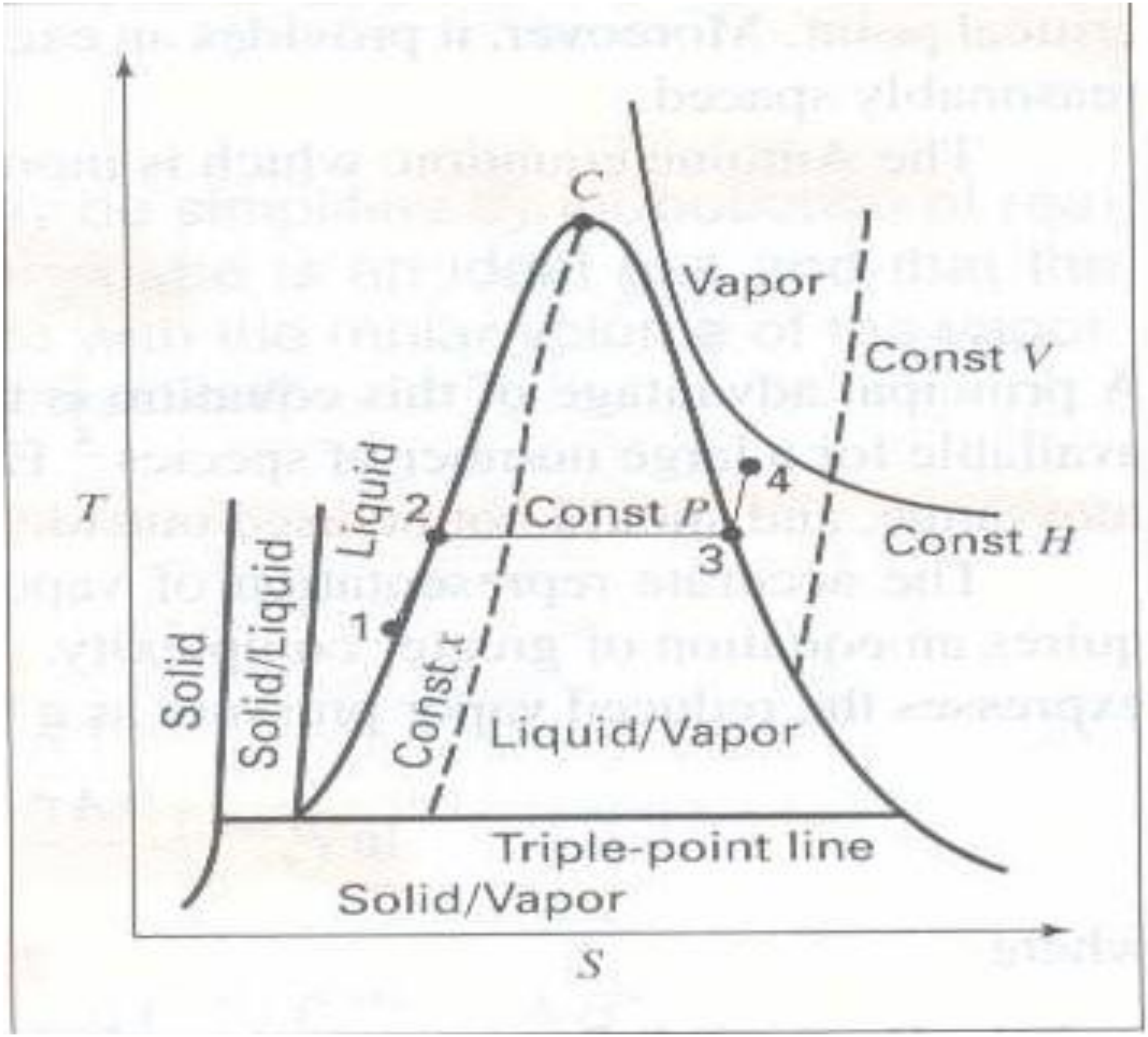


Fig. 6.3

Thermodynamic diagrams

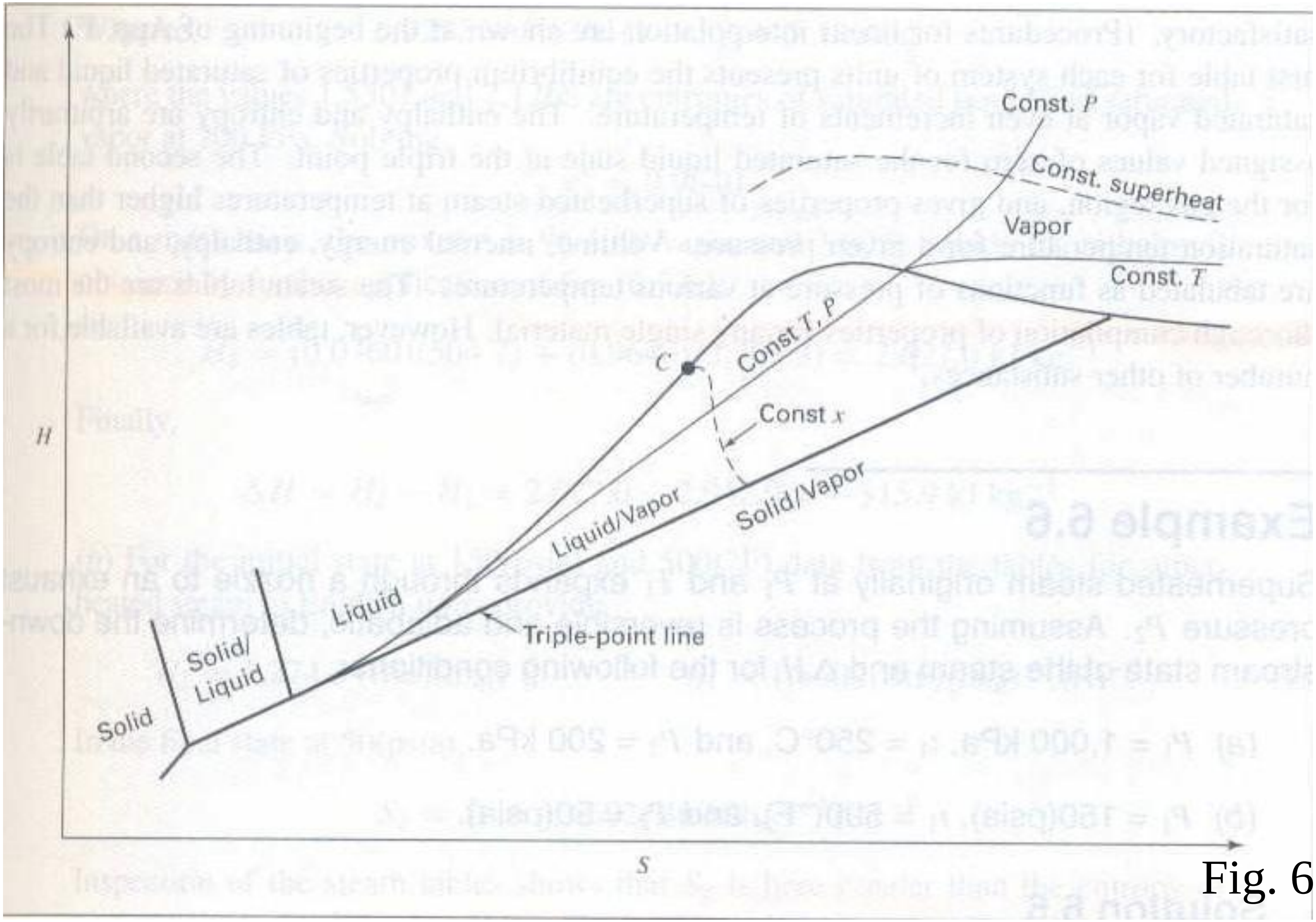


Fig. 6.4

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 conditions:

(a) $P_1 = 1000$ kPa, $T_1 = 250^\circ$C, and $P_2 = 200$ kPa.

(b) $P_1 = 150$ psia, $T_1 = 500^\circ$F, and $P_2 = 50$ psia.

Since the process is both reversible and adiabatic, the entropy change of the steam is zero.

(a) From the steam stable and the use of interpolation,

At $P_1 = 1000$ kPa,: $T^{sat} = 179.88 < T_1 = 250^\circ\text{C} \rightarrow$(Superheated):

$H_1 = 2942.9$ kJ/kg, $S_1 = 6.9252$ kJ/kg.K

At $P_2 = 200$ kPa: $S^v = 7.1268$ kJ/kg.K; $S^l = 1.5301$kJ/kg.K

$S^l < S_2 = S_1 = 6.9252$ kJ/kg.K $< S^v$

the final state is in the two-phase liquid-vapor region:

$$\boxed{S_2 = (1 - x_2^v)S_2^l + x_2^v S_2^v} \longrightarrow \boxed{6.9252 = 1.5301(1 - x_2^v) + 7.1268 x_2^v}$$

$$\downarrow$$

$$\boxed{x_2^v = 0.9640}$$

$$\downarrow$$

$$\boxed{\Delta H = H_2 - H_1 = -315.9\,\frac{kJ}{kg}} \longleftarrow \boxed{H_2 = (1 - 0.964)(504.7) + (0.964)(2706.3) = 2627.0}$$

(b) From the steam stable and the use of interpolation,

At $P_1 = 150$ psia: $T^{sat} = 358.43 < T_1 = 500^\circ F \rightarrow$(Superheated):

$H_1 = 1274.3$ Btu/lbm, $S_1 = 1.6602$ Btu/lbm.R

At $P_2 = 50$ psia: $S^v = 1.5454$

$S_2 = S_1 = 1.6602$ Btu/lbm.R $> S^v$,

the final state is in the superheat region:

$$T_2 = 283.28^\circ F \qquad H_2 = 1175.3\ Btu/lbm$$

$$\boxed{\Delta H = H_2 - H_1 = -99.0\,\frac{Btu}{lbm}}$$

Example 6.8. A 1.5 m^3 tank contains 500 kg of liquid water in equilibrium with pure water vapor, which fills the remainder of the tank. The temperature and pressure are 100°C, and 101.33 kPa. From a water line at a constant temperature of 70°C and a constant pressure somewhat above 101.33 kPa, 750 kg of liquid is bled into the tank. If the temperature and pressure in the tank are not to change as a result of the process, how much energy as heat must be transferred to the tank?

Energy balance:

$$\boxed{\frac{d(mU)_{cv}}{dt} = \dot{Q} + H'\dot{m}'} \longrightarrow \boxed{\frac{d(mU)_{cv}}{dt} = \dot{Q} + H'\frac{dm_{cv}}{dt}}$$

$$\downarrow$$

$$\boxed{Q = \Delta(mU)_{cv} - H'\Delta m_{cv}}$$

$$\downarrow \quad \boxed{H = U + PV}$$

$$\boxed{Q = \Delta(mH)_{cv} - \Delta(PmV)_{cv} - H'\Delta m_{cv}}$$

$$\downarrow$$

$$\boxed{Q = (m_2H_2)_{cv} - (m_1H_1)_{cv} - H'\Delta m_{cv}}$$

At the end of the process, the tank still contains saturated liquid and saturated vapor in equilibrium at 100°C and 101.33 kPa.

$$\boxed{Q = (m_2 H_2)_{cv} - (m_1 H_1)_{cv} - H'\Delta m_{cv}}$$

$$\boxed{H' = 293.0\frac{kJ}{kg} \quad saturated\ liquid\ @\,70^\circ C}$$

$$\boxed{H_{cv}^{l} = 419.1\frac{kJ}{kg} \quad saturated\ liquid\ @\,100^\circ C}$$

$$\boxed{H_{cv}^{v} = 2676.0\frac{kJ}{kg} \quad saturated\ vapor\ @\,100^\circ C}$$

From the steam table, the specific volumes of saturated liquid and saturated vapor at 100°C are 0.001044 and 1.673 m^3/kg , respectively.

$$\boxed{(m_1 H_1)_{cv} = m_1^l H_1^l + m_1^v H_1^v = 500(419.1) + \frac{1.5-(500)(0.001044)}{1.673}(2676.0) = 211616 kJ}$$

$$\boxed{m_2 = 500 + \frac{1.5-(500)(0.001044)}{1.673} + 750 = m_2^l + m_2^v} \quad \boxed{1.5 = 1.673 m_2^v + 0.001044 m_2^l}$$

$$\boxed{(m_2 H_2)_{cv} = m_2^l H_2^l + m_2^v H_2^v = 524458 kJ}$$

$$\boxed{Q = (m_2 H_2)_{cv} - (m_1 H_1)_{cv} - H'\Delta m_{cv} = 524458 - 211616 - (750)(293.0) = 93092 kJ}$$

Generalized Properties Correlations for Gases

$$\boxed{P = P_c P_r} \qquad \boxed{T = T_c T_r}$$

$$\boxed{\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}} \longrightarrow \boxed{\frac{H^R}{RT_c} = -T_r^2\int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}}$$

$$\boxed{\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P}} \longrightarrow \boxed{\frac{S^R}{R} = -T_r\int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z-1)\frac{dP_r}{P_r}}$$

$$\boxed{Z = Z^0 + \omega Z^1}$$

$$\boxed{\frac{H^R}{RT_c} = \left[-T_r^2\int_0^{P_r} \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}\right] - \omega\left[-T_r^2\int_0^{P_r} \left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}\right]}$$

$$\boxed{\frac{S^R}{R} = \left[-T_r\int_0^{P_r} \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z^0-1)\frac{dP_r}{P_r}\right] - \omega\left[-T_r\int_0^{P_r} \left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z^1-1)\frac{dP_r}{P_r}\right]}$$

$$\downarrow$$

$$\boxed{\frac{H^R}{RT_c} = \left[\frac{(H^R)^0}{RT_c} + \omega\frac{(H^R)^1}{RT_c}\right] = HRB(TR, PR, OMEGA)}$$

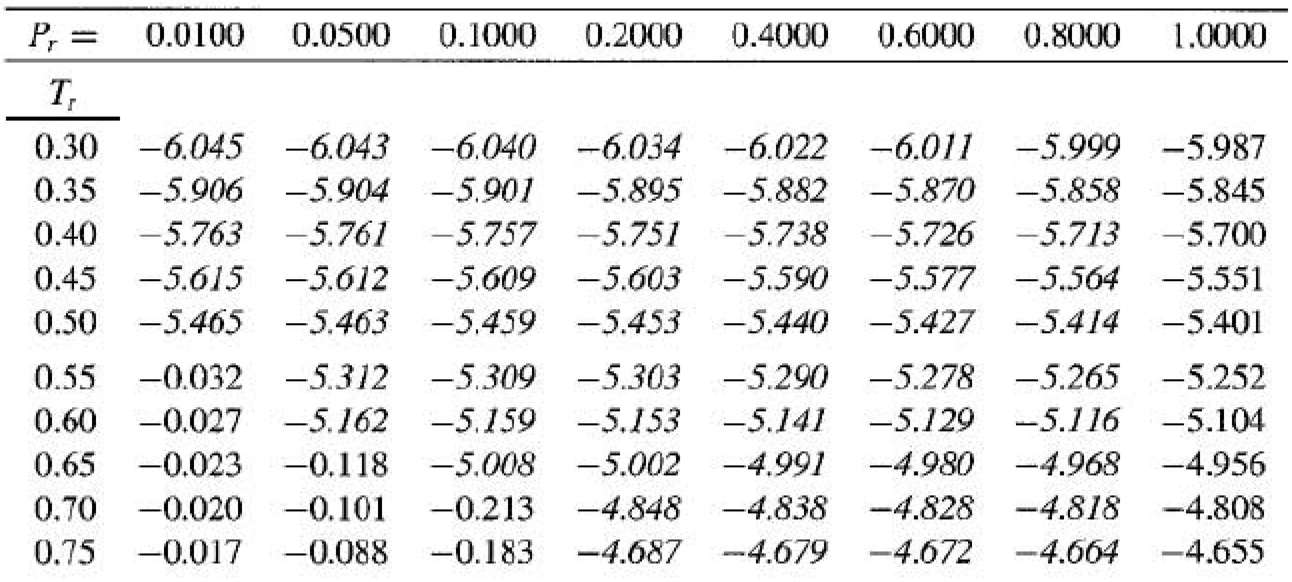
$$\boxed{\frac{S^R}{R} = \left[\frac{(S^R)^0}{R} + \omega\frac{(S^R)^1}{R}\right] = SRB(TR, PR, OMEGA)}$$

- Appendix D1 for programming
- Appendix E, Table E5 ~ E12 to get values.

Generalized Properties Correlations for Gases

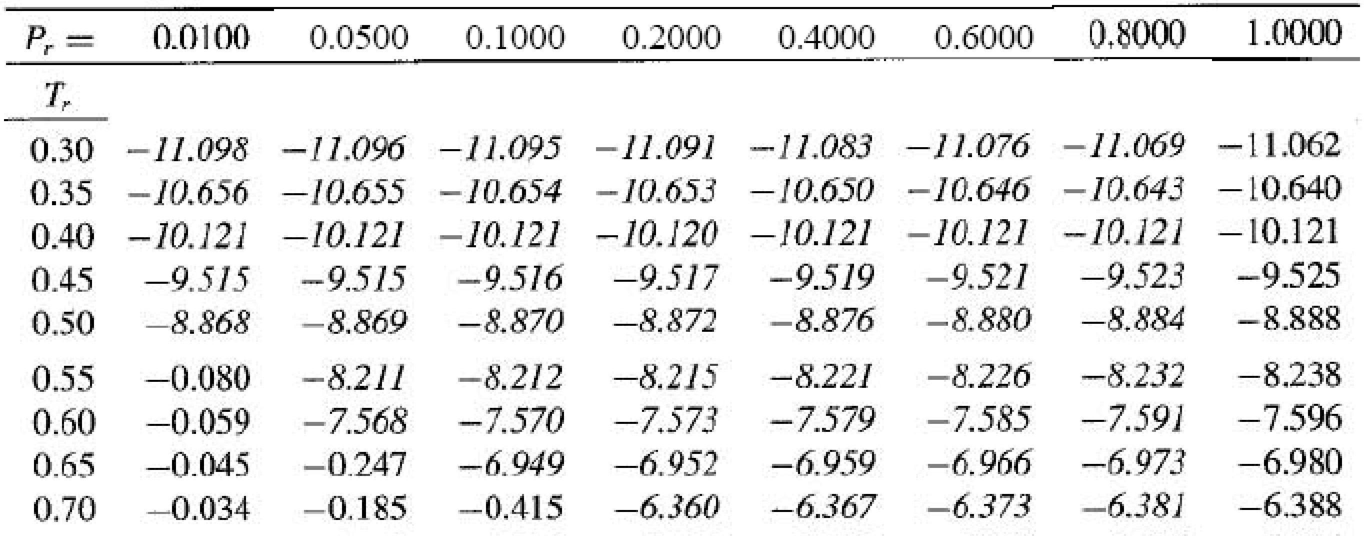
See Appendix E, Tables E5 ~ E1 for higher Tr

Table E.5 Values of $(H^R)^0/RT_c$



$P_r =$ T_r	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
0.30	−6.045	−6.043	−6.040	−6.034	−6.022	−6.011	−5.999	−5.987
0.35	−5.906	−5.904	−5.901	−5.895	−5.882	−5.870	−5.858	−5.845
0.40	−5.763	−5.761	−5.757	−5.751	−5.738	−5.726	−5.713	−5.700
0.45	−5.615	−5.612	−5.609	−5.603	−5.590	−5.577	−5.564	−5.551
0.50	−5.465	−5.463	−5.459	−5.453	−5.440	−5.427	−5.414	−5.401
0.55	−0.032	−5.312	−5.309	−5.303	−5.290	−5.278	−5.265	−5.252
0.60	−0.027	−5.162	−5.159	−5.153	−5.141	−5.129	−5.116	−5.104
0.65	−0.023	−0.118	−5.008	−5.002	−4.991	−4.980	−4.968	−4.956
0.70	−0.020	−0.101	−0.213	−4.848	−4.838	−4.828	−4.818	−4.808
0.75	−0.017	−0.088	−0.183	−4.687	−4.679	−4.672	−4.664	−4.655

Table E.6 Values of $(H^R)^1/RT_c$



$P_r =$ T_r	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
0.30	−11.098	−11.096	−11.095	−11.091	−11.083	−11.076	−11.069	−11.062
0.35	−10.656	−10.655	−10.654	−10.653	−10.650	−10.646	−10.643	−10.640
0.40	−10.121	−10.121	−10.121	−10.120	−10.121	−10.121	−10.121	−10.121
0.45	−9.515	−9.515	−9.516	−9.517	−9.519	−9.521	−9.523	−9.525
0.50	−8.868	−8.869	−8.870	−8.872	−8.876	−8.880	−8.884	−8.888
0.55	−0.080	−8.211	−8.212	−8.215	−8.221	−8.226	−8.232	−8.238
0.60	−0.059	−7.568	−7.570	−7.573	−7.579	−7.585	−7.591	−7.596
0.65	−0.045	−0.247	−6.949	−6.952	−6.959	−6.966	−6.973	−6.980
0.70	−0.034	−0.185	−0.415	−6.360	−6.367	−6.373	−6.381	−6.388

Generalized Properties Correlations for Gases

See Appendix E, Tables E5 ~ E1 for higher Tr

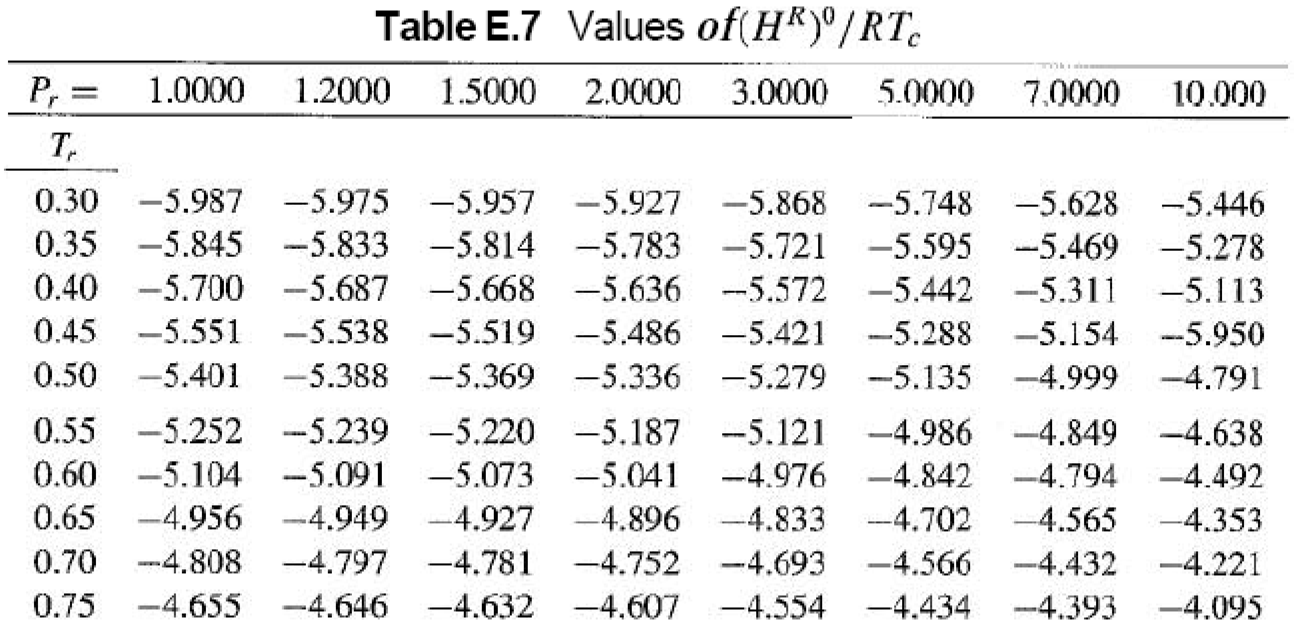


Table E.7 Values of $(H^R)^0/RT_c$

$P_r =$	1.0000	1.2000	1.5000	2.0000	3.0000	5.0000	7.0000	10.000
T_r								
0.30	−5.987	−5.975	−5.957	−5.927	−5.868	−5.748	−5.628	−5.446
0.35	−5.845	−5.833	−5.814	−5.783	−5.721	−5.595	−5.469	−5.278
0.40	−5.700	−5.687	−5.668	−5.636	−5.572	−5.442	−5.311	−5.113
0.45	−5.551	−5.538	−5.519	−5.486	−5.421	−5.288	−5.154	−5.950
0.50	−5.401	−5.388	−5.369	−5.336	−5.279	−5.135	−4.999	−4.791
0.55	−5.252	−5.239	−5.220	−5.187	−5.121	−4.986	−4.849	−4.638
0.60	−5.104	−5.091	−5.073	−5.041	−4.976	−4.842	−4.794	−4.492
0.65	−4.956	−4.949	−4.927	−4.896	−4.833	−4.702	−4.565	−4.353
0.70	−4.808	−4.797	−4.781	−4.752	−4.693	−4.566	−4.432	−4.221
0.75	−4.655	−4.646	−4.632	−4.607	−4.554	−4.434	−4.393	−4.095

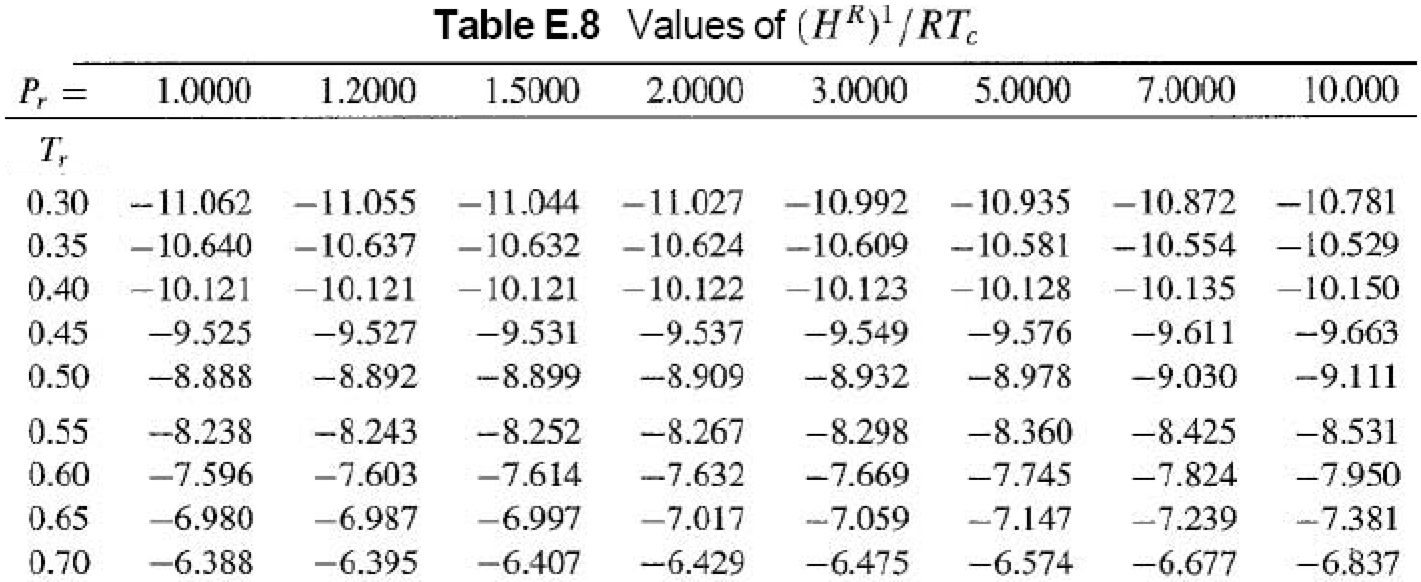


Table E.8 Values of $(H^R)^1/RT_c$

$P_r =$	1.0000	1.2000	1.5000	2.0000	3.0000	5.0000	7.0000	10.000
T_r								
0.30	−11.062	−11.055	−11.044	−11.027	−10.992	−10.935	−10.872	−10.781
0.35	−10.640	−10.637	−10.632	−10.624	−10.609	−10.581	−10.554	−10.529
0.40	−10.121	−10.121	−10.121	−10.122	−10.123	−10.128	−10.135	−10.150
0.45	−9.525	−9.527	−9.531	−9.537	−9.549	−9.576	−9.611	−9.663
0.50	−8.888	−8.892	−8.899	−8.909	−8.932	−8.978	−9.030	−9.111
0.55	−8.238	−8.243	−8.252	−8.267	−8.298	−8.360	−8.425	−8.531
0.60	−7.596	−7.603	−7.614	−7.632	−7.669	−7.745	−7.824	−7.950
0.65	−6.980	−6.987	−6.997	−7.017	−7.059	−7.147	−7.239	−7.381
0.70	−6.388	−6.395	−6.407	−6.429	−6.475	−6.574	−6.677	−6.837

Generalized Properties Correlations for Gases

See Appendix E, Tables E5 ~ E1 for higher Tr

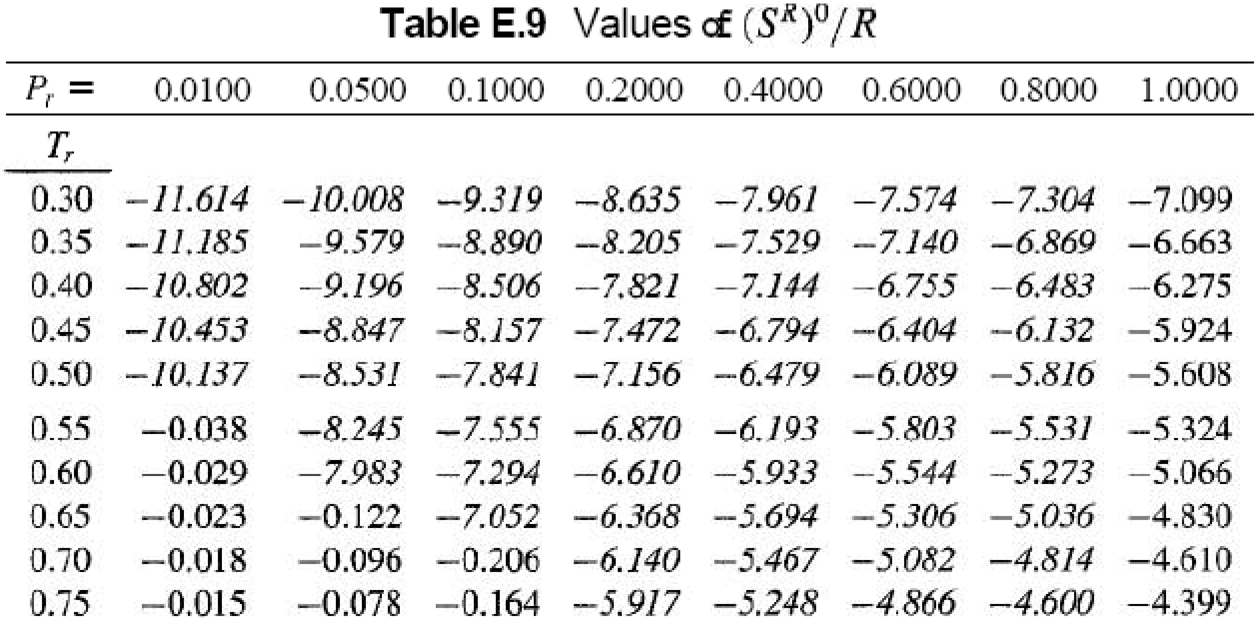


Table E.9 Values of $(S^R)^0/R$

P_r = / T_r	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
0.30	−11.614	−10.008	−9.319	−8.635	−7.961	−7.574	−7.304	−7.099
0.35	−11.185	−9.579	−8.890	−8.205	−7.529	−7.140	−6.869	−6.663
0.40	−10.802	−9.196	−8.506	−7.821	−7.144	−6.755	−6.483	−6.275
0.45	−10.453	−8.847	−8.157	−7.472	−6.794	−6.404	−6.132	−5.924
0.50	−10.137	−8.531	−7.841	−7.156	−6.479	−6.089	−5.816	−5.608
0.55	−0.038	−8.245	−7.555	−6.870	−6.193	−5.803	−5.531	−5.324
0.60	−0.029	−7.983	−7.294	−6.610	−5.933	−5.544	−5.273	−5.066
0.65	−0.023	−0.122	−7.052	−6.368	−5.694	−5.306	−5.036	−4.830
0.70	−0.018	−0.096	−0.206	−6.140	−5.467	−5.082	−4.814	−4.610
0.75	−0.015	−0.078	−0.164	−5.917	−5.248	−4.866	−4.600	−4.399

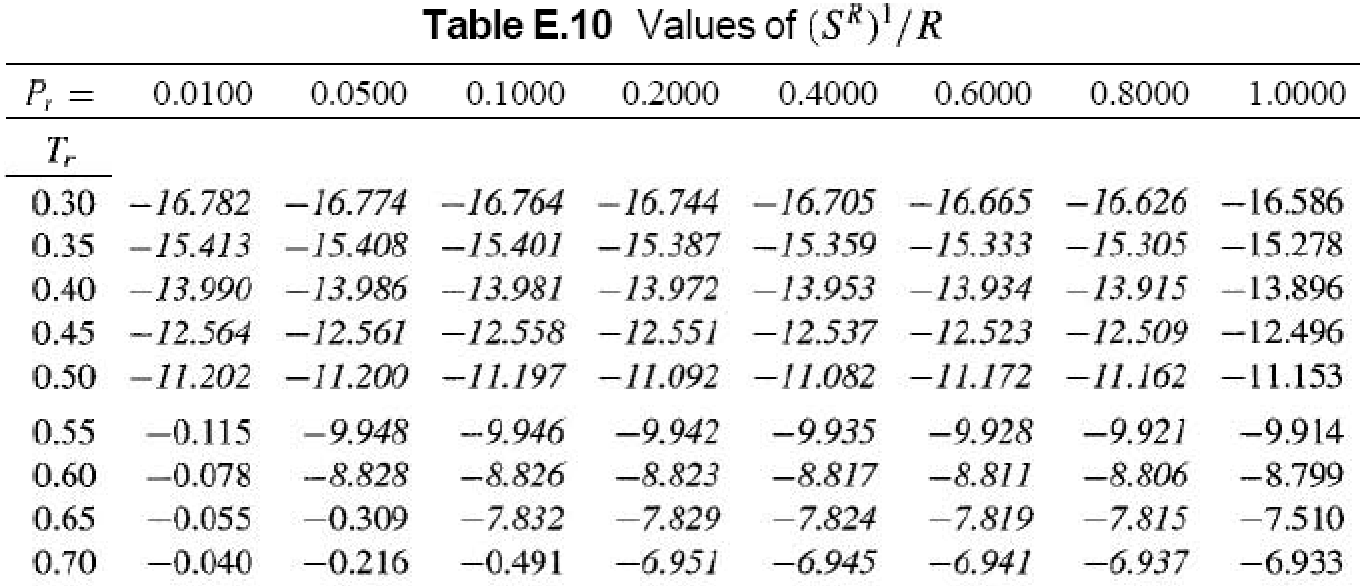


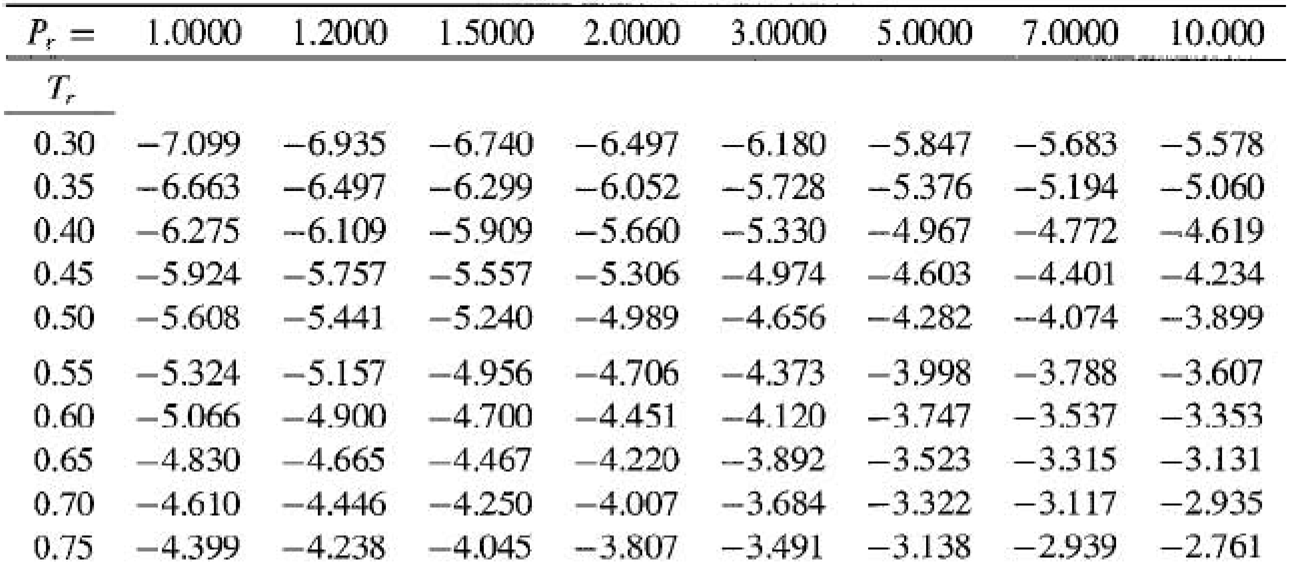
Table E.10 Values of $(S^R)^1/R$

P_r = / T_r	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
0.30	−16.782	−16.774	−16.764	−16.744	−16.705	−16.665	−16.626	−16.586
0.35	−15.413	−15.408	−15.401	−15.387	−15.359	−15.333	−15.305	−15.278
0.40	−13.990	−13.986	−13.981	−13.972	−13.953	−13.934	−13.915	−13.896
0.45	−12.564	−12.561	−12.558	−12.551	−12.537	−12.523	−12.509	−12.496
0.50	−11.202	−11.200	−11.197	−11.092	−11.082	−11.172	−11.162	−11.153
0.55	−0.115	−9.948	−9.946	−9.942	−9.935	−9.928	−9.921	−9.914
0.60	−0.078	−8.828	−8.826	−8.823	−8.817	−8.811	−8.806	−8.799
0.65	−0.055	−0.309	−7.832	−7.829	−7.824	−7.819	−7.815	−7.510
0.70	−0.040	−0.216	−0.491	−6.951	−6.945	−6.941	−6.937	−6.933

Generalized Properties Correlations for Gases

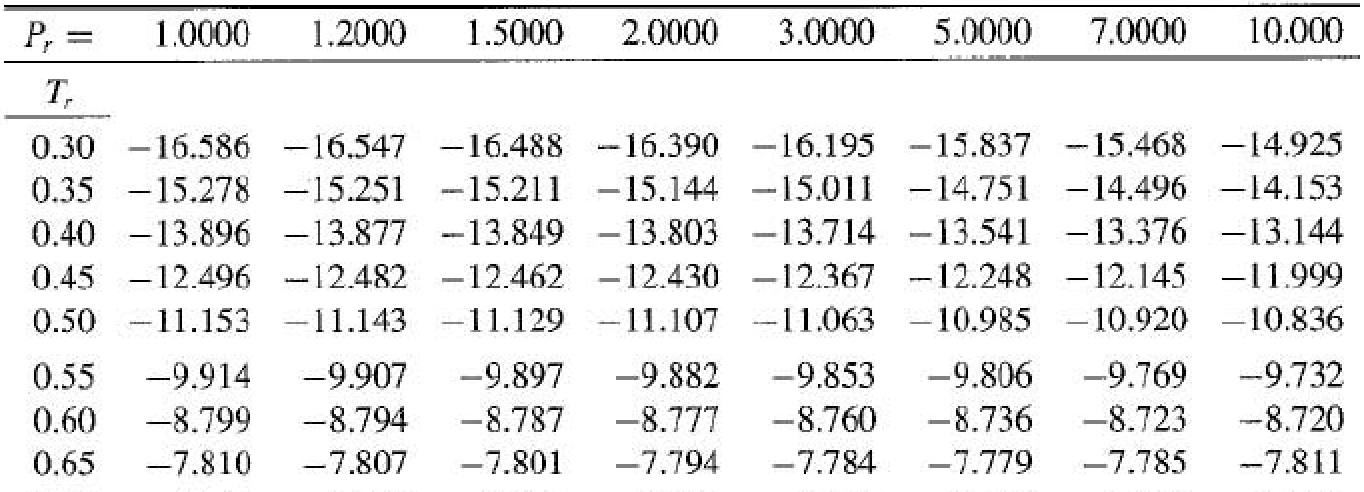
See Appendix E, Tables E5 ~ E1 for higher Tr

Table E.11 Values of $(S^R)^0/R$



$P_r =$ T_r	1.0000	1.2000	1.5000	2.0000	3.0000	5.0000	7.0000	10.000
0.30	−7.099	−6.935	−6.740	−6.497	−6.180	−5.847	−5.683	−5.578
0.35	−6.663	−6.497	−6.299	−6.052	−5.728	−5.376	−5.194	−5.060
0.40	−6.275	−6.109	−5.909	−5.660	−5.330	−4.967	−4.772	−4.619
0.45	−5.924	−5.757	−5.557	−5.306	−4.974	−4.603	−4.401	−4.234
0.50	−5.608	−5.441	−5.240	−4.989	−4.656	−4.282	−4.074	−3.899
0.55	−5.324	−5.157	−4.956	−4.706	−4.373	−3.998	−3.788	−3.607
0.60	−5.066	−4.900	−4.700	−4.451	−4.120	−3.747	−3.537	−3.353
0.65	−4.830	−4.665	−4.467	−4.220	−3.892	−3.523	−3.315	−3.131
0.70	−4.610	−4.446	−4.250	−4.007	−3.684	−3.322	−3.117	−2.935
0.75	−4.399	−4.238	−4.045	−3.807	−3.491	−3.138	−2.939	−2.761

Table E.12 Values of $(S^R)^1/R$



$P_r =$ T_r	1.0000	1.2000	1.5000	2.0000	3.0000	5.0000	7.0000	10.000
0.30	−16.586	−16.547	−16.488	−16.390	−16.195	−15.837	−15.468	−14.925
0.35	−15.278	−15.251	−15.211	−15.144	−15.011	−14.751	−14.496	−14.153
0.40	−13.896	−13.877	−13.849	−13.803	−13.714	−13.541	−13.376	−13.144
0.45	−12.496	−12.482	−12.462	−12.430	−12.367	−12.248	−12.145	−11.999
0.50	−11.153	−11.143	−11.129	−11.107	−11.063	−10.985	−10.920	−10.836
0.55	−9.914	−9.907	−9.897	−9.882	−9.853	−9.806	−9.769	−9.732
0.60	−8.799	−8.794	−8.787	−8.777	−8.760	−8.736	−8.723	−8.720
0.65	−7.810	−7.807	−7.801	−7.794	−7.784	−7.779	−7.785	−7.811
0.70	−6.933	−6.930	−6.926	−6.922	−6.919	−6.929	−6.952	−7.002

Thermodynamic properties using residual and ideal properties

The generalized correlations for *H^R and S^R, together with ideal-gas heat capacities,* allow calculation of enthalpy and entropy and their changes values of gases at any temperature and pressure as follows:

$$\left.\begin{array}{l}\boxed{H_2 = H_0^{ig} + \int_{T_0}^{T_2} C_P^{ig}\,dT + H_2^R} \\ \boxed{H_1 = H_0^{ig} + \int_{T_0}^{T_1} C_P^{ig}\,dT + H_1^R}\end{array}\right\} \longrightarrow \boxed{\Delta H = \int_{T_1}^{T_2} C_P^{ig}\,dT + H_2^R - H_1^R}$$

$$\downarrow$$

$$\boxed{\Delta H = \left\langle C_P^{ig} \right\rangle_H (T_2 - T_1) + H_2^R - H_1^R}$$

$$\left.\begin{array}{l}\boxed{S_2 = S_0^{ig} + \int_{T_0}^{T_2} C_P^{ig}\,\frac{dT}{T} - R\ln\frac{P_2}{P_0} + S_2^R} \\ \boxed{S_1 = S_0^{ig} + \int_{T_0}^{T_1} C_P^{ig}\,\frac{dT}{T} - R\ln\frac{P_1}{P_0} + S_1^R}\end{array}\right\} \longrightarrow \boxed{\Delta S = \int_{T_1}^{T_2} C_P^{ig}\,\frac{dT}{T} - R\ln\frac{P_2}{P_1} + S_2^R - S_1^R}$$

$$\downarrow$$

$$\boxed{\Delta S = \left\langle C_P^{ig} \right\rangle_S \ln\frac{P_2}{P_1} + S_2^R - S_1^R}$$

Example 6.9. Estimate V, U, H, and S for 1-butene vapor at 200°C and 70 bar if H and S are set equal to zero for saturated liquid at 0°C. Assume that only data available are:

$$T_c = 420K \qquad P_c = 40.43\, bar \qquad \omega = 0.191 \qquad T_n = 266.9K\ (nomal\ boiling\ \ pt.)$$

$$C_P^{ig} / R = 1.967 + 31.630 \times 10^{-3} T - 9.837 \times 10^{-6} T^2$$

$$\boxed{T_r = 1.127} \qquad \boxed{P_r = 1.731}$$

$$\begin{aligned} Z &= Z^0 + \omega Z^1 \\ &= 0.485 + (0.191)(0.142) \\ &= 0.512 \end{aligned}$$

$$\boxed{V = \frac{ZRT}{P} = 287.8 \frac{cm^3}{mol}}$$

Assuming four steps:

(a) Vaporization at T_1 and $P_1 = P^{sat}$

(b) Transition to the ideal-gas state at (T_1, P_1)

(c) Change to (T_2, P_2) in the ideal-gas state

(d) Transition to the actual final state at (T_2, P_2)

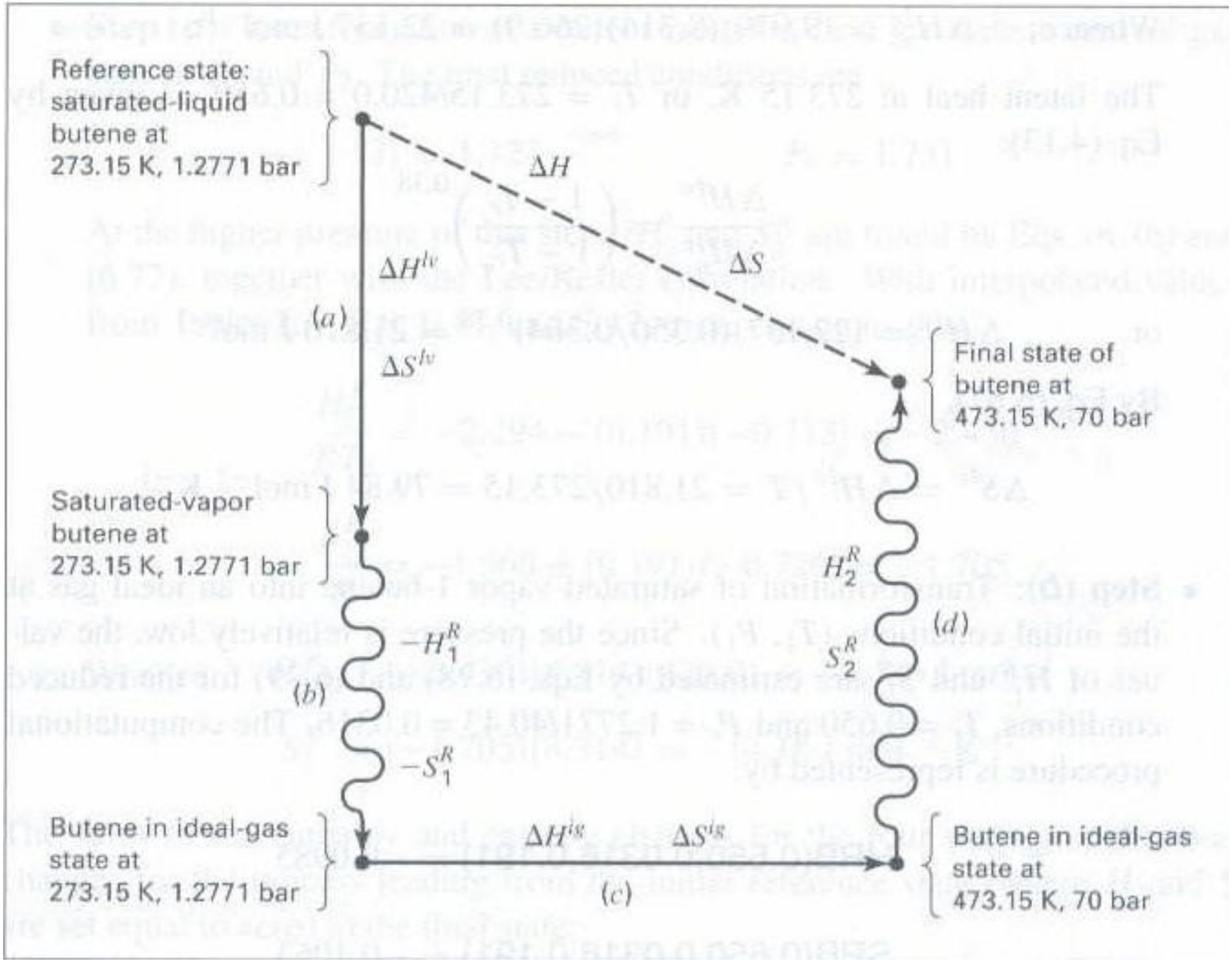

Reference state: saturated-liquid butene at 273.15 K, 1.2771 bar
ΔH
ΔS
ΔH^{lv}
(a)
ΔS^{lv}
Final state of butene at 473.15 K, 70 bar
Saturated-vapor butene at 273.15 K, 1.2771 bar
H_2^R
(d)
S_2^R
$-H_1^R$
(b)
$-S_1^R$
Butene in ideal-gas state at 273.15 K, 1.2771 bar
ΔH^{ig}
ΔS^{ig}
(c)
Butene in ideal-gas state at 473.15 K, 70 bar

Fig 6.7

Step (a)

Using Clausius/Clapeyron equation $\boxed{\ln P^{sat} = A - \frac{B}{T}}$

$$B = -\frac{\ln P^{sat}(T) - \ln P_c^{sat}}{1/T \ - 1/T_c}$$

$T_n = 266.9K$ at P^{sat} =1atm =1.0133 bar

$$B = -\frac{\ln(1.0133/40.43)}{1/266.9 \ - 1/420} = 2699.11$$

$$\boxed{A = \ln P_c + \frac{B}{T_c} = \ln(40.43) + 2699.11/420 = 10.1260}$$

T1 = 273.15K: $\boxed{\ln P^{sat} = A - \frac{B}{T} = 10.126 - 2699.11/273.15 \rightarrow P^{sat} = 1.2771\,\text{bar}}$

$$\boxed{T_{rn} = \frac{266.9}{420} = 0.636}$$

$$\boxed{\frac{\Delta H_n^{lv}}{RT_n} = \frac{1.092\left(\ln P_c - 1.013\right)}{0.930 - T_{rn}} \rightarrow \Delta H_n^{lv} = 22137 \ \text{J/mol}}$$

$$\boxed{\begin{aligned} T_{r1} &= \frac{T_n}{T_c} = 0.636 \\ T_{r1} &= \frac{273}{420} = 0.650 \end{aligned}}$$

$$\boxed{\frac{\Delta H^{lv}(T_1)}{\Delta H^{lv}(T_n)} = \left(\frac{1 - T_{r1}}{1 - T_{rn}}\right)^{0.38} \rightarrow \Delta H^{lv}(T_1) = 21810 \ \text{J/mol}}$$

Step (a)

$$\boxed{dH = TdS + VdP = TdS} \longrightarrow \boxed{\Delta H^{lv} = T\Delta S^{lv}}$$

$$\boxed{\Delta H^{lv} = 21810 \frac{J}{mol}}$$

$$\boxed{\Delta S^{lv} = \frac{\Delta H^{lv}}{T} = \frac{21810}{273.15} = 79.84 \frac{J}{mol \cdot K}}$$

Step (b)

$$\boxed{T_r = 0.650} \quad \boxed{P_r = 0.0316}$$

$$\boxed{\frac{H^R}{RT_c} = \left[\frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c}\right] = HRB(TR, PR, OMEGA) = -0.0985} \quad \boxed{-H_1^R = 344 \frac{J}{mol}}$$

$$\boxed{\frac{S^R}{R} = \left[\frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R}\right] = SRB(TR, PR, OMEGA) = -0.1063} \quad \boxed{-S_1^R = 0.88 \frac{J}{mol \cdot K}}$$

Table E5 ~ E12 to get values

Step (c)

$$\boxed{\Delta H^{ig} = 8.314 \times ICPH(273.15, 473.15; 1.967, 31.630E-3, -9.837E-6, 0.0) = 20564 \frac{J}{mol}}$$

$$\boxed{\begin{aligned}&\Delta S^{ig} = 8.314 \times ICPS(273.15, 473.15; 1.967, 31.630E-3, -9.837E-6, 0.0) - 8.314 \ln \frac{70}{1.2771}\\&= 22.18 \frac{J}{mol \cdot K}\end{aligned}}$$

Step (d) $\boxed{T_r = 1.127}$ $\boxed{P_r = 1.731}$ Table E5 ~ E12 to get values

$$\boxed{\frac{H^R}{RT_c} = \left[\frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} \right] = -2.430}$$

$$\boxed{H_2^R = -8485 \frac{J}{mol}}$$

$$\boxed{\frac{S^R}{R} = \left[\frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R} \right] = -1.705}$$

$$\boxed{S_2^R = -14.18 \frac{J}{mol \cdot K}}$$

Total

$$\boxed{H = \Delta H = 21810 - (-344) + 20564 - 8485 = 34233 \frac{J}{mol}}$$

$$\boxed{S = \Delta S = 79.84 - (-0.88) + 22.18 - 14.18 = 88.72 \frac{J}{mol \cdot K}}$$

$$\boxed{U = H - PV = 34233 - (70)(287.8)/10 = 32218 \frac{J}{mol}}$$

Gas mixtures

- Pseudocritical parameters resulting from simple linear mixing rules:

$$\boxed{\omega \equiv \sum_i y_i \omega_i} \quad \boxed{T_{Pc} \equiv \sum_i y_i T_{ci}} \quad \boxed{P_{Pc} \equiv \sum_i y_i P_{ci}}$$

Example 6.10. Estimate V, H^R, and S^R for an equimolar mixture of carbon dioxide and propane at 450 K and 140 bar

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$$\boxed{T_{Pc} \equiv \sum_i y_i T_{ci} = (0.5)(304.2) + (0.5)(369.8) = 337K} \rightarrow \boxed{T_{pr} = 1.335}$$

$$\boxed{P_{Pc} \equiv \sum_i y_i P_{ci} = (0.5)(73.83) + (0.5)(42.48) = 58.15 bar} \rightarrow \boxed{P_{pr} = 2.41}$$

$$\left.\begin{matrix} T_{pr} = 1.335 \\ P_{pr} = 2.41 \end{matrix}\right\} \quad \boxed{Z^0 = 0.697} \quad \boxed{Z^1 = 0.205}$$

$$\boxed{\omega \equiv \sum_i y_i \omega_i = (0.5)(0.224) + (0.5)(0.152) = 0.188} \rightarrow \boxed{Z = Z^0 + \omega Z^1 = 0.736}$$

$$\boxed{V = \frac{ZRT}{P} = 196.7 \frac{cm^3}{mol}} \quad \boxed{\frac{H^R}{RT_{pc}} = \left[\frac{\left(H^R\right)^0}{RT_{pc}} + \omega \frac{\left(H^R\right)^1}{RT_{pc}}\right] = -1.762} \quad \boxed{\frac{S^R}{R} = \left[\frac{\left(S^R\right)^0}{R} + \omega \frac{\left(S^R\right)^1}{R}\right] = -1.029}$$

$$\boxed{H^R = -4937 \ J/mol} \quad \boxed{S^R = -8.56 \ J/mol \cdot K}$$