# CHEMICAL ENGINEERING THERMODYNAMICS CHE F213

## Thermodynamic Properties of Fluid

### Thermodynamic Property Relations

# Contents


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# Work done & Helmholtz free energy

Consider the energy and entropy balances for a closed, isothermal, constant-volume system:

$$U_2 - U_1 = Q + W$$

and

$$S_2 - S_1 = \frac{Q}{T} + S_{gen}$$

Eliminating Q between the two equations, and using $T=T_1=T_2$,

$$W = (U_2 - T_2 S_2) - (U_1 - T_1 S_1) + TS_{gen}$$

$$\boxed{W = (A_2 - A_1) + TS_{gen}}$$

# Helmholtz free energy

A new thermodynamic variable, the Helmholtz energy, is define as

$$A = U - TS$$

The work required for a reversible ($S_{gen}$ =0), isothermal, constant-volume process is,

$$\boxed{W^{rev} = (A_2 - A_1)}$$

Reversible work done for a process is equal to the change in Helmholtz energy.

Work for irreversible, isothermal, constant volume process,

$$\boxed{W = W^{rev} + TS_{gen}}$$

# Work done & Gibbs Energy

Now, consider a process occurring in a closed system at fixed temperature and pressure:

$$U_2 - U_1 = Q + W \; - (P_2 V_2 - P_1 V_1)$$

$$S_2 - S_1 = \frac{Q}{T} + S_{gen}$$

Thus,

$$W = (U_2 + P_2 V_2 - T_2 S_2) - (U_1 + P_1 V_1 - T_1 S_1) + TS_{gen}$$

$$\boxed{W = (G_2 - G_1) + TS_{gen}}$$

# Gibbs Energy

Another new thermodynamic variable, the Gibbs energy, is define as

$$G = U + PV - TS = H - TS$$

Thus, $\boxed{W^{rev} = (G_2 - G_1)}$

For a closed system change at constant temperature and pressure,

$$W = W^{rev} + TS_{gen}$$

# Property Relation Objective

- To develop from the first and second laws the fundamental property relations which underlie the mathematical structure of thermodynamics.
  - Derive equations which allow calculation of enthalpy and entropy values from PVT and heat capacity data.
  - Discuss diagrams and tables by which property values are presented for convenient use.
  - Develop generalized correlations which provide estimated of property values in the absence of complete experimental information.

# Property relations for homogeneous phases

First law for a closed system

$$d(nU) = dQ + dW$$

a special reversible process

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

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

$$d(nU) = Td(nS) - Pd(nV)$$

**Eq 6.1**

Only properties 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.

# Mathematical preliminaries

[1] For a function of the form $P = P(X,Y)$ one can write the following total differential:

$$dP = \left(\frac{\partial P}{\partial X}\right)_Y dX + \left(\frac{\partial P}{\partial Y}\right)_X dY = MdX + NdY$$

Where: $M = \left(\frac{\partial P}{\partial X}\right)_Y \quad and \quad N = \left(\frac{\partial P}{\partial Y}\right)_X$

Further, $\left(\frac{\partial M}{\partial Y}\right)_X = \left(\frac{\partial^2 P}{\partial Y \partial X}\right) \quad and \quad \left(\frac{\partial N}{\partial X}\right)_Y = \left(\frac{\partial^2 P}{\partial X \partial Y}\right)$

It follows: $\left(\frac{\partial M}{\partial Y}\right)_X = \left(\frac{\partial N}{\partial X}\right)_Y$

[2] $$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}$$

$$d(nU) = Td(nS) - Pd(nV)$$

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

The enthalpy: $H \equiv U + PV$ **Eq 2.11**

The Helmholtz energy: $A \equiv U - TS$ **Eq 6.2**

The Gibbs energy: $G \equiv H - TS$ **Eq 6.3**

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For one mol of homogeneous fluid of constant composition:

**Fundamental Property Relation**

$$dU = TdS - PdV$$ **Eq 6.7**

$$dH = TdS + VdP$$ **Eq 6.8**

$$dA = -PdV - SdT$$ **Eq 6.9**

$$dG = VdP - SdT$$ **Eq 6.10**

## Maxwell's equations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$ **Eq 6.13**

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$ **Eq 6.14**

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$ **Eq 6.15**

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$ **Eq 6.16**

# Enthalpy and Entropy as Functions of T and P

❖ Temperature derivatives:

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \qquad \textbf{Eq 2.20}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \qquad \textbf{Eq 6.17}$$

❖ **Pressure derivatives:**

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \textbf{Eq 6.18}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \qquad \textbf{Eq 6.19}$$

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

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

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

$$dH = TdS + VdP$$

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

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

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

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

From Maxwell →

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

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

**Eq 6.20**

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

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

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

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

**Eq 6.21**

$$H \equiv U + PV$$

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

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

**Eq 6.22**

# Enthalpy and Entropy relation for liquids

$$dH = C_P dT + \left( V - T\left(\frac{\partial V}{\partial T}\right)_P \right) dP$$ **Eq 6.20**

$$\left(\frac{\partial V}{\partial T}\right)_P = \beta V$$ **Eq 3.2**

$$dH = C_P dT + (1 - \beta T) V dP$$ **Eq 6.28**

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$ **Eq 6.21**

$$dS = C_P \frac{dT}{T} - \beta V dP$$ **Eq 6.29**

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

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

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

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

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

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

**Eq 6.15**

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

**Eq 6.32**

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

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

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

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

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

**Eq 6.33**

- Using the definition of β and *K* , the ratio β / *K* can be represent as

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}} \qquad \textbf{Eq 6.34}$$

- Alternative forms of the equations 6.32 and 6.33, are:

$$dU = C_V\, dT + \left[\frac{\beta}{\kappa} T - P\right] dV \qquad \textbf{Eq 6.35}$$

$$dS = C_V\, \frac{dT}{T} + \frac{\beta}{\kappa}\, dV \qquad \textbf{Eq 6.36}$$

# Problem 1

Derive an expression for enthalpy change of a gas during an isothermal process assuming using the following EOS:

$$P\,(V-b) = R\,T$$

# Thermodynamic Identities

FROM FUNDAMENTAL PROPERTY RELATION, WE CAN DERIVE FOLLOWING THERMODYNAMIC IDENTITIES:

$$\boxed{\left(\frac{\partial H}{\partial S}\right)_P \equiv \left(\frac{\partial U}{\partial S}\right)_V = T}$$

$$\boxed{\left(\frac{\partial G}{\partial P}\right)_T \equiv \left(\frac{\partial H}{\partial P}\right)_S = V}$$

$$\boxed{\left(\frac{\partial A}{\partial T}\right)_V \equiv \left(\frac{\partial G}{\partial T}\right)_P = -S}$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_S \equiv \left(\frac{\partial A}{\partial V}\right)_T = -P}$$

# The Gibbs Energy as Generating Function

From fundamental property relations,

$$dG = V\,dP - S\,dT$$

Gibbs energy is functionally related to pair of variable (P and T): $G = G(T,P)$

Since these variables can be directly measured and controlled, the Gibbs free energy is a thermo-dynamic property of great potential utility

An alternative form of a fundamental property relation as defined in dimensionless terms:

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

$$\boxed{G \equiv H - TS} \qquad \boxed{dG = VdP - SdT}$$

$$\boxed{d\left(\frac{G}{RT}\right) \equiv \frac{V}{RT}dP - \frac{H}{RT^2}dT} \longleftrightarrow \boxed{d\left(\frac{G}{RT}\right) = \left(\frac{\partial(G/RT)}{\partial P}\right)_T dP + \left(\frac{\partial(G/RT)}{\partial T}\right)_P dT}$$

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

The Gibbs energy when given as a function of T and P therefore serves as a generating function for the other thermodynamic properties, and implicitly represents complete information.

Show that from an equation of state relating to Gibbs energy, temperature and pressure, equations of state for all other state functions can be obtained by appropriate differentiation

An equation of state of the form G = G (T,P)

Function of temperature and entropy can be obtained using

dG = VdP - SdT

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

Now the enthalpy and internal energy can be found as follows:

$$H(T,P) = G(T,P) + TS(T,P) = G(T,P) - T\left(\frac{\partial G}{\partial T}\right)_P$$

and

$$U(T,P) = G(T,P) + TS(T,P) - PV(T,P) = G(T,P) - T\left(\frac{\partial G}{\partial T}\right)_P - P\left(\frac{\partial G}{\partial P}\right)_T$$

The Helmholtz energy is obtained from

$$A(T,P) = G(T,P) - PV(T,P) = G(T,P) - P\left(\frac{\partial G}{\partial P}\right)_T$$

and the constant-pressure and constant-volume heat capacities can be found as follows:

$$C_p(T,P) = \left(\frac{\partial H}{\partial T}\right)_P = \frac{\partial}{\partial T}\bigg|_P \left[G(T,P) - T\left(\frac{\partial G}{\partial T}\right)_P\right] = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

and

$$C_V(T,P) = C_P + \frac{T(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P - T\left(\frac{\partial^2 G}{\partial T.\partial P}\right)^2 \left(\frac{\partial^2 G}{\partial P^2}\right)_T^{-1}$$

The isothermal compressibility and volume expansivity are found as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{(\partial^2 G/\partial P^2)_T}{(\partial G/\partial P)_T}$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{(\partial^2 G/\partial P \partial T)}{(\partial G/\partial P)_T}$$

# Residual Property Relations

- An alternate method of computing energy and entropy changes for real gases involves the definition of *residual property*
- The definition for the generic residual property is:

$$M^R = M\,(T,P) - M^{ig}\,(T,P)$$

  - M is the molar value of any extensive thermodynamics property: V, U, H, S, G.
  - M, $M^{ig}$ are the actual and ideal gas properties which are at the same temperature and pressure.

- **Residual Gibbs energy:**

$$G^R \equiv G - G^{ig}$$

- G & $G^{ig}$ are the actual and ideal gas values of the Gibbs energy at the same temperature and pressure.

- **Residual volume:**

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

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

The residual properties are usually used for gases *only.*

# Fundamental property relation for residual properties

- The fundamental property relation for residual preperties applies to fluids of constant composition.

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}dP - \frac{H^R}{RT^2}dT \ldots (6.42)$$

$$\frac{V^R}{RT} = \left[\frac{\partial\left(G^R / RT\right)}{\partial P}\right]_T \ldots (6.43)$$

$$\frac{H^R}{RT} = -T\left[\frac{\partial\left(G^R / RT\right)}{\partial T}\right]_P \ldots (6.44)$$

$$From \quad Eq.(6.43), \qquad d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}\,dP \qquad (const\ \ T)$$

$$\frac{G^R}{RT} = \left(\frac{G^R}{RT}\right)_{P=0} + \int_0^P \frac{V^R}{RT}\,dP = \int_0^P (Z-1)\frac{dP}{P} \ldots (6.45) \qquad for\ ideal\ \ gas\ \left(\frac{G^R}{RT}\right)_{P=0} = J$$

$$Eq.(6.45+6.44); \qquad \frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \ldots (6.46)$$

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

$$So, \qquad \frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P} \qquad (const\ \ T) \qquad \ldots (6.48)$$

# Enthalpy and Entropy from Residual Properties

*Applied to H and S;* $H = H^{ig} + H^{R}$ $\qquad S = S^{ig} + S^{R}$

*Integration of Eq.(6.23)and(6.24);*

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

*Substitution;*

$$\boxed{H = H_0^{ig} + \int_{T_0}^{T} C_P^{ig}\,dT + H^{R}} \qquad \ldots(6.50)$$

$$S = S_0^{ig} + \int_{T_0}^{T} C_P^{ig}\,dT - R\ln\frac{P}{P_0} + S^{R} \qquad \ldots(6.51)$$

**The true worth of the Eq. for ideal gases is now evident. They are important because they provide a convenient base for the calculation of real-gas properties.**

# Example 6.3

Calculate H and S of saturated iso-butane vapor at 360 K from the following information:

1. Table 6.1 gives compressibility-factor data
2. The vapor pressure of iso-butane at 360 K is 15.46 bar
3. Set $H_0^{ig}$ = 18,115 $Jmol^{-1}$ and $S_0^{ig}$ = 295.976 $Jmol^{-1}K^{-1}$ for the ideal-gas reference state at 300 K, 1 bar
4. $C_p^{ig}/R = 1.7765+33.037x10^{-3}T$ (T/K)

**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 | | |

## Solution

Eqs. (6.47) and (6.48) are used to calculate $H^R$ and $S^R$.

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

- Plot $(\partial Z/\partial T)_P/P$ and $(Z-1)/P$ vs. P
- From the compressibility-factor data at 360 K $\rightarrow$ $(Z-1)/P$
- The slope of a plot of Z vs. T $\rightarrow$ $(\partial Z/\partial T)_P/P$
- Data for the required plots are shown in Table 6.2.

**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) |

$$\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} = 26.37\times10^{-4}\,K^{-1} \qquad \int_0^P (Z-1)\frac{dP}{P} = -0.2596$$

$$By\ Eq.\ (6.46), \qquad \frac{H^R}{RT} = -(360)(26.37\times10^{-4}) = -0.9493$$

$$By\ Eq.\ (6.48), \qquad \frac{S^R}{R} = -0.9493 - \left(-0.2596\right) = -0.6897$$

$$For\ R = 8.314\ \ Jmol^{-1}K^{-1}$$

$$H^R = \left(-0.9493\right)\left(8.314\right)\left(360\right) = -2{,}841.3\ \ Jmol^{-1}$$

$$S^R = \left(-0.6897\right)\left(8.314\right) = 5.734\ \ Jmol^{-1}K^{-1}$$

$$H = H_0^{ig} + \int_0^{T_1} C_P^{ig} dT + H^R$$

$H_0^{ig}$ = 18,115 Jmol$^{-1}$

$C_p^{ig}/R = 1.7765+33.037\times10^{-3}T$ (T/K)

$$\int_0^{T_1} C_P^{ig} dT = 6324.73 \text{ Jmol}^{-1}$$

$$H^R = -2{,}841.3 \ \ Jmol^{-1}$$

$$H = 21598.5 \ \ Jmol^{-1}$$

# Residual Properties by Equations of State

- Residual Properties from the Virial EoS

$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT} = 1 + B^{'}P$$

$$\frac{G^R}{RT} = \int_0^P (Z-1)\frac{dP}{P}(const\ \ T) = \frac{BP}{RT} \qquad (6.54)$$

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

$$or \qquad \frac{H^R}{RT} = \frac{P}{R}\left(\frac{B}{T} - \frac{dB}{dT}\right) \qquad (6.55)$$

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT} = -\frac{P}{R}\frac{dB}{dT} \qquad (6.56)$$

- **Pressure Explicit Form**
  - Expressions for $G^R/RT$, $H^R/RT$ and $S^R/RT$ are evaluative by integrating the derivative of P (dP) and are incompatible with pressure-explicit equations of state.
  - These equations are transformed to make V (or ρ) the variable of integration. ρ is more convenient variable and the equation PV = ZRT, is written as,

$$P = Z \rho RT \qquad (6.57)$$

Differentiation gives: $dP = RT (Z\, d\rho + \rho\, dZ)$ (Const T)

$$\frac{dP}{P} = \frac{d\rho}{\rho} + \frac{dZ}{Z} \quad \text{(Const T)}$$

# Residual functions as Pressure explicit form

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

Integral evaluated at constant T and ρ→ 0 as P→0

$$\frac{H^R}{RT^2}dT = \frac{V^R}{RT}dP - d\left(\frac{G^R}{RT}\right) = \frac{(Z-1)}{P}dP - d\left(\frac{G^R}{RT}\right)$$

Division by dT and restriction to constant $\rho$ gives

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

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

# Residual Properties by Cubic EoS

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

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

$$where, \qquad q = \frac{a}{bRT} \quad , \quad \rho = \frac{1}{V}$$

These equations results in following expressions :

$$\int_0^{\rho} (Z-1)\frac{d\rho}{\rho} = -\ln(1-\rho b) - qI \qquad \int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho} = -\frac{dq}{dT}I$$

$$\text{where,} \quad I \equiv \int_0^{\rho} \frac{d(\rho b)}{(1+\varepsilon\rho b)(1+\sigma\rho b)} \qquad (\text{const T})$$

- The generic EoS presents two cases for evaluation of integral

$$\text{Case 1: } \varepsilon \neq \sigma \qquad \mathrm{I} = \frac{1}{\sigma - \varepsilon} \ln\left(\frac{1+\sigma\rho b}{1+\varepsilon\rho b}\right)$$

$$\text{Case 1: } \varepsilon = \sigma \qquad \mathrm{I} = \frac{\rho b}{1+\varepsilon\rho b}$$

Evaluation of these Integrals result :

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

$$\frac{H^R}{RT} = Z - 1 + T\left(\frac{dq}{dT}\right)I$$

$$\frac{S^R}{R} = \ln(1-\rho b)Z + \left(q + T\frac{dq}{dT}\right)I$$

# Illustration

- Determine the expressions for $G^R$, $H^R$ and $S^R$ implied by van der Waals equation of state

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\varepsilon b)(V+\sigma b)} \qquad a(T) = \psi \frac{\alpha(T_r)R^2T_c^2}{P_c} \qquad b = \Omega \frac{RT_c}{P_c}$$

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

| Eq. of State | $\alpha(T_r)$ | $\sigma$ | $\epsilon$ | $\Omega$ | $\Psi$ |
|---|---|---|---|---|---|
| vdW (1873) | 1 | 0 | 0 | 1/8 | 27/64 |

$$G^R(T,P) = PV - RT - \frac{a}{V} - RT\ln\frac{P(V-b)}{RT}$$

$$H^R(T,P) = PV - RT - \frac{a}{V} \qquad S^R(T,P) = R\ln\frac{P(V-b)}{RT}$$

# Other form of enthalpy & entropy departure function

- Volume explicit form

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

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

- Pressure explicit form

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

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

# Peng Robinson EoS

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

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

$$b = 0.07780 \frac{RT_c}{P_c}$$

$$\alpha = \left[1 + S\left(1 - \sqrt{T_r}\right)\right]^2$$

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

$$T_r = \frac{T}{T_c}$$

- Enthalpy changes for the Peng-Robinson EoS

$$H(T,P) - H^{ig}(T,P) = RT\left(Z-1\right) + \frac{T\left(\frac{da}{dT}\right) - a}{2\sqrt{2b}} \ln\left[\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right]$$

where Z = PV/RT and B = Pb/RT

# Residual Enthalpy and Entropy from Generalized property correlations

$$Z = Z^0 + \omega Z^1$$

$$\left(\frac{\partial Z}{\partial T_r}\right)_{P_r} = \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} + \omega\left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r}$$

$$\frac{H^R(T,P)}{RT_c} = -T_r^2 \int_{P_r=0,T_r}^{P_r,T_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}$$

$$\frac{H^R(T,P)}{RT_c} = -T_r^2 \int_{P_r=0,T_r}^{P_r,T_r} \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \omega T_r^2 \int_{P_r=0,T_r}^{P_r,T_r} \left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}$$

The integrals on the right sides of the equations may be evaluated numerically or graphically for various values of $T_r$ and $P_r$ from data for $Z^0$ and $Z^1$.

$$\frac{H^R(T,P)}{RT_c} = \frac{\left(H^R\right)^0}{RT_c} + \omega\frac{\left(H^R\right)^1}{RT_c} \qquad \frac{S^R(T,P)}{R} = \frac{\left(S^R\right)^0}{R} + \omega\frac{\left(S^R\right)^1}{R}$$

# Extension to Gas Mixtures

$$\omega \equiv \sum_i y_i \omega_i \ldots (6.97) \qquad T_{pc} \equiv \sum_i y_i T_{ci} \ldots (6.98) \qquad P_{pc} \equiv \sum_i y_i P_{ci} \ldots (6.99)$$

$$T_{\mathrm{Pr}} = \frac{T}{T_{pc}} \quad \ldots (6.100) \qquad P_{\mathrm{Pr}} = \frac{P}{P_{pc}} \quad \ldots (6.101)$$

**These replace $T_r$ and $P_r$ for reading entries from the table of App. E, and lead to values of Z by Eq.(3.57), and $H^R/RT_{pc}$ by Eq.(6.85), and $S^R/R$ by Eq.(6.86).**

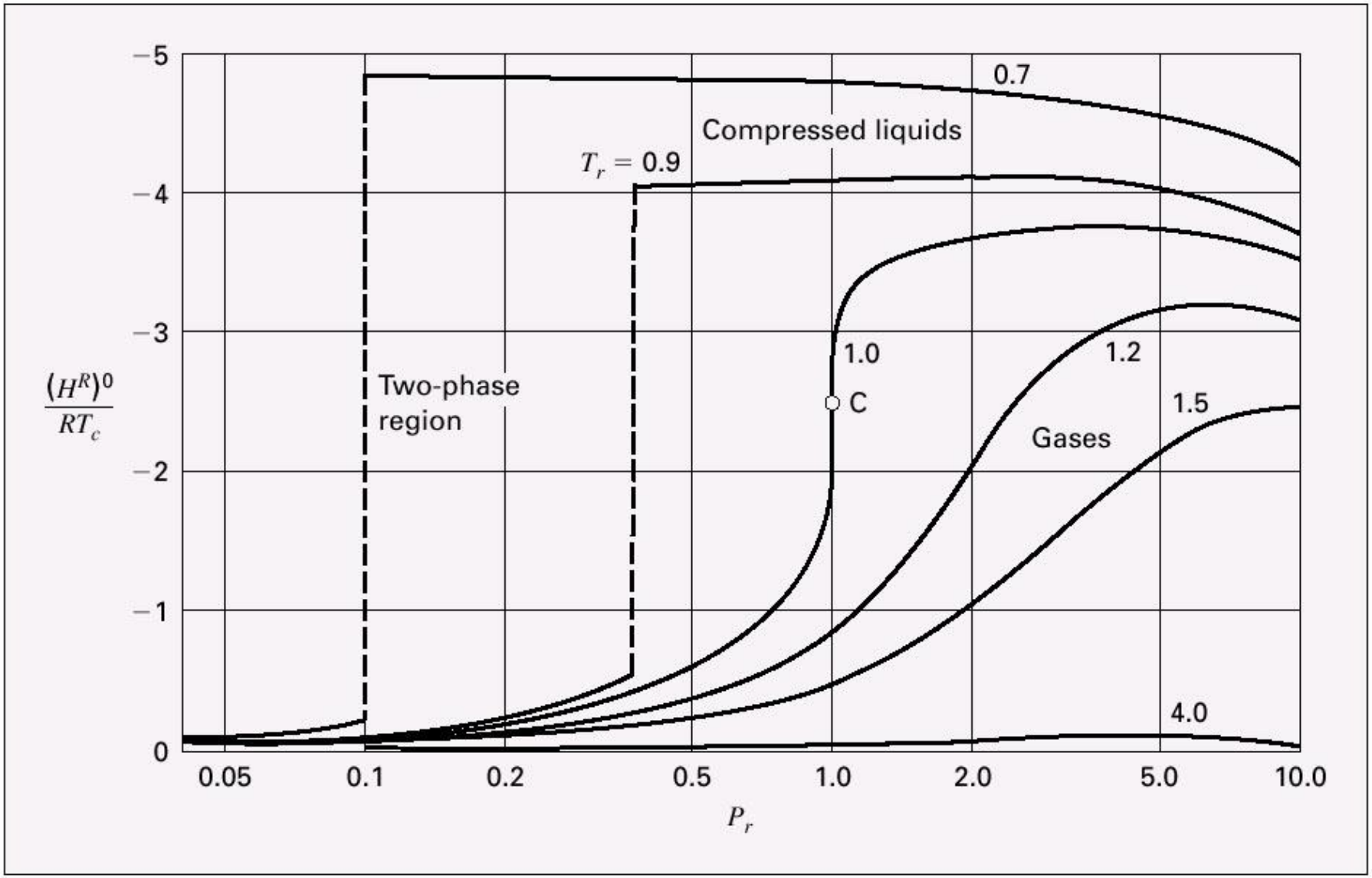
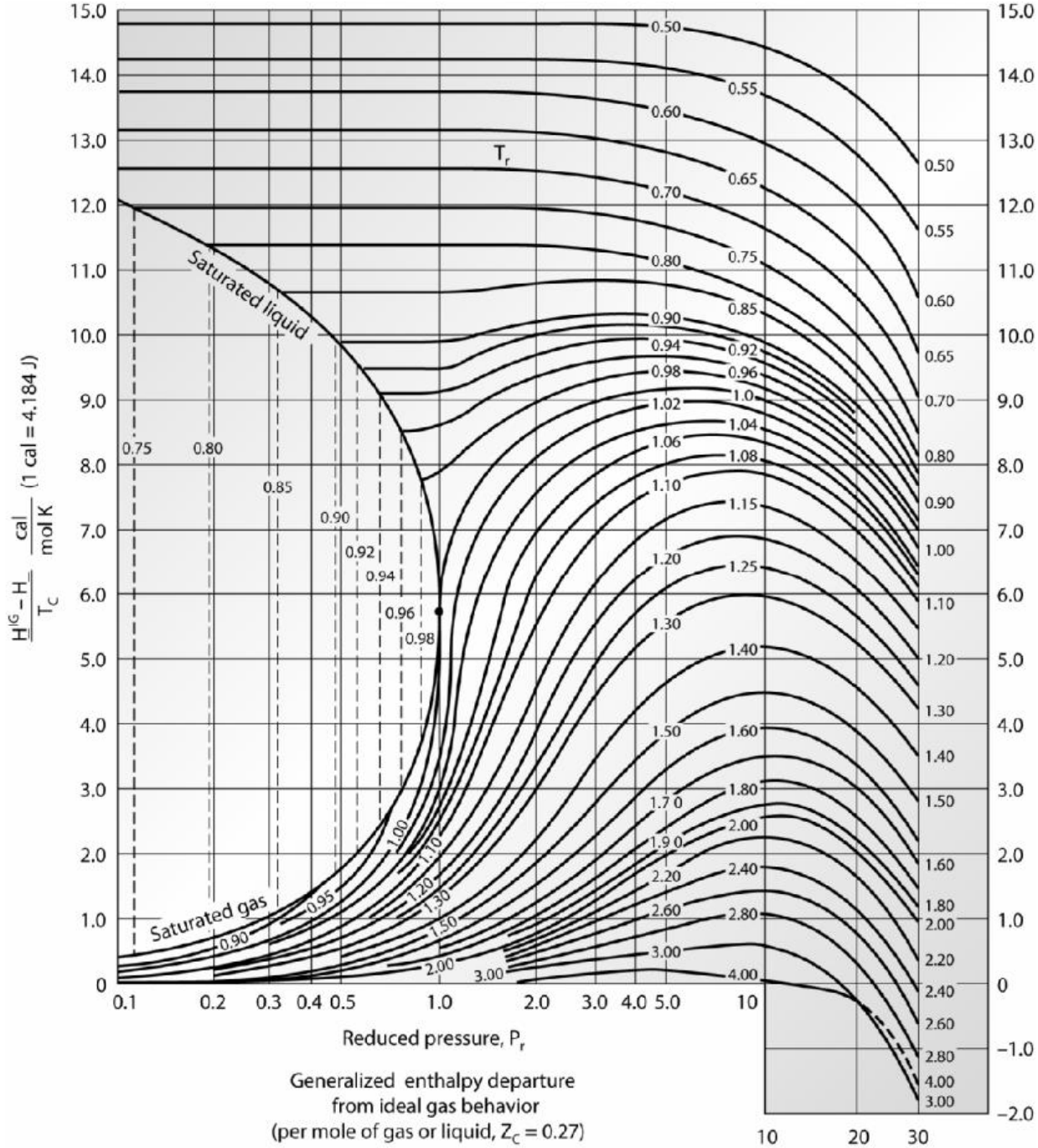
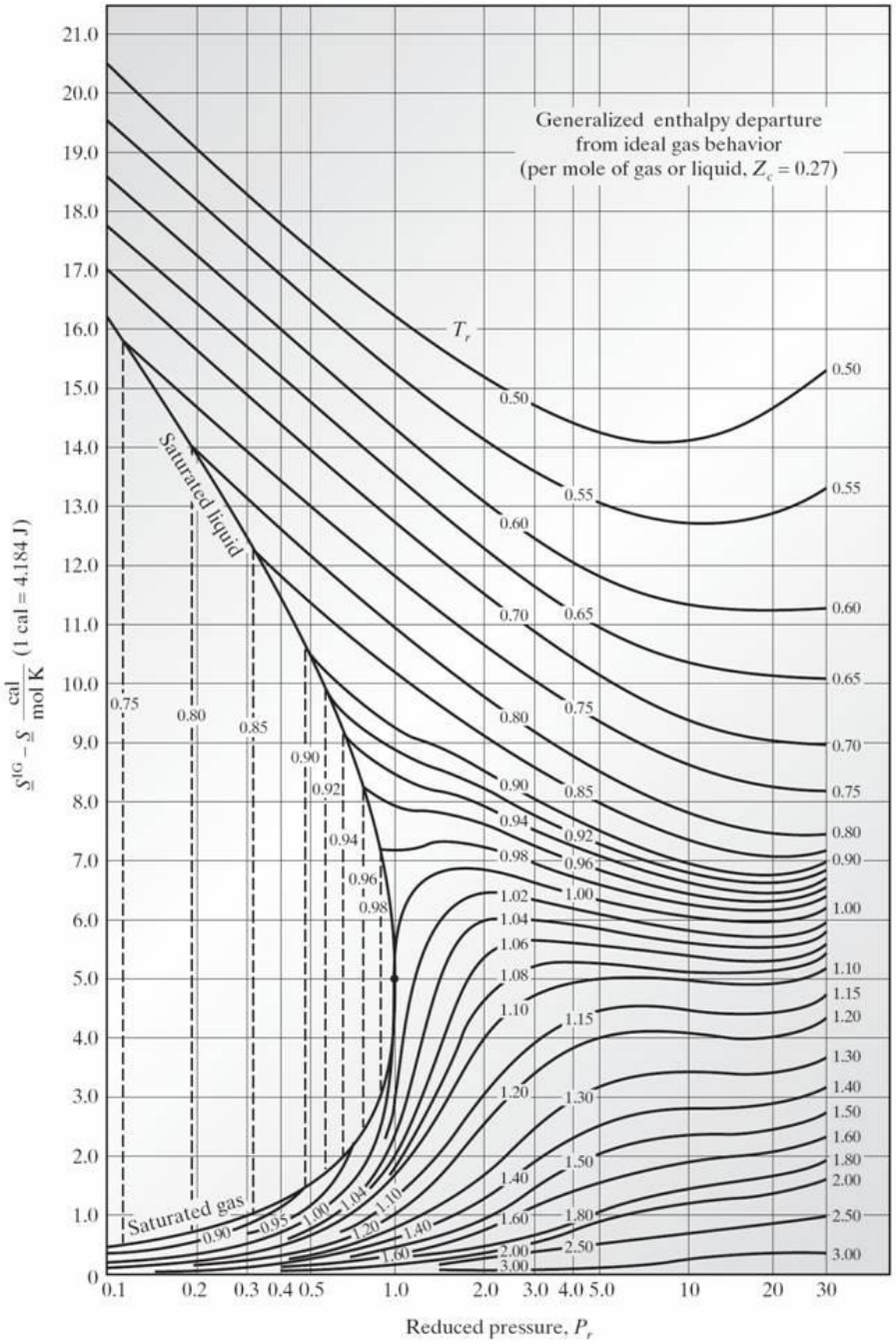



**Figure 6.5**: The Lee/Kesler correlation for $(H^R)^0/RT_c$ as a function of $T_r$ and $P_r$.




Generalized enthalpy departure
from ideal gas behavior
(per mole of gas or liquid, $Z_C = 0.27$)

Ref. :
Sandler

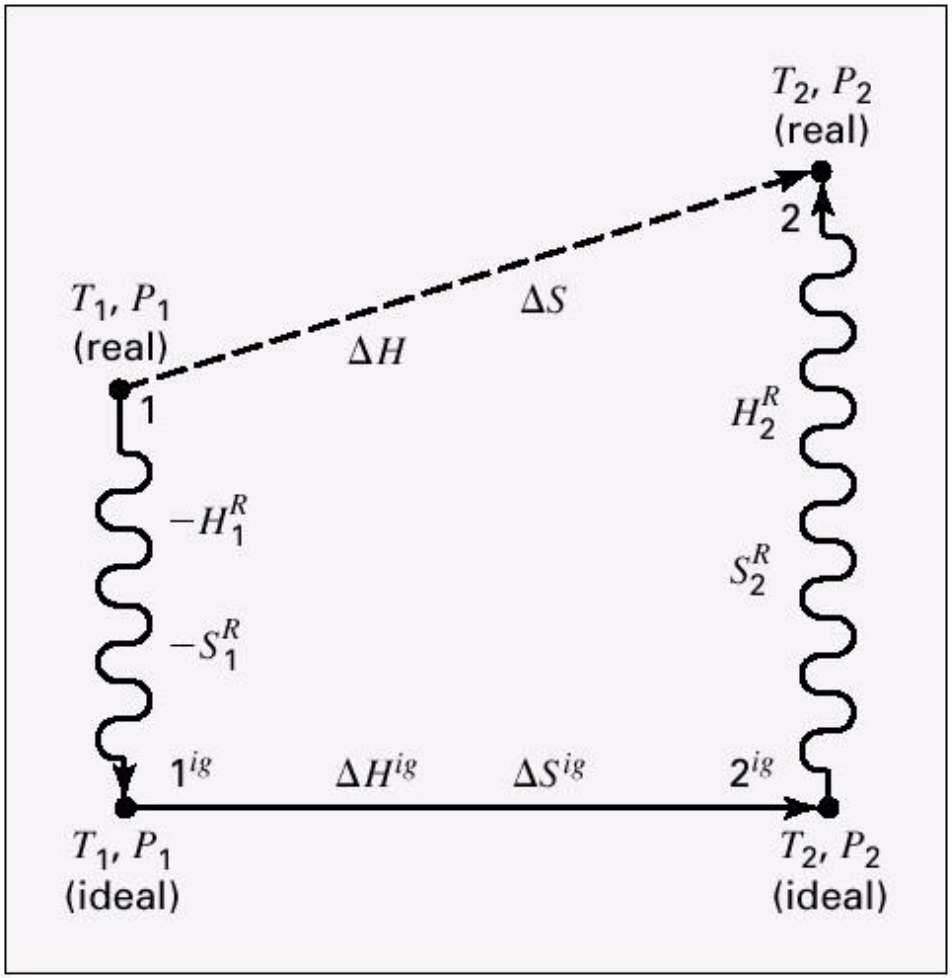

Generalized enthalpy departure
from ideal gas behavior
(per mole of gas or liquid, $Z_c = 0.27$)
$T_r$
Saturated liquid
Saturated gas
$\underline{S}^{IG} - \underline{S}$ $\frac{\text{cal}}{\text{mol K}}$ (1 cal = 4.184 J)
Reduced pressure, $P_r$

Ref. :
Sandler

# Calculational path for property changes ΔH and ΔS

$$\Delta H = \int_{T_1}^{T_2} C_P^{ig}\, dT + H_2^R - H_1^R \ldots (6.91)$$

$$\Delta S = \int_{T_1}^{T_2} C_P^{ig}\, \frac{dT}{T} - R \ln \frac{P_2}{P_1} + S_2^R - S_1^R \ldots (6.92)$$



# TWO-PHASE SYSTEMS

- A phase transition at constant temperature and pressure occurs whenever the phase boundary is crossed (recollect P-T curve for pure fluid).
- As a result of the phase change thermodynamic properties e.g., molar or specific volume, internal energy, enthalpy and entropy change abruptly.
- Molar or specific Gibbs energy is the exception, which does not change during a phase transition such as melting.
- For two phases in equilibrium α and β: $G^{\alpha} = G^{\beta}$

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

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

$$Integration\ of\ Eq.(6.8);\ \ \Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta}\ \ (The\ latent\ heat\ of\ phase\ transition)$$

$$Thus,\ \ \Delta S^{\alpha\beta} = \Delta H^{\alpha\beta} / T \Rightarrow \frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}} \quad \ldots(6.71) \quad : The\ Clapeyron\ equation$$

- # Clapeyron Equation

$$Phase\ transition\ from\ liquid\ to\ vapor;\quad \frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{T\Delta V^{lv}} \quad \ldots(6.72)$$

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

Compressibility factor of phase change (vaporization)

$$\frac{d\ln P^{sat}}{dT} = \frac{\Delta H^{lv}}{RT^2\Delta Z^{lv}} \quad \ldots(6.73)$$

$$or \qquad \frac{d\ln P^{sat}}{d(1/T)} = \frac{\Delta H^{lv}}{R\Delta Z^{lv}} \quad \ldots(6.74)$$

- # Clausius /Clapeyron Equation

The Clapeyron Equation for vaporization may be simplified by approximating the vapor phase as an ideal gas and the molar volume of liquid negligible compared to molar volume of vapor.

These assumptions alter the Clapeyron equation to Clausius /Clapeyron Equation

$$\Delta V^{lv} = V^{v} = \frac{RT}{P^{sat}} \quad \text{or} \quad \Delta Z^{lv} = 1 \qquad \text{Thus,}\quad \Delta H^{lv} = -R\frac{d\ln P^{sat}}{d(1/T)}$$

# Temperature Dependence of the Vapor Pressure of Liquids

- The knowledge of vapor-pressure and temperature relation is required for the calculation of the latent heats of vaporization
- Generally a plot of ln $P^{sat}$ vs. $1/T$ yields nearly a straight line:

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

$$The\ \ Antoine\ \ eq.:\ \ \ln P^{sat} = A - \frac{B}{T+C} \quad \ldots(6.76)$$

$$Antoine\ \ cons\tan ts\ \ are\ \ given\ \ in\ \ Table\ \ B.2,\ App.B$$

**Wagner Equation**

$$A\ \ function\ \ of\ \ T_r;\ \ \ln P_r^{sat}(T_r) = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1-\tau} \ldots(6.77)$$

$$where \qquad \tau \equiv 1 - T_r$$

# Two-Phase Liquid/Vapor System

$$nV = n^l V^l + n^v V^v \qquad n = n^l + n^v \quad (moles)$$

$$V = x^l V^l + x^v V^v \qquad x: \ mass \ fraction$$

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

$$The \ generic \ equation:$$

$$M = (1 - x^v) M^l + x^v M^v \quad \ldots (6.82a)$$

$$where \ M \equiv V, U, H, S, etc. \ An \ alternative \ form:$$

$$M = M^l + x^v \Delta M^{lv} \quad \ldots (6.82b)$$

# THERMODYNAMIC DIAGRAMS

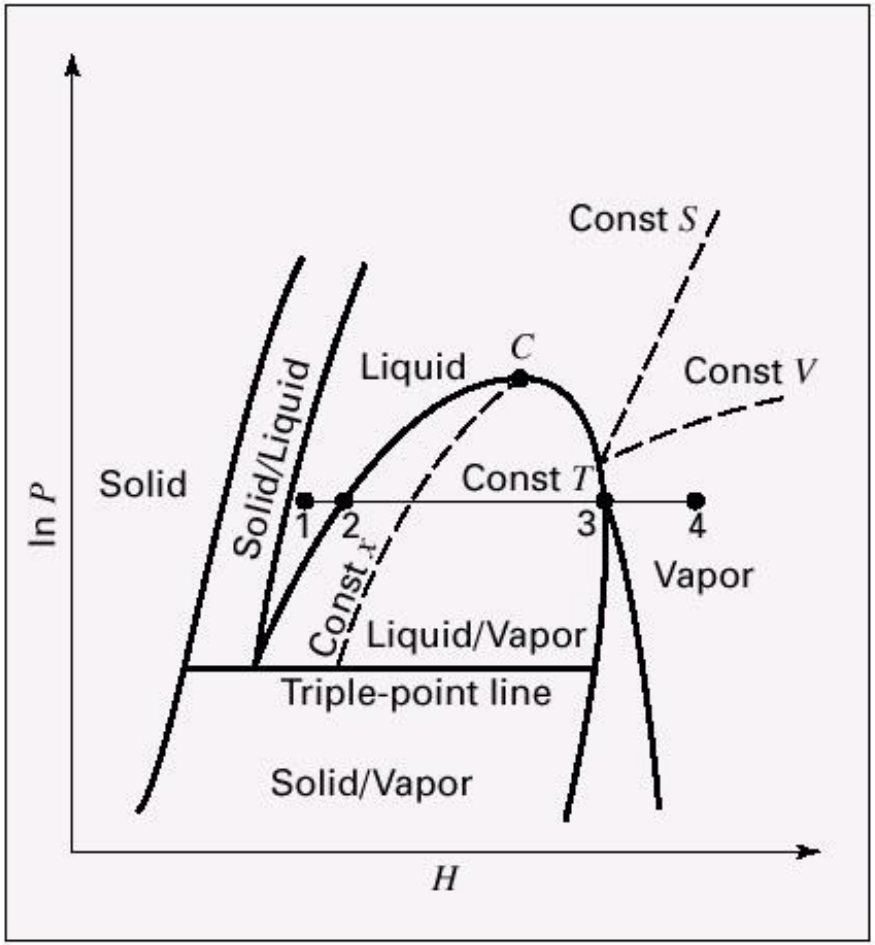



**Figure 6.2**: $PH$ diagram.

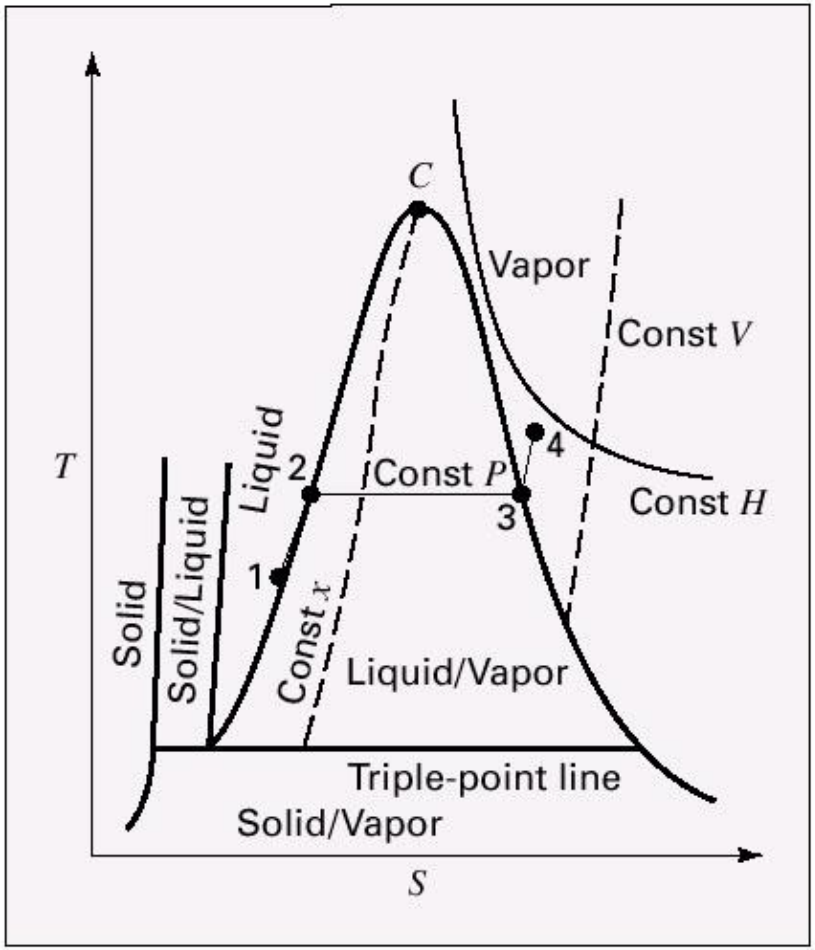
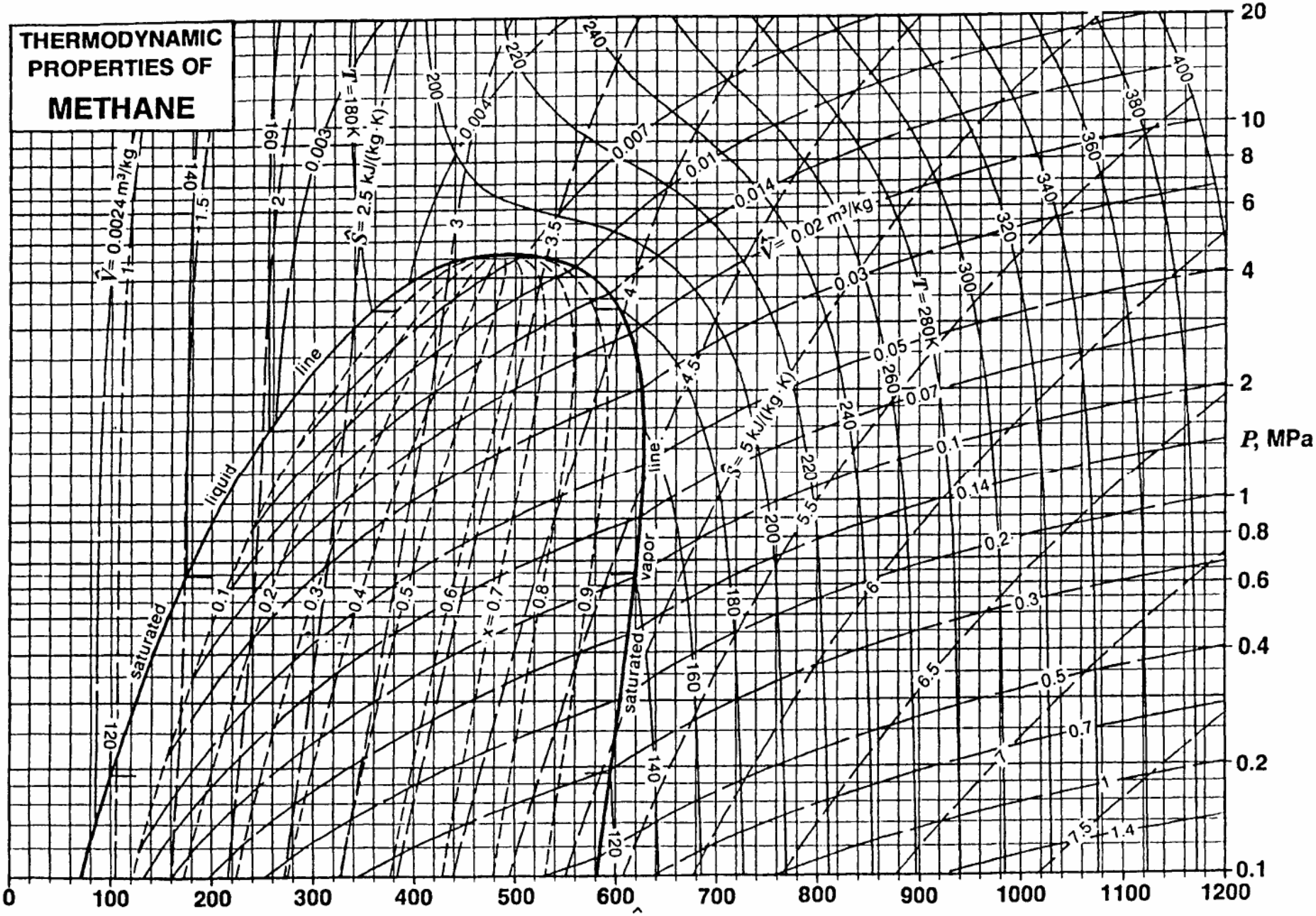
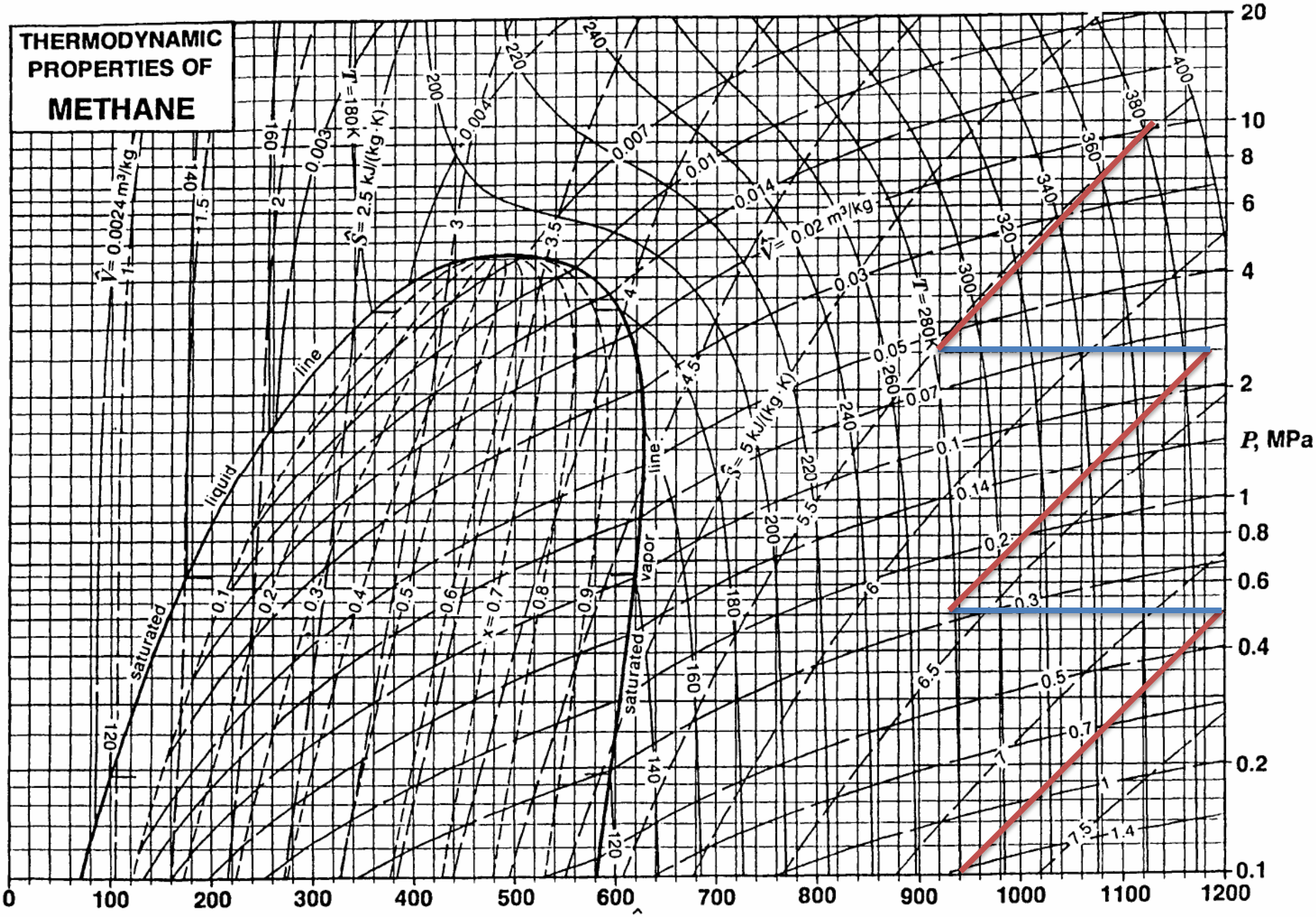



**Figure 6.3**: $TS$ diagram.

# Thermodynamic diagram for process calculations



# Illustration

- It is desired to produce liquefied natural gas (LNG), which is considered as pure methane, from that gas at 1 bar and 280 K. In a Linde liquefaction process, a three stage compressor with intercooling is used which operates reversibly and adiabatically. The first stage compress the gas from 1 bar to 5 bar, the second stage from 5 bar to 25 bar, and the third stage from 25 bar to 100 bar. Between stages the gas is isobarically cooled to 280 K.
- Calculate the amount of work required for each kilogram of methane that passes through the compressor in the simple liquefaction process

# Thermodynamic diagram for process calculations