Chapter 6
Thermodynamic Properties Of Fluids

In this chapter:

1. Develop fundamental property relations for fluids. (based on the 1-st & 2^{nd} laws).
2. Use these relations to derive equations to calculate enthalpy and entropy values from PVT data and heat capacity data.
3. Calculate actual property values, by introducing Residual properties and learn how to estimate it by equation of state.
4. Explain the criteria of phase equilibria for a pure substances and its utilization in the Clapeyron equation.
5. Follow this by discussion of the most common used diagrams and tables in thermodynamic.

6.1 Property Relations For Homogenous Phases

- For n moles, 1-st law of closed system is

$$d(nU) = dQ + dW \qquad (2.6)$$

For reversible process, 2-nd law

$$dQ_{rev} = T\, dS^t \qquad (5.12)$$

And

$$dW_{rev} = -P\, d(nV) \qquad (1.2)$$

Substitute back,

$$d(nU) = Td(nS) - Pd(nV) \qquad (6.1)$$

Equation 6.1:

1. based on the combination of 1-st and 2-nd laws.
2. Good for closed system (constant mass).
3. Applicable to reversible as well as to irreversible process.

- Define additional thermodynamic properties:

Enthalpy $H = U + PV$ (2.11)

The Helmholtz free energy $A = U - T\,S$ (6.2)

The Gibbs free energy $G = H - T\,S$ (6.3)

- For one mole (or a unit mass) of a homogenous fluid of constant composition,

Fundamental property relations for a closed system

$$dU = TdS - PdV \qquad (6.7)$$

$$dH = TdS + V\,dP \qquad (6.8)$$

$$dA = -P\,dV - S\,dT \qquad (6.9)$$

$$dG = V\,dP - S\,dT \qquad (6.10)$$

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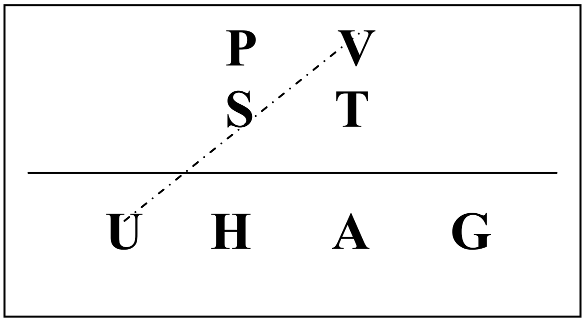

- The criterion of exactness for a differential expression:

If $F = F(x,y)$

The differential of F $dF = (\delta F/\delta x)_y\, dx + (\delta F/\delta y)_x\, dy$

Let $M = (\delta F/\delta x)_y$ and $N = (\delta F/\delta y)_x$

Then $dF = M\, dx + N\, dy$ (6.11)

By further differentiation,

$$(\delta M/\delta y)_x = \delta^2 F/\delta x\, \delta y \quad \text{and} \quad (\delta N/\delta x)_y = \delta^2 F/\delta y\, \delta x$$

Since the order of differentiation is immaterial, then

$$(\delta M/\delta y)_x = (\delta N/\delta x)_y \qquad (6.12)$$

Thus, do the same thing for the total differential equations 6.7 – 6.10:

Maxwell's equations

$$(\delta T/\delta V)_S = -(\delta P/\delta S)_V \qquad \textbf{(6.13)}$$

$$(\delta T/\delta P)_S = (\delta V/\delta S)_P \qquad \textbf{(6.14)}$$

$$(\delta P/\delta T)_V = (\delta S/\delta V)_T \qquad \textbf{(6.15)}$$

$$(\delta V/\delta T)_P = -(\delta S/\delta P)_T \qquad \textbf{(6.16)}$$

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1- TV, PS (Horiz. +), (Vert. -)
2- The opposite.

$$\frac{T}{P} = \frac{V}{S} \qquad \frac{P}{T} = \frac{S}{V}$$

$$\frac{T}{V} = -\frac{P}{S} \qquad \frac{V}{T} = -\frac{S}{P}$$

Enthalpy and Entropy as Function of T & P

- Most useful equations of H and S result when these properties expressed as function of T and P.

- How H and S are vary with T and P?
  Or what is $(\delta H/\delta T)_P$, $(\delta S/\delta T)_P$, $(\delta H/\delta P)_T$ and $(\delta S/\delta P)_T$?

- The aim is to express H=H(T,P) and S=S(T,P)

Find $\mathbf{dH = (\delta H/\delta T)_P\, dT + (\delta H/\delta P)_T\, dP}$

And $\mathbf{dS = (\delta S/\delta T)_P\, dT + (\delta S/\delta P)_T\, dP}$

We know that $\underline{(\delta H/\delta T)_P = C_P}$ (2.20)

And from equation 6.8, dH = TdS + V dP

Dividing by dT and keeping P constant, gives

$$\mathbf{(\delta H/\delta P)_T = T\,(\delta S/\delta T)_P}$$

Combine with equation 2.20,

$$\underline{(\delta S/\delta T)_P = C_P / T} \qquad (6.17)$$

From 6.16 (Maxwell),

$$\underline{(\delta S/\delta P)_T = -\,(\delta V/\delta T)_P} \qquad (6.18)$$

Divide 6.8 by dP while keeping T constant

$$\underline{(\delta H/\delta P)_T = T\,(\delta S/\delta P)_T + V}$$

From 6.18 it becomes,

$$\underline{(\delta H/\delta P)_T = V - T\,(\delta V/\delta T)_P} \qquad (6.19)$$

Substitute for the partial derivatives,

$$\boxed{\mathbf{dH = C_P\, dT + [V - T\,(\delta V/\delta T)_P\,]\, dP}} \qquad (6.20)$$

and

$$\boxed{\mathbf{dS = C_P\, dT/T - (\delta V/\delta T)_P\, dP}} \qquad (6.21)$$

The Ideal-Gas State

$$PV^{ig} = RT$$

$$\boxed{\mathbf{(\delta V/\delta T)_P = R/P}}$$

Substitute into 6.20,

$$dH^{ig} = C_P^{ig}\, dT + [V^{ig} - T\, R/P]\, dP$$

Or

$$\boxed{\mathbf{dH^{ig} = C_P^{ig}\, dT}} \qquad (6.23)$$

Substitute into 6.21,

$$\boxed{\mathbf{dS^{ig} = C_P^{ig}\, dT/T - R/P\, dP}} \qquad (6.24)$$

Same equations were developed for dH (2.6) and dS (5.18) of ideal gas.

Example 1:

Prove that $\mathbf{(\delta H/\delta P)_T = 0}$
Or
Prove that enthalpy is not function of pressure for an ideal gas.

Example 2:

Prove that $\mathbf{(\delta S/\delta P)_T = 0}$
Or
Prove that entropy is not function of pressure for an ideal gas.

Alternative Forms for Liquids

Express 6.18 and 6.19 in terms of the volume expansivity β, recall from 3.2 that

$$\beta = 1/V\ (\delta v/\delta T)_P$$

Rewrite 6.18.

$$\boxed{(\delta S/\delta P)_T = -\ (\delta V/\delta T)_P = -\ \beta V} \quad (6.25)$$

And 6.19,

$$\boxed{(\delta H/\delta P)_T = V - T\ (\delta V/\delta T)_P = V - \beta TV} \quad (6.26)$$

The partial change of internal energy with pressure is obtained as follows,

$$U = H - PV$$

Differentiate with P at constant T,

$$(\delta U/\delta P)_T = (\delta H/\delta P)_T - P\ (\delta V/\delta T)_P - V$$

Since Isothermal compressibility, $\kappa = -1/V\ (\delta v/\delta p)_T$ (3.3)

From 6.25,

$$(\delta U/\delta P)_T = (\kappa T - \beta T) \quad (6.27)$$

Equations 6.25 through 6.27 applies only for liquids.

Replacing $(\delta V/\delta T)_P$ in 6.20 and 6.21 yields,

$$\boxed{dH = C_P\ dT + V\ (1 - \beta T)\ dP} \quad (6.28)$$

$$\boxed{dS = C_P\ dT/T - \beta V\ dP} \quad (6.29)$$

Both and V are weak function of P and can be considered constants at an average value of integration of the last term of the above two equations.

Read Example 6.1

The Gibbs Energy as a Generating Function

$$dG = V\,dP - S\,dT \qquad (6.10)$$

G = G (P,T). Both P and T can be directly measured and controlled. G a property of interest and important.

It is more convenient to deal with a dimensionless for of 6.10.

$$\boxed{d(G/RT) = V/RT\,dP - H/RT^2\,dT} \qquad (6.37)$$

Advantages of this equation: All terms are dimensionless. Moreover, in contrast to 6.10, enthalpy rather than entropy appears on the right side.

6.10 and 6.37 are too general for direct practical application, then at constant T

$$\boxed{V/RT = [\delta(G/RT) / \delta P]_T} \qquad (6.38)$$

And at constant P,

$$\boxed{H/RT = -T\,[\delta(G/RT) / \delta T]_P} \qquad (6.39)$$

Thus, if (G/RT) is known as function of T and P, then V/RT and H/RT can be determined by simple differentiation. The remaining properties are given by defining equations. For example,

$$S/R = H/RT - G/RT \qquad \text{and} \qquad U/RT = H/RT - PV/RT$$

The Gibbs energy when given as a function of T and P serves as a generating function for the other thermodynamic properties.

6.2 Residual Properties

- ***Is the difference between a certain thermodynamic property in the <u>ideal gas</u> state and its value in the <u>real gas</u> state both at the same T and P.***

  The residual Gibbs energy is: $G^R = G - G^{ig}$

  In a similar fashion other properties can be defined,

  $$V^R = V - V^{ig}$$
  $$= V - RT/P$$

  But V = ZRT/P, Then

  $$V^R = RT/P(Z\text{-}1) \qquad (6.40)$$

  In general,

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

  Where M is the molar value of any extensive thermodynamic property, V, H, U, S, A or G.

- Now rewrite 6.37 for an ideal gas

  $$d(G^{ig}/RT) = V^{ig}/RT\ dP - H^{ig}/RT^2\ dT$$

  Subtract fro 6.37

  $$\boxed{d(G^R/RT) = V^R/RT\ dP - H^R/RT^2\ dT} \qquad (6.42)$$

  This *Fundamental residual property* relation applies to fluid of constant composition.

  $$\boxed{V^R/RT = [\delta(G^R/RT) / \delta P]_T} \qquad (6.43)$$

  $$\boxed{H^R/RT = -T\ [\delta(G^R/RT) / \delta T]_P} \qquad (6.44)$$

  In addition, G = H – TS and for an ideal gas $G^{ig} = H^{ig} - TS^{ig}$ by the difference,

  $$G^R = H^R - TS^R$$

  Then the residual entropy,

  $$S^R/R = H^R/RT - G^R/RT \qquad (6.47)$$

  Thus, the residual Gibbs energy serves as a generating function for the other thermodynamic properties.

- However, equation 6.43 provide a direct link with experimental data

$$d(G^R/RT) = V^R/RT\ dP \quad \text{(constant T)}$$

Integrate from P = 0 to P (arbitrary value)

$$G^R/RT = \int_0^P V^R/RT\ dP \quad \text{(constant T)}$$

From 6.40 $V^R = RT/P(Z-1)$

$$G^R/RT = \int_0^P (Z-1)\ dP/P \quad \text{(constant T)} \qquad (6.49)$$

Differentiating with respect to T in accordance to 6.44

$$\boxed{H^R/RT = -T \int_0^P (\delta Z / \delta T)_P\ (dP/P) \quad \text{(constant T)}} \qquad (6.46)$$

Combine 6.46 and 6.49 into 6.47, yields

$$\boxed{S^R/R = -T \int_0^P (\delta Z / \delta T)_P\ (dP/P) - \int_0^P (Z-1)\ dP/P \quad \text{(constant T)}} \qquad (6.48)$$

Importance of residual property:

- $Z = PV/ RT$
- Z and may be calculated from PVT data.
- The two integrals evaluated by numerical or graphical methods. Alternatively, they may be evaluated analytically if Z expressed by equation of state.

Enthalpy and Entropy from Residual Properties

$$H^R = H - H^{ig} \qquad S^R = S - S^{ig}$$

H and S from integration of 6.23 and 6.24

$$H^{ig} = H_o^{ig} + \int_{T0}^{T} C_P^{ig}\ dT \qquad S^{ig} = S_o^{ig} + \int_{T0}^{T} C_P^{ig}\ dT - R \ln P/P_o$$

Using the appropriate mean heat capacities for enthalpy and entropy,

$$H^{ig} = H_o^{ig} + C_P^{ig} (T-T_o) + H^R \qquad (6.52)$$

$$S^{ig} = S_o^{ig} + C_P^{ig} \ln T/T_o - R \ln P/P_o + S^R \qquad (6.53)$$

6.3 Residual Properties by Equations of State

❖ Residual properties from the Virial equation of state

A) Two terms Virial equation $Z-1 = BP / RT$ (3.38)

6.49 reduce to

$$G^R /RT = BP /RT \quad (6.54)$$

And 6.44 becomes

$$H^R /RT = P /R (B/T - dB/dT) \quad (6.55)$$

Substitute both equations into 6.47

$$S^R /R = -P /R \, dB/dT \quad (6.56)$$

Good for low pressure up to 15 bar.

B) Three terms Virial equation $Z = PV/RT = 1 + B/V + C/V^2$ (3.39)

In terms of density $Z-1 = B\rho + C\rho^2$

Then,

$$G^R /RT = 2B\rho + 3/2\, C\rho^2 - \ln Z \quad (6.61)$$

$$H^R /RT = T[(B/T - dB/dT) + (C/T - \tfrac{1}{2}\, dC/dT)\, \rho^2] \quad (6.62)$$

$$S^R /R = \ln Z - T[(B/T + dB/dT)\, \rho + 1/2\, (C/T + dC/dT)\, \rho^2] \quad (6.63)$$

Useful for gases up to 50 bar. Solution required iteration procedure.

- **Residual properties by Cubic Equations of State**

Cubic Equation of State:
$P = (RT/V\text{-}b) - (\alpha\ (T) / (V+\varepsilon b)(V + \sigma b))$ (3.42)

Find the value of integrals and substitue in equations, 6046, 6.48 and 6.49

$\boxed{G^R/RT = Z\text{-}1 - \ln (Z\text{-}\beta) - q\ I}$ (6.66b)

$\boxed{H^R /RT = Z\text{-}1 + [d\ln\alpha(T_r)/ d \ln T_r \text{-}1]\ q\ I}$ (6.67)

$\boxed{S^R /R = \ln (Z\text{-} \beta) + d\ln\alpha(T_r)/ d \ln T_r\ \ q\ I}$ (6.68)

Where,

1. $\beta = \Omega\ \ P_r/T_r$ (3.53)

2. $q = \psi\ \alpha(T)/ \Omega\ T_r$ (3.54)

3. For I:
   Case 1: $\varepsilon \neq \sigma$ $I = 1/\sigma-\varepsilon\ \ \ln(Z+\sigma\beta / Z+\varepsilon\ \beta\ )$ (6.65b)
   Case 2: $\varepsilon = \sigma$ $I = \beta/Z$

4. Derivative for RK = - 0.5
   Derivative for SRK = $-C\ (T_r/\alpha)^{0.5}$
   Where $C = 0.48 + 1.574\omega - 0.176\ \omega^2$
   Derivative for PR = $-C\ (T_r/\alpha)^{0.5}$
   Where $C = 0.37464 + 1.54226\omega - 0.26992\ \omega^2$

5. Solve for Z first as in Ch.3.
   For vapor phase
   $Z = 1 + \beta + q\ \beta\ (Z\text{-}\ \beta\ ) / (Z+\ \varepsilon\beta)(Z + \sigma\beta)$ (3.52)

   For liquid phase
   $Z = \beta + (Z+\ \varepsilon\beta)\ (Z + \sigma\beta)\ (1+ \beta\ \text{-}\ Z/\ q\beta\ )$ (3.56)

   Iteration procedures are needed (Ex. 3.8)

Example 6.4

- **Generalized property Correlations for Gases (Sec. 6.7)**

1. **Lee-Kessler Generalized Equation (high pressure above 15 bar)**

$$\boxed{H^R/RT_C = (H^R)^0 / RT_C + \omega (H^R)^1 / RT_C} \qquad \mathbf{(6.85)}$$

$$\boxed{S^R/R = (S^R)^0 / R + \omega (S^R)^1 / R} \qquad \mathbf{(6.86)}$$

$(H^R)^0 / RT_C$	**Table E.5, E.7**
$(H^R)^1 / RT_C$	**Table E.6, E.8**
$(S^R)^0 / R$	**Table E.9, E.11**
$(S^R)^1 / R$	**Table E.10, E.12**

2. **Generalized second Virial coefficient correlation (low pressure up to 15 bar)**

$$\boxed{H^R/RT_C = P_r\,[B^0 - T_r\, dB^0/dT_r + \omega\,(B^1) - T_r\, dB^1/dT_r)]} \qquad \mathbf{(6.87)}$$

$$\boxed{S^R/R = - P_r\,(dB^0/dT_r + \omega\, dB^1/dT_r)} \qquad \mathbf{(6.88)}$$

Where,

$$\boxed{B^0 = 0.083 - 0.422/ T_r^{1.6}} \qquad \mathbf{(3.65)}$$

$$\boxed{B^1 = 0.139 - 0.172/ T_r^{4.2}} \qquad \mathbf{(3.66)}$$

$$\boxed{dB^o/dT_r = 0.675/T_r^{2.6}} \qquad \mathbf{(6.89)}$$

$$\boxed{dB^1/dT_r = 0.722/T_r^{5.2}} \qquad \mathbf{(6.90)}$$

No iteration.

6.4 Two-Phase System

- In Fig. 3.1, Curves represent phase boundary for a pure substance.
- A phase transition occurs when one of the curves is crossed.
- When a phase transition occurs at a given constant T and P, the molar value or specific values change too.

  $$V_{sat}^{liq} \neq V_{sat}^{vap}$$

  This is true for U, H, S, but not G.

- For n moles or 1 mole at constant T and P, at the phase transition;

  $dU = TdS - PdV$ (U will change)

  $dH = TdS + V\,dP$ (H will change 6.8)

  $dA = -P\,dV - S\,dT$ (A will change 6.9)

  $dG = V\,dP - S\,dT$ ($\underline{dG = 0}$)

  If a differential amount of liquid is evaporate at constant T and P^{sat}

  $$G^{liq} = G^{vap}$$

- In general, for any two phases (α, β) coexisting in equilibrium at constant T and P^{sat}

  $$G^{\alpha} = G^{\beta} \qquad (6.69)$$

  Then, along a two-phase boundary curve

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

  Substitute into the fundamental equation of dG for and

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

  Arranging,

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

  Integrate equation 6.8 for this change, yield the latent heat of phase transition

  $$\Delta H^{\alpha\beta} = T\,\Delta S^{\alpha\beta} \qquad (6.70)$$

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

  Substitute in the preceding equation,

  $$dP^{sat}/dT = \Delta H^{\alpha\beta}/T\,\Delta V^{\alpha\beta} \qquad (6.71)$$

  Clpeyron equation.

  For transition from liquid to vapor phase,

  $$dP^{sat}/dT = \Delta H^{Lv}/T\,\Delta V^{Lv} \qquad (6.72)$$

<u>Example 6.5.</u>

- Application of the clasius –clapeyron equation
  A plot of $\ln P^{sat}$ vs. $1/T$ yields nearly a straight line

  $$\ln P^{sat} = A - B/T \qquad (6.75)$$

  Where A and B are constants for a given species.
  It is a rough application of PV relation.

- Antoine equation is more accurate

  $$\ln P^{sat} = A - B/T + C \qquad (6.76)$$

  Where A, B and C are constants for a given species and given in the footnote.

- Wagner equation more accurate over a wide range of temperatures.

  $$\ln P_r^{sat} = A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6 / 1- \tau \qquad (6.77)$$

  Where $\tau = 1-T_r$
  A, B, C and D are constants.

Two Phase Liquid/Vapor systems

$$nV = n^L V^L + n^V V^V$$

Where $n = n^L + n^V$
Divide by n gives, $V = X^L V^L + X^V V^V$
Where X^L and X^V are the fraction of the total system that are liquid and vapor.

Since, $X^L + X^V = 1$

$$V = (1- X^V) V^L + X^V V^V$$

Where, X^V is called the quality.
In general for other extensive properties (V, U, H, S, etc),

$$M = (1- X^V) M^L + X^V M^V \qquad (6.82)$$

Other form,

$$M = M^L + X^V \Delta M^{LV} \qquad (6.82b)$$

6.5 Thermodynamic Diagrams

- **PT diagram (Fig. 3.1)**

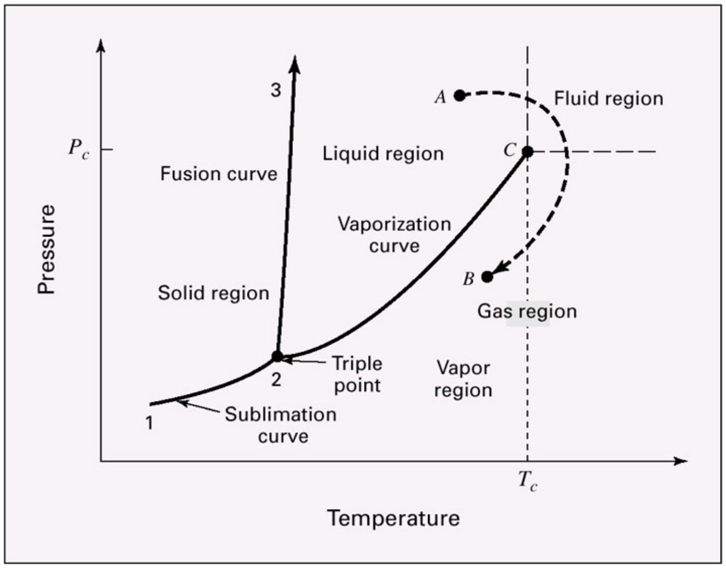

Figure 3.1: PT diagram for a pure substance.

Characteristics of PT diagram:

a. Two-phase region is represented by a line.
b. Triple point is represented by a point.
c. Critical point is represented by a point.

- **PV diagram (Fig. 3.2)**

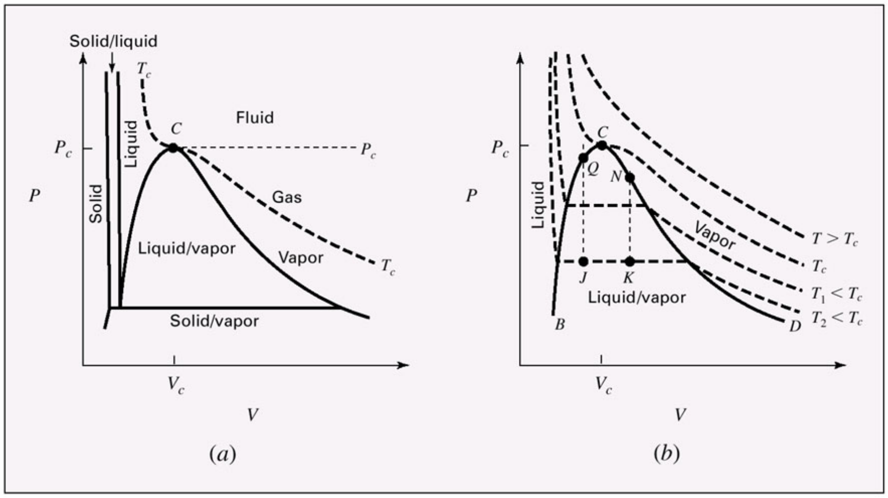

Figure 3.2: PV diagrams for a pure substance. (*a*) Showing solid, liquid, and gas regions. (*b*) Showing liquid, liquid/vapor, and vapor regions with isotherms.

Characteristics of PT diagram:

a. Two-phase region is represented by an area under the curve.
b. Triple point is line.
c. Critical point is line.

- PH diagram (Fig. 6.2)

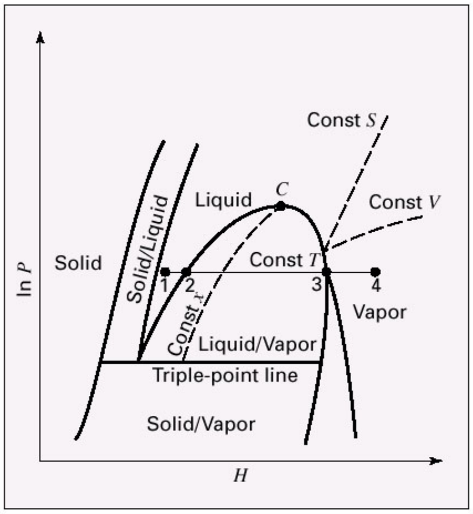

Figure 6.2: PH diagram.

Similar to PV diagram.

- TS diagram (Fig. 6.3) and HS diagram (Fig.6.4) (Mollier diagram)

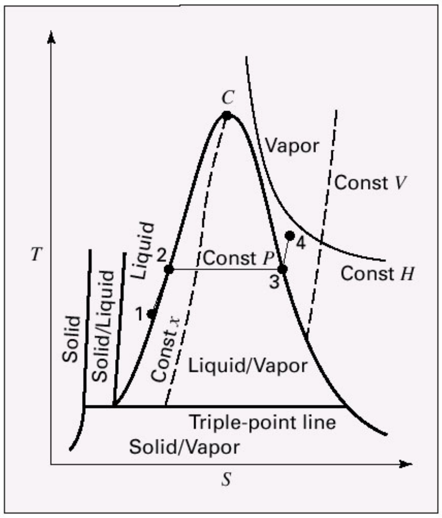

Figure 6.3: TS diagram.

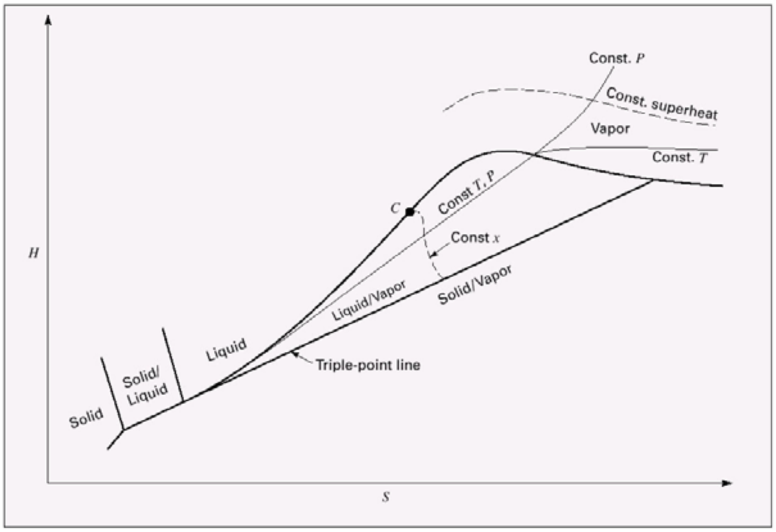

Figure 6.4: Mollier diagram.

Similar to PV and PH diagrams.

6.6 Tables of Thermodynamic Properties

Steam tables (APP. F) both in SI units and English units. (P.688)

SI units:
F1 : Saturated liquid & vapor (T intervals).

F2 : Superheated region for $T \geq T^{sat}$ of a given pressure.

F3&F4: English units.

Sub cooled liquid Sat. → **liquid &saturated vapor** → **Superheated vapor**.

Example 6.7