Chapter 5.
Calculation of Properties

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Introductory remark

- So far we have encountered several thermodynamic properties, all state functions, meaning that they are fixed once the state is fixed.
- Tables are impractical for mass-calculations such as those involved in large scale design, and of course it is impractical to tabulate properties of all conceivable substances under all conceivable states.
- Methodologies for the *numerical calculation of thermodynamic properties* are needed.
- Two things are focused on this chapter: (a) *to develop relationships among the various thermodynamic properties*; (b) *to develop methodologies for the calculation of enthalpy and entropy as a function of pressure and temperature*.

Instructional Objectives

- Manipulate the differential of thermodynamic properties
- Generate relationships between properties
- Calculate properties using the equation of state
- Properly apply reference states in the calculation of absolute properties

Calculus of Thermodynamics

- In dealing with pure substances we have two independent variables. Though we prefer to choose pressure and temperature, *any two variables from the set {V, P, T, S, H ···} may be used for this purpose.* For instance, Isotherms and isobars on the PV graph are expressed functions of H and S. In addition, in the PV graph, we have chosen P and V as the independent variables.

- *The same thermodynamic property may be written in various equivalent forms, depending on the pair that is chosen as the independent variables*.

- The logic is provided by *the tools of multivariable calculus*.

Tools of multivariate calculus

$$F = F(X, Y)$$

$$dF = \left(\frac{\partial F}{\partial X}\right)_Y dX + \left(\frac{\partial F}{\partial Y}\right)_X dY$$

“Triple-product rule” ~ dF = 0

$$[0 = \left(\frac{\partial F}{\partial X}\right)_Y dX + \left(\frac{\partial F}{\partial Y}\right)_X dY]_{\text{const.F}}$$

$$[\left(\frac{\partial F}{\partial X}\right)_Y \frac{dX}{dY} = -\left(\frac{\partial F}{\partial Y}\right)_X]_{\text{const.F}}$$

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

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

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$$

Exact differential
dF = AdX+BdY

$$A = \left(\frac{\partial F}{\partial X}\right)_Y, B = \left(\frac{\partial F}{\partial Y}\right)_X \qquad \left(\frac{\partial B}{\partial X}\right)_Y = \left(\frac{\partial A}{\partial Y}\right)_X$$

$$\left(\frac{\partial B}{\partial X}\right)_Y = \frac{\partial^2 F}{\partial Y \partial X} = \frac{\partial^2 F}{\partial Y \partial X} = \left(\frac{\partial A}{\partial Y}\right)_X$$

Calculus vs. Thermodynamics: There is a correspondence bet thermodynamic language and mathematics.

Thermodynamics		**Calculus**
State function	⟷	Exact differential
Path function	⟷	Inexact differential
Reversible process	⟷	Integration path

Integration of Differentials

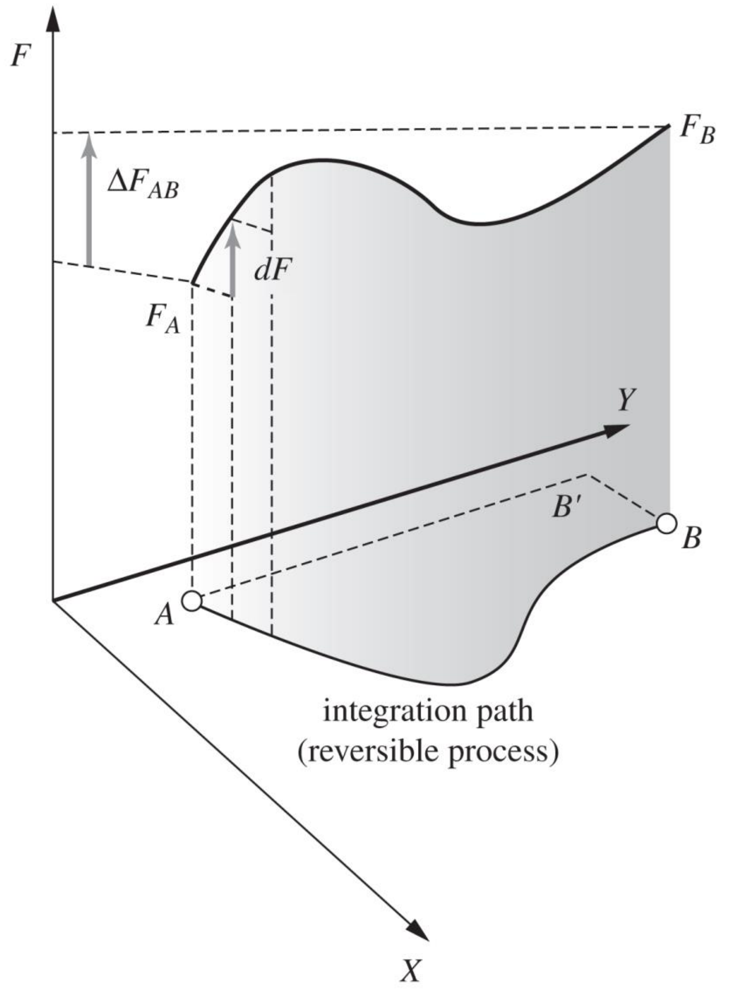

Figure 5-1

Geometric interpretation of the integration path. As the state traces the integration path on the XY plane, property F traces a line on the $F(X,Y)$ surface.

Fundamental Relationships

$$dU = TdS - PdV$$

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

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

$$dH = TdS + VdP$$

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

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

$$dG = -SdT + VdP$$

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

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

$$dA = -SdT - PdV$$

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

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

Example 5.1. Change of variables

- Express the partial derivative $(\alpha H/ \alpha P)T$ in terms of P, V, and T.

- Ans. $dH = T\ dS + V\ dP$

Equations for Enthalpy and Entropy

- The stated goal for this chapter is to obtain equations for the enthalpy and entropy in terms of pressure and temperature.

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

$$dH = \left(\frac{\partial H}{\partial T}\right)PdT + \left(\frac{\partial H}{\partial P}\right)TdP$$

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

$$dS = \frac{dH}{T} - \frac{V}{T}dP$$

Ideal-Gas State

Equation of state	**$PV^{ig} = RT$**
Compressibility factor	$Z^{ig} = 1$
Heat capacities	$C_p^{ig} - C_v^{ig} = R$
Enthalpy	$dH^{ig} = C_p^{ig}\, dT,\ \Delta H_{12}^{ig} = \int_{T_1}^{T_2} C_p^{ig}\, dT$
Internal energy	$dU^{ig} = C_v^{ig}\, dT,\ \Delta U_{12}^{ig} = \int_{T_1}^{T_2} C_v^{ig}\, dT$
Entropy	$dS^{ig} = \frac{C_p^{ig} dT}{T} - \frac{RdP}{P}, \Delta S_{12}^{ig} = \int_{T_1}^{T_2} \frac{C_p^{ig} dT}{T} - R \ln \frac{P_2}{P_1}$

Incompressible Phases

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \ , \ \left(\frac{\partial V}{\partial T}\right)_P = \beta V$$

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

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

- For condensed phases (solid, liquids away from the critical point), both β and V are small. Accordingly, the contribution of the terms V(1-βT)dP and –VdP to the enthalpy and entropy is generally negligible when compare to the contribution of the temperature term. -> this is the reason why we often take the enthalpy and entropy of compressed liquids to be independent of pressure.

Residual Properties

- The simplicity of the ideal-gas state is lost when we move away from the ideal-gas state, which further simplifies the calculation.

- The difficulty is removed through the introduction of residual properties.

- The calculation is done in two parts: first, we obtain enthalpy and entropy as if the substance were in the ideal state, then we add an appropriate correction that makes the result exact. This correction is the residual property.

  $F(P, T) = F^{ig}(P, T) + F^{R}(P, T)$, F^{ig} is the ideal-gas property at P and T, the property obtained by applying the ideal-gas equations.

$$\Delta H_{12} = \int_{T_1}^{T_2} C_p{}^{ig}\, dT + H_2{}^R - H_1{}^R$$

$$\Delta S_{12} = \int_{T_1}^{T_2} C_p{}^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_1} + S_2{}^R - S_1{}^R$$

Residual Enthalpy

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

$$dH^R = dH - dH^{ig}\ (Constant\ T)$$

$$dH^R = \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP\ (Constant\ T)$$

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

This is the desired result: it gives
the residual enthalpy in state (P, T)
in the form of an integral that may be
evaluated if the equation of state is known.

Residual Entropy

$$dS^R = dS - dS^{ig}\ (Constant\ T)$$

$$dS^R = \left[\frac{R}{P} - \left(\frac{\partial V}{\partial T}\right)_P\right] dP\ (Constant\ T)$$

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

Residual Volume

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

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

Other Residual Properties

- It is not necessary to derive equations for any other residual properties because these can all be related to V^R, H^R, and S^R.

- In general, all relationships among “regular” properties can also be written among the corresponding residual properties. For example, internal energy is related to enthalpy through the relationship,

$$U = H - PV$$

In the ideal-gas state, this becomes,

$$U^{ig} = H^{ig} - PV^{ig}$$

$$U^R = H^R - PV^R$$

Applications

- The general procedure is, first express the volume in terms of pressure and temperature, compute the partial derivative and finally perform the integrations in H^R, S^R.

- The simplest possible equation of state is the ideal-gas law; the residuals should vanish. Next simplest case is the truncated virial equation. Cubic equations of state may be another choice but it require some additional work

Example 5.2. Residual properties in the ideal-gas state

- Obtain the residual enthalpy, entropy, and volume in the ideal-gas state.

- Ans. $V=RT/P$

Example 5.3. Residual properties from the truncated virial equation

- Obtain the residual enthalpy, entropy, and volume from the truncated virial equation.

- Ans. $V=RT/P + B$

Pressure-Explicit Relations

$$H^R = PV - RT + \int_{\infty}^{V} \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV \text{ (Constant T)}$$

$$S^R = R\ln\frac{PV}{RT} + \int_{\infty}^{V} \left[\left(\frac{\partial P}{\partial T}\right)_V - \frac{R}{V}\right] dV \text{ (Constant T)}$$

Applications to Cubic Equations

Generalized Correlations

$$\frac{H^R}{RTc} = h(0) + \omega\, h(1)$$

$$\frac{S^R}{R} = s(0) + \omega\, s(1)$$

Example 5.4. Residual properties from corresponding states

- Obtain the residual enthalpy and entropy of ethylene at 250 K, 30 bar using the Lee-Kesler charts.

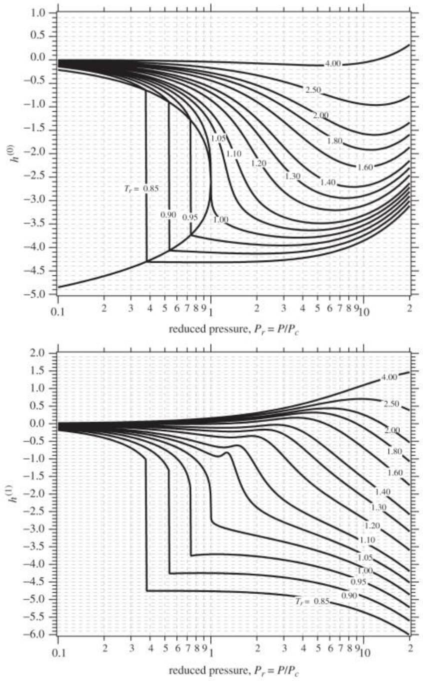

Figure 5-2

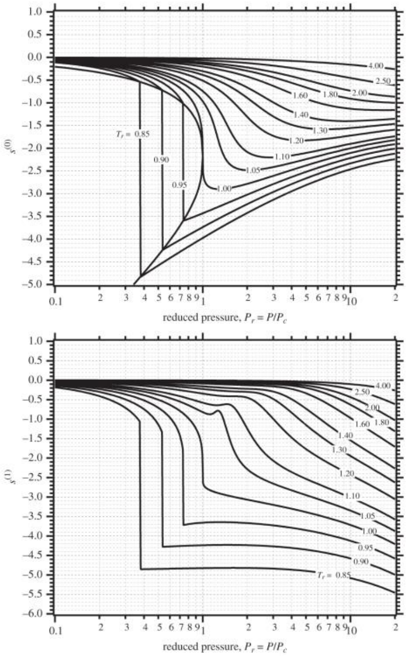

Figure 5-3

Pressure-Enthalpy Chart

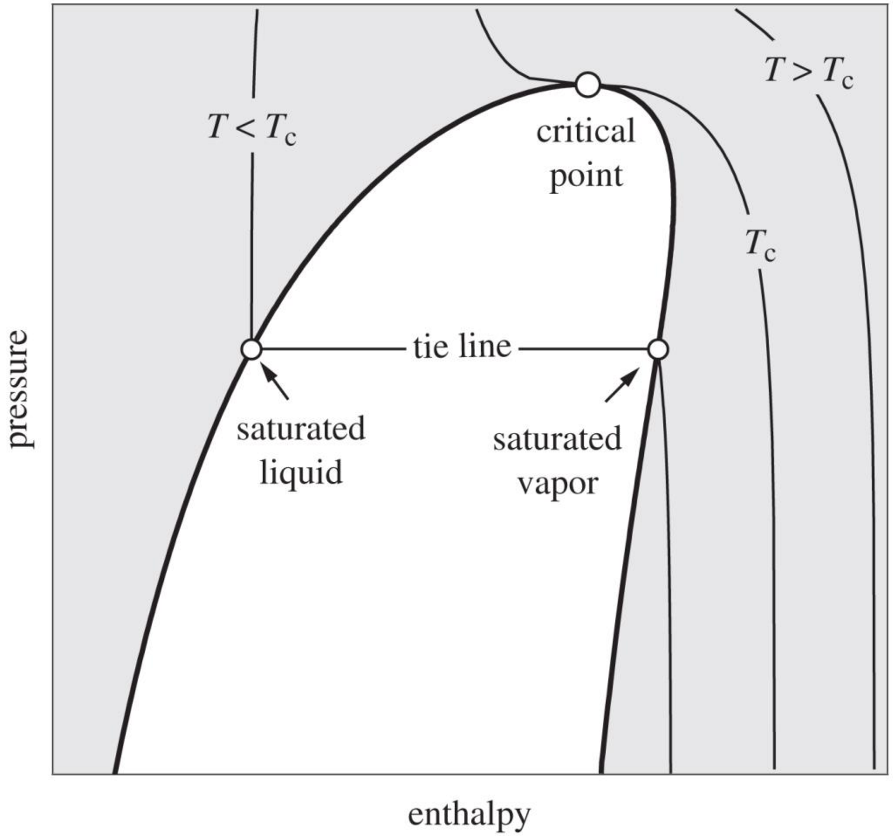

Figure 5-4

Pressure-enthalpy chart.

Temperature-Entropy Chart

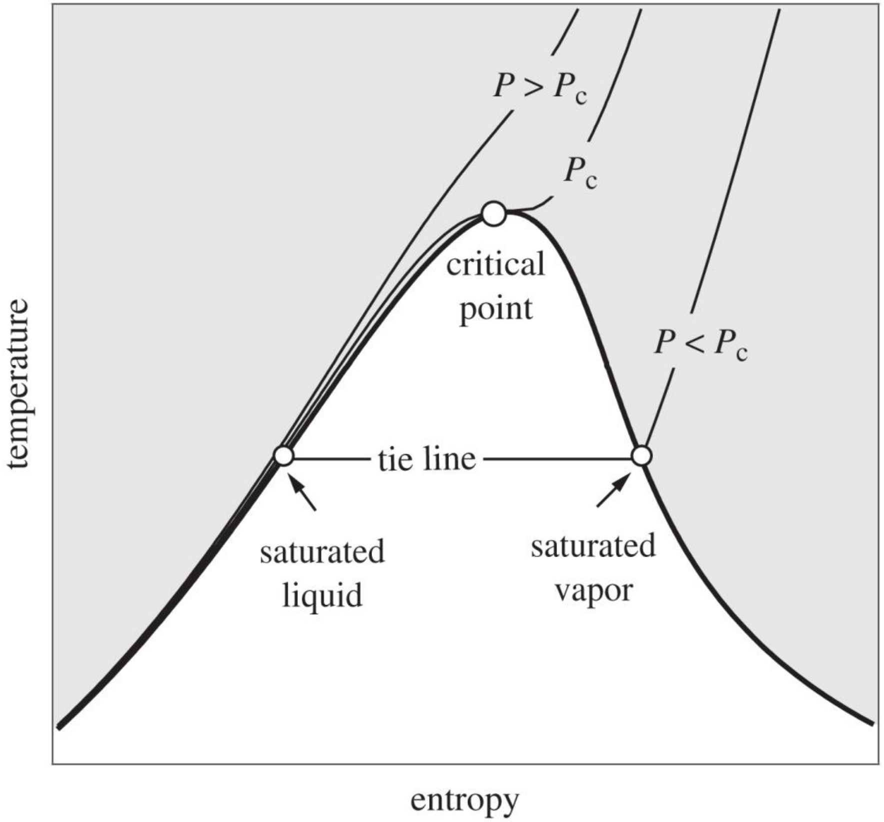

Figure 5-5

Temperature-entropy chart.

Enthalpy-entropy Chart

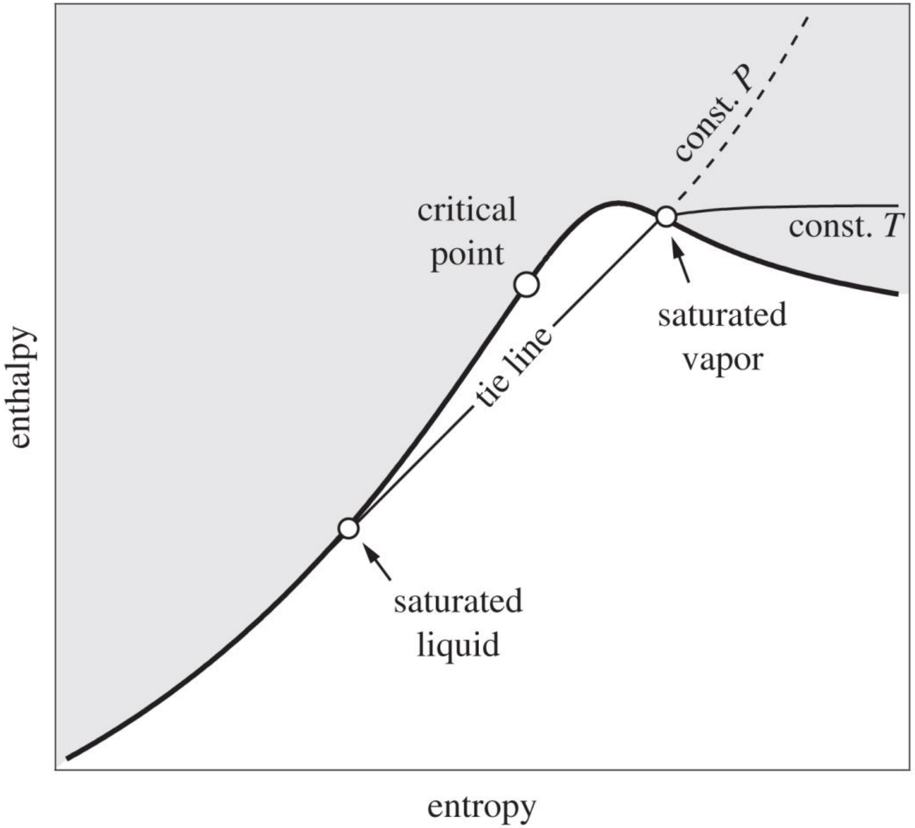

Figure 5-6

Enthalpy-entropy (Mollier) chart.