EG3029 Chemical Thermodynamics

Thermodynamic Properties of Pure Fluids

Property Relations for Homogeneous Phases

- Important definitions for state functions
  - Enthalpy $$\boxed{H = U + P\,V}$$
  - Helmholtz energy $$\boxed{A = U - T\,S}$$
  - Gibbs energy $$\boxed{G = H - T\,S}$$

Property Relations for Homogeneous Phases

- For 1 mol of homogeneous fluid at const. comp.

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -PdV - SdT$$

$$dG = VdP - SdT$$

- Maxwell's equations

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

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

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

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

Property Relations for Homogeneous Phases

- Enthalpy and entropy as functions of *T* and *P*

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

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

- Ideal gas:

$$dH = C_P dT$$

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

- Liquid:

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

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

Property Relations for Homogeneous Phases

- Internal energy and entropy as functions of *T* and *V*

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

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

- Worked example: Develop the property relations appropriate to the incompressible fluid, a model fluid for which both β and κ are zero.

Property Relations for Homogeneous Phases

- Gibbs energy as generating function

$$dG = VdP - SdT$$

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

- After substitution and algebraic reduction

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

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

The Gibbs energy when given as *G(T,P)* serves as a generating function for the other thermodynamic properties, and implicitly represents complete property information.

Residual Properties General Approach

- Residual Gibbs energy is defined as

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

G actual Gibbs energy
G^{ig} ideal gas value

and results in

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

and the restricted forms

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

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

Residual Properties by Equations of State

- Alternative approach to numerical integration: analytical evaluation by EOS
- Virial EOS: $Z-1=\frac{BP}{RT}$

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

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

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

Residual Properties by Equations of State

- Cubic EOS:

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

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

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

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

Two-Phase Systems
General

- Phase transition: many extensive properties change abruptly during phase transition at given *P* and *T*: specific volume, internal energy, enthalpy, entropy
- Exception: molar Gibbs energy
- For 2 phases α and β of pure species at equilibrium:

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

- Clapeyron equation:

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

Two-Phase Systems
General

- Temperature dependence of vapour pressure: empirical approaches for practical applications
  - Simplest case $$\ln P^{sat} = A - \frac{B}{T}$$
  - Antoine equation $$\ln P^{sat} = A - \frac{B}{T + C}$$
  - Wagner equation $$\ln P_r^{sat} = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1 - \tau} \qquad \tau = 1 - T_r$$

Two-Phase Systems Liquid/Vapour Systems

- System with saturated vapour and saturated liquid in equilibrium: total value of any extensive property is the sum of the total properties of the phases

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

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

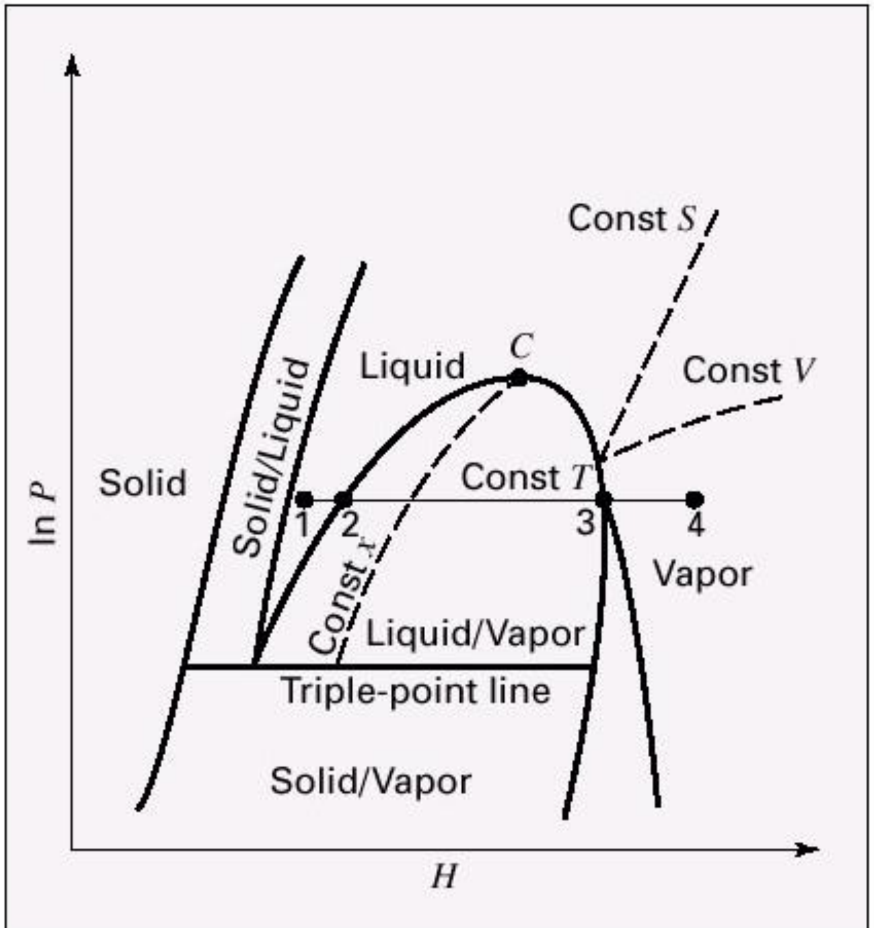
$$x^l = 1 - x^v$$

- Generic equations for V, U, H, S, etc

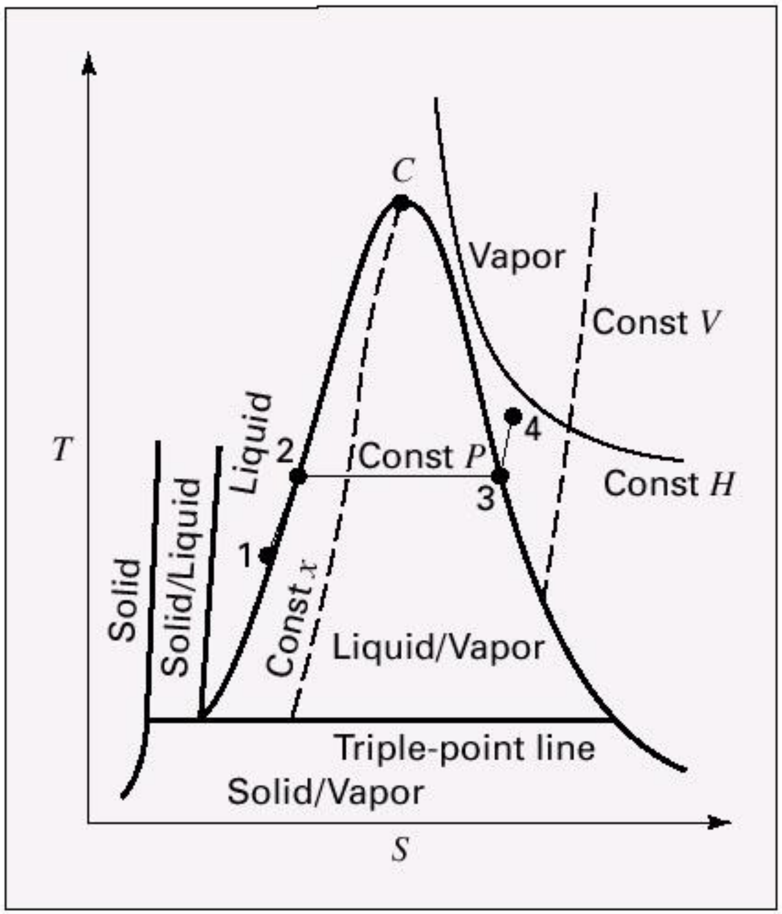
$$M = (1 - x^v) M^l + x^v M^v$$

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

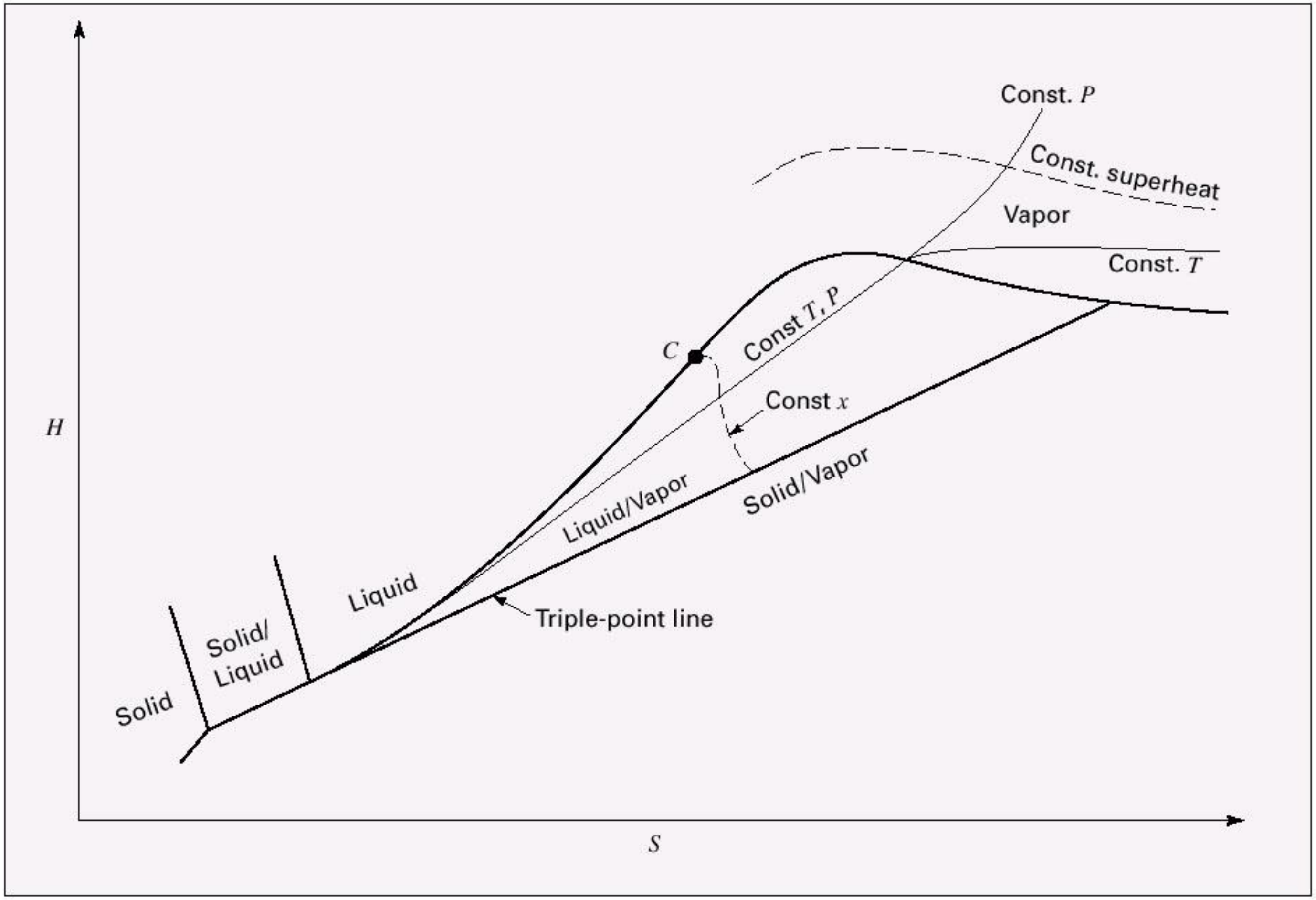
Thermodynamic Diagrams P H diagram



Thermodynamic Diagrams
T S diagram



Thermodynamic Diagrams
Mollier diagram (H S)



Tables of Thermodynamic Properties Steam Tables

Worked example:

Superheated steam originally at P_1 = 1000 kPa and T_1 = 250 degC expands through a nozzle to an exhaust pressure P_2 = 200 kPa.

What is the downstream state of the steam and the change in enthalpy assuming a reversible and adiabatic process?