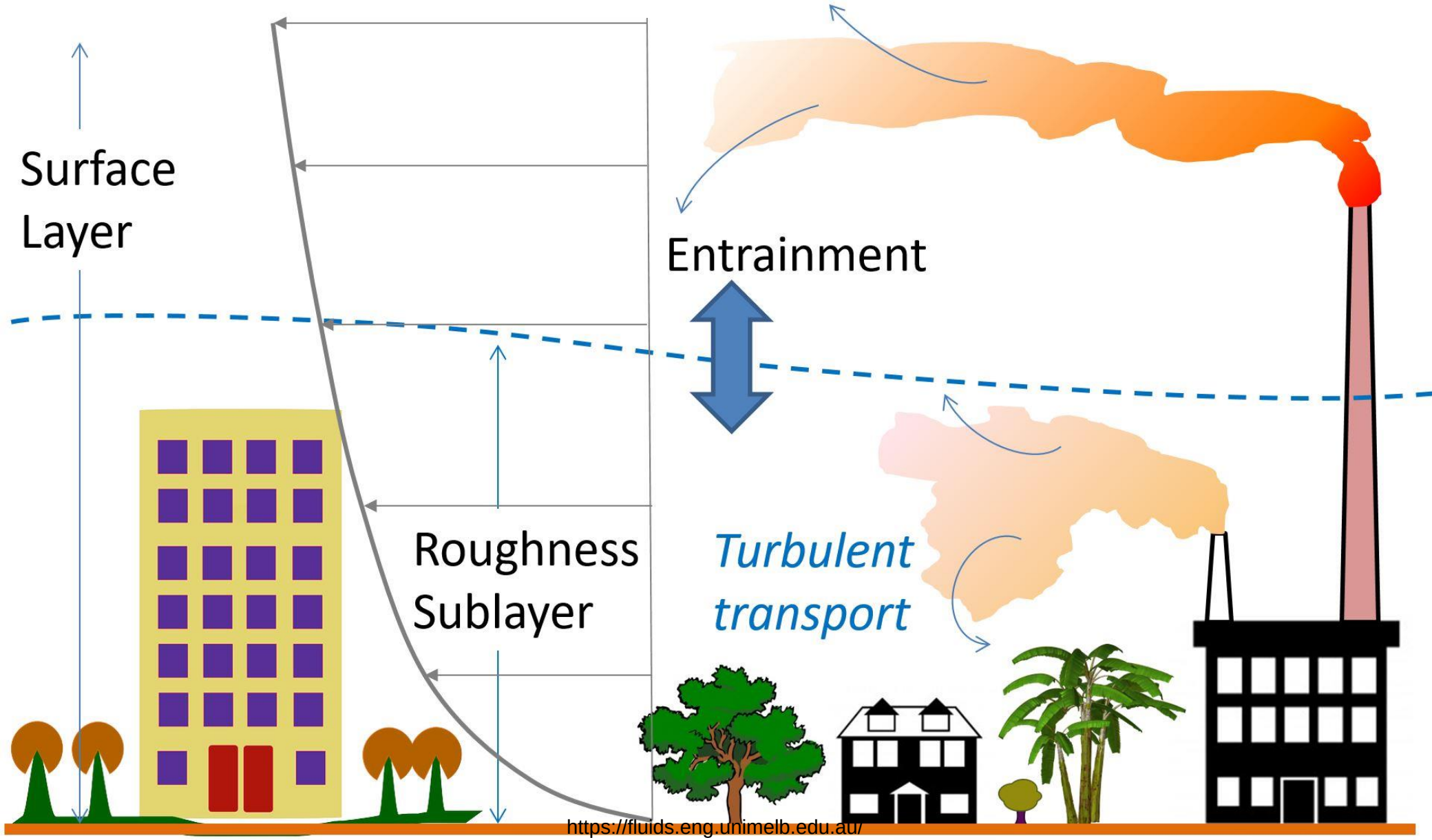
Aero Thermo Hydro Engineers Nexus Application

Department of Nuclear Engineering, Seoul National University



A Quick Look

- Independent Properties of the Pure Substance Model
- Equilibrium Liquid-Vapor States
- Equilibrium Liquid-Solid and Vapor-Solid States
- Equilibrium Solid-Liquid-Vapor States
- Gibbs Phase Rule
- Energy Interactions During Changes of Phase
- Phase Equilibrium
- Thermodynamic Surfaces
- Tabulation of the Thermodynamic Properties
- Metastable States
- Applications of the Pure Substance Model

Simple System

1) no surface forces (from capillarity & surface tension)
2) no forces due to gravity, electric charge, magnetic fields
3) no shear forces
4) no bulk motion

- p is uniform and hydrostatic at equilibrium $\int \boldsymbol{pdV}$ is the only mode of reversible work transfer
- No chemical reactions
- Pure Substance: a simple (sub)system invariant in chemical composition

- State Principle
  - Any two independent properties are sufficient to establish a stable equilibrium thermodynamic state of a system
  - For each indentifiable departure from the requirements for a simple system, one additional independent property is required
- Properties of Pure Substance Model
  - simple system

↓

pure substance state principle → one independent property per reversible mode of energy interactions

Properties of Pure Substance Model

- 1st law $dU = TdS - pdV = \delta Q_{rev} - \delta W_{rev},\ U = U(S,V)$
  - If irreversible, TdS > δQ by the same amount that pdV > δW
- Intensive & Extensive Properties

  $$d(U/m) = Td(S/m) - pd(V/m),\ du = Tds - pdv$$

  - intensive properties: mass independent -T, p, u, s, v
  - extensive properties: dependent on the extent of system U, S, V
- Phase: All parts of a system which have identical and uniform values for each of the specific properties as well as identical and uniform T and p are said to constitute one phase

Properties of Pure Substance Model

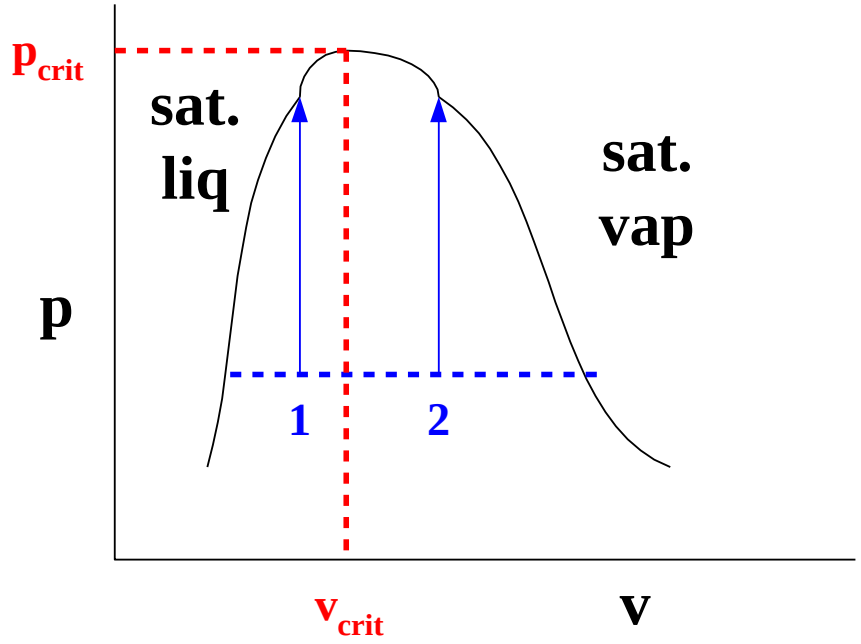
- Saturation Temperature
  - temperature @ which two phases coexist in equilibrium with one another at a given pressure
- Saturation pressure
  - pressure @ which two phases coexist at a given temperature
- Boiling, Evaporation, Vaporization
  - change in phase from sat. liquid to sat. vapor
- Condensation, Liquefaction
  - change in phase from sat. vapor to sat. liquid

Properties of Pure Substance Model

- Saturated Vapor
  - all saturation properties for which $v > v_{crit}$
- Saturated Liquid
  - all saturation properties for which $v > v_{crit}$

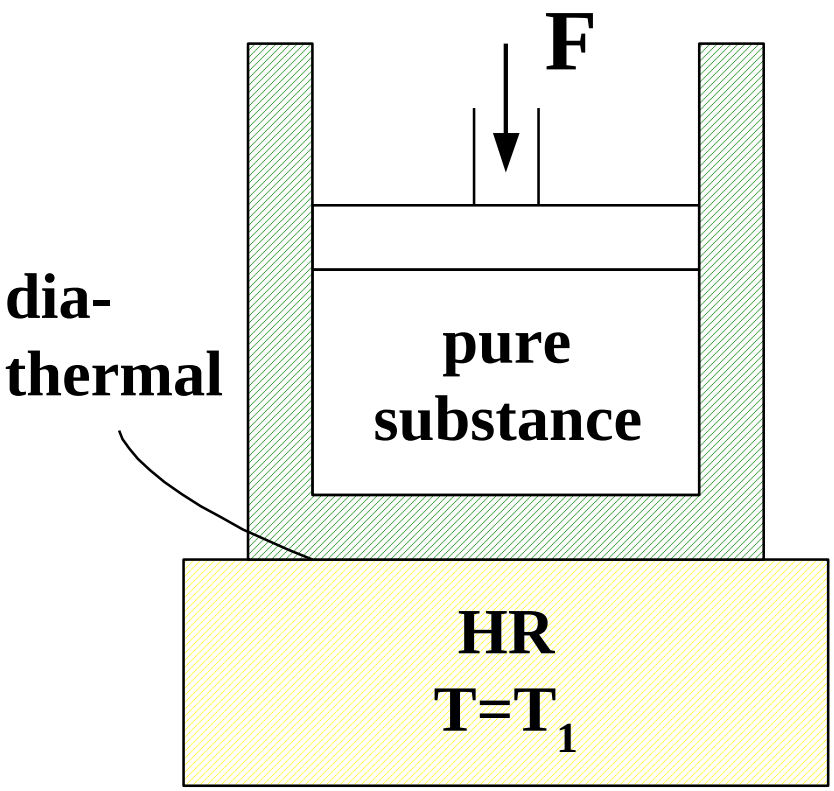
1 reaches sat. liquid
with positive δQ
at constant v

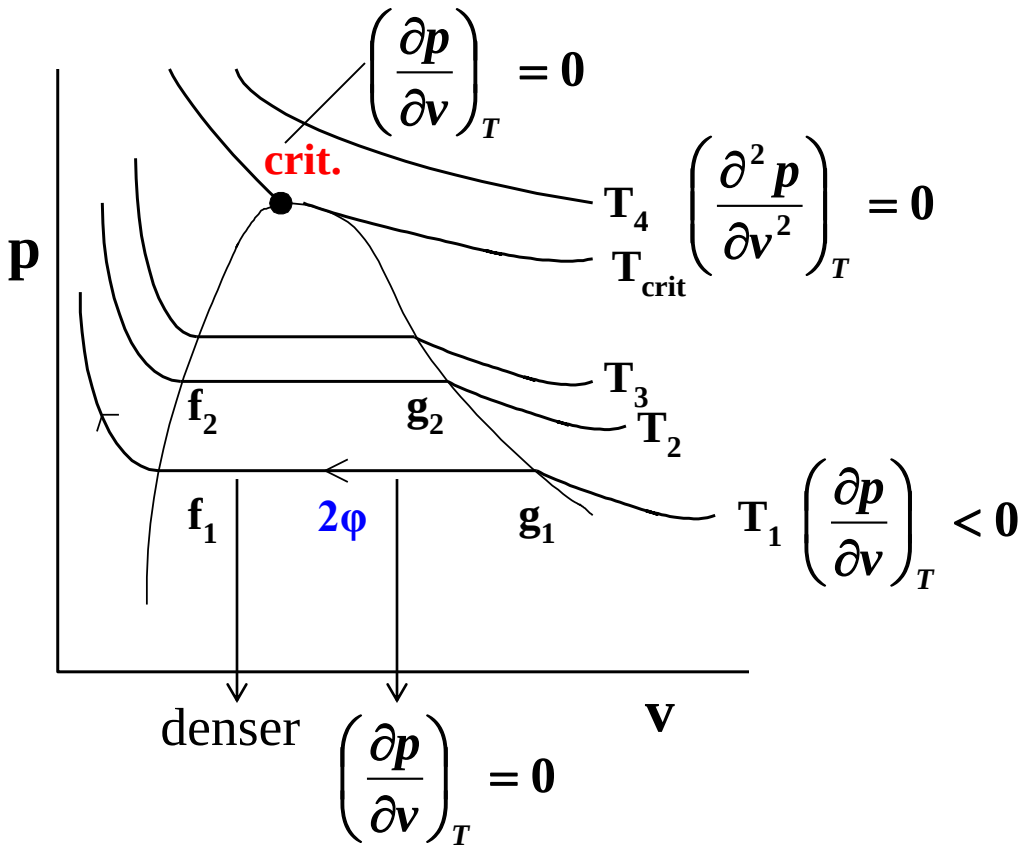
2 reaches sat. vapor
with positive δQ
at constant v



Properties of Pure Substance Model

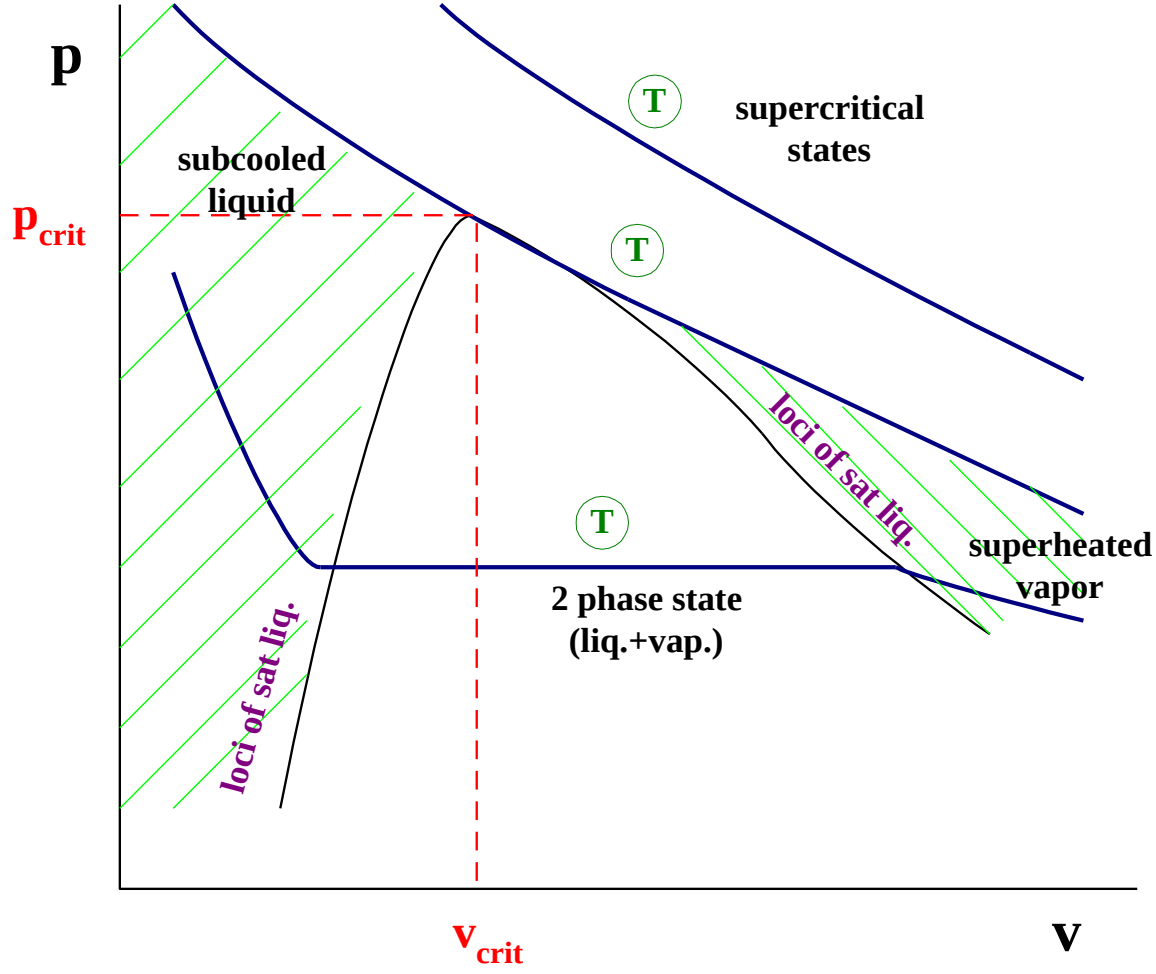
Piston-cylinder Apparatus for Isothermal Process





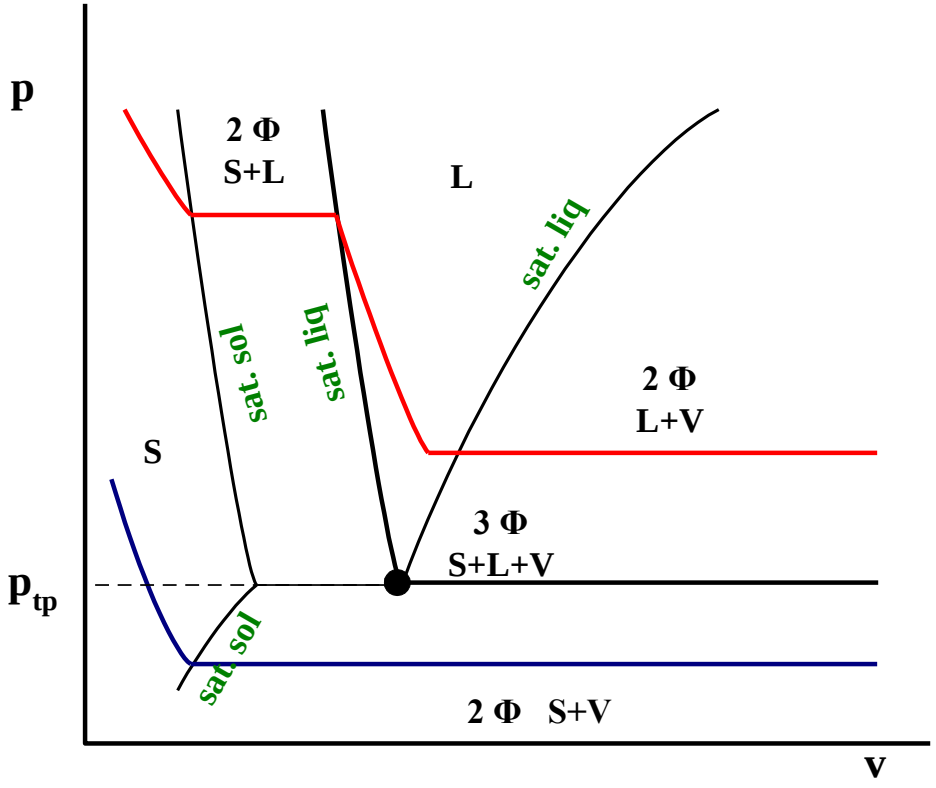
Properties of Pure Substance Model

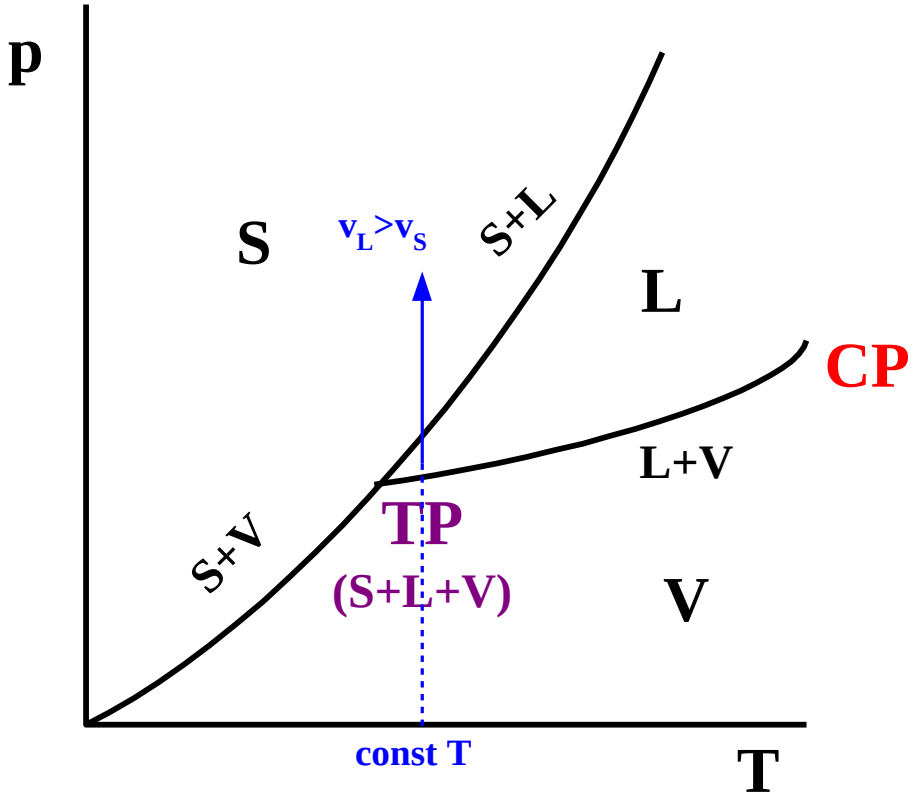
Piston-cylinder Apparatus for Isothermal Process



Properties of Pure Substance Model

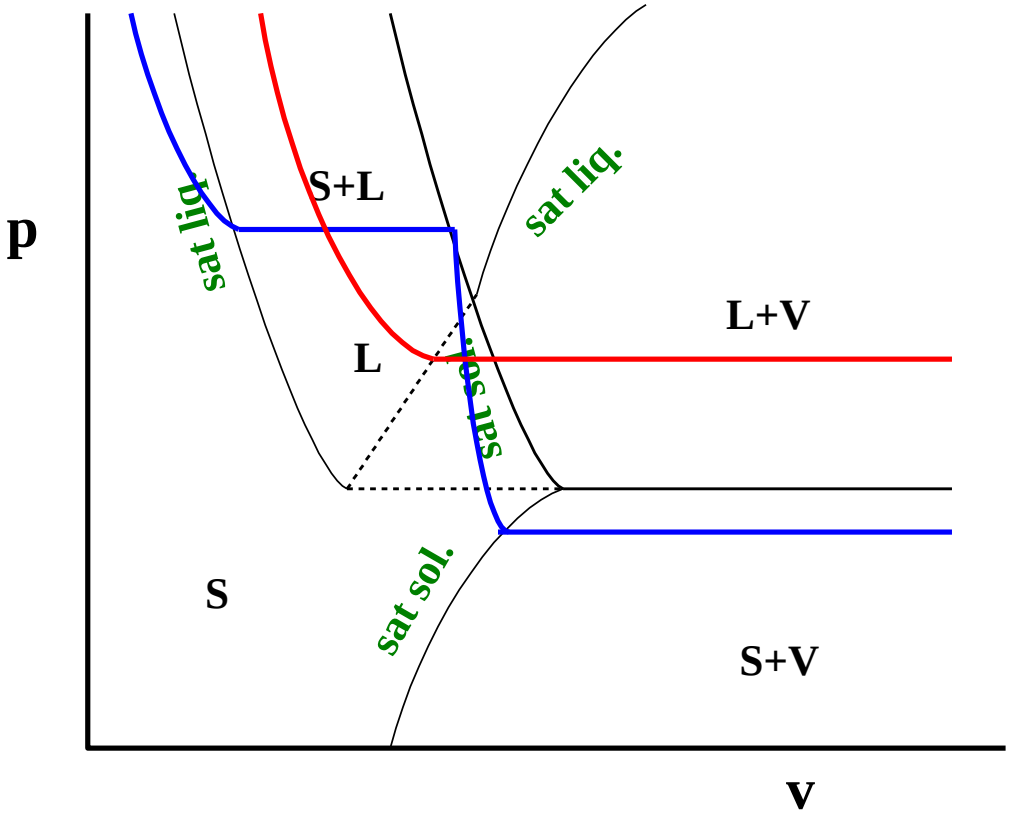
Substance that Contracts upon Freezing

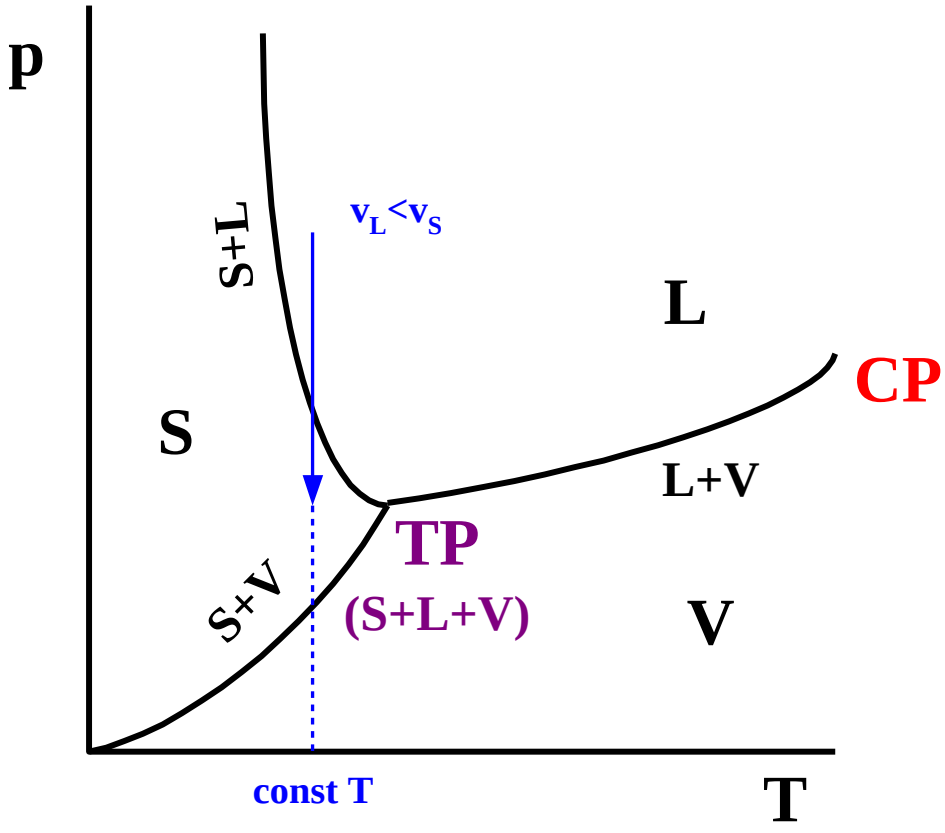




Properties of Pure Substance Model

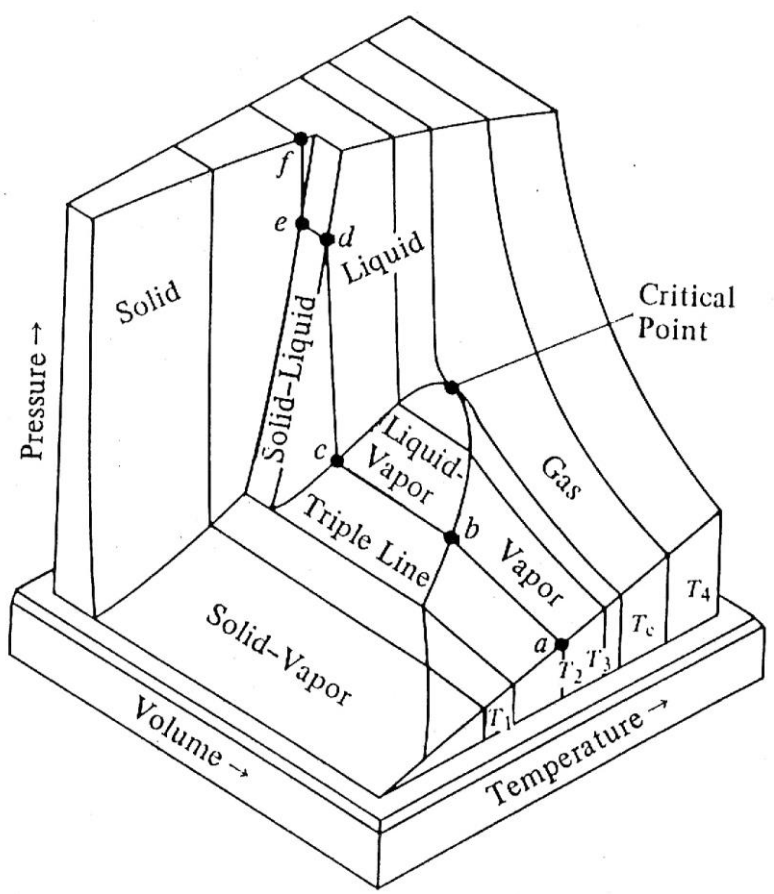
- Substance Expands upon Freezing

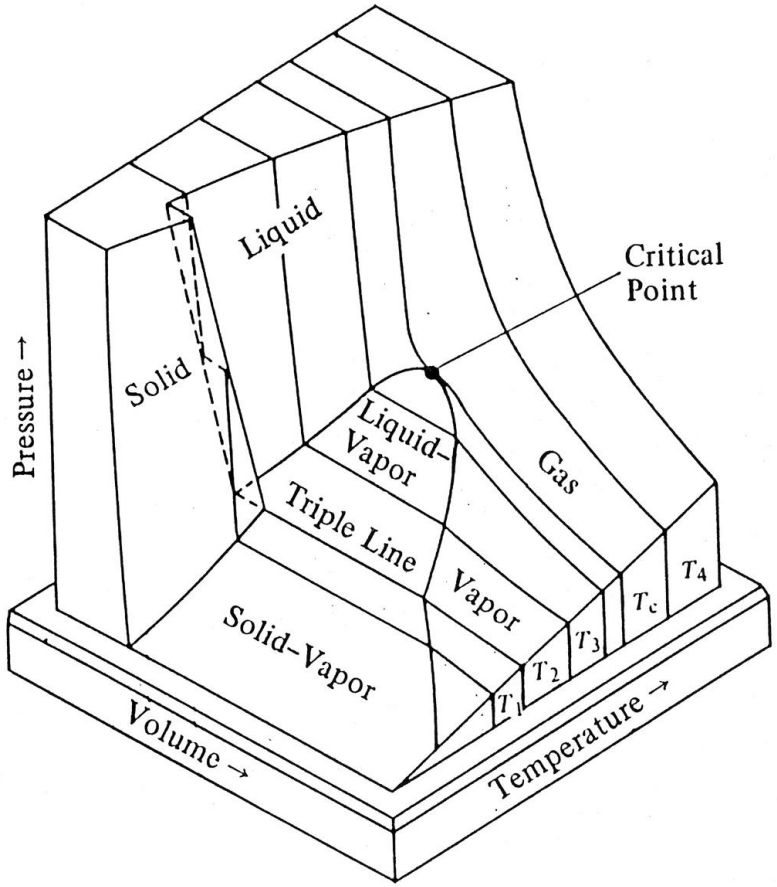




Properties of Pure Substance Model

Substance that Contracts & Expands upon Freezing



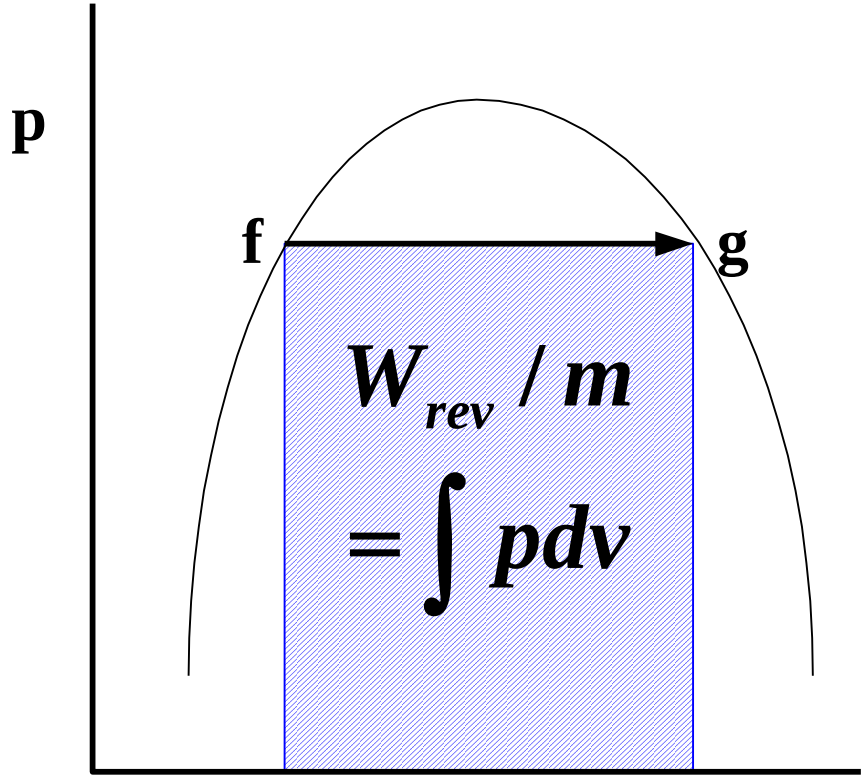


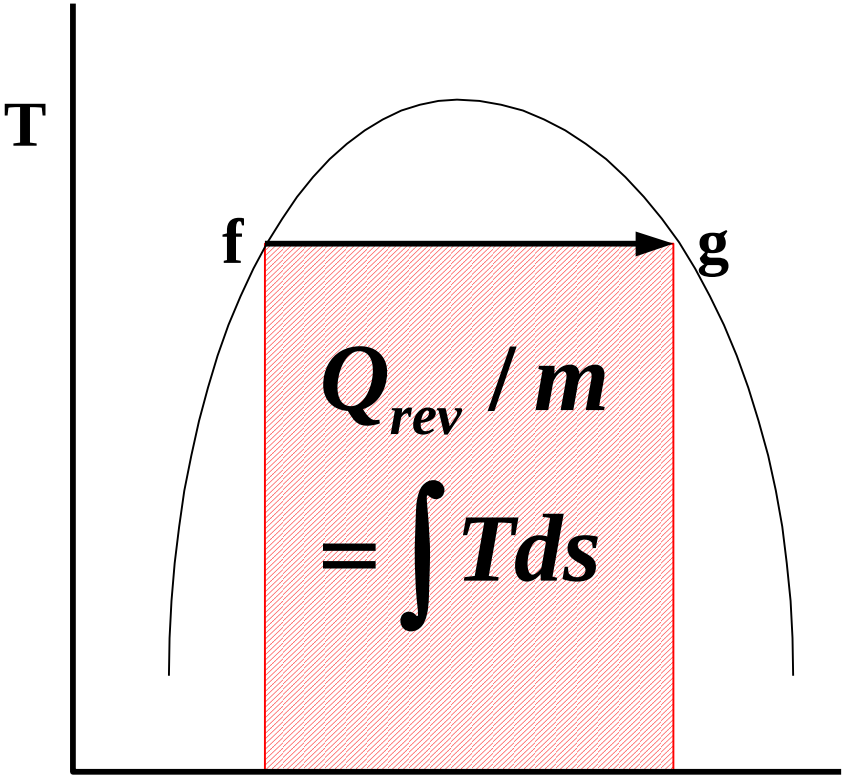
Properties of Pure Substance Model

- Gibbs phase Rule
  - f: number of thermodynamic degrees of freedom (number of independent intensive properties)
  - c: number of chemically independent species
  - ζ: number of phases $f = 2 + c - \varsigma$
  - For a pure substance c=1
    - 1 phase (f=2): p and T can be fixed arbitrarily. (divariant)
    - 2 phase (f=1): p or T can be fixed arbitrarily (monovariant)
    - 3 phase (f=0): (invariant)
      - » No intensive property can be arbitrarily fixed.
      - » Intensive state is automatically specified by virtue of equilibrium

Properties of Pure Substance Model

Energy change (constant p phase from sat. L to sat. V)





$$W_{fg,rev} = mp\left(v_g - v_f\right)$$

Properties of Pure Substance Model

Energy change (constant p phase from sat. L to sat. V)

1st law

$$Q_{fg} - W_{fg} = m\left(u_g - u_f\right)$$

$$Q_{fg} = m\left(h_g - h_f\right)$$

$$Q_{fg,rev} = mh_{fg}$$

h_{fg}:latent heat of vaporization

2nd law

$$Q_{fg} = m\int_f^g Tds = mT\left(s_g - s_f\right)$$

$$= mTs_{fg} = mh_{fg}$$

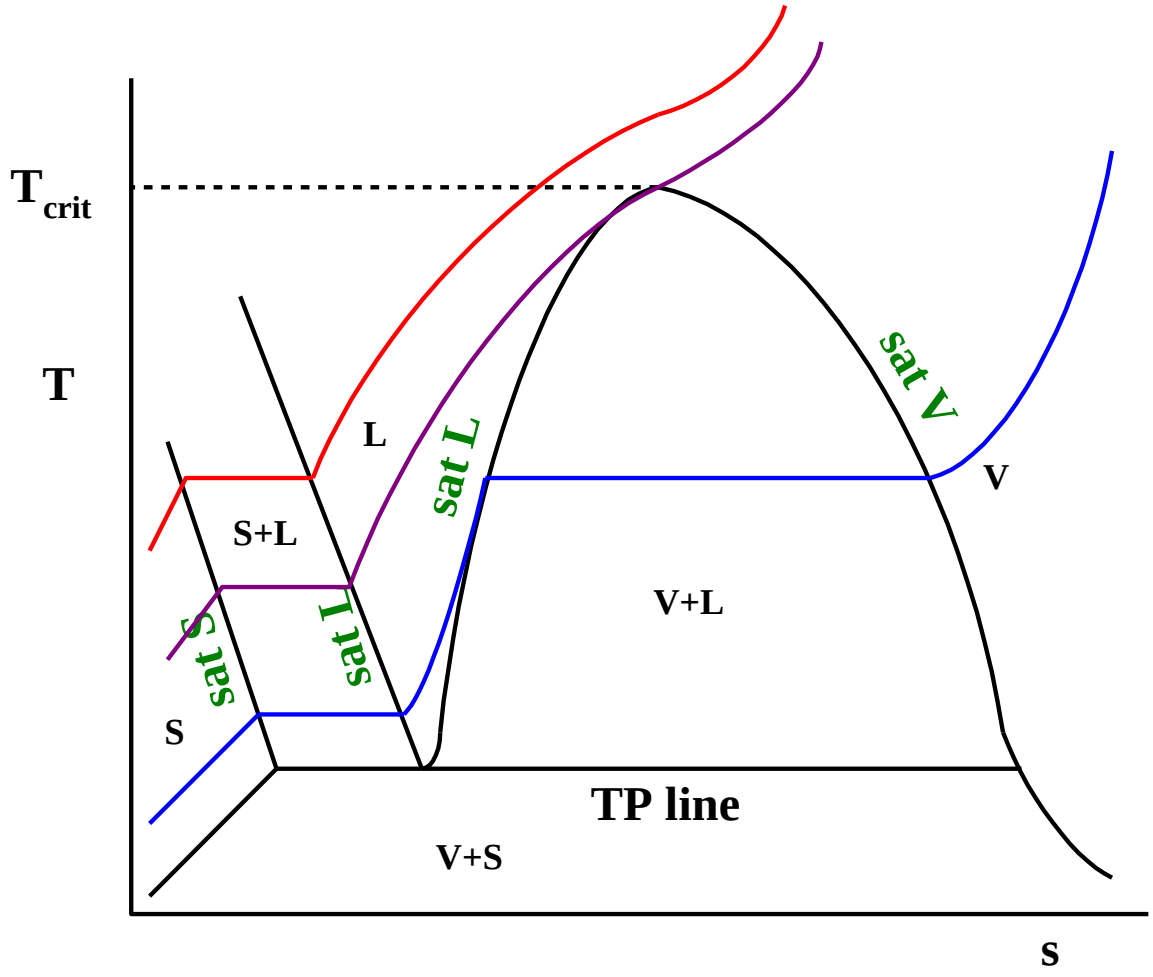
$$\therefore Ts_{fg} = h_{fg}$$

$$\left(h - Ts\right)_g = \left(h - Ts\right)_f \quad or \quad g_g = g_f$$

g: Gibbs free energy / mass

Properties of Pure Substance Model

Temperature-Entropy Diagram of Pure Substance



Properties of Pure Substance Model

Tabulation of Data

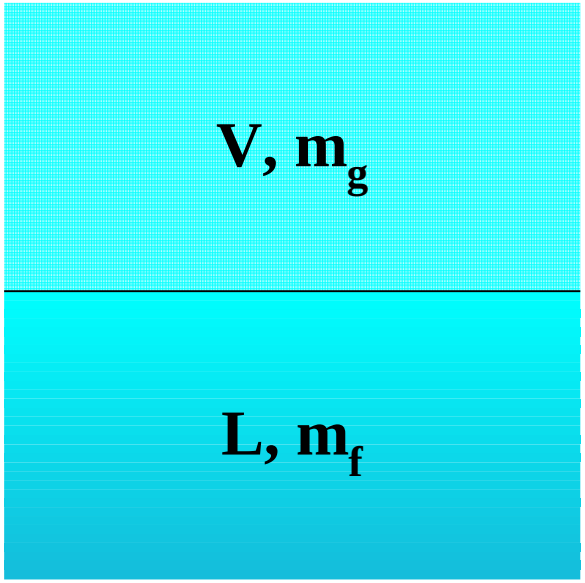
$$v = v_f + v_g$$

$$mv = m_f v_f + m_g v_g$$

$$v = v_f + \frac{m_g}{m_f + m_g} v_g$$

$$x = \frac{m_g}{m_f + m_g}$$

$$v = v_f + x v_{fg}, \; s = s_f + x s_{fg}$$



Steam table data $u = u_f + x u_{fg}, \; h = h_f + x h_{fg}, \; \rho = \rho_f + \alpha \rho_{fg}$

Properties of Pure Substance Model

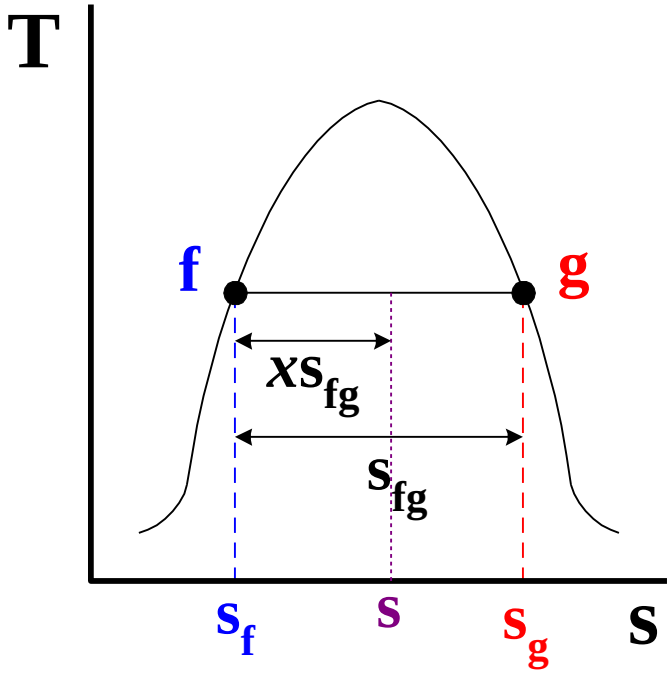
Tabulation of Data

Ex.1 A system with a total volume of 3 m^3 contains 2 kg of H_2O at $p=7\times10^4$ N/m^2. What is S?

$$x = \frac{v - v_f}{v_g - v_f}$$

$$s = s_f + x s_{fg}$$

$$S = ms$$



Properties of Pure Substance Model

Metastable States

- In stable equilibrium states, a system can change from one stable equilibrium to another only if there is a corresponding, finite, permanent change of state of the environment.
- In metastable states, a system can change states from metastable to some other stable equilibrium state by means of a finite, but temporary, change of state of the environment.
- Example 1: very clean deaerated water may be heated at constant p in a new unscratched glass container significantly above TBP(p) W/O the appearance of bubbles ------ superheated liquid
  - metastable: introduction of vapor will cause the rapid, explosive change to a stable 2 phase state consisting of a liquid phase and a vapor phase in mutual equilibrium

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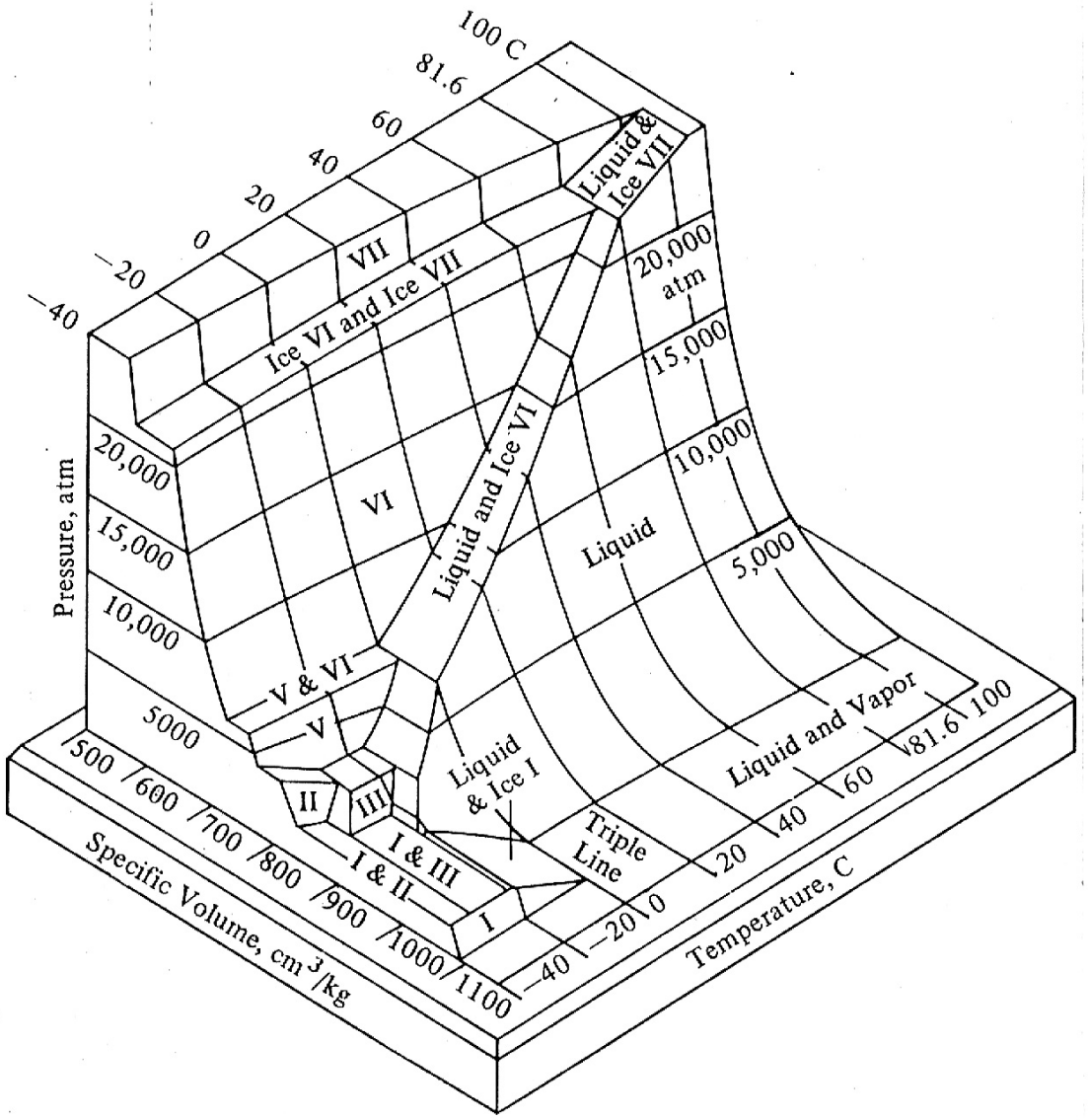


Thermofluid Properties

Thermodynamic Functions

- Define a canonical relation of thermodynamics for a closed system

  - mathematically

$$du = Tds - pdv \qquad u = u(s,v)$$

  - definitions of temperature and pressure in an abstract mathematical sense (at hand prosuppose that the actual function u(s,v) is

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv, \quad T = \left(\frac{\partial u}{\partial s}\right)_v, \quad -p = \left(\frac{\partial u}{\partial v}\right)_s$$

- Think of the independent variables(properties) as a set of coordinates, so that various characteristic thermodynamic functions should be obtainable from one another by means of a suitable transformation of coordinates

Thermodynamic Functions

- The Legendre transformation for the canonical relation
- To replace one of the independent variables in an exact differential with its conjugate variable(property), subtract from the differential of the dependent variable the differential of the product of the two conjugate variables

Enthalpy h=h(s,p)	Helmholtz free energy f=f(T,v)	Gibbs free energy g=g(T,p)
$dh = Tds + vdp$	$df = -sdT - pdv$	$dg = -sdT + vdp$
$\because (h = u + pv)$	$\because (f = u - Ts)$	$\because (g = h - Ts)$
$dh = \left(\frac{\partial h}{\partial s}\right)_p ds + \left(\frac{\partial h}{\partial s}\right)_s dp$	$df = \left(\frac{\partial f}{\partial T}\right)_v dT + \left(\frac{\partial f}{\partial v}\right)_T dv$	$dg = \left(\frac{\partial g}{\partial T}\right)_p dT + \left(\frac{\partial g}{\partial p}\right)_T dp$
$T = \left(\frac{\partial h}{\partial s}\right)_p,\ v = \left(\frac{\partial h}{\partial s}\right)_s$	$-s = \left(\frac{\partial f}{\partial T}\right)_v,\ -p = \left(\frac{\partial f}{\partial v}\right)_T$	$-s = \left(\frac{\partial g}{\partial T}\right)_p,\ v = \left(\frac{\partial g}{\partial p}\right)_T$

Maxwell Relations

- user the fact that the order of differentiation is immaterial. Given z=z(x,y) with an exact differential dz
- Apply to the canonical relation

$$\left\{\frac{\partial}{\partial x}\left[\left(\frac{\partial z}{\partial y}\right)_x\right]\right\}_y = \left\{\frac{\partial}{\partial y}\left[\left(\frac{\partial z}{\partial x}\right)_y\right]\right\}_x$$

u=u(s,v)

$$\left\{\frac{\partial}{\partial v}\left[\left(\frac{\partial u}{\partial s}\right)_v\right]\right\}_s = \left\{\frac{\partial}{\partial s}\left[\left(\frac{\partial u}{\partial v}\right)_s\right]\right\}_v \qquad \left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$$

h=h(s,p)

$$\left\{\frac{\partial}{\partial p}\left[\left(\frac{\partial h}{\partial s}\right)_p\right]\right\}_s = \left\{\frac{\partial}{\partial s}\left[\left(\frac{\partial h}{\partial p}\right)_s\right]\right\}_p \qquad \left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_v$$

f=f(T,v)

$$\left\{\frac{\partial}{\partial T}\left[\left(\frac{\partial f}{\partial v}\right)_T\right]\right\}_v = \left\{\frac{\partial}{\partial v}\left[\left(\frac{\partial f}{\partial T}\right)_v\right]\right\}_T \qquad \left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

g=g(T,p)

$$\left\{\frac{\partial}{\partial p}\left[\left(\frac{\partial g}{\partial T}\right)_p\right]\right\}_T = \left\{\frac{\partial}{\partial T}\left[\left(\frac{\partial g}{\partial p}\right)_T\right]\right\}_p \qquad -\left(\frac{\partial s}{\partial p}\right)_T = \left(\frac{\partial v}{\partial T}\right)_p$$

The Clapeyron Relation (Along the sat. line)

$$dp = \left(\frac{dp}{dT}\right)_{sat} dT \qquad dg = -sdT + vdp$$

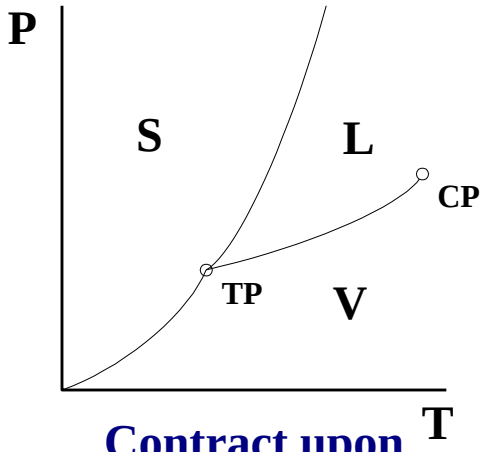
$$dg = \left[-s + v\left(\frac{dp}{dT}\right)_{sat}\right] dT$$

$$dg = \left[-s_f + v_f\left(\frac{dp}{dT}\right)_{sat} - x\left(-s_{fg} + v_{fg}\left(\frac{dp}{dT}\right)_{sat}\right)\right] dT$$

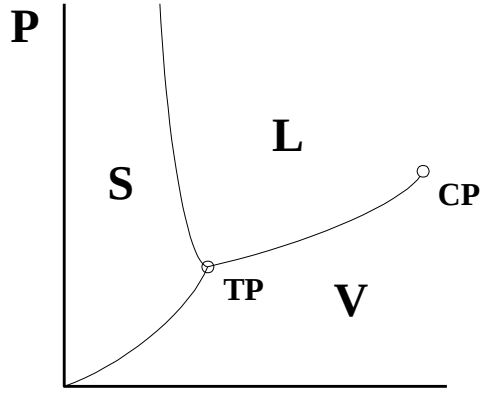
$$g_{fg} = 0 \quad or \quad g_g = g_f$$

$$\left(\frac{dp}{dT}\right) = \frac{s_{fg}}{v_{fg}} = \frac{h_{fg}}{Tv_{fg}}$$ The Clapeyron relation

→This result is general and holds for any two phases in equilbiruim



Contract upon freezing



Expand upon freezing

The Clapeyron Relation (Along the sat. line)

- obtain the equation for the vapor pressure curve by integrating:

$$\int_1^2 dp = \int_1^2 \frac{h_{fg}}{v_{fg}} \frac{dT}{T}$$

$$p_2 - p_1 = \int_{T_1}^{T_2} \frac{h_{fg}}{v_{fg}} \frac{dT}{T}$$

- Exercise: Alternate method of deriving the Clapeyron relation

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \qquad \left(\frac{\partial s}{\partial v}\right)_T = \frac{s_g - s_f}{v_g - v_f} \qquad \left(\frac{\partial p}{\partial T}\right)_v = \frac{s_g - s_f}{v_g - v_f}$$

Incompressible Fluid: v=constant

$$dh = \left(\frac{\partial h}{\partial p}\right)_T dp + \left(\frac{\partial h}{\partial T}\right)_p dT$$

$$\left(\frac{\partial h}{\partial T}\right)_p = c_p = T\left(\frac{\partial s}{\partial T}\right)_p$$

$$\left(\frac{\partial h}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T + v = -T\left(\frac{\partial v}{\partial T}\right)_p + v$$

$$dh = vdp + c_p dT \qquad (v \ \ const.)$$

$$\left(\frac{\partial}{\partial p} c_p\right)_T = \left[\frac{\partial}{\partial p}\left(\frac{\partial h}{\partial T}\right)_p\right]_T$$

$$= \left[\frac{\partial}{\partial T}\left(\frac{\partial h}{\partial p}\right)_T\right]_p = \left(\frac{\partial v}{\partial T}\right)_p = 0$$

c_p(T only)

$$h_2 - h_1 = v(p_2 - p_1) + \int_{T_1}^{T_2} c_p(T)dT$$

$$u_2 - u_1 = \int_{T_1}^{T_2} c_p(T)dT$$

$$\left(\frac{\partial u}{\partial T}\right)_v = c_v = c_p = c$$

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{cdT}{T}, \quad W_{1-2} = m\int_{v_1}^{v_2} pdv = 0$$

$$Q_{1-2} = U_2 - U_1 = m\int_{T_1}^{T_2} cdT$$

v is constant →rev. work transfer associated with normal displacement of the boundary is zero

Ideal Gas: pv=RT, p=p(T,v), u=u(T,v)

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$du = T\left(\frac{\partial s}{\partial T}\right)_v dT + \left[T\left(\frac{\partial s}{\partial v}\right)_T - p\right]dv$$

$$\left(\frac{\partial u}{\partial T}\right)_v = c_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - p$$

$$= T\left(\frac{\partial p}{\partial T}\right)_v - p = p - p = 0$$

$$du = c_v dT$$

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v(T)dT$$

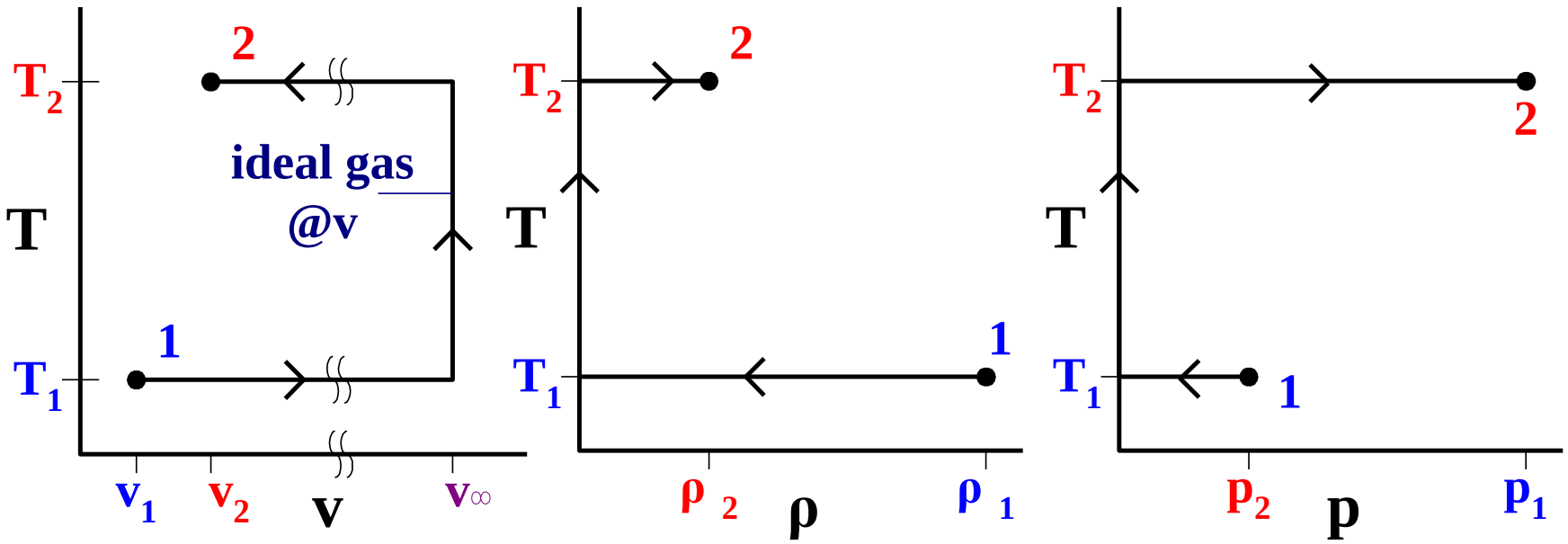
$$h = u + pv = u + RT$$

$$h_2 - h_1 = R(T_2 - T_1) + \int_{T_1}^{T_2} c_v(T)dT$$

$$dh = (R + c_v)dT = c_p dT$$

More General Cases

- 2 Methods
  - p=p(v,T), u=u(v,T), h=h(v,T), s=s(v,T)
  - v=v(p,T), u=u(p,T), h=h(v,T), s=s(v,T)



Compute the difference in internal energy between states 1&2

More General Cases

- p=p(T,v)

$$du = c_v dT + \left[T\left(\frac{\partial p}{\partial T}\right)_T - p \right] dv$$

$$u_2 - u_1 = \left\{ \int_{v_1}^{v_\infty} \left[T\left(\frac{\partial p}{\partial T}\right)_T - p \right] dv \right\}_{T=T_1}$$

$$+ \int_{T_1}^{T_2} c_v dT + \left\{ \int_{v_\infty}^{v_2} \left[T\left(\frac{\partial p}{\partial T}\right)_T - p \right] dv \right\}_{T=T_2}$$

→p (T,v) and c_{v_∞} are two complex to be integrated in closed form

→evaluated numerically

$$ds = \left[\left(\frac{\partial p}{\partial T}\right)_v - \frac{R}{v} \right] dv + \frac{R}{v} dv + \frac{c_v}{T} dT$$

$$s_2 - s_1 = R \ln \frac{v_2}{v_1} + \left[\int_{T_1}^{T_2} \frac{c_v}{T} dT \right]$$

$$+ \left\{ \int_{v_1}^{v_\infty} \left[\left(\frac{\partial p}{\partial T}\right)_v - \frac{R}{v} \right]_{T=T_1} dv \right\}$$

$$+ \left\{ \int_{v_\infty}^{v_2} \left[\left(\frac{\partial p}{\partial T}\right)_v - \frac{R}{v} \right]_{T=T_2} dv \right\}$$

$$h = u(v,T) + v\, p(v,T)$$

$$f = u(v,T) - T\, s(v,T)$$

$$g = h(v,T) - T\, s(v,T)$$

More General Cases

- v=v(T,p)

$$ds = \left[\frac{R}{p} - \left(\frac{\partial v}{\partial T}\right)_p\right]dp - \frac{R}{p}dp + \frac{c_p}{T}dT$$

$$s_2 - s_1 = -R\ln\frac{p_2}{p_1} + \left[\int_{T_1}^{T_2} c_p dT\right]_{p=0}$$

$$+\left\{\int_{p_1}^{0}\left[\frac{R}{p} - \left(\frac{\partial v}{\partial T}\right)_p\right]dp\right\}_{T=T_1}$$

$$+\left\{\int_{0}^{p_2}\left[\frac{R}{p} - \left(\frac{\partial v}{\partial T}\right)_p\right]dp\right\}_{T=T_2}$$

$$dh = \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]dp + c_p dT$$

$$h_2 - h_1 = \left\{\int_{p_1}^{0}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]dp\right\}_{T=T_1}$$

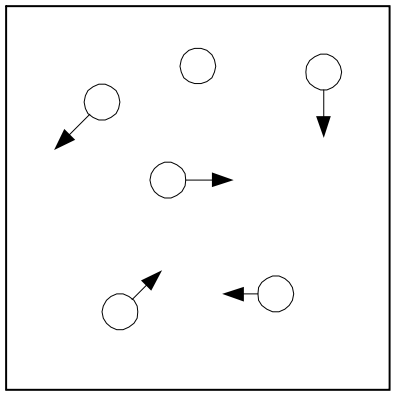
$$+\left[\int_{T_1}^{T_2} c_p dT\right] + \left\{\int_{0}^{p_2}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]dp\right\}_{T=T_2}$$

$$u(p,T) = h(p,T) - p\,v(p,T)$$

$$f(p,T) = u(p,T) - T\,s(p,T)$$

$$g(p,T) = h(p,T) - T\,s(p,T)$$

Special Formulation of the p-v-T Data



van der Waals Equation of State

- suggested by J.D. van der Waals (1873)
- represent the p-v-T characteristics of both L+V
- has a critical state
- approaches the ideal gas behavior as p→0
- the simplest model of a substance explaining the departure from the ideal gas behavior
- a molecular model in which the molecules have a finite volume and exert long range attractive forces on one another

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

b: volume excluded by the dimensions of molecules
a: accounts for attractive forces between molecules

Special Formulation of the p-v-T Data

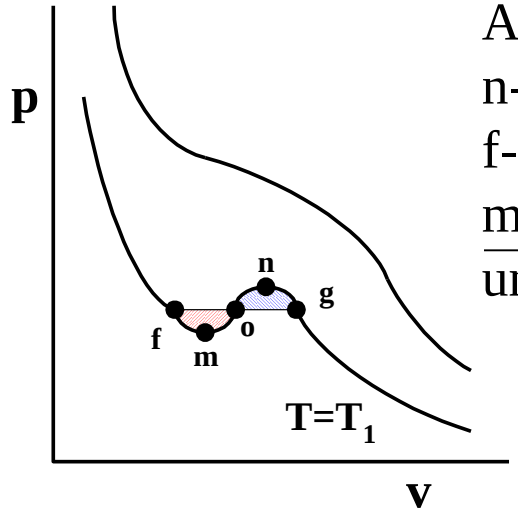
van der Waals Equation of State

- result 1 not all of the physical volume of the container is available to the molecules of the gas 2 the force that the molecules exert on the container wall is reduced by the attractive force exerted on a molecule by its neighbors
- Example

$$\left(\frac{\partial p}{\partial v}\right)_{T_c} = \left(\frac{\partial^2 p}{\partial v^2}\right)_{T_c} = 0$$

$$a = \frac{27}{64}\frac{R^2 T_c^{\,2}}{p_c}, \quad b = \frac{1}{8}\frac{RT_c}{p_c}$$

$$pv^3 - (bp + RT)v^2 + av - ab = 0$$



Area(f-m-o)=Area(o-m-g)
n-g: metastable vapor
f-m: metastable liquid
m-n: gas is mechanically unstable

$$\left(\frac{\partial p}{\partial v}\right)_T > 0$$

Special Formulation of the p-v-T Data

Virial Equation of State

$$\frac{pv}{RT} = 1 + \frac{f_1(T)}{v} + \frac{f_2(T)}{v^2} + \frac{f_3(T)}{v^3} + \cdots\cdots$$

- f_1, f_2, f_3 = functions (T only) 2nd, 3rd, 4th virial coefficient
- first proposed by Clausius as an improvement over the ideal gas model
- virial coefficients account for interaction forces among molecules
- magnitudes of interaction forces depend on the nature of the microscopic model used to describe the forces of interaction

Special Formulation of the p-v-T Data

Generalized Equation of State

First define reduced properties:

$$p_r = \frac{p}{p_c} \quad T_r = \frac{T}{T_c} \quad v_r = \frac{v}{v_c}$$

All substances follow the same equation of state expressed in terms of reduced properties

compressibility factor

$$Z = \frac{pv}{RT} (\neq 1)$$

$$Z = \frac{pv}{RT} = f_1(T_r, v_r) = f_2(T_r, p_r)$$

Summary

Incompressible Fluid

$$v = const. \quad c_v = c_p = c$$

-Not 100% accurate
-Pretty good for subcooled (compressed) liquid
-mechanical / thermal aspects only weakly coupled

$$u_2 - u_1 = \int_{T_1}^{T_2} c(T)dT$$

$$h_2 - h_1 = v(p_2 - p_1) + \int_{T_1}^{T_2} c(T)dT$$

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c(T)}{T}dT$$

Summary

Ideal Gas

$$pv = RT$$

-In fact u_2-u_1 holds regardless of whether v remains constant or not

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v(T)dT$$

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p(T)dT$$

$$s_2 - s_1 = -R\ln\frac{p_2}{p_1} + \int_{T_1}^{T_2}\frac{c_p(T)}{T}dT$$

$$c_p - c_v = R$$

Summary of Thermodynamic Relation

The characteristic thermodynamic functions

Property	Function	Total Derivative
$u = u$	$u = u(s,v)$	$du = Tds - pdv$
$h = h + pv$	$h = h(s,p)$	$dh = Tds + pdv$
$f = u - Ts$	$f = f(T,v)$	$df = -sdT - pdv$
$g = h - Ts$	$g = g(T,p)$	$dg = -sdT + vdp$

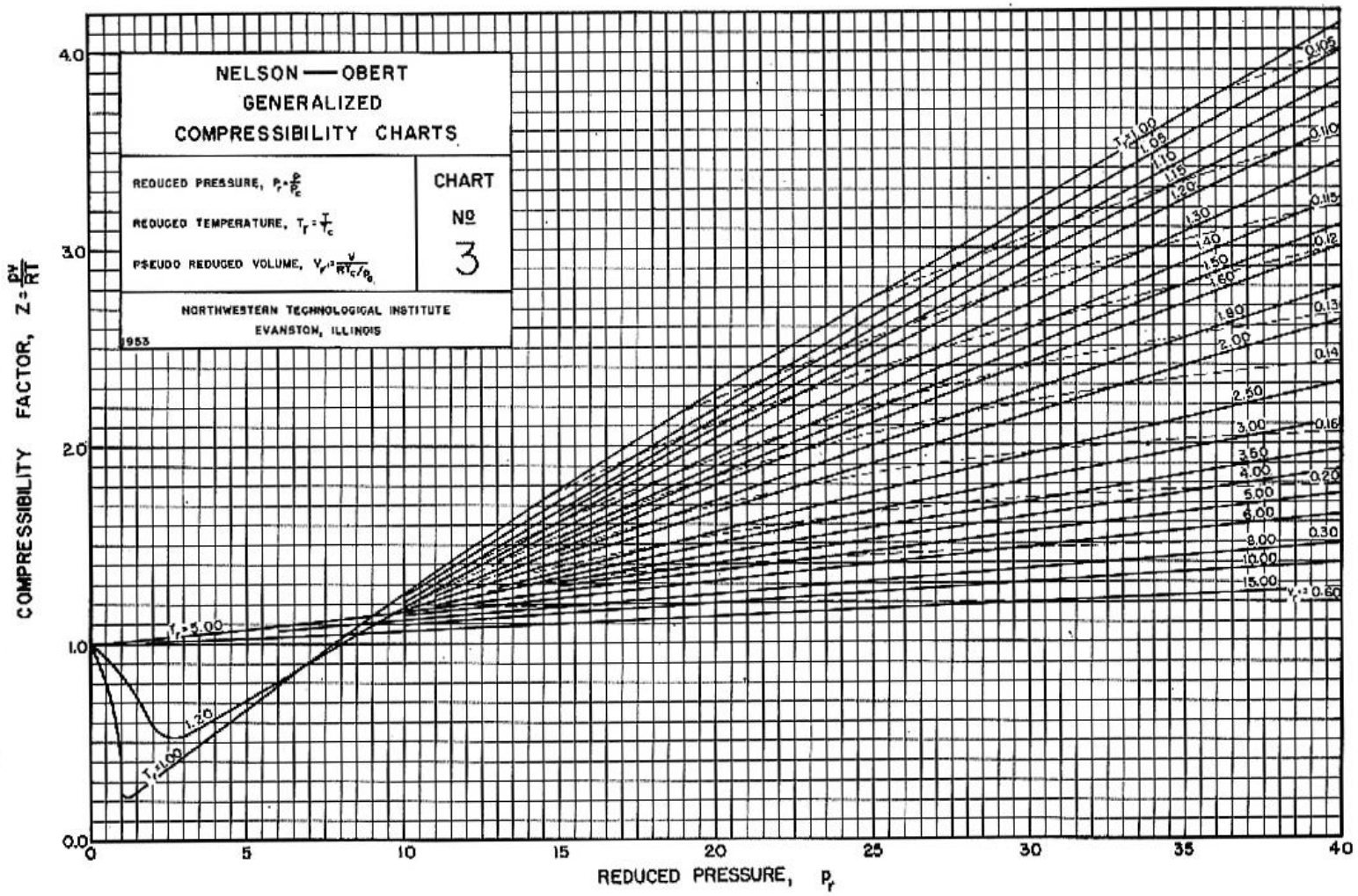
The First partial derivatives of the characteristic functions

$$T \equiv (\partial u/\partial s)_v \equiv (\partial h/\partial s)_p$$
$$-p \equiv (\partial u/\partial v)_s \equiv (\partial f/\partial v)_T$$
$$-s \equiv (\partial f/\partial T)_v \equiv (\partial g/\partial T)_p$$
$$v \equiv (\partial h/\partial p)_s \equiv (\partial g/\partial p)_T$$

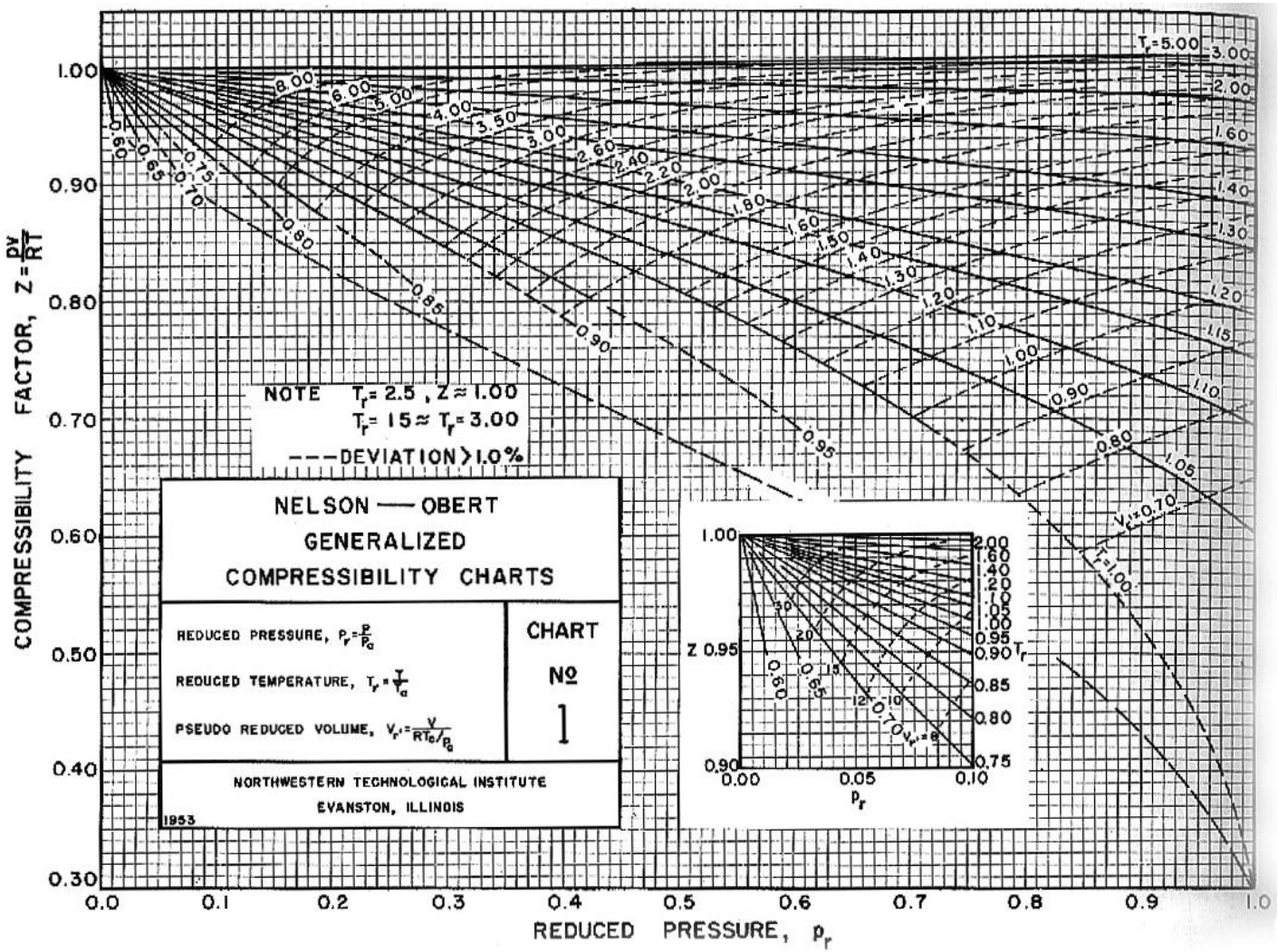
The mixed second partial derivatives of the characteristic functions, the Maxwell relation

$$\frac{\partial^2 u}{\partial s \partial v} = \left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$$
$$\frac{\partial^2 h}{\partial s \partial p} = \left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$$
$$\frac{\partial^2 f}{\partial T \partial v} = -\left(\frac{\partial s}{\partial v}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_v$$
$$\frac{\partial^2 g}{\partial T \partial p} = -\left(\frac{\partial s}{\partial p}\right)_T = \left(\frac{\partial v}{\partial T}\right)_p$$

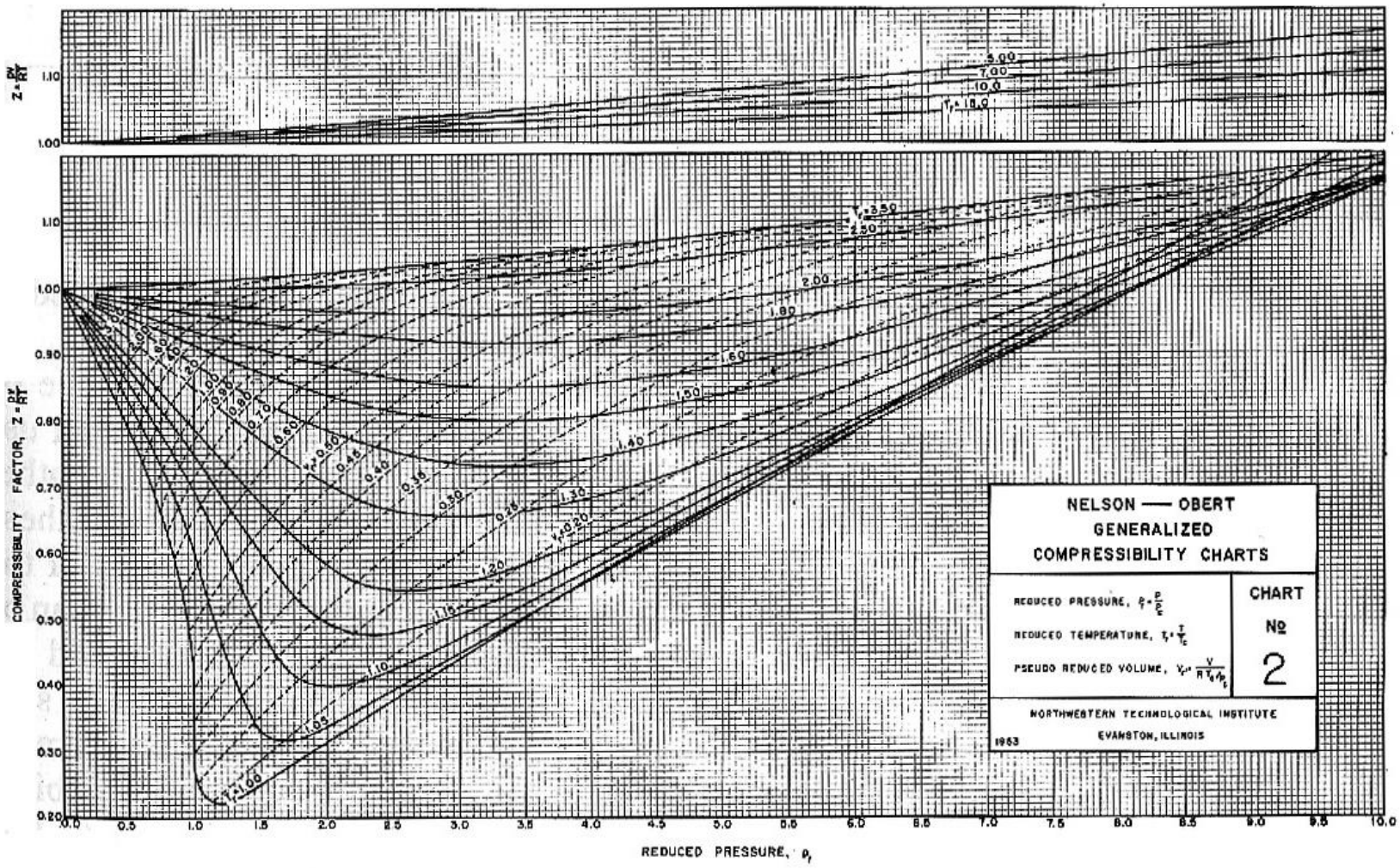
Compressibility Charts



Generalized Compressibility Chart No.1



Aero Thermo Hydro Engineers Nexus Application

Department of Nuclear Engineering, Seoul National University

➢ Generalized Compressibility Chart No.2