CHEMICAL ENGINEERING THERMODYNAMICS
Course no: CHE C311 / F213
1st Semester 2014 – 2015

Phase Behavior of Pure Fluids

Volumetric Properties of Pure Fluids

Contents

- Phase equilibrium of a pure substance (*T - v, P– v and P-T diagrams)*

- Saturation pressure, saturation temperature and vapor pressure curve

- Equations of state

- Concept of an ideal gas

- Real gas: Compressibility

- Empirical Equations of state

- Generalized Co-relations

Phase Relations

Phase

- <mark>Homogeneous distinct form of matter</mark> that is solid, liquid or gas
- Continuous or dispersed
- One phase is separated from another phase by boundary surfaces at which some or all physical properties change in stepwise fashion

Components

- The substance or compounds used to make up the system (in absence of reaction)

Variance

- The number of intensive variables that must be fixed to fix completely all intensive properties of all the phases

Phase Rule

- The phase rule presents the general relationship between the variance (degree of freedom) and the number of components and phases present:

$$F = 2 - \pi + N$$

where π =number of phases   N= no of chemical species   F = degree of freedom

- J W Gibbs deducted it by theoretical reasoning in 1875.

The pure substance

We define a

- Pure substance: a material with homogeneous and invariable composition.

- To elaborate,

  - Pure substances can have multiple phases: an ice-water mixture is still a pure substance.

  - An air-steam mixture is not a pure substance.

  - Air, being composed of a mixture of N_2, O_2, and other gases, is formally not a pure substance. However, experience shows that we can often treat air as a pure substance with little error.

Vapor-liquid-solid phase equilibrium

- Different phases of pure substances can exist in equilibrium with one another
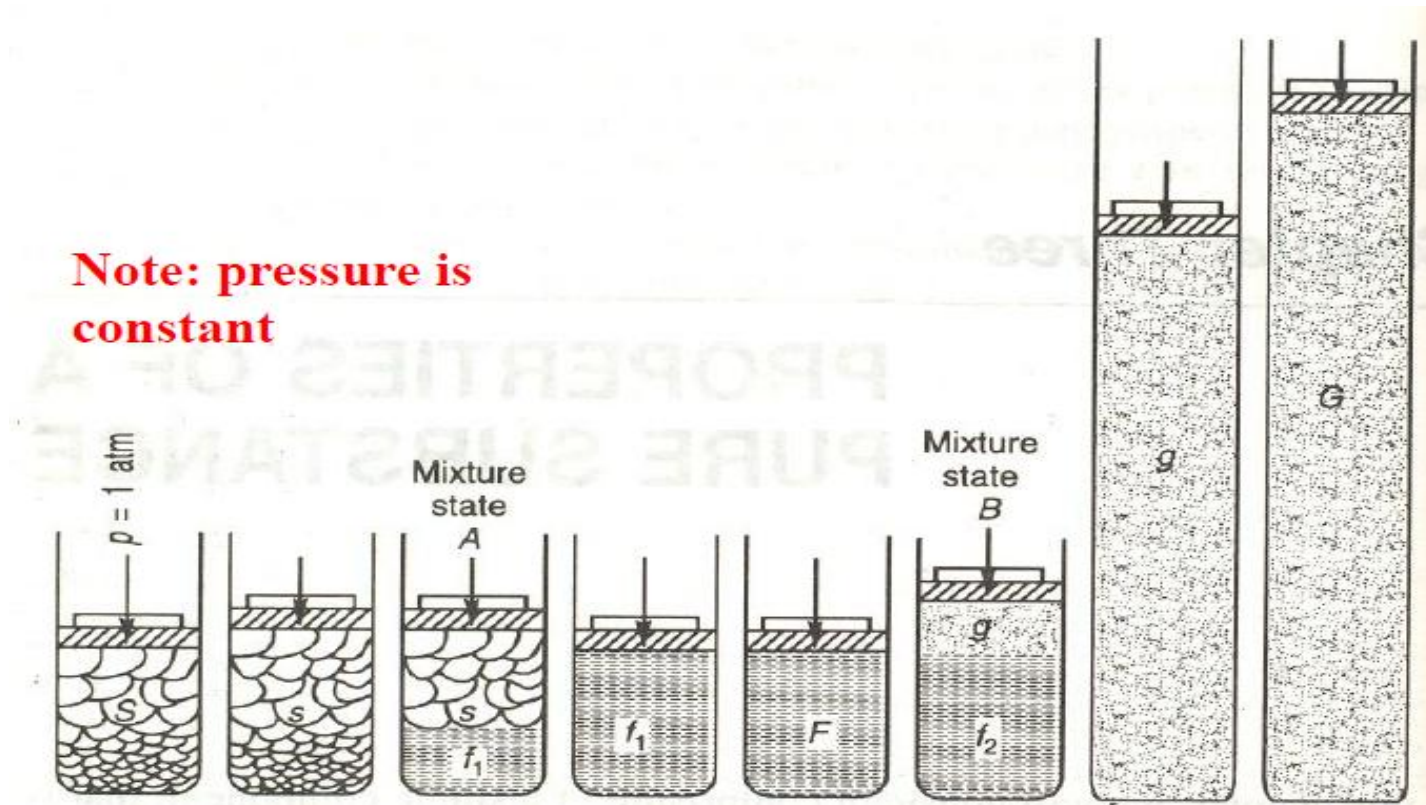
Water in different thermodynamic states

- Sketch of experiment in which heat is added isobarically to ice in a *closed* piston-cylinder arrangement.

- The pressure remains constant at a value of 1 atm. This is an isobaric process.

- The total volume increases slightly as heat is added.

- The temperature of the ice increases significantly as heat is added.

- At a special value of temperature, we have all solid, but cannot add any more heat and retain all solid. We will call this state the *saturated solid state and the corresponding temperature saturation temperature*

Water in different thermodynamic states

- *As we* continue to add heat, The temperature remains constant (this is *isothermal now as well as isobaric).*

- The total volume continues to increase
  - We notice *two phases present: solid and liquid, with a distinct phase boundary.*

- As more heat is added, more vapor appears, all while P = 100 kPa and T = 99.62 ∘C.
  - The liquid is dense relative to the vapor. That is $\rho_f > \rho_g$, where f denotes fluid or liquid and g denotes gas or vapor. Thus, $v_g > v_f$

- At a certain volume, we have all vapor and no liquid, still at P = 100 kPa,T = 99.62 ∘C. We call this state the *saturated vapor state.* As heat is added, we find both the temperature and the volume rise, with the pressure remaining constant. The water remains in the all vapor state.
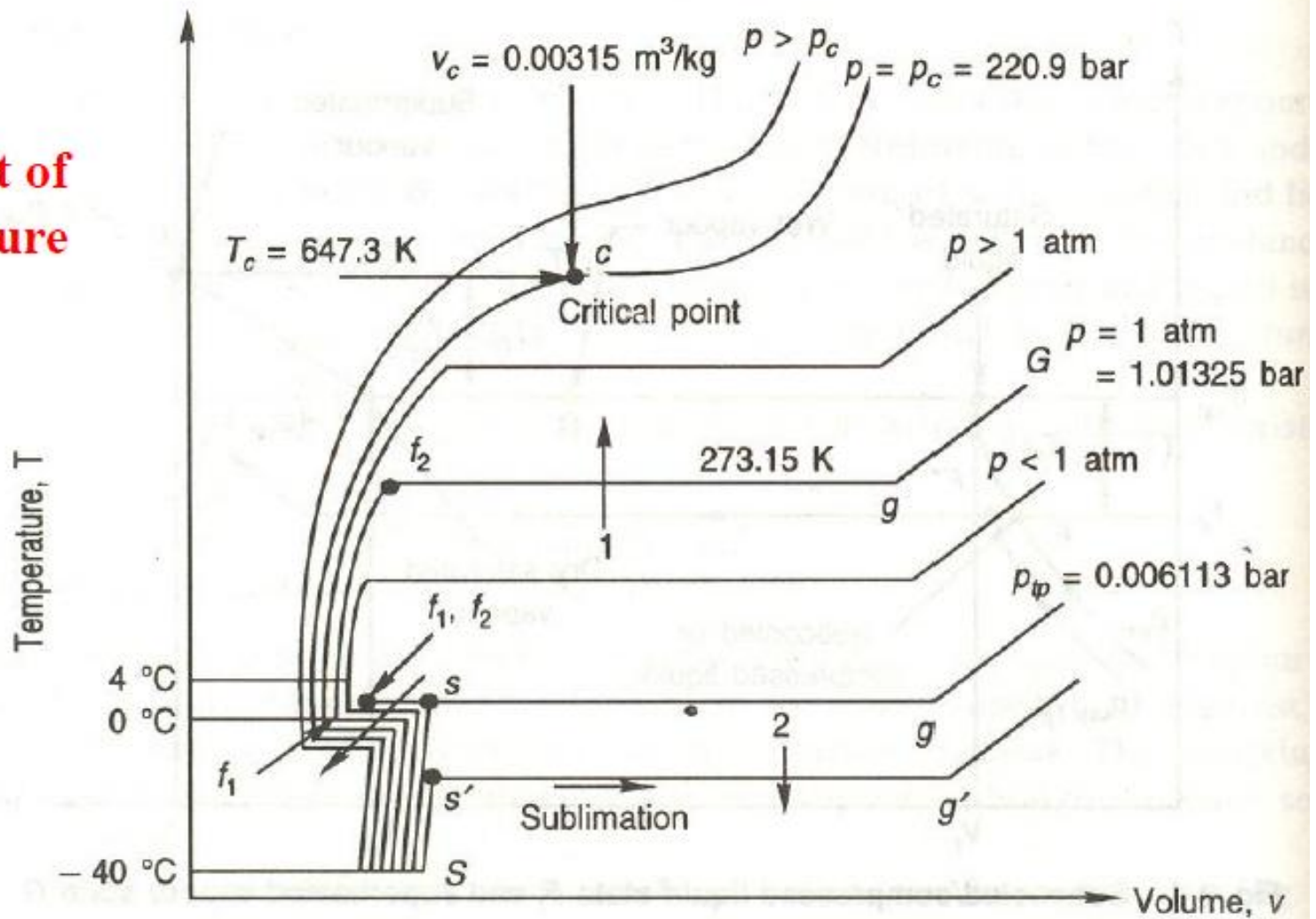
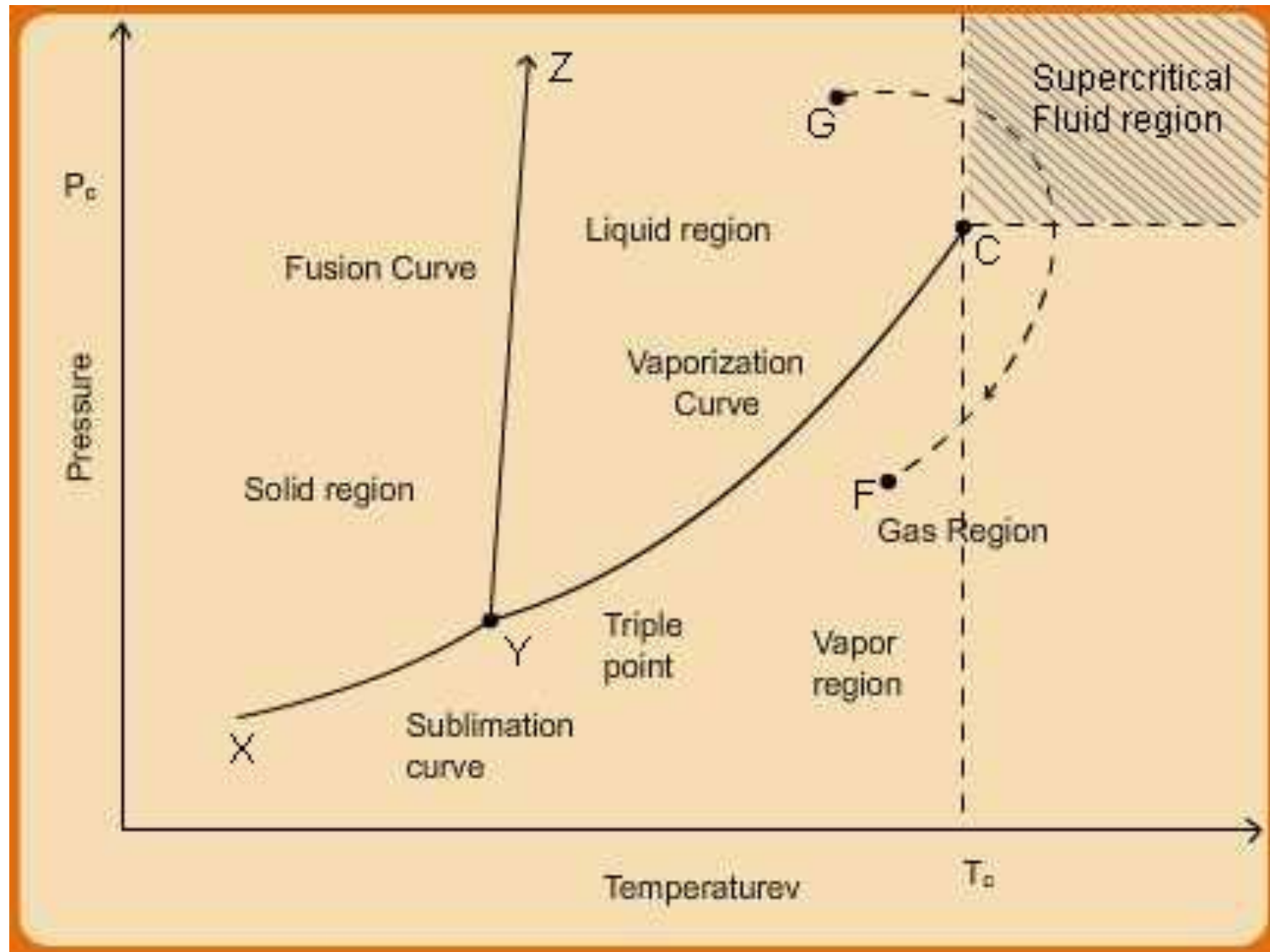# Phase equilibrium of a pure substance on a T-v diagram
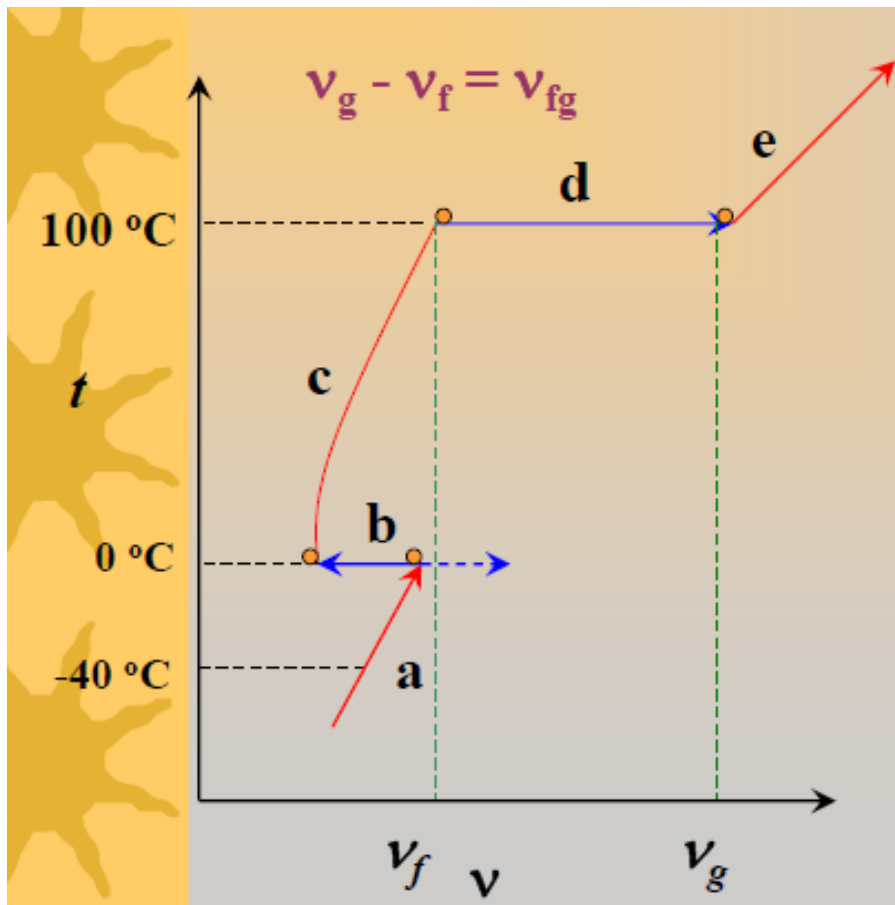
- **Process a:** Ice at −40 °C to ice at 0 °C (no phase change)

- **Process b:** Ice at 0 °C to water at 0 °C (phase change)

- **Process c:** Water at 0 °C to water at 100 °C (no phase change)

- **Process d:** Waterat 100 °C to steam at 100 °C (phase change)

- **Process e:** Steam at 100 °C to higher temperature (no phase change)

- *NOTE: PRESSURE CONSTANT*

Changes of state of water at different pressure on T-v diagram

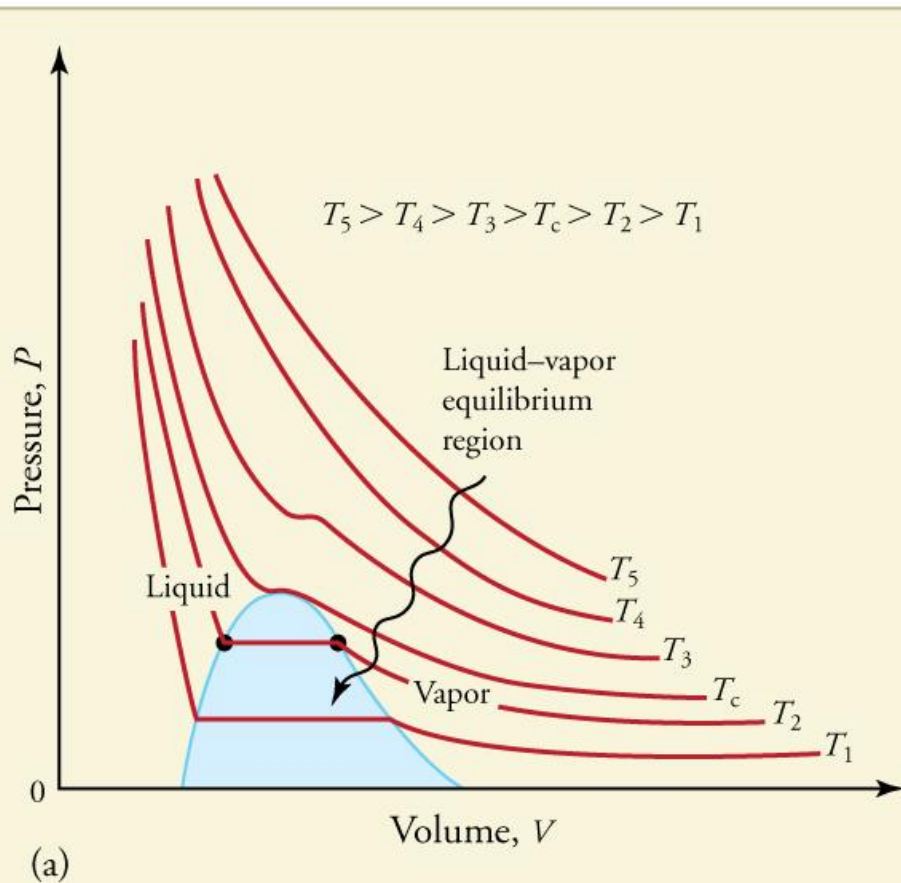# PT diagram for a pure substance

P-v diagram for a pure substance

- On P-v diagram the boundaries (on a PT diagram) becomes areas, regions where two phases exists in equilibrium
- The figure shows P-v diagram with 5 isotherms superimposed
- The line labeled T_1 and T_2 are subcritical regions
- The line labeled T_3 is critical region
- The line labeled T_4 and T_5 are subcritical regions

Equation of State

Properties can be correlated through a functional relation of the form

f(P, v, T) = 0

This is called the equation of state

They are put in 3 categories:

Empirical: Curve fitting data from experiments. Most accurate, but could be limited by range

Generalized: Makes use of Z or compressibility factor

Theoretical: Derived based on kinetic theory and statistical thermodynamics

Equation of state

- An equation of state may be solved for any one of the three quantities P, V, or T as a function of the other two.
  - For example consider V as function of T and P,

$$V = V(P, T)$$

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

- Here defining two new terms
  - **Volume expansivity**

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

  - **Isothermal Compressibility**

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

Equation of state

The generic equation of state can be written as

$$\frac{dV}{V} = \beta.dT - \kappa.dP$$

For liquids, which are relatively incompressible, the factors β *and* κ *are generally show an weak dependence on T and P and hence averaged values of these parameters may be used for* estimating the liquid volume at any temperature using the following integrated form of the equation

$$\ln\frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1)$$

PVT Relation : Ideal gas behavior

In isotherm for gases and vapors V decreases as P increases, and can be present as power series in P for an isotherm

PV = a + b P + c P^2 +....

- This is shown experimentally by measurement of volumetric data, the limiting value of PV as P→0 is same for all gases

$$(PV)^* = f (T) = a$$

$(PV)_t^* = 22{,}711.8 \text{ cm}^3 \text{ bar mol}^{-1}$

$T = 273.16 \text{ K} = \text{triple point of water}$
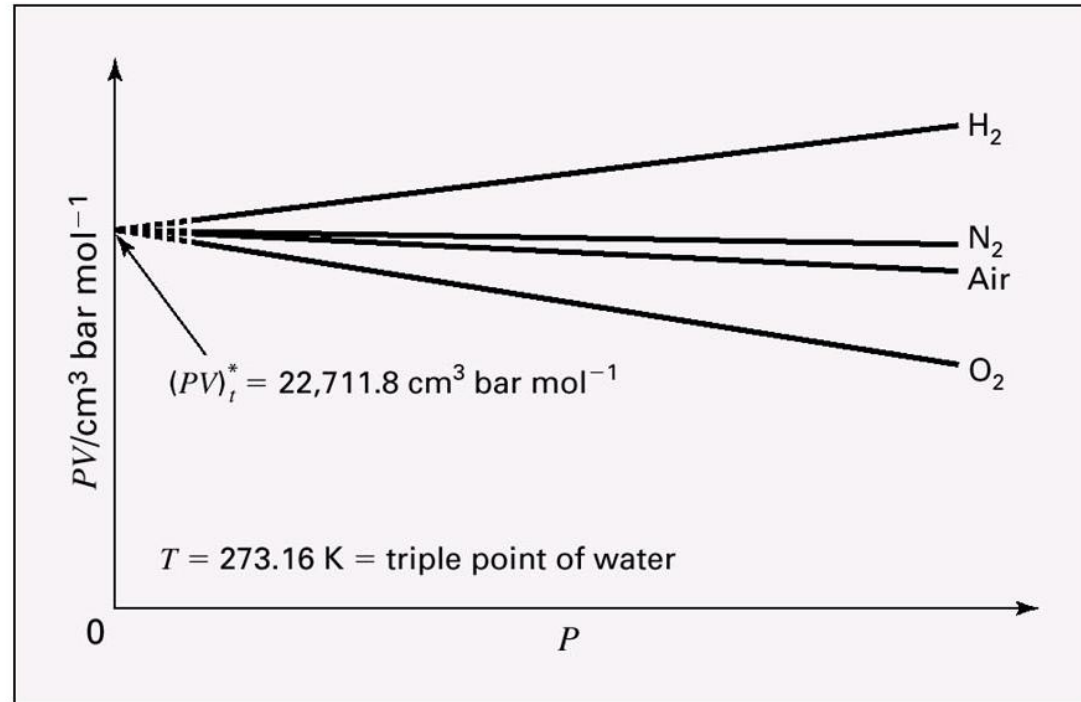
Ideal-Gas Temperature

- Considering (PV)* proportional to T with proportionality constant *R*

$$(PV)^* = f(T) = R\,T$$

- This forms a basis for absolute temperature scale (Kelvin scale)
  - Assign the value 273.16 K to the temperature of the triple point of water (denoted by subscript t)

$$(PV)_t^* = R \times 273.16 \text{ K}$$

$$T = 273.16 \frac{(PV)^*}{(PV)_t^*}$$

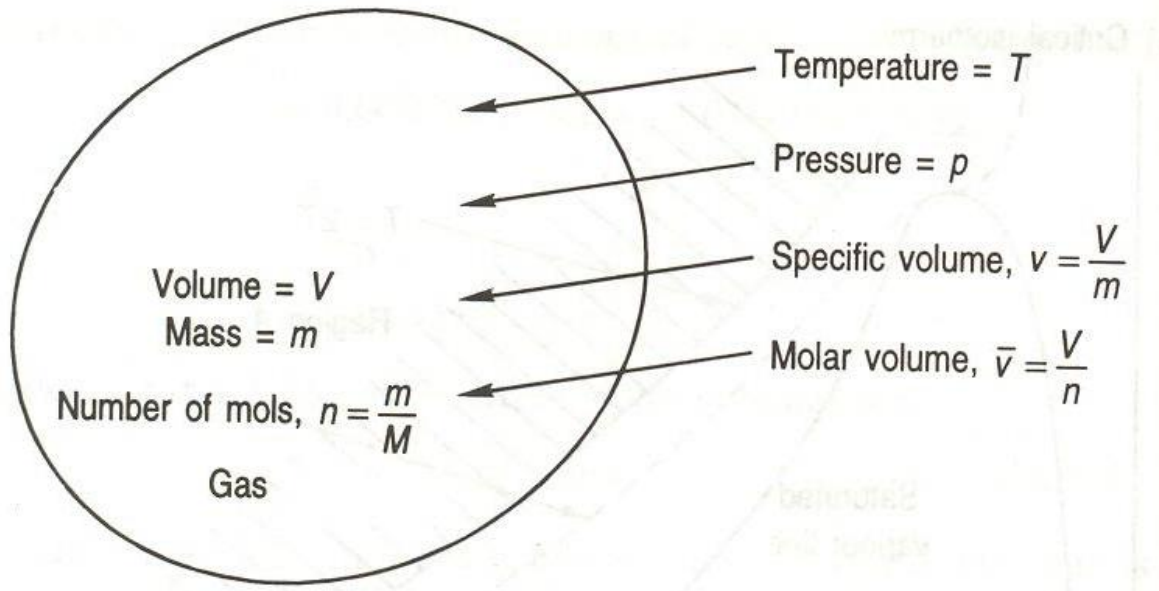Above equation establishes the ideal-gas temperature scale

Universal Gas Constant

- The proportionality constant R (in ideal gas equation) is called the universal gas constant

- It's numerical value is determined using: $(PV)_t^*$ = R x 273.15 K, from experimental PVT data;

$$R = \frac{(PV)_t^*}{273.16K}$$

- Since PVT data can not be taken at zero pressure, data taken at finite pressures are extrapolated to a zero pressure state

  - Accepted value of (PV)* is 22711.8 cm^3 bar/mol, leads to following value of R = 8.31447 J/(mol.K)

  - Through unit conversions R may be expressed in various units

Ideal Gas Law

Temperature = T

Pressure = p

Specific volume, $v = \dfrac{V}{m}$

Molar volume, $\bar{v} = \dfrac{V}{n}$

Volume = V
Mass = m
Number of mols, $n = \dfrac{m}{M}$
Gas

Unit mass basis
$$Pv = RT$$
Total mass basis
$$PV = mRT$$
Total mole basis
$$PV = nR'T$$
Unit mole basis
$$Pv' = R'T$$

Note R is specific gas constant (J / kg. K)
R' is the universal gas constant = R x M
where M is molecular weight
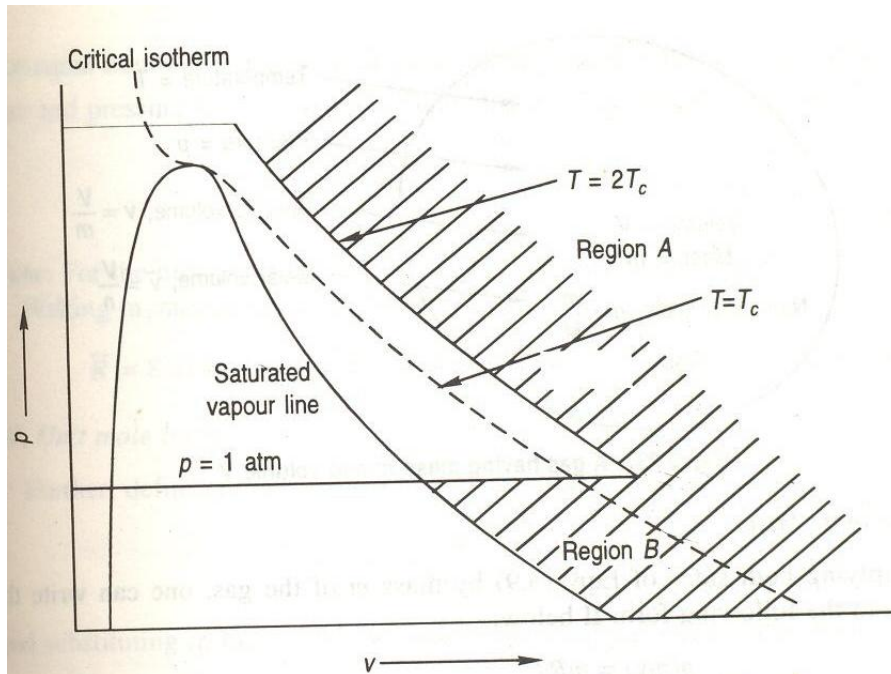**R'= 8314.4 J / kmol.K**

Concept of an ideal gas

Fig. 3.22   Regions A and B of ideal gas behaviour

- Region A: High temperature in excess of critical temperature
- Region B: Low pressure
- At a certain point both intersect
- Behavior of gases under these conditions is characterized by ideal gas behavior

Concept of an ideal gas

An ideal gas is one in which

- Intermolecular forces of attraction or repulsion are negligible

- Molecules are perfectly elastic and rigid. No loss of momentum after collisions with container walls

- Volume occupied by gas molecules is negligible as compared to the container volume

- The macroscopic behavior is characterized by:

$$PV = RT \quad \text{and} \quad U = U(T)$$

Implied Property Relation for an Ideal Gas

- Heat Capacity at constant volume, for an ideal gas is a function of temperature only

$$\mathbf{d}u = c_v(T)\,\mathbf{d}T$$

$$\Delta u = u_2 - u_1 = \int c_v(T)\,\mathrm{d}T$$

- Heat Capacity at constant pressure, for an ideal gas is also a function of temperature only

$$\mathbf{d}h = c_P(T)\,\mathbf{d}T$$

$$\Delta h = h_2 - h_1 = \int c_P(T)\,\mathrm{d}T$$

A useful relation between C_p and C_v for an ideal gas comes

$$C_p - C_v = R$$

Equations for Process Calculations for Ideal Gases

- The work for mechanically reversible closed system process is given by $\delta W = -P\,dV$

- For an ideal gas in any closed system process, first law ($\delta Q + \delta W = dU$) can be written as

$$\delta Q = C_v dT + PdV$$

For ideal gas $P = RT/V$

$$dQ = C_V dT + RT\frac{dV}{V} \qquad\qquad dW = -RT\frac{dV}{V}$$

With $V = RT/P$ and $C_p - C_v = R$

$$dQ = C_P dT - RT\frac{dP}{P} \qquad\qquad dW = -RdT + RT\frac{dP}{P}$$?

Isothermal Process

$$\Delta U = \Delta H = 0$$

$$Q = -W = RT\frac{\ln V_2}{V_1} = -RT\frac{\ln P_2}{P_1} \quad \text{(Const T)}$$

Isobaric Process

$$\Delta U = \int C_v(T)\,dT \quad \text{and} \quad \Delta H = \int C_P(T)\,dT$$

$$Q = \int C_P(T)\,dT \quad and \quad W = -R(T_2 - T_1)$$

Isochoric Process

$$\Delta U = \int C_v(T)\,dT \quad \text{and} \quad \Delta H = \int C_P(T)\,dT$$

$$Q = \int C_v(T)\,dT \quad and \quad W = 0$$

Adiabatic Process

- For an adiabatic process, there is no heat transfer between the system and surroundings; $\delta Q = 0$

$$PV^\gamma = \text{Constant} \qquad (\text{where } \gamma = C_p/C_v)$$

$$dW = dU = C_v dT$$

$$W = C_V \Delta T = \frac{R\Delta T}{\gamma - 1}$$

$$W = \frac{RT_2 - RT_1}{\gamma - 1} = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

T_2 and V_2 are usually unknown, eliminate V_2

$$W = \frac{P_1 V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right] = \frac{RT_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right]$$

Polytropic Process

- Polytropic process suggest a model of some versatility
- With δ constant, it is defined as a process represented by empirical equation:

$$PV^{\delta} = \text{constant}$$

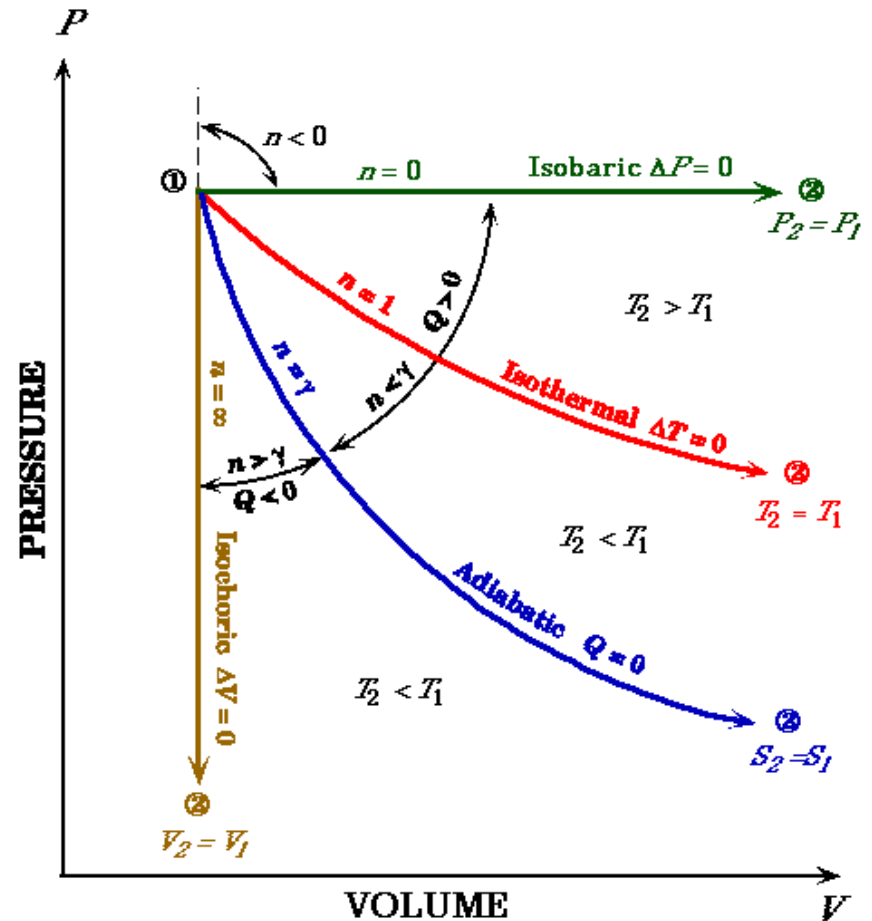For an ideal gas equations

$$TV^{\delta-1} = \text{constant} \qquad TP^{(1-\delta)/\delta} = \text{constant}$$

$$W = \frac{RT_1}{\delta - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right]$$

$$Q = \frac{(\delta - \gamma)RT_1}{(\delta - 1)(\gamma - 1)}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right]$$

Polytropic Process

- Isobaric Process $\delta=0$

- Isothermal process $\delta=1$

- Adiabatic process $\delta=\gamma$

- Isochoric process $\delta = \infty$

Irreversible Process

- So far, relations are developed for reversible closed system processes for ideal gases, however property change ΔU and ΔH are valid for ideal gases regardless of process.

- The work for an *irreversible* process is calculated by a two-step procedure:

  - First, W is determined for a mechanically reversible process accomplishing same change of state as irreversible process.

  - Second, this result is multiplied or divide by an efficiency to give the actual work.

  - If the process produces work, the absolute values of reversible work should be multiplied by efficiency. If the process requires work, the value of the reversible work should be divided by an efficiency

Real Gases & Compressibility

- Deviation from ideality occurs due to assumptions that are not strictly valid
  - Volume of gas is comparable to vessel volume and also intermolecular attraction cannot be ignored
- Several equations of state exist accounting for this deviation
- One term used to signify departure from ideality is named compressibility factor **Z** *or* just compressibility

$$Z \equiv \frac{PV}{RT}$$

Virial Equation of State

- For sophisticated calculations fitting equations with more adjustable parameters are used. These are called virial equations or Virial Expansions

$$Z = 1 + B'P + C'P^2 + D'P^3 + \ldots\ldots$$

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots$$

where B (or B') and C (or C') are the temperature dependent second and third virial coefficients

- The coefficients B',C' are related to B,C as:

$$B' = \frac{B}{RT}, \qquad C' = \frac{C - B^2}{(RT)^2}$$

Virial EoS

- The virial equations are firmly based on statistical mechanics, which provides physical significance to the virial coefficients

- For the expansion in $1/V$, the term B/V account for two body interaction between pair of molecules; the C/V^2 term account for three-body interactions, etc.

- The contributions to Z of successively higher-ordered terms decreases rapidly.

- Applicable for practical purpose, if two or three terms suffice for close approximations to the value of the series.

Application of the Virial Equations

- With sufficient number of coefficients, the virial equation can give excellent vapor-phase predictions, but it is not applicable to liquid phase

- Figure shows compressibility factor graph for methane

- All isotherm originate at the value of $Z = 1$ for $P = 0$, are nearly straight line at low pressures, thus a tangent to isotherm at $P = 0$, is good approximation
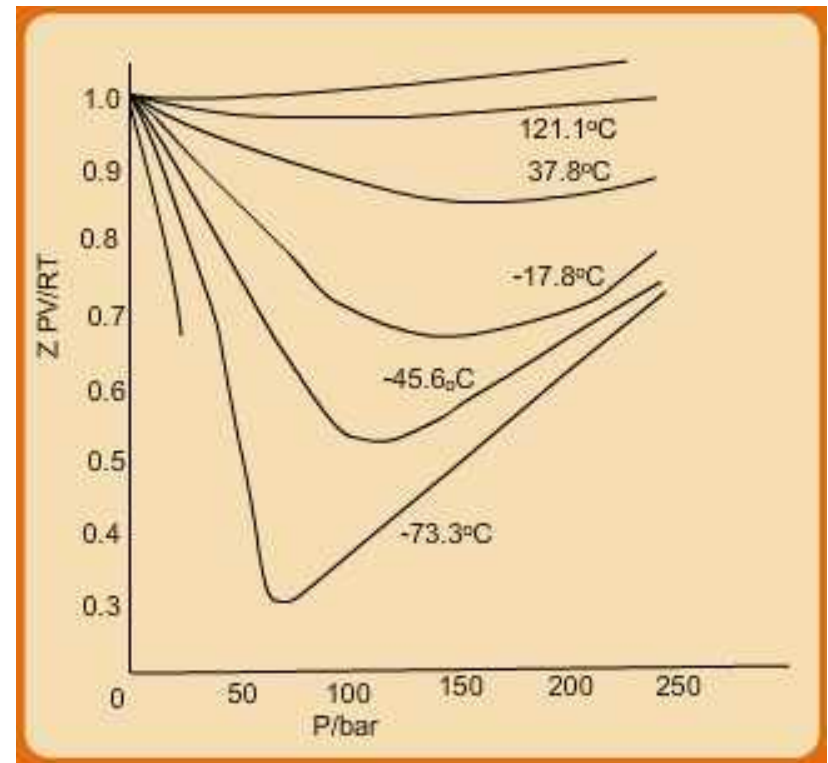
$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT} = 1 + B'P$$

Application of the Virial Equations

- For pressures above the range of applicability with two term virial expansion, but below the critical pressure, the virial equation truncated to three terms provides excellent results

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}$$

  - The equation can be directly solve for pressure, but is cubic in volume
  - Values for B and C depends on substance and temperature.
  - Data for B and C can be found in literature

- Virial expansion with more than three terms are unwieldy and uncommon

- **Benedict/Webb/Rubin equation:** Complex but used in petroleum and natural-gas industries for light HC's and other gases

Cubic Equations of State

- Cubic equations are the simplest equations to represents the behavior of both liquids and gases

- Several empirical "cubic" equations have been invented to relate P to V and T for non-ideal gases.

- General class of equations of state:

$$P = \frac{RT}{V-b} - \frac{\theta(V-\eta)}{(V-b)(V^2 + \kappa V + \lambda)}$$

  - **van der Waals**
  - **Redlich Kwong**
  - **Peng Robinson**
  - **Soave Redlich Kwong**

van der Waals EoS

One of the earliest and simplest EoS (by J.D. van der Waals in 1873)

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

At small specific volumes, the molecules occupy considerable space, result in lesser free volume

At small specific volumes, the attractive term is significant and proportional to density square

Here a and b are positive constants

The values of a and b are different for different substance, but they are related in <u>the same way</u> to each substance's Critical properties T_c and P_c

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

Isotherm as given by Cubic EoS

– P-V diagram showing three isotherms

– Superimposed dome showing states of saturated liquid and vapor

– <mark>Cubic EoS have three volume roots</mark>

– Physical meaningful values of V are real, positive and greater than constant b

– The smallest root is a 'liquid' and the largest is the 'vapor' root, the third root lying in between is of no use.
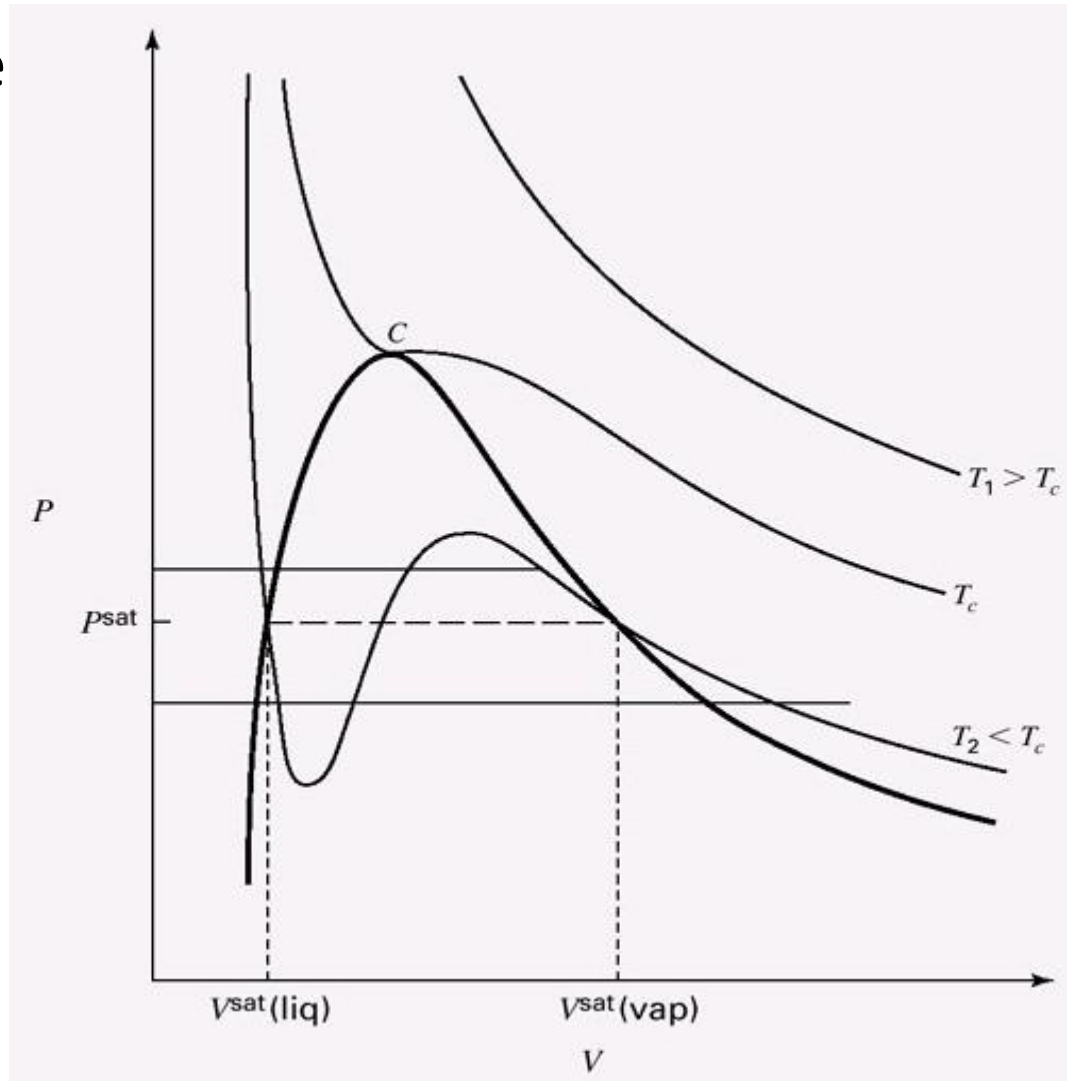
A Generic Cubic EoS

- After the van der Waals equation, several hundred cubic equations has been proposed

- All are the special case of the general equation

$$P = \frac{RT}{V-b} - \frac{\theta(V-\eta)}{(V-b)(V^2 + \kappa V + \lambda)}$$

where, b, θ, κ, η, λ are the parameters which depends on temperature and composition (for mixture)

- An important class of EoS results with assigning these parameters as: $\eta = b$, $\theta = a(T)$, $\kappa = (\epsilon + \sigma)b$, $\lambda = \epsilon\sigma\, b^2$

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\varepsilon b)(V+\sigma b)} \qquad ..(3.42)$$

- For a given equation,

  - ϵ and σ are pure numbers, the same for all substances

  - Parameters $a(T)$ and b, are substance dependent

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\varepsilon b)(V+\sigma b)} \qquad ..(3.42)$$

$$a(T) = \psi \frac{\alpha(T_r)R^2 T_c^2}{P_c} \qquad (3.45) \qquad\qquad b = \Omega \frac{RT_c}{P_c} \qquad (3.46)$$

Parameter Assignments for Equations of State

Eq. of State	$\alpha(T_r)$	σ	ϵ	Ω	Ψ	Z_c
vdW (1873)	1	0	0	1/8	27/64	3/8
RK (1949)	$T_r^{-1/2}$	1	0	0.08664	0.42748	1/3
SRK (1972)	$\alpha_{\mathrm{SRK}}(T_r;\omega)^\dagger$	1	0	0.08664	0.42748	1/3
PR (1976)	$\alpha_{\mathrm{PR}}(T_r;\omega)^\ddagger$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724	0.30740

$$^\dagger\alpha_{\mathrm{SRK}}(T_r;\omega) = \left[1 + (0.480 + 1.574\,\omega - 0.176\,\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$$

$$^\ddagger\alpha_{\mathrm{PR}}(T_r;\omega) = \left[1 + (0.37464 + 1.54226\,\omega - 0.26992\,\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$$

Peng-Robinson

- This equation is **nice balance of accuracy vs complexity**

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \qquad (3.47)$$

- The a and b parameters are related empirically to the critical properties:

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T) \qquad b = 0.07780 \frac{RT_c}{P_c}$$

- The α parameter is **temperature dependent** and also **depends on** another tabulated, molecule specific parameter, called the **"acentric factor"**

Solving for volume root

- The complex equations can be solved using spreadsheet
- Because of the way the equation is written, finding the volume when T and P are given requires trial and error calculations (root finding)
- Below T_c – care must be taken to make sure that the correct root is obtained
  - There is one root near the ideal gas law (The large volume)
    - In Excel, make the first guess the ideal gas law – program will find the "vapor root"
      - There is one root near b (liquid root)
      - There is one root near 3xb (physically meaningless root the middle one)
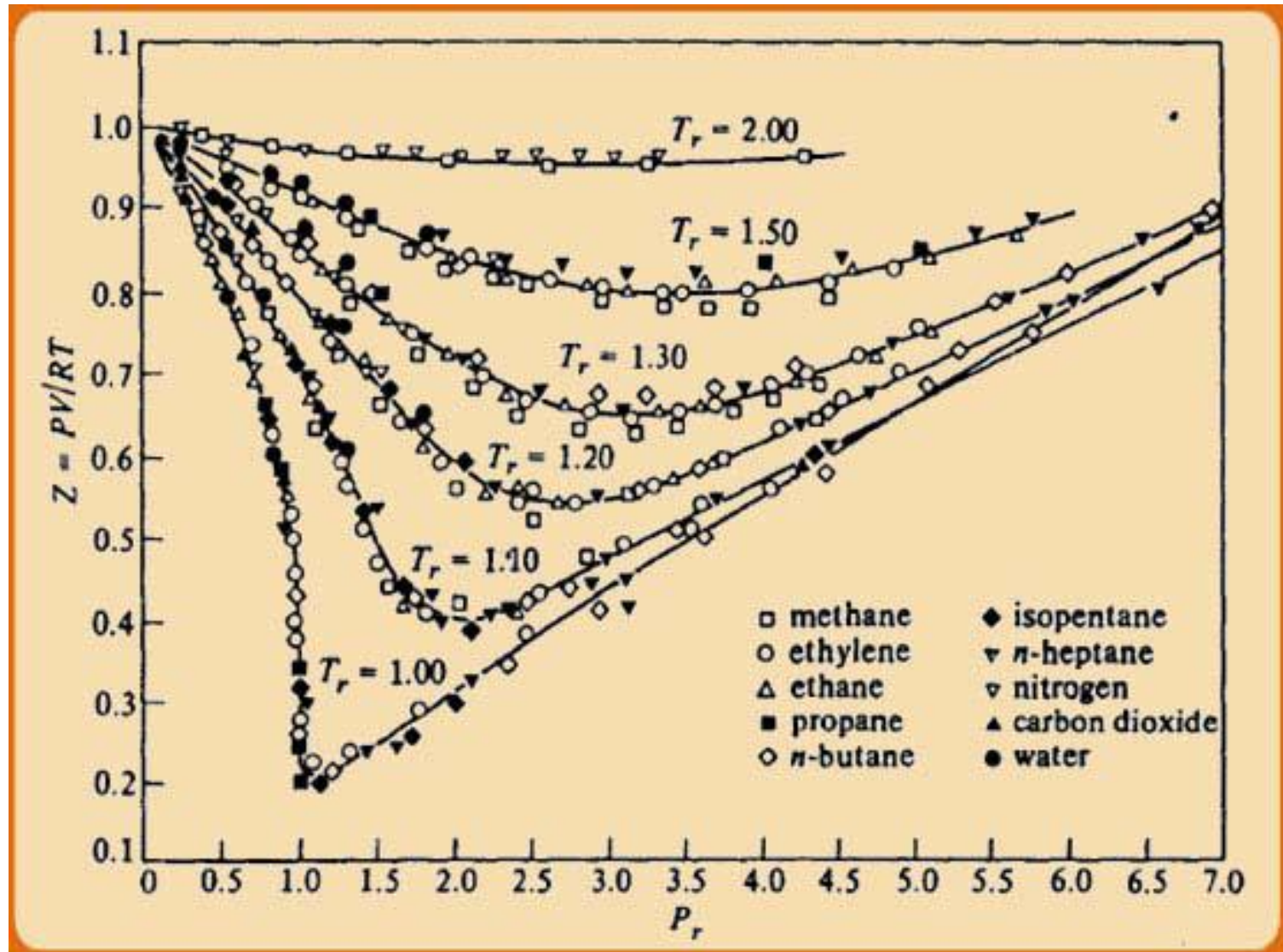
Real gas & Compressibility

- Each of the EoS can be written in the form

$$z^3 + \alpha.z^2 + \beta.z + \gamma = 0$$

- *Z being in terms of P, T and v is a property*

- *An equation of state can be written having form z=f(P, T) and can be plotted keeping T constant (compressibility chart)*

- Different charts will be needed for different gases. One single chart can however be developed based on **Law of corresponding states** when pressure temperature are expressed in dimensionless form using **P_r ; T_r**

Generalized Compressibility chart

Theorem of Corresponding States

- Experimental observations proves that,when correlated at dimensionless reduced temperature (T_r) and reduced pressure (P_r), compressibility factor Z for different fluids exhibits similar behavior.

$$T_r = T / T_c \qquad P = P / P_c$$

- **If two substance have the same reduced pressure and reduced temperature they have approximately the same compressibility factor and all deviate from ideal-gas behavior to about the same degree**

- Corresponding – state correlations of Z based on this theorem are called *two-parameter* correlations as they use two parameters T_c and P_c.

Acentric Factor

- Two-parameter correlation are closely exact for simple fluid but not complex fluids.

- To address this gap Pitzer and coworkers introduced <mark>a third corresponding-states parameter, characteristic of molecular structure, more particularly the "degree of sphericity" of the molecule</mark>; the most widely used one is acentric factor 'ω'

$$\text{Acentric factor } \omega \equiv -1 - \log (P_r^{sat})_{Tr = 0.7}$$

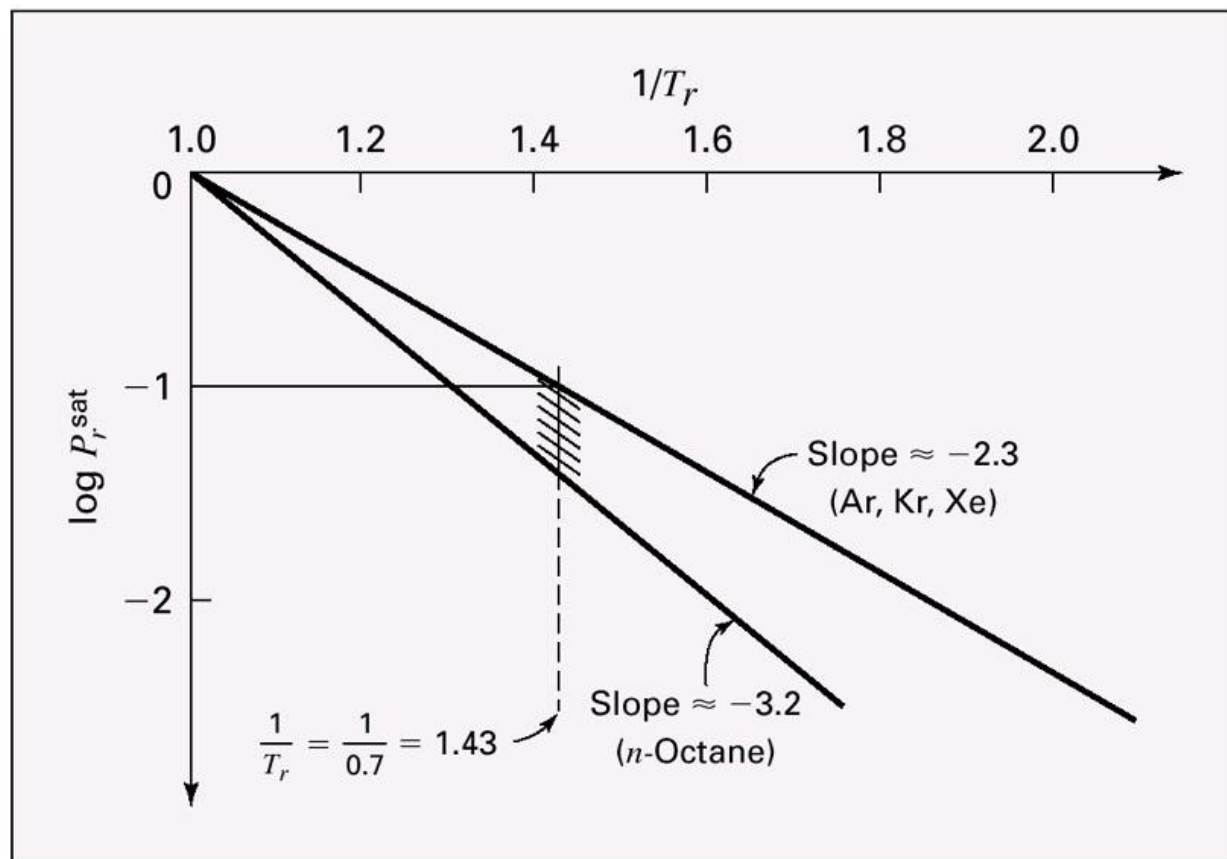Here $(P_r^{sat})_{Tr=0.7}$ is the vapor pressure of fluid at $Tr=0.7$

$$Z = Z (P_r, T_r, \omega)$$

Three-parameter theorem of corresponding states:

All fluids having the same value of ω when compared at the same T_r and P_r, have the same value of Z, and all deviate from ideal-gas behavior to about the same degree

Figure 3.12: Approximate temperature dependence of the reduced vapor pressure.

Generalized Compressibility factor Approach to EOS: **Pitzer Correlations**

According to this approach, compressibility factor is decomposed as follows: $Z = Z^0 + \omega Z^1$

Where Z^0 and Z^1 are function of both T_r and P_r

- *When $\omega = 0$ (for simple fluid), second term disappears and Z^0 becomes identical with Z*

Lee and Kesler Correlation:

- *Development is based on modified Benedict/Webb/Rubin EoS*
- *It takes the form of tables which contains Z^0 and Z^1 as functions of T_r and P_r*
- *The Lee/Kesler correlation provides reliable results for nonpolar/ slightly polar substances*

Pitzer Correlations for the Second Virial Coefficient

Accurate representation of Z^0 and Z^1 includes complex equations.

However using simplest form of the virial equation one can approximate the analytical expression to these functions for limited range of pressures.

$$Z = 1 + \frac{BP}{RT} = 1 + \hat{B}\frac{P_r}{T_r}$$

where $\hat{B}$ is a reduced second virial coefficien t,

given by $\hat{B} = \dfrac{BP_c}{RT_{cr}}$

Pitzer Correlations for the Second Virial Coefficient

Thus, Pitzer and coworkers proposed a second correlation, which yield value for $\hat{B}$

$$\hat{B} = B^0 + \omega B^1 \qquad (3.63)$$

$$Z = 1 + B^0 \frac{P_r}{T_r} + \omega B^1 \frac{P_r}{T_r} = Z^0 + \omega Z^1$$

Above comparison provides the following identities:

$$Z^0 = 1 + B^0 \frac{P_r}{T_r} \qquad \text{and} \qquad Z^1 = B^1 \frac{P_r}{T_r} \qquad (3.64)$$

B^0 and B^1 are functions of T_r only and represented as:

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad (3.65) \qquad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \qquad (3.66)$$
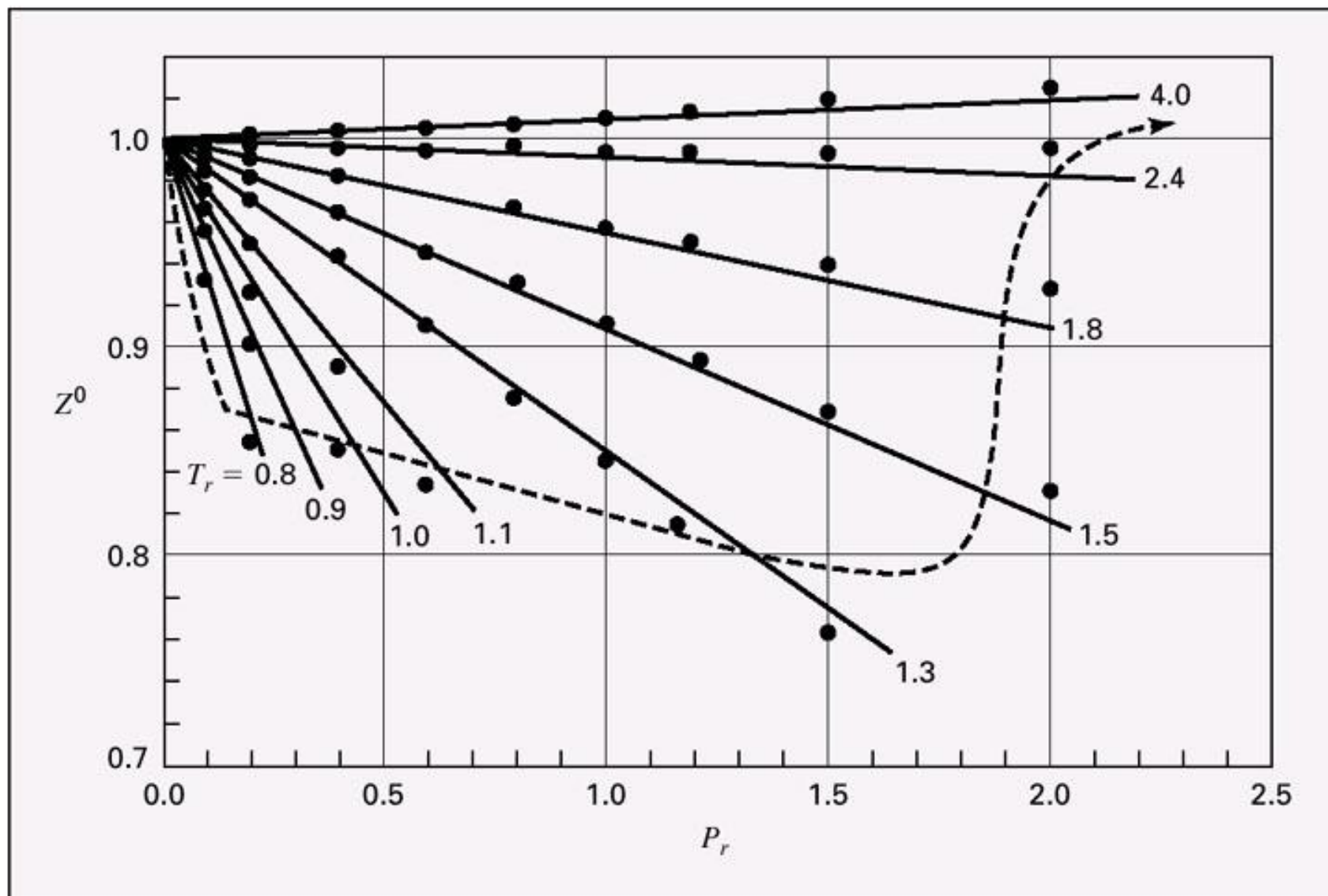
Figure 3.14: Comparison of correlations for Z^0. The virial-coefficient correlation is represented by the straight lines; the Lee/Kesler correlation, by the points. In the region above the dashed line the two correlations differ by less than 2%.

Illustration

Determine the molar volume of n-butane at 510 K and 25 bar by

    a) The ideal-gas equation

    b) The generalized compressibility-factor correlation

<u>Data:</u> T_c = 425.1 K, P_c = 37.96 bar, ω = 0.20

P_r	0.6	0.8
T_r	1.2	1.2
z^0	0.8779	0.8330
z^1	0.326	0.0499

<u>Answer:</u> a) V^{ig} = 1696.1 cm³/mol

             b) V = 1480.7 cm³/mol

Generalized Correlations for Liquids

- **Molar volumes of saturated liquids**
  - Proposed by Rackett

$$V^{Sat} = V_c Z_c (1 - T_r)^{2/7}$$

- **Lydersen, Greenkorn and Hougen**
  - Two parameter corresponding states correlation
  - Correlate reduced density as function of T_r and P_r

$$\rho_r \equiv \frac{\rho}{\rho_c} = \frac{V_c}{V}$$

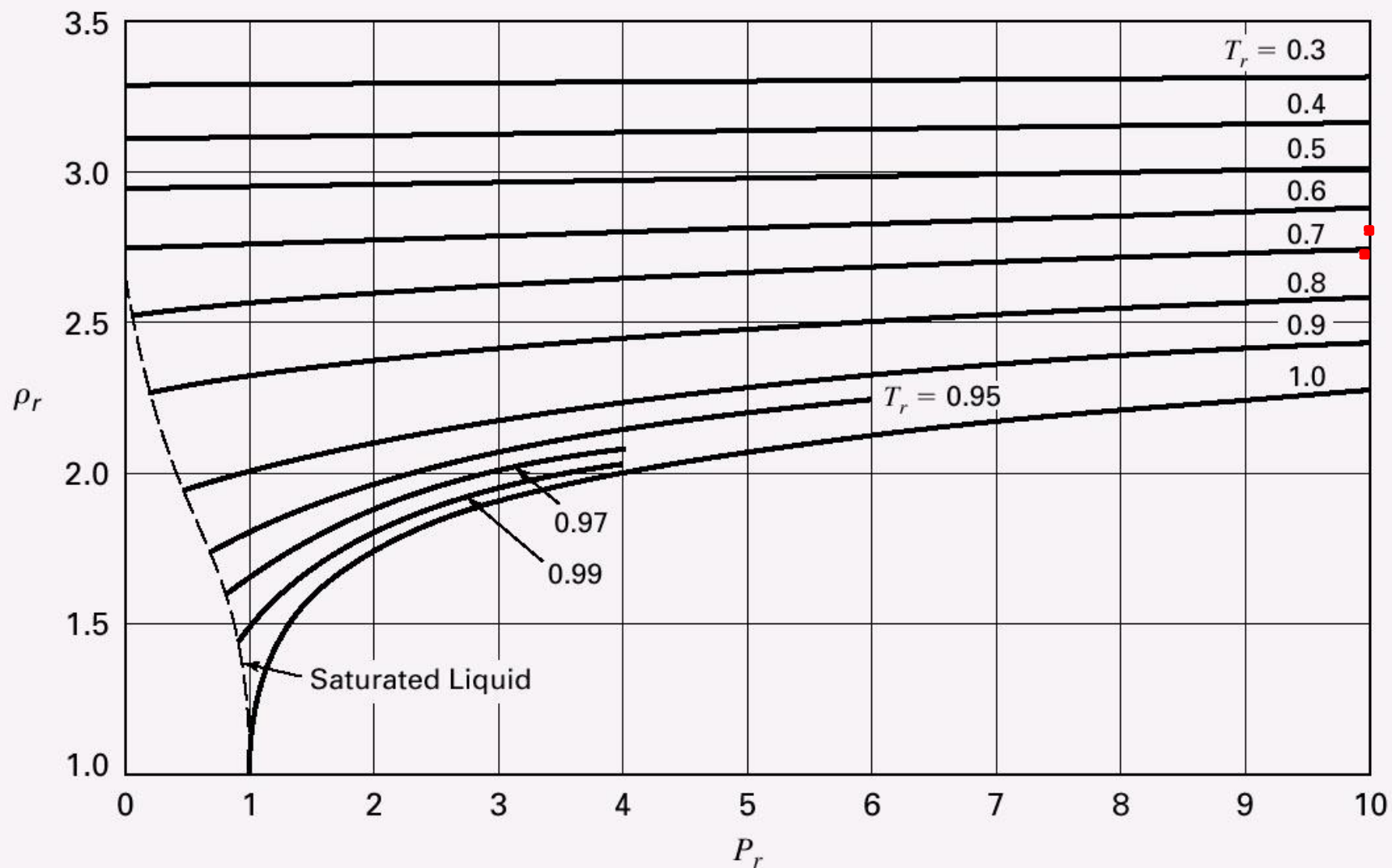or

$$V_2 = V_1 \frac{\rho_{r1}}{\rho_{r2}}$$

[Figure 3.16]

Figure 3.16: Generalized density correlation for liquids.