Exact Differential

$z(x + \Delta x, y + \Delta y)$

$z(x, y + \Delta y)$

z

Δz

$z(x, y)$

y

$z(x + \Delta x, y)$

(x, y)

x

z

y

$(x, y + \Delta y)$

$(x + \Delta x, y + \Delta y)$

(x, y)

$(x + \Delta x, y)$
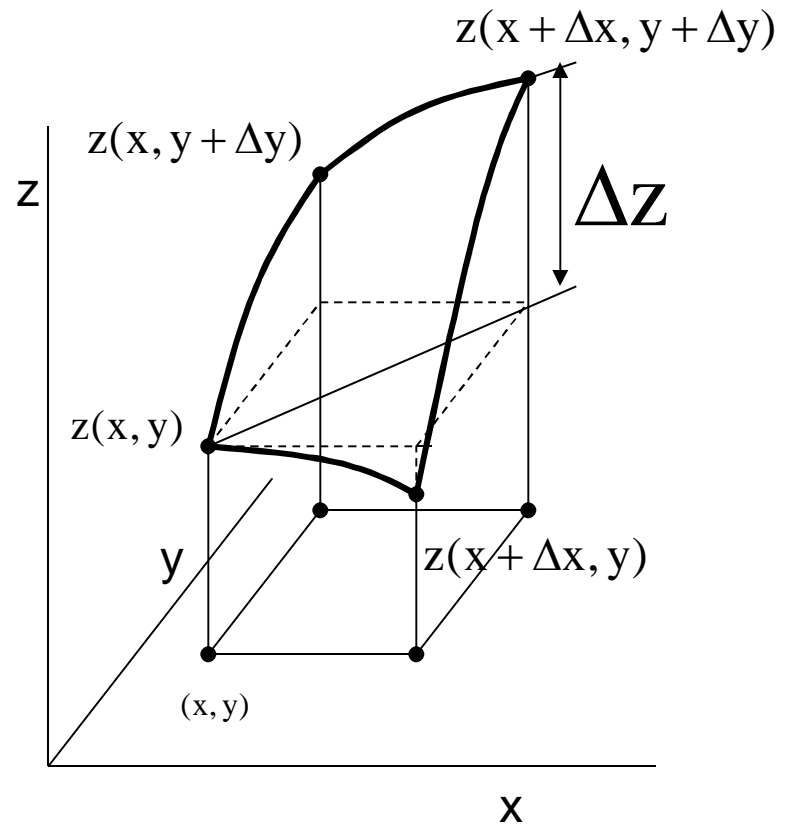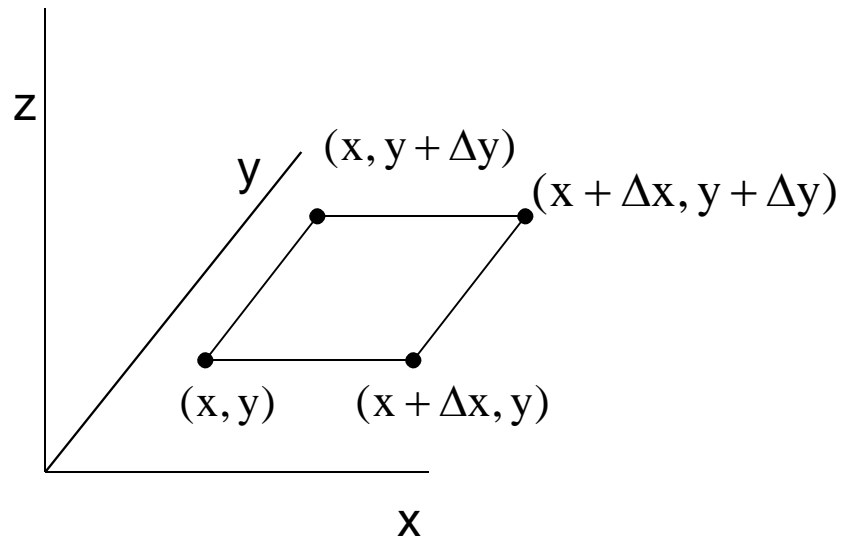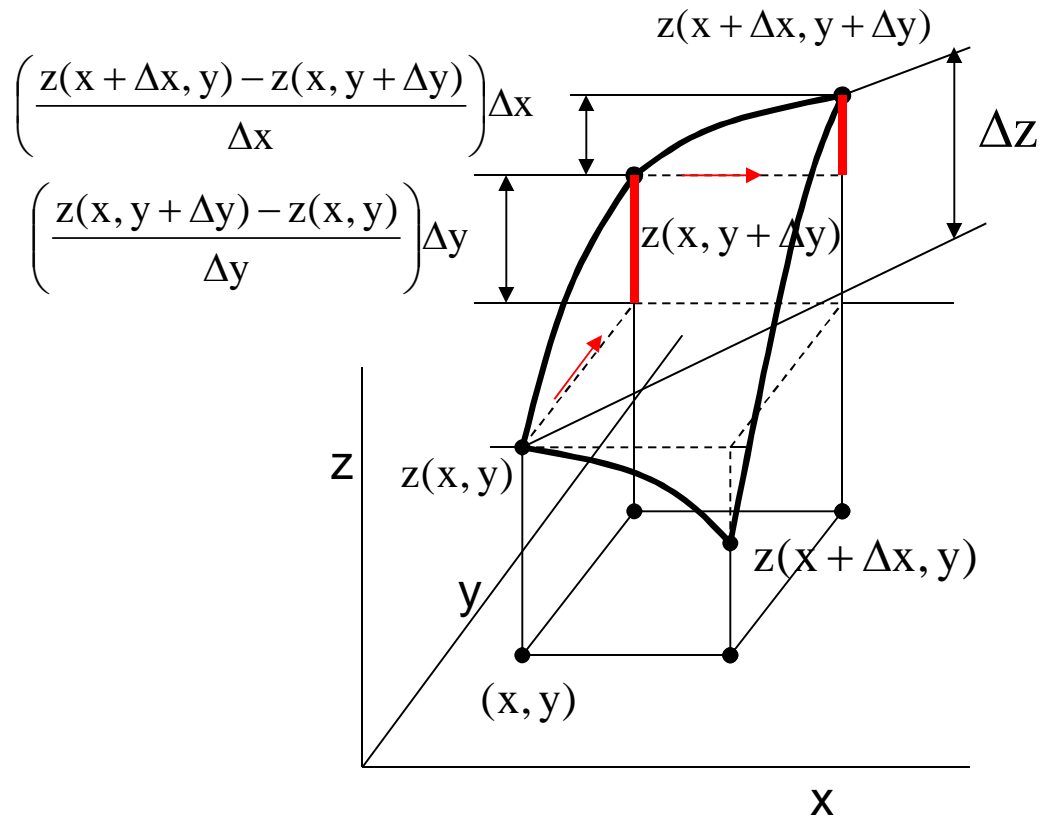
x

Exact Differential

Theorm :

If the function $z = f(x, y)$

has continuous first partial

deriviatives in the domain,

then the function z has

a differential

$$dz = \frac{\partial z}{\partial x}\, x + \frac{\partial z}{\partial y}\, y$$

at every point in the domain.

$$\left(\frac{z(x+\Delta x, y) - z(x, y+\Delta y)}{\Delta x}\right)\Delta x$$

$$\left(\frac{z(x, y+\Delta y) - z(x, y)}{\Delta y}\right)\Delta y$$

$z(x + \Delta x, y + \Delta y)$

Δz

$z(x, y+\Delta y)$

z $z(x, y)$

y

$z(x + \Delta x, y)$

(x, y)

x

$$z = \left(\frac{z(x+\ x, y) - z(x, y+\ y)}{x}\right)\ x + \left(\frac{z(x, y+\ y) - z(x, y)}{y}\right)\ y$$

$$\underset{=0}{\text{limit}}\ \frac{z(x+\ x, y) - z(x, y)}{x} = \left(\frac{\partial z}{\partial x}\right)_{y=\text{const}}$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_{y=\text{const}} dx + \left(\frac{\partial z}{\partial y}\right)_{x=\text{const}} dy \quad (12\text{-}3)$$

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$$dz = \left(\frac{\partial z}{\partial x}\right)_{y=\text{const}} dx + \left(\frac{\partial z}{\partial y}\right)_{x=\text{const}} dy$$

differentiating the partial deriviatives again,

$$\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right) \text{ since order is immaterial}$$

Since $x = x(y, z)$

$$dx = \left(\frac{\partial x}{\partial y}\right)dy + \left(\frac{\partial x}{\partial z}\right)dz \quad \text{and} \quad dy = \left(\frac{\partial y}{\partial x}\right)dx + \left(\frac{\partial y}{\partial z}\right)dz$$

subsistuting into dz,

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = 1$$

and $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad (12\text{-}19)$

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Maxwell Relation Derivation

$q = du + pdv$ First Law

$q = Tds$ Second Law

Combining,

$du = [T]ds + [-p]dv$

Since u is a property, independent of path

and a function of any two other properties,

$u = u(s, v)$, du is an exact differential.

$$du = \left[\left(\frac{\partial u}{\partial s}\right)_v\right]ds + \left[\left(\frac{\partial u}{\partial v}\right)_s\right]dv$$

comparing the quantaties in bracket,

$$T = \left(\frac{\partial u}{\partial s}\right)_v \quad \text{and} \quad -p = \left(\frac{\partial u}{\partial v}\right)_s$$

differentating again,

$$\left(\frac{\partial T}{\partial v}\right)_s = \frac{\partial}{\partial v}\left(\frac{\partial u}{\partial s}\right)_v \quad \text{and}$$

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

order does not affect the

result of differentiation and,

$$\frac{\partial}{\partial v}\left(\frac{\partial u}{\partial s}\right)_v = \frac{\partial}{\partial s}\left(\frac{\partial u}{\partial v}\right)_s$$

substituting,

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \quad (12\text{-}16)$$

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Using $du = Tds - pdv$ (12-10)

three realtionships were derived

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

$$-p = \left(\frac{\partial u}{\partial v}\right)_s$$

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \quad (12-16)$$

Using three additional equations,

First Law + h definition

$dh = Tds + vdp$ (12-11)

Helmholtz function

a property composed of properties

$a = u - Ts$ (12-12)

GibbvsFunction (Availability)

a property composed of properties

$g = h - Ts$ (12-13)

using this same technique 9 addditional

 relationships can be derived.

Maxwell Relations

from $u = u(s, v)$

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

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \quad (12\text{-}16)$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \quad (12-18)$$

from $h = h(s, p)$

$$T = \left(\frac{\partial h}{\partial s}\right)_p \quad v = \left(\frac{\partial h}{\partial p}\right)_s$$

$$\left(\frac{\partial T}{\partial p}\right)_s = -\left(\frac{\partial v}{\partial s}\right)_p \quad (12\text{-}17)$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T \quad (12-19)$$

Additional Relations

Helmholtz Function $a = u - Ts$

from $a = a(v, T)$

$$-p = \left(\frac{\partial a}{\partial v}\right)_T \quad v = \left(\frac{\partial a}{\partial T}\right)_p$$

Gibbs Functiong $g = h - Ts$

from $g = g(T, p)$

$$v = \left(\frac{\partial g}{\partial p}\right)_T \quad v = \left(\frac{\partial g}{\partial T}\right)_p$$

$$\left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial h}{\partial s}\right)_p$$

$$\left(\frac{\partial u}{\partial v}\right)_s = -\left(\frac{\partial a}{\partial v}\right)_T$$

$$\left(\frac{\partial h}{\partial p}\right)_s = \left(\frac{\partial g}{\partial p}\right)_T$$

$$\left(\frac{\partial a}{\partial T}\right)_v = -\left(\frac{\partial g}{\partial T}\right)_p$$

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

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Given that enthalpy of a gas is known everywhere as a function of pressure and entropy, $h = h(s,p)$ find t, v, u, g and a as functions of s and p.

$$dh = \left(\frac{\partial h}{\partial s}\right)_p ds + \left(\frac{\partial h}{\partial p}\right)_s dp \quad \text{exact differential of the property } h$$

$$dh = Tds + vdp \quad \text{First Law and definition of enthalpy}$$

a) comparing equations, $T(s,p) = \left(\dfrac{\partial h}{\partial s}\right)_p$

b) comparing equations, $v(s,p) = \left(\dfrac{\partial h}{\partial p}\right)_s$

c) $u = h - pv$ definition of h

$$u(s,p) = h(s,p) - p\left(\frac{\partial h}{\partial p}\right)_s$$

d) $a(s,p) = u - Ts$

$$a(s,p) = h(s,p) - p\left(\frac{\partial h}{\partial p}\right) - \left(\frac{\partial h}{\partial s}\right)_p s$$

e) $g(s,p) = h - Ts$

$$g(s,p) = h(s,p) - \left(\frac{\partial h}{\partial s}\right)_p s$$

$$z = z(x, y)$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

$$h = h(p, T)$$

$$\left(\frac{\partial p}{\partial T}\right)_h \left(\frac{\partial T}{\partial h}\right)_p \left(\frac{\partial h}{\partial p}\right)_T = -1$$

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p \text{ Specific Heat}$$

at constant pressure

$$JT = \left(\frac{\partial T}{\partial p}\right)_h \text{ Joule Tompson}$$

coefficient

$$c = \left(\frac{\partial h}{\partial p}\right)_T \text{ constant temperature}$$

coefficient

$$\frac{1}{JT} \times \frac{1}{c_p} \times c = -1$$

$$c = -JT \times c_p$$

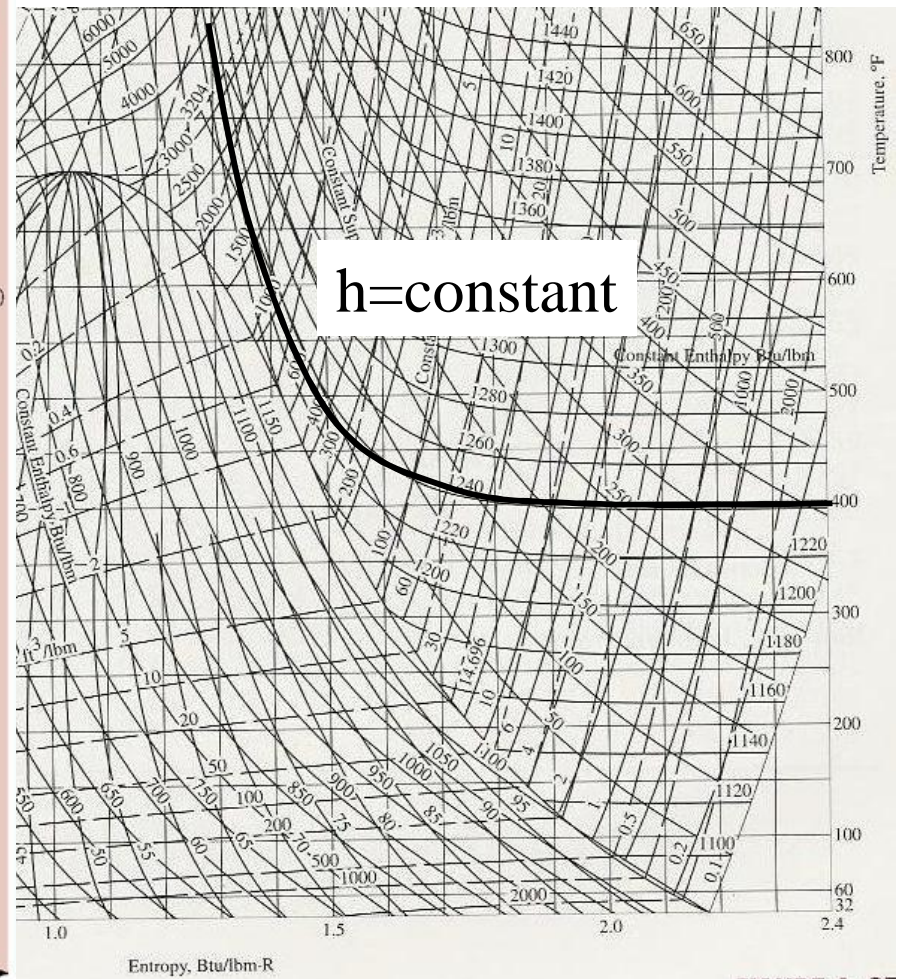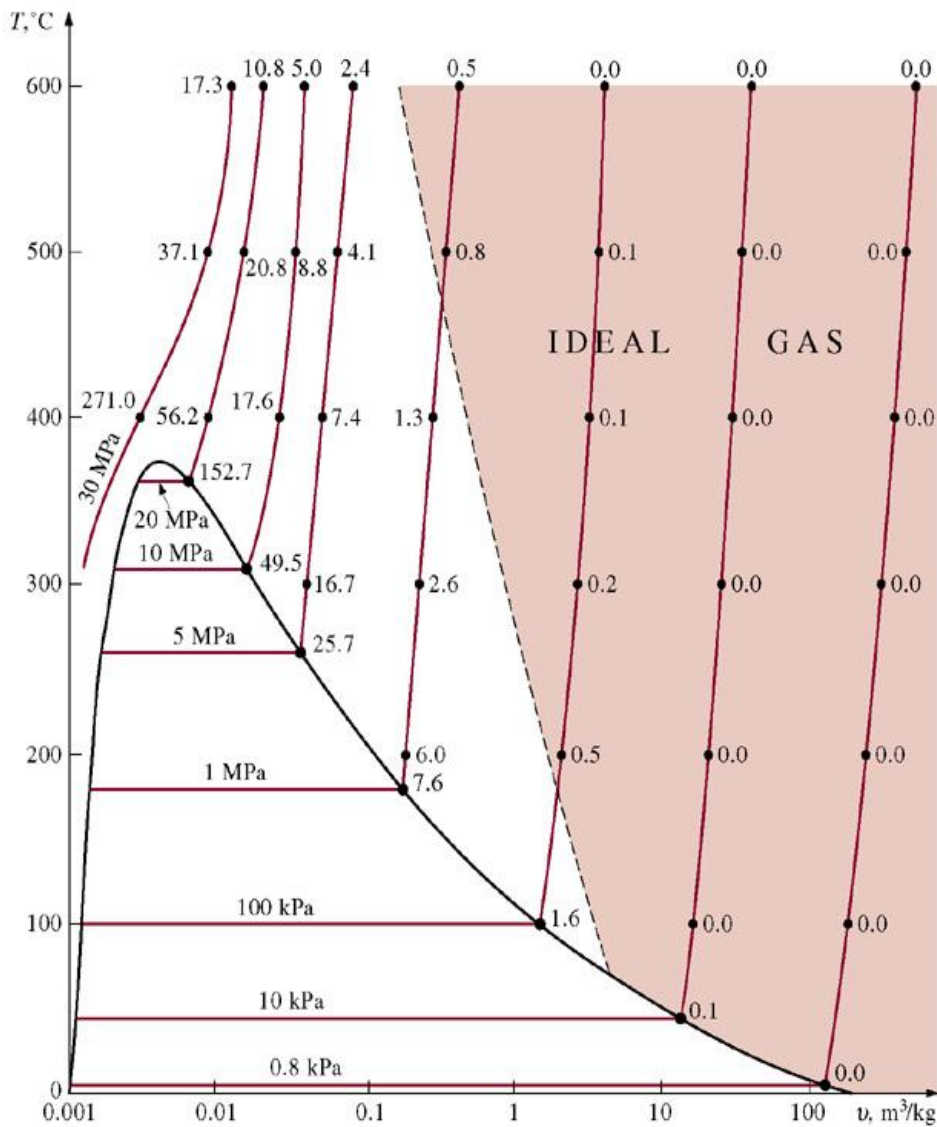$$\left(\frac{\partial T}{\partial p}\right)_h = \text{JT Coefficient}$$

IDEAL GAS

h=constant

T-s diagram for water. [*Source:* Joseph H. Keenan, Frederick G. Keyes, Philip G. Hill, and Joan G. Moore, *Steam Tables* (New York: John Wiley & Sons, 1969).]

FIGURE A–9E

Clapeyron Relation

Using the Maxwell Realtion,

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \qquad (12.18)$$

for

a two phase mixture

of a pure substance

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{s_{fg}}{v_{fg}}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

2 phase

$\Rightarrow$ p is a function only of T

$$\left(\frac{s_{fg}}{v_{fg}}\right)_T = \frac{dp}{dT}$$

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

$$\frac{h_{fg}}{s_{fg}} = T$$

$$s_{fg} = \frac{h_{fg}}{T}$$

substituting gives the Clapeyron Relation

$$\left(\frac{dp}{dT}\right)_{sat} = \frac{h_{fg}}{T\, v_{fg}} \qquad (12.22)$$

relates h_{fg} and v_{fg} simply to p, v, T data

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PRINCIPAL OF CORRERSPONDING STATES COMPRESSIBILITY FACTOR Z

Z is **about** the same for all gases at the same reduced temperature and the same reduced pressure where:

$$Z = \frac{pv}{RT}$$

$$Z = \frac{pV}{mRT}$$

Figure 3-51

$$P_R = \frac{p}{p_{critical}} \quad (3-22)$$

$$T_R = \frac{T}{T_{critical}}$$
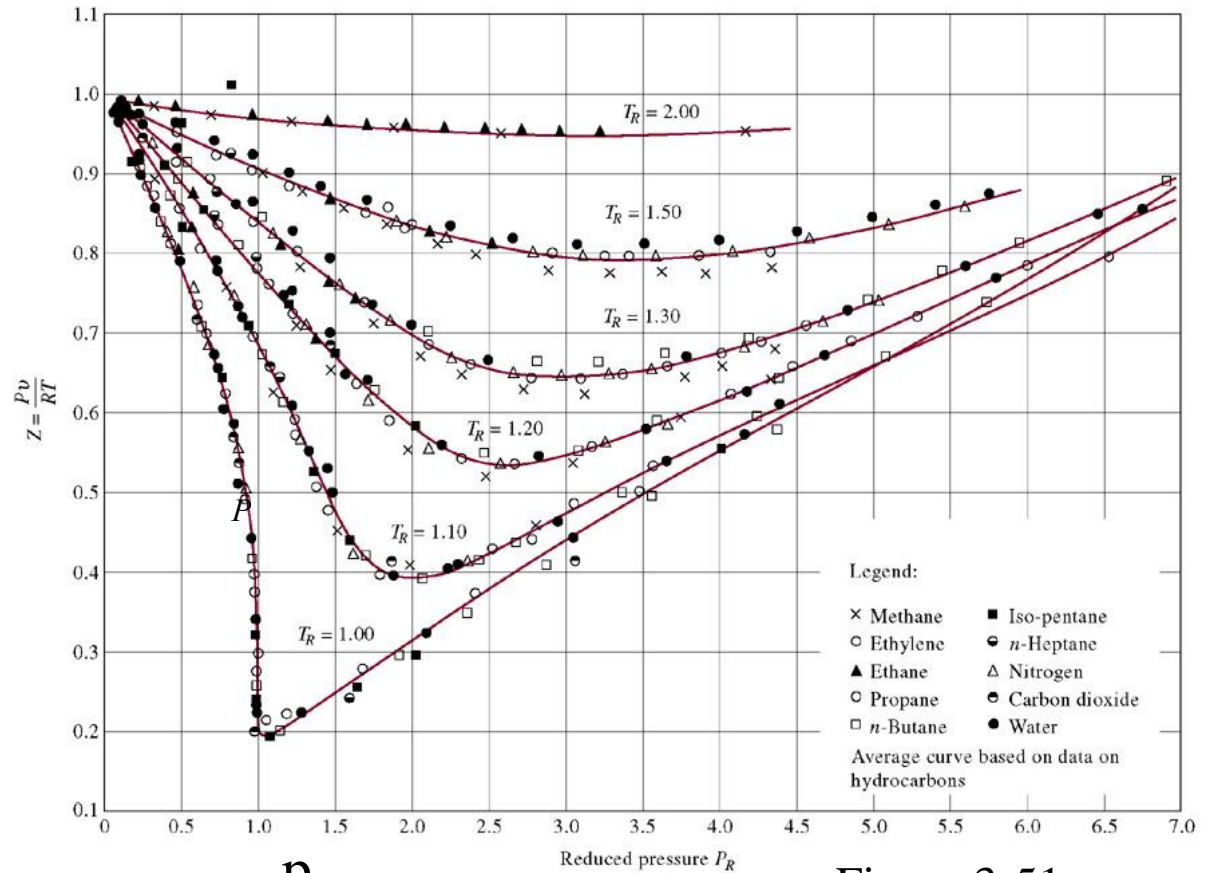
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VAN DER WAALS EQUATION OF STATE - 1873

$$\left(\mathbf{p} + \frac{\mathbf{a}}{\mathbf{v^2}} \right) (\mathbf{v} - \mathbf{b}) = \mathbf{RT} \qquad \mathbf{(3-22)}$$

$$\frac{a}{v^2} - \text{intermolecular forces}$$

$$b - \text{volume of gas molecules}$$

$$p = \frac{RT_{critical}}{v_{critical} - b} - \frac{a}{v^2_{critical}}$$

$$\left(\frac{\partial p}{dv} \right)_{T_{critical}} = 0 \qquad \left(\frac{\partial^2 p}{dv^2} \right)_{T_{critical}} = 0$$

$$a = \frac{27\, R^2\, T^2_{critical}}{64\, p_{critical}} \qquad b = \frac{R\, T_{critical}}{8\, p_{critical}}$$

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

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

critical point

p

v

Equations of State

Ideal Gas Law $pv = RT$

Compessibility $pv = ZRT$

Figure $3 - 51$

Variable Specific Heat

$$c_p(T)$$

$$h = \int c_p(T)dT$$

TableA $- 17$ to 23

Table A $-17E$ to $23E$

Van der Waals Equation

1873 $(3 - 22)$

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

Beattti Bridgman 1928 $(3 - 24)$

5 constants Table $3 - 4$ coefficients

Redlich Kwong 1949

Benedict Webb Rubin $(3 - 26)$

8 constants Table A $- 24$ coefficients

Virial Equation

$$p = \frac{RT}{v} + \frac{a(T)}{v^2} + \frac{b(T)}{v^3} + ... \quad (3 - 27)$$

Spread Sheet World air equation $- 32$ constants

Many, many others.

Thermodynamic Properties are Measurements

p,T,v, u ,h,s   - measure directly

-measure by change $\left(\dfrac{\partial s}{\partial v}\right)_T = \left(\dfrac{\partial p}{\partial T}\right)_v$

Tables

```
              ┌──→ Tables
              │
Property ─────┼──→ Curve fits ──────────────→ Tables
Data          │
              ├──→ Correlation's,  Boyles Law ──→ Tables
              │         pv=c@T=c        ↘  limited hand
              │                            calculations
              │
              └──→ Equations of State,  pv=RT ──→ Tables
                                            ↘ Calculation Modules
                                   NIST, EES, HYSYM
                                   interactive, callable
```

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