Chapter 3
Properties of Pure Substances
純質的性質

3.1 Pure Substance (純質)

- *A substance that has a fixed chemical composition throughout is called a* **Pure Substance.**
- **Pure Substance:**
  - ***- N_2, O_2, gaseous Air***
  - ***- A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous Air is not.***

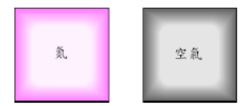


圖3-1 氮與氣態空氣為純質。

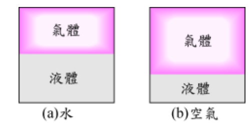


圖3-2 液態和汽態水的混合物是純質，液態和汽態空氣的混合物不是純質。

3.2 Phases of a Pure Substance (純質的相)

- ***Solid:***
  - *-The molecules in a solid are kept at their positions by the large spring like intermolecular forces.*
  - *-The attractive and repulsive forces between the molecules tend to maintain them at relatively constant distances from each other.*
- ***Liquid: Groups of molecules move about each other.***
- ***Gas: Molecules move about at random.***

3.2 純質的相

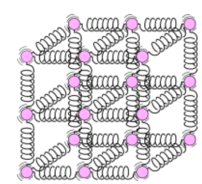


圖3-3 固體內的分子是以如彈簧般的分子力保持分子的位置。

圖3-4 固體內分子之間的吸引力與排斥力將分子維持在固定的距離。

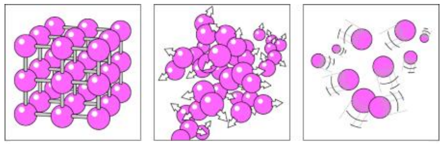


圖 **3-5** 不同相態的原子排列(a)固體內分子在相當固定的位置；(b) 液態之分子群彼此相對運動；(c)氣相之分子隨意運動。

Phase Rule (no chemical reaction)

Remind:

- ***F=C-P+2***

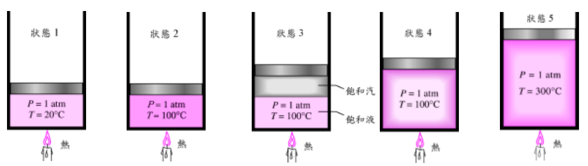
  - ***F*** ***: # of intensive (internal) properties need to fix the state of the system***
  - ***C*: # of components**
  - ***P*: # of phases**

  For pure liquid or gas (vapor) *F* =2 (*C*=1, *P*=1)

  For un-saturated water *F* =1 (*C*=1, *P*=2)

  For triple line (points) *F* =0 (*C*=1, *P*=3)

3.3 Phase-Change Processes of Pure Substance
(純質的相變化過程)



在1 atm 與20℃，水以液相存在(壓縮液)

100℃，為即將汽化的液體(飽和液)

加入更多的熱，部分飽和液汽化(飽和液汽混合物)

溫度固定在100℃，直到最後一滴液體汽化(飽和汽)

更多的熱加入汽體的溫度開始上升(過熱汽)

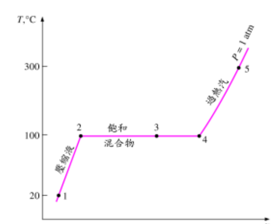


圖**3-11** 水在**定壓下(1atm)**加熱過程的***T-v*** 圖。

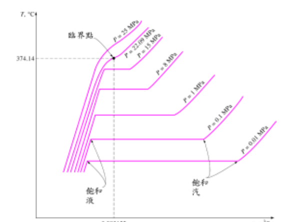


圖**3-16** 純質在**不同壓力**下之等壓相變化的***T- v***圖。

3.3 Phase-Change Processes of Pure Substance
- Terminologies (專門用語)

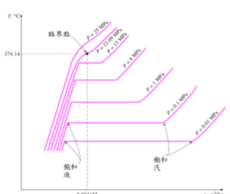
- *Compressed liquid* (壓縮液) *or a subcooled liquid* (過冷液) : *A liquid that is not about to vaporize.*
- *Saturated liquid* (飽和液) : *A liquid that is about to vaporize.*
- *Saturated vapor* (飽和汽) : *A vapor that is about to condense.*
- *Saturated liquid-vapor mixture* (飽和液汽混合物) : *the liquid and vapor phases coexist in equilibrium.*
- *Superheated vapor* (過熱汽) : *A vapor that is not about to condense*

3.3 Phase-Change Processes of Pure Substance

- *Saturated temperature* (飽和溫度), *Tsat: At a given pressure, the temperature at which a pure substance changes phase.*
- *Saturated pressure* (飽和壓力), *Psat: At a given temperature, the pressure at which a pure substance changes phase.*
- *Latent heat* (潛熱)*: the amount of energy absorbed or released during a phase-change process.*
- *Latent heat of fusion* (溶解熱)*: the amount of energy absorbed during melting.*
- *Latent heat of vaporization* (蒸發熱)*: the amount of energy absorbed during vaporization.*

表 **3-1** 水在不同溫度的飽和(沸騰)壓力

溫度 T, ℃	飽和壓力 P_{sat}, kPa
−10	0.26
−5	0.40
0	0.61
5	0.87
10	1.23
15	1.71
20	2.34
25	3.17
30	4.25
40	7.38
50	12.35
100	101.3 (1atm)
150	475.8
200	1554
250	3973
300	8581



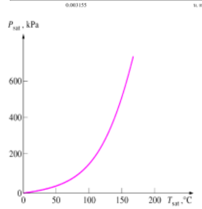
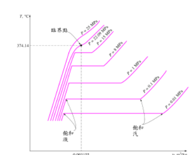
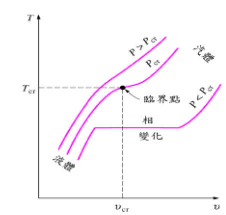


圖 **3-12** 純質的液-汽飽和曲線(水)。

高度 m	大氣壓力 kPa	沸騰溫度 ℃
0	101.33	100.0
1,000	89.55	96.3
2,000	79.50	93.2
5,000	54.05	83.0
10,000	26.50	66.2
20,000	5.53	34.5

表 **3-2** 依高度變化的標準大氣壓力及水的飽和(沸騰)溫度





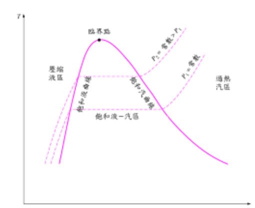


圖 **3-16, 17** 高於臨界壓力($P > P_c$)將無法區別相的變化過程(沸騰)。

臨界點 **(Critical Point)**, T_c(臨界溫度), P_c(臨界壓力)

$T_c = 373.95$ C = 647 K

$P_c = 22.064$ MPa

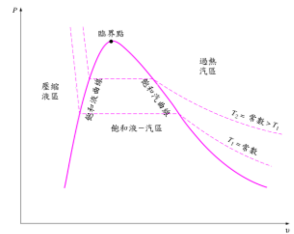
$v_c = 0.003106\ m^3/kg$

$u_f = u_g = 2015.7$ kJ/kg

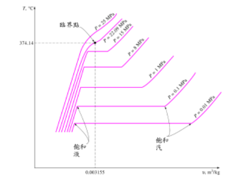
3.4 Property Diagrams（性質圖）for Phase-Change Processes

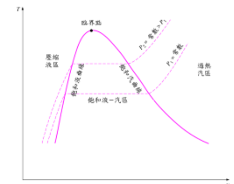
- ***The T-v diagram:***
  - ***Critical point**: the point at which the saturated liquid and saturated vapor states are identical.*
  - ***Saturated liquid line:***
  - ***Saturated vapor line:***
  - ***Compressed liquid region:***
  - ***Superheated vapor region:***
  - ***Saturated liquid-vapor mixture region:***

相變化過程的性質圖 - *P-v* 圖



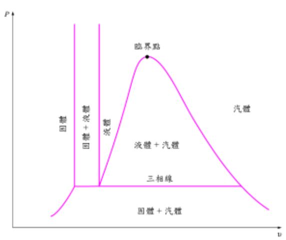
純質的*P-v*圖





純質的*T-v*圖

三相 - 固、液、汽相



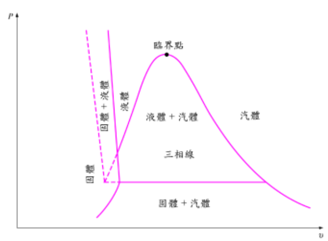
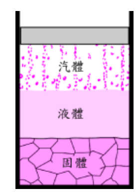
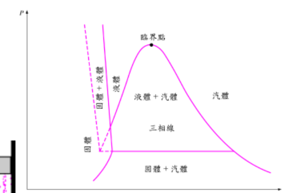
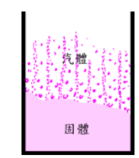


圖 **3-20 (a)** 凝固時收縮的物質 *P-v* 圖，(b)凝固時膨脹之物質(例如水)的 *P-v* 圖。







在**三相點(triple point)**的壓力與溫度，物質以三相平衡共存。

低壓時(低於三相點)固體未溶解就蒸發(昇華)**(sublimation)**。

Note: 嚴格而言，不是**三相點(triple point)**，是**三相線(triple points line)**，在此線上各點的物質鈞以三相平衡共存。**[*T, P,*** fixed; need (x_v,x_l) or (v,x_l) …to locate the point**]**.

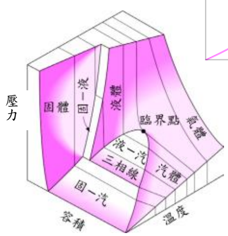


圖 3-24 凝固時收縮的物質之**P-v-T** 圖。

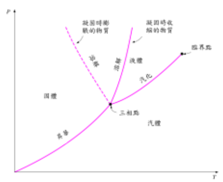


圖 3-23純質的 ***P-T*** 圖。

P-v-T surface
P(v,T), T(P,v), v(T,P), or z(x,y)

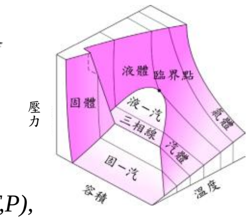
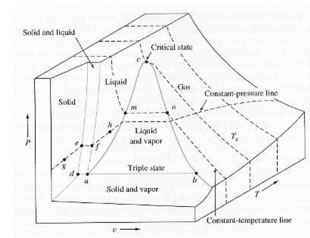
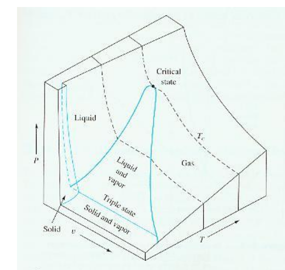


圖 3-25 凝固時膨脹的物質之 **P-v-T** 圖。





2-8

3.5 Property Tables (性質表)

- ***Table A-4:***
  Saturated water - Temperature table
- ***Table A-5:***
  Saturated water - Pressure table
- ***Table A-6:***
  Superheated water
- ***Enthalpy, H***
  H= U + PV (kJ)
  h= u + Pv (kJ/kg)
- ***Entropy, S***

3.5 性質表

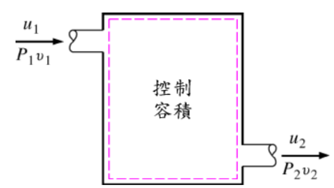


圖**3-26** 在控容的分析中常討論到 ***u + Pv*** 的結合。

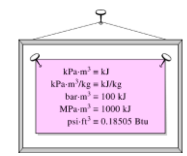
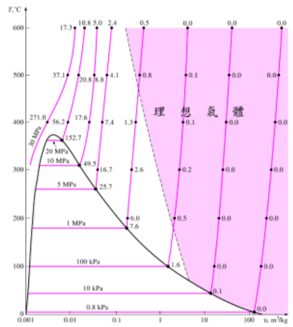


圖**3-27** 壓力(P)× 容積(V)可表示能量
kPa x m^3 = 10^3 N/m^2 x m^3
= 10^3 N·m = 10^3 J = 1 kJ

u
h = u + pv



溫度 °C T	飽和壓力 kPa P_{sat}	比容 m³/kg 飽和液 v_f	比容 m³/kg 飽和汽 v_g
85	57.83	0.001 033	2.828
90	70.14	0.001 036	2.361
95	84.55	0.001 040	1.982

指定溫度　　對應之飽和壓力　　飽和液之比容　　飽和汽之比容

圖**3-28** 表A-4 的部分表列。

Example 3-3

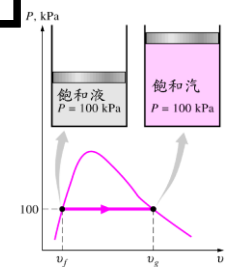
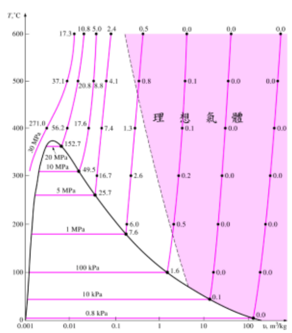
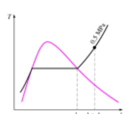


圖 **3-31** 範例 3-3 示意圖與 *P-v* 圖。



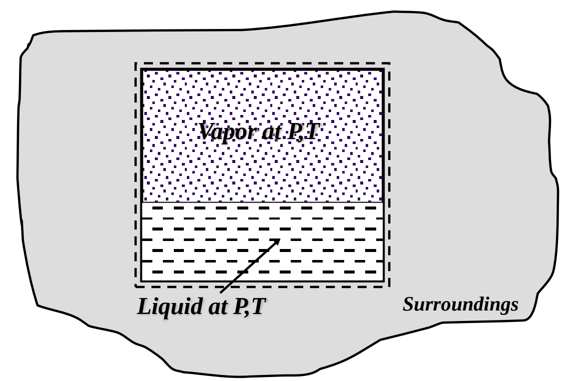
T,°C	v, m³/kg	u, kJ/kg	h, kJ/kg
	P = 0.1 MPa (99.63°C)		
飽和	1.6940	2506.1	2675.5
100	1.6958	2506.7	2676.2
150	1.9364	2582.8	2776.4
⋮	⋮	⋮	⋮
1300	7.260	4683.5	5409.5
	P = 0.5 MPa (151.86°C)		
飽和	0.3749	2561.2	2748.7
200	0.4249	2642.9	2855.4
250	0.4744	2723.5	2960.7

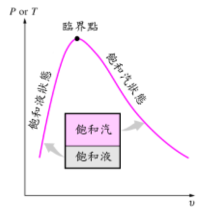
圖 **3-40** 表 A-6 的部分表列 。

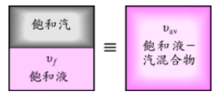


在指定壓力下過熱汽體的 *h* 值
大於飽和汽的 *h* 值。

Liquid-vapor equilibrium







為了方便，可以將兩相系統視為均質性混合物處理。

quality (乾度) $x = \dfrac{m_{vapor}}{m_{total}} = \dfrac{m_{vapor}}{m_{liquid} + m_{vapor}}$

圖 3-32 以乾度 x 表示飽和混合物中液相和汽相的相對量。

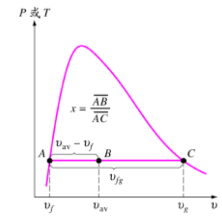


圖 3-34 P-v 圖和 T-v 圖上乾度與水平距離的關係。

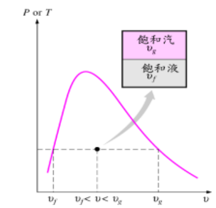


圖 3-35 飽和液汽混合物的 v 值在指定下 T 或 P 的 v_f 與 v_g 之間。

$V = V_f + V_g, \quad m_t = m_f + m_g$

$m_t v = m_f v_f + m_g v_g$

$(m_f + m_g) v = m_f v_f + \underline{(m_g v_f - m_g v_f)} + m_g v_g$

$\quad = m_t v_f + m_g (v_g - v_f)$

$v = v_f + x v_{fg}, \quad v_{fg} = v_g - v_f$

Note : $v = v_f + x v_{fg} \neq v_f + v_g$

$v = v_f + x v_{fg}, \quad V = V_f + V_g, \quad m_t = m_f + m_g$

$m_t v = m_f v_f + m_g v_g$

$v = (m_f / m_t) v_f + (m_g / m_t) v_g$

$v = (1 - x) v_f + x v_g$

Similar to U (u), H (h), S (s)

$u = u_f + x u_{fg} = (1 - x) u_f + x u_g$

$h = h_f + x h_{fg} = (1 - x) h_f + x h_g$

$s = s_f + x s_{fg} = (1 - x) s_f + x s_g$

$A_g > A_f$
or $A_{fg} > 0$

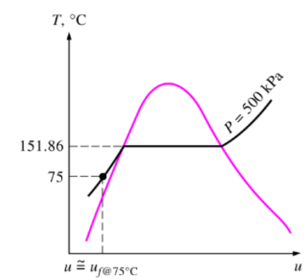


圖 3-42 在已知的 P 與 T，$P > P_{sat}@T$ 或 $T < T_{sat}@P$，
(or $v < v_f$, $u < u_f$, $h < h_f$ at a given P or T)
物質為壓縮液。

已知：P 和 T

$$v \cong v_{f@T}$$
$$u \cong u_{f@T}$$
$$h \cong h_{f@T}$$

壓縮液的性質可以近似視為已知溫度的飽和液。

For more accurate

$$h \cong h_{f@T} + v_{f@T}(P - P_{sat@T})$$

Example 3-8

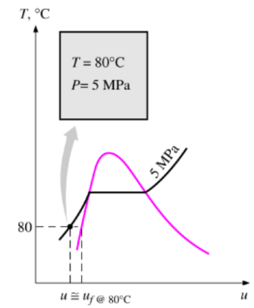


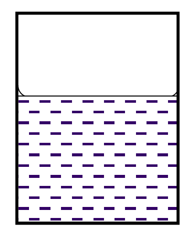
圖 **3 - 41** 範例 3-8 示意圖與T-u圖。

~ 0.34% deviation

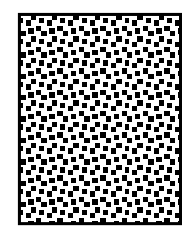
3.6 The Ideal-Gas Equation of State (理想氣體狀態方程式)

- *Equation of state:*
  Any equation that relates the pressure, temperature, and specific volume of a substance.
- *Gas: The vapor phase of a substance*
- *Vapor: A gas that is not far from a state of condensation*

Fluids and gases



A liquid will take the shape of its container but exhibits a free surface.



$$V_{gas} = V_{container}$$
$$T_{gas}, P_{gas}$$

A gas will fill its container completely and does not exhibit a free surface.

3.6 The Ideal-Gas Equation of State

$PV = NR_uT,$

$PV = mRT$

$Pv = RT, v = V / m$

$P\hat{v} = R_uT, \hat{v} = V / N$

This implies:

(1) very little molecular interaction (p = 0),

(2) molecules are point masses, i.e.,

molecules occupy zero volume.

3.6 The Ideal-Gas Equation of State

The universal gas constant

$R_u = 8.314 \ kJ / kmol \cdot K$

$= 1545 \ ft \cdot lbf / lbmol \cdot R$

M, molar mass, the mass of 1 mole of substance in grams, or 1 kmol in kilograms. [in SI

6.023×10^{23} *molecules / mole*].

For Air

M = 28 kg/kmol = 28 g/mole

***= 28 lbm/lbmol* (definition)**

The gas constants, *$R = R_u / M$*

物質	R, kJ/kg·K
空氣	0.2870
氦	2.0769
氬	0.2081
氮	0.2968

The ideal gas state surface – *a 3 dimensional surface*

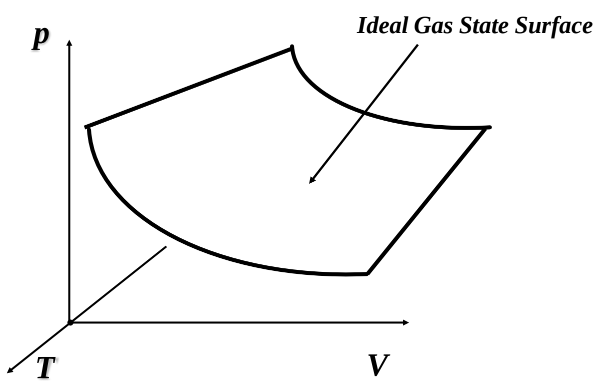
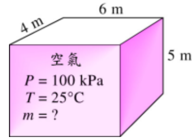


圖 3-45 理想氣體經常不適用於真實氣體；
因此使用時須注意。

Example 3-10



$$PV = mRT$$

$$m = \frac{PV}{RT} = \frac{(100kPa)(4\cdot5\cdot6)m^3}{(0.287kJ/(kg\cdot K)(25+273)K}$$

$$= \frac{(100\cdot10^3\frac{N}{m^2})(4\cdot5\cdot6)m^3}{(0.287\cdot10^3\cdot N\cdot m/(kg\cdot K)(25+273)K} = 140.3kg$$

圖3-48 範例 3-10 的示意圖。

The ideal gas $\frac{Pv}{RT} = 1$

The perfect gas $\frac{Pv}{RT} = 1$

$c_v = constant$

$c_P - c_v = R$

3.7 Compressibility Factor- A Measure of Derivation from Ideal-Gas Behavior

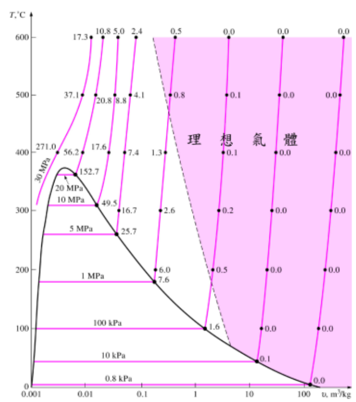


圖 3-47 水蒸汽為理想氣體的百分誤差([($v_{表}$-$v_{理想}$)/$v_{表}$]×100)小於1的區域

3.7 Compressibility Factor- A Measure of Derivation from Ideal-Gas Behavior

- *Compressibility Factor* (壓縮係數), *Z*

  $Z = Pv/RT$

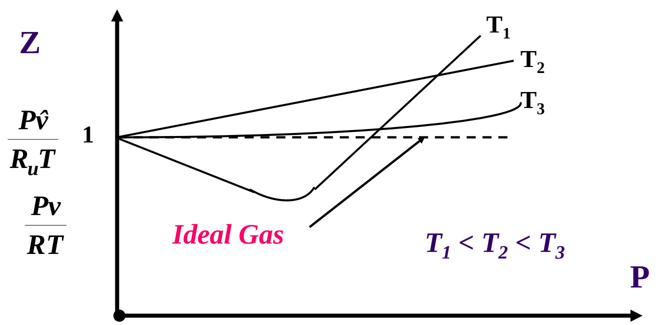
  $Z = v_{actual}/v_{ideal}$
- *Ideal gas*: $Z = 1$
- *Real gases*:

  $Z > 1$

  $Z = 1$

  $Z < 1$

Real Gases



3.7 Compressibility Factor- A Measure of Derivation from Ideal-Gas Behavior

- ***The normalization:***
  - *Reduced pressure, P_R*

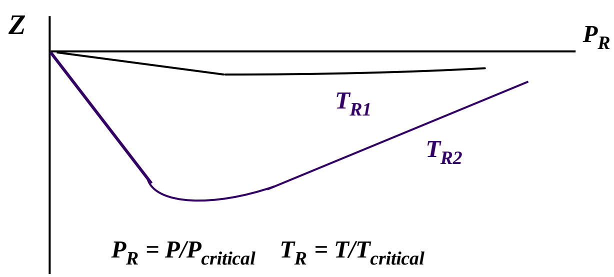
    $P_R = P/P_{cr}$
  - *Reduced temperature, T_R*

    $T_R = T/T_{cr}$
- ***The principle of corresponding states:***

  The Z factor for all gases is approximately the same at the same reduced pressure and temperature.

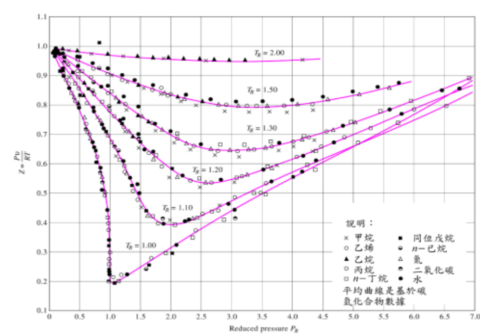
Reduced pressure and temperature

Generalized Compressibility Chart



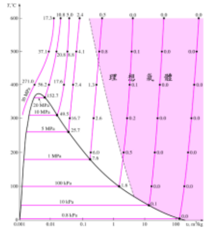
$P_R = P/P_{critical}$ $T_R = T/T_{critical}$

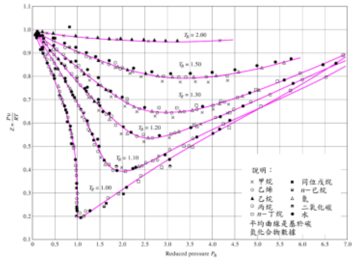
Generalized Compressibility Chart

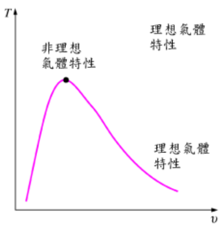


$$P_R = \frac{P}{P_{cr}} \quad T_R = \frac{T}{T_{cr}}$$

Reduced pressure and temperature
Corresponding State (P_R, T_R)







1. 不論溫度，在非常低的壓力下所有氣體均接近理想氣體。
2. 不論壓力，在非常高的溫度下(T_R>2)所有氣體均接近理想氣體。
3. 臨界點附近的氣體狀態與理想氣體特性有最大的偏離。

Example 3-11 Use of Generalized Charts – determine v

Errors ; ideal gas ~ 20%
charts ~ 2%

$$P_R = \frac{P}{P_{cr}}$$

$$T_R = \frac{T}{T_{cr}}$$

pseudo – reduced specific volume

$$v_R = \frac{v_{actural}}{RT_{cr} / P_{cr}}, \neq \frac{v_{actural}}{v_{cr}}$$

Example 3-12 Use of Generalized Charts – determine P

$$\left.\begin{aligned} P_R &= \frac{P}{P_{cr}} \\ v_R &= \frac{v}{RT_{cr}/P_{cr}} \end{aligned}\right\} Z = \ldots \text{ (Fig. A–15)}$$

圖 3-52 亦可由P_R和v_R決定可壓縮性因數的因素。(A-15 figure)

水, T = 350 C, v = 0.035262 m3/kg,
P = ?
Sol. Exact 7.0 MPa, Z chart 6.84 MPa,
Ideal gas 8.15 MPa

3.8 其他的狀態方程式

van der Waals
Berthelet
Redlich-Kwang
Beattie-Bridgeman
Benedict-Webb-Rubin
Strobridge
Virial

圖 3-55 歷史上曾經提出的數種狀態方程式。
Pages 141-144

van der Waals equation of state

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

a/v^2: intermolecular force
b: volume occupied by the molecular

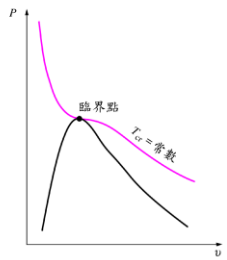


圖 **3-56** 純質的臨界等溫線在臨界點
有轉折點。

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_{cr}} = 0 \qquad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_{cr}} = 0$$

for van der Waals equation of state

$$a = \frac{27R^2T_{cr}^2}{64P_{cr}} \qquad b = \frac{RT_{cr}}{8P_{cr}}$$

圖 **3-57** 複雜的狀態方程式使氣體的 *P-v-T* 特
性可以在更大的使用範圍更準確。

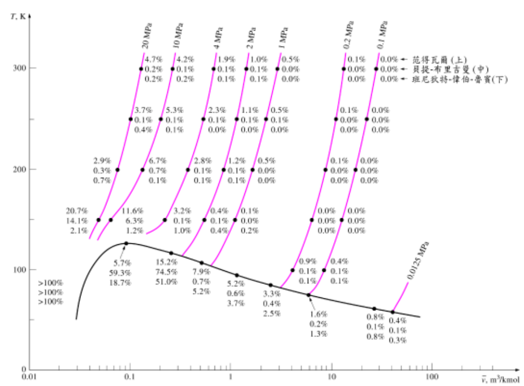


圖3-58 應用於氮之各種狀態方程式的誤差百分率(%)
$= [(v_{表}-v_{方程式})/v_{表}] \times 100$。

第三章習題

11, 26, 35, 44, 56, 68, 77, 84, 93, 103, 112, 123