Chapter 4　Volumetric Properties of Pure Fluids

§4-1.The Ideal gas

1. The model of the ideal gas:

❶The gas particles can be considered zero-volume points in space.

❷The total volume of the ideal gas can't be neglected.

❸There are no interactions, attractive or repulsive, between the individual gas particles.

❹當 gas particle 碰撞時，無能量的產生 or 消耗。

❺The mass of the gas particles cannot be neglected.

2. The ideal gas law ➔ $PV = nRT$ or $P\hat{V} = RT$

§4-2. PVT Behavior of Pure Substances

1.Pure substances ➔ Measure the vapor pressure at different temperature

↳ Fig. 3.1. is a figure of pressure-vs.-temperature curves

(1)Line 1-2:

❶the sublimation curve, separates the solid and gas regions.

❷solid-vapor line, points on the solid-vapor line describe those state in which solid and vapor are in equilibrium.

(2)Line 2-3:

❶the fusion curve, separates the solid and liquid regions.

❷solid-liquid line, points on the solid-liquid line describe those state in which liquid and solid are in equilibrium.

(3)Line 2-C:

❶the vaporization curve, separates the liquid and gas regions.

❷liquid-vapor line, points on the liquid-vapor line describe those state in which liquid and vapor are in equilibrium.

(4)All three lines meet at the triple point, where the three phases coexist in equilibrium.

(5)Point C ➔ critical point

↳對應到 critical pressure P_c, 與 critical temperature T_c
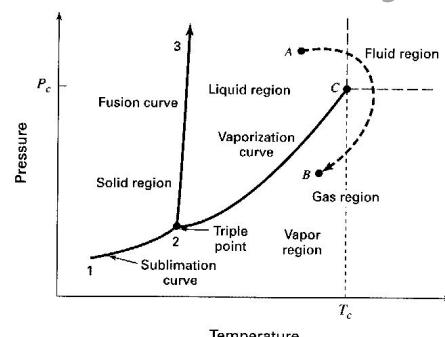
Figure 4-1

❶The highest pressure and highest temperature at which a pure chemical
　species can exist in vapor/liquid equilibrium.

❷Homogeneous fluids are usually classified as liquids or gases.
　↳The distinction cannot always be sharply drawn, because the two phases
　　become indistinguishable at the critical point.

❸point B → vapor，如何變成 liquid？
　※當 B 點的溫度超過 T_c 時，再如何加壓(定溫下)亦無法使其變成液體。
　　∴T_c 是使氣體可以藉定溫加壓而變成液體的最高溫度。
　　　一般而言，分子間的吸引力越大 ➔ T_c 越 ＿＿。

❹The region, $T > T_c$ and $P > P_c$ ➔ fluid region.
　↳●No phase boundaries ➔ 無法區分 liquid or gas。
　　●Reduce the pressure at constant temperature ➔ no vaporization occurs.
　　●Reduce the temperature at constant pressure ➔ no condensation occurs.

❺The gas region is sometimes divided into two parts by the vertical line
　across T_c.
　①vapor: A gas to the left of this line, which can be condensed either by
　　　　　compression at constant temperature or by cooling at constant
　　　　　pressure.
　②supercritical fluid : $T > T_c$, including the fluid region.
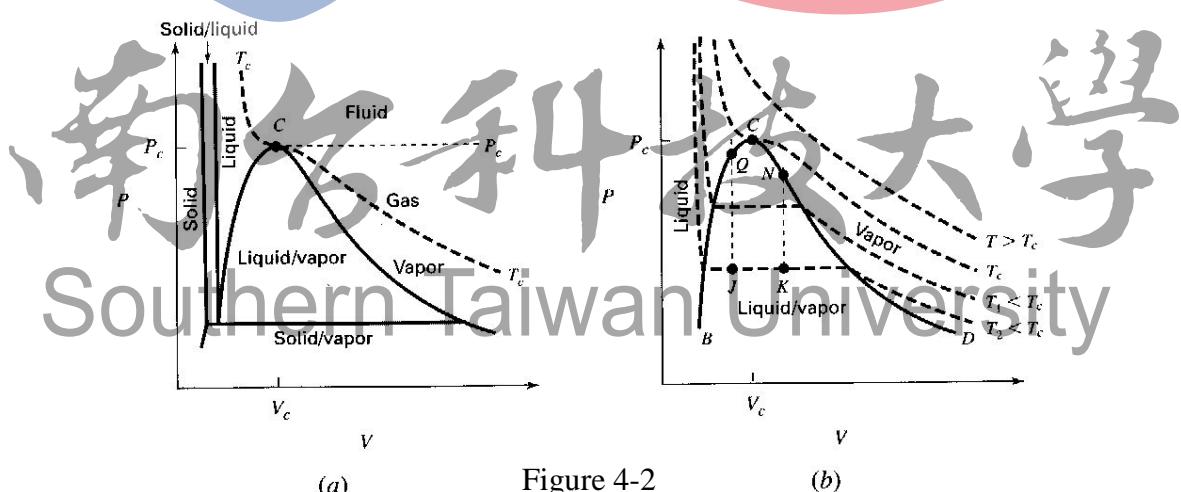
Figure 4-2

2.PV diagram:
　(1)Figure 4.2(b) shows the liquid, liquid/vapor, and vapor regions of the PV
　　diagram, with four isotherms superimposed.

4-2

❶Isotherms on Fig. 4.1

↳●vertical lines

●$T > T_c$ ➔ do not cross a phase boundary.

❷Isotherms on Fig. 4.2(b)

↳●not vertical lines

●$T < T_c$ ➔ a discontinuous line.

●$T > T_c$ ➔ a smooth line.

(2)Figure 4.2(b):

❶The horizontal line in the dome-shaped curve BCD

↳●the mixtures of liquid and vapor in equilibrimn.

●from 100% liquid at the left end to 100% vapor at the right end.

❷The left half of curve BCD (from B to C)

↳the single-phase (saturated) liquids at their boiling temperatures.

❸The right half of curve BCD (from C to D)

↳the single-phase (saturated) vapors at their condensation temperatures.

❹The horizontal segments of the isotherms in the two-phase region become progressively shorter at higher temperatures, being ultimately reduced to a point at C.

↳exhibits a horizontal inflection at the critical point C at the top of the dome.

↳Here the liquid and vapor phases cannot be distinguished from each other, because their properties are the same.
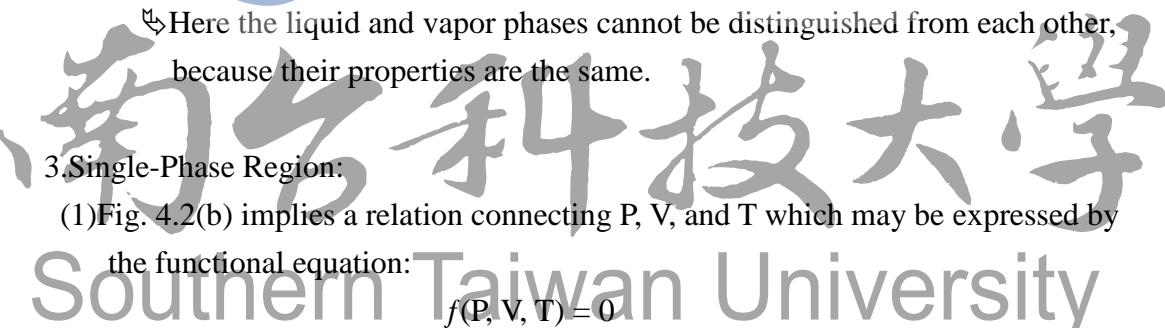
3.Single-Phase Region:

(1)Fig. 4.2(b) implies a relation connecting P, V, and T which may be expressed by the functional equation:

$$f(P, V, T) = 0$$

●The simplest equation of state is for an ideal gas, $P\hat{V} = RT$.

●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.

(2) If V is considered a function of T and P, then $\hat{V} = \hat{V}(T, P)$

4-3

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

●Define:

❶Volume expansivity: $\beta \equiv \frac{1}{\hat{V}}(\frac{\partial \hat{V}}{\partial T})_P$

❷Isothermal compressibility: $\kappa \equiv -\frac{1}{\hat{V}}(\frac{\partial \hat{V}}{\partial P})_T$

$$\therefore \frac{d\hat{V}}{\hat{V}} = \beta\, dT - \kappa\, dP$$

◆For the liquid phase
　↳①Both β and κ are small.
　　②β is almost always positive (liquid water of 0～4℃ is an exception), and κ is necessarily positive.
　　③At conditions not close to the critical point, β and κ are weak functions of temperature and pressure.

◆For liquids outside the critical region ➔ incompressible fluid.
　　∴視 β = 0　and　κ = 0

❸Integration of $\frac{d\hat{V}}{\hat{V}} = \beta\, dT - \kappa\, dP$ then yields:

$$\ln\frac{\hat{V}_2}{\hat{V}_1} = \beta(T_2\text{-}T_1) - \kappa(P_2\text{-}P_1)$$
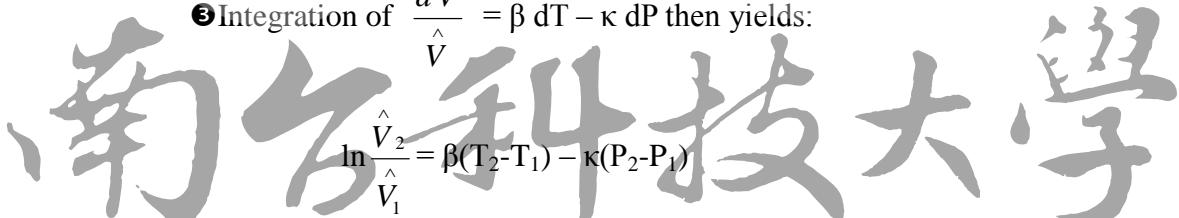
Example 4-1:
For liquid acetone at 20℃ and 1 bar,

β= 1.487 x 10⁻³℃⁻¹　　κ = 62 x 10⁻⁶ bar⁻¹　　V = 1.287 cm³g⁻¹

For acetone, find:

(a)The value of $(\frac{\partial P}{\partial T})_V$.

(b)The pressure generated by heating at constant V from 20℃ and 1 bar to 30℃.
(c)The change in volume for a change from 20℃ and 1 bar to 0℃ and 10 bar.

§4-3. Real gases

1. 目前已有若干 real gas 的狀態方程式被導出來，而這些方程式都含有一些由實驗所得的常數，用來修正理想氣體方程式，使其適用於一些真實氣體或某種情況下的真實氣體。

2. Principle of corresponding states:
   (1) critical constant：
   - critical temperature T_c
   - critical pressure P_c
   - critical volume $\hat{V}_C$: 一氣體在臨界壓力與臨界溫度時的 molar volume。

   (2) 由 Tab. 4-1 知不同物質在臨界狀態時，臨界壓縮因子 Z_c ($Z_c = \dfrac{P_C \hat{V}_C}{RT_C}$) 大致相等。
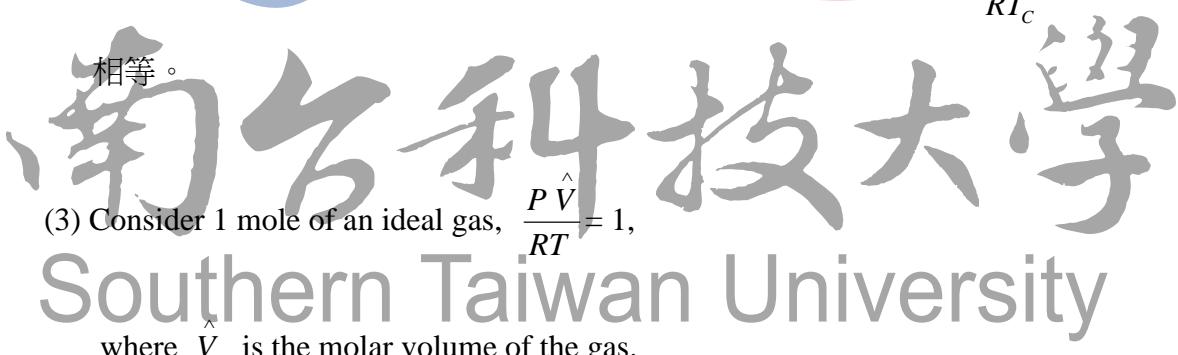
   (3) Consider 1 mole of an ideal gas, $\dfrac{P\hat{V}}{RT} = 1$,

   where $\hat{V}$ is the molar volume of the gas.

   ❶ For a nonideal gas, this quotient may not equal *1*.

   Defined the compressibility factor z, then $\dfrac{P\hat{V}}{RT} \equiv Z$ or $\dfrac{PV}{nRT} = Z$

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✶The values of compressibility factor depend on the pressure, volume, and temperature of the real gas.

❷Define: reduced temperature：$T_r \equiv \dfrac{T}{T_c}$

reduced pressure $P_r \equiv \dfrac{P}{P_c}$ ；reduced molar volume $\hat{V}_r = \dfrac{\hat{V}}{\hat{V}_C}$

Table 4-1

氣　　體	熔點 °K	沸點 °K	T_c °K	沸點/T_c	P_c atm	$\bar{V}_c$ l/mole	$\dfrac{P_c \bar{V}_c}{RT_c}$
			簡單非極性分子（註）				
He	0.9	4.2	5.3	0.79	2.26	0.0578	0.300
H₂	14.0	20.4	33.3	0.68	12.8	0.0650	0.304
Ne	24.5	27.2	44.5	0.61	25.9	0.0417	0.296
A	83.9	87.4	151	0.58	48	0.0752	0.291
Xe	133	164.1	289.81	0.57	57.89	0.1202	0.293
N₂	63.2	77.3	126.1	0.61	33.5	0.0901	0.292
O₂	54.7	90.1	154.4	0.58	49.7	0.0744	0.292
CH₄	89.1	111.7	190.7	0.59	45.8	0.0990	0.290
CO₂	...	194.6	304.2	0.64	72.8	0.0942	0.274
			極性分子（註）				
H₂O	273.1	373.1	647.3	0.58	217.7	0.0566	0.232
NH₃	195.4	239.7	405.5	0.59	112.2	0.0720	0.243
CH₃OH	175.4	337.9	513.2	0.66	78.67	0.118	0.220
CH₃Cl	175.5	249.7	416.3	0.60	65.8	0.148	0.285
C₂H₅Cl	134.2	285.9	460.4	0.62	52	0.196	0.269
			烴類 (Hydrocarbons)				
乙烷 C₂H₆	89.98	184.6	305.5	0.60	48.2	0.139	0.267
丙烷 C₃H₈	185.51	281.1	305.5	0.60	48.2	0.139	0.267
異丁烷 C₄H₁₀(iso)	113.6	261.5	407	0.64	37	0.250	0.276
正丁烷 C₄H₁₀(n)	134.9	272.7	426	0.64	36	0.250	0.257
正己烷 C₆H₁₄	178.8	342.1	507.9	0.67	29.6	0.367	0.260
正辛烷 C₈H₁₈	216.6	397.7	570	0.70	24.7	0.490	0.259
苯 C₆H₆	278.6	352.7	561.6	0.63	47.9	0.256	0.265
環己烷 C₆H₁₂	279.7	353.9	554	0.64	40.57	0.312	0.230
乙烯 C₂H₄	103.7	169.3	282.8	0.60	50.5	0.126	0.274
乙炔 C₂H₂	191.3	189.5	308.6	0.61	61.6	0.113	0.275

✶Experimental observation shows;
For different fluids ➔ T_r & P_r 相同時 ➔ exhibit similar behavior

> All fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor, and all deviate from ideal-gas behavior to about the same degree.

✸根據此理論，可藉由 T_c、P_c、T_r、P_r 等資料求得 Z 值。其方法約略如下：

①由質能均衡(化工計算)、熱力學或物理化學或化工手冊等書本找出該氣體的 critical pressure P_c, critical temperature T_c ---等 critical constant。

②再依下列公式求出該氣體的對比變數(reduced variables)

　　$P_r = P/P_c$; $T_r = T/T_c$ -----

③有了 P_r 、 T_r 、V_r 其中的兩個，即可由質能均衡(化工計算)、熱力學或物理化學上所附的圖去找出 Z 值。

✸此法特別適用於高壓下的氣體。特別是在已知 T, P 而要求 V 時，頗為方便。但若是已知 T, V 而要求 P 或已知 P, V 而要求 T 時，會多 2, 3 個步驟。

Example 4-2:　已知 T, P ➔ 求 V

A tank is filled with 170 g of NH_3. The pressure and temperature in the tank are 40.8 atm and 384 K, respectively. Find the volume of these ammonium gases by using compressibility factor Z.

壓力一體積因子，$p_r v'_r = Z T_r$

一致壓力，P_r

✱若是已知 T, V 而要求 P，則需要 ideal reduced volume ($\hat{V}_{ri}$，理想一致體積)：

$$\hat{V}_{ri} = \frac{\hat{V}}{\hat{V}_{Ci}}$$
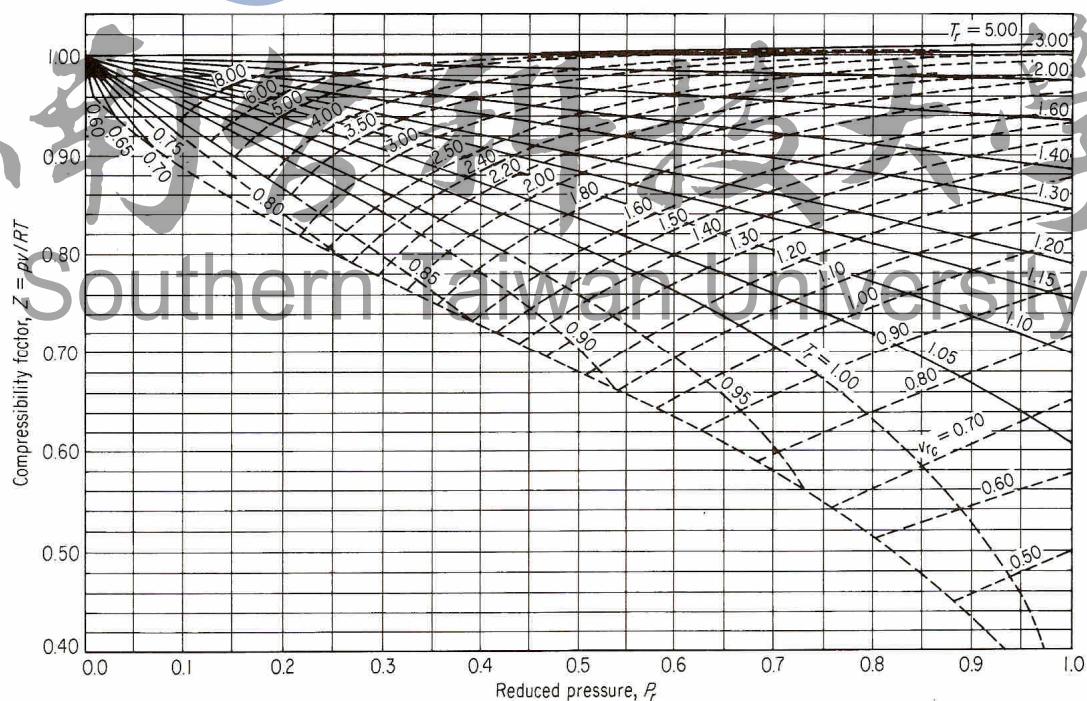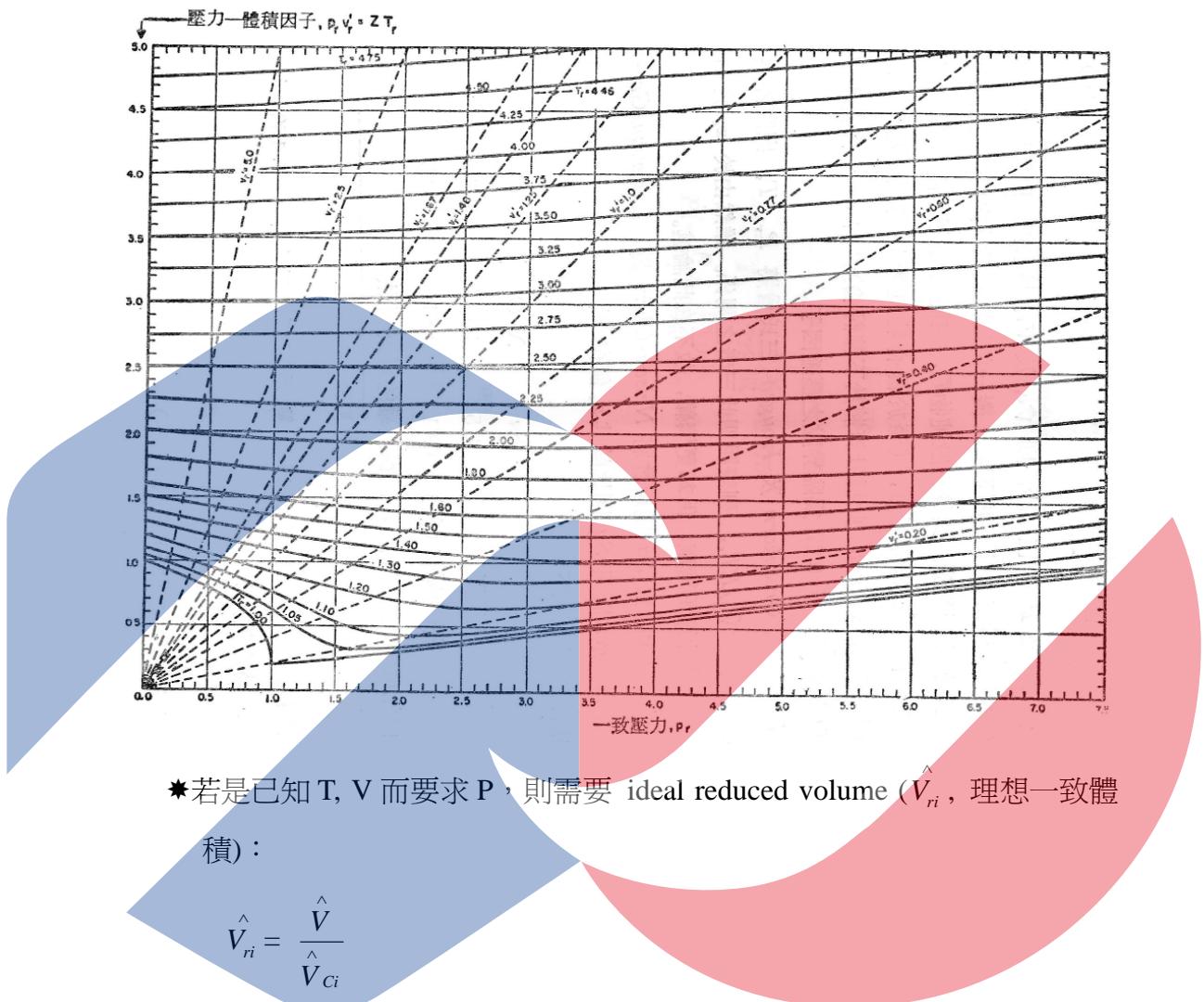
● $\hat{V}$: the molar volume of the gas

● $\hat{V}_{Ci}$: 在臨界條件下，把該氣體當成 ideal gas 而得到的莫耳體積。

∴ $P_c \hat{V}_{Ci} = RT_c$

Example 4-3: 已知 T, V ➔ 求 P

A tank (28.32 liter) is filled with 109.8 mole of O_2 at -25℃. Find the pressure of these O_2 gases by using compressibility factor z.   71.1 atm

2. The Virial Equations：

  (1) Virial equation of state implies that gases are nonideal because of the forces between the atoms or molecules.

  (2) A virial equation is simply a power series in terms of one of the state variables, either P or V.

$$Z = \frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \frac{D}{\hat{V}^3} + \text{----} \quad \text{(I)} \qquad Z：\text{compressibility factor}$$

❶where B, C, D --- are called the virial coefficients and are dependent on the nature of the gas and the temperature.

❷B is called the second virial coefficient; C is the third virial coefficient, and so forth.

❸一般的 real gas 之 $\hat{V}$ >> 1 → 上述 Virial equation 的第三項、第四項 --- 的重要性便不及第二項 → B 值便較受注意。

❹Virial equations of state in terms of pressure instead of volume are:

$$Z = \frac{P\hat{V}}{RT} = 1 + B'P + C'P^2 + D'P^3 + \text{----} \quad \text{(II)}$$

B', C', D' --- are called the virial coefficients

the third virial coefficient

the second virial efficient
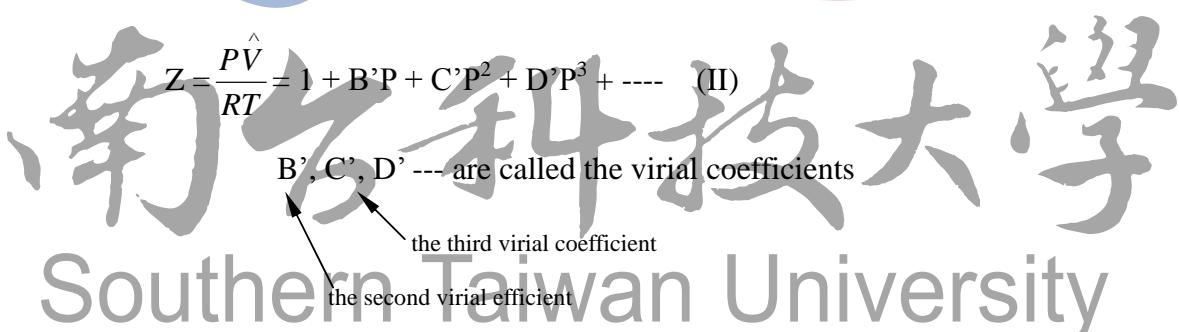
●此兩種表示法，可推導得：
B'=B/RT；C'=(C-B²)/(RT)²；D'=(D-3BC+2B³)/(RT)³

❺Virial equations 也有以下的表示法：

$$P\hat{V} = RT + B'P + C'P^2 + D'P^3 + \text{----}$$

由 $Z = \dfrac{P\hat{V}}{RT} = 1 + \dfrac{B}{\hat{V}} + \dfrac{C}{\hat{V}^2} + \dfrac{D}{\hat{V}^3} + \cdots$ ➔ $P = \dfrac{RT}{\hat{V}} + \dfrac{BRT}{\hat{V}^2} + \dfrac{CRT}{\hat{V}^3}$ (只看 3 項)

代入(II) 得

$$\frac{P\hat{V}}{RT} = 1 + B'\left(\frac{RT}{\hat{V}} + \frac{BRT}{\hat{V}^2} + \frac{CRT}{\hat{V}^3}\right) + C'\left(\frac{RT}{\hat{V}} + \frac{BRT}{\hat{V}^2} + \frac{CRT}{\hat{V}^3}\right)^2$$

$$+ D'\left(\frac{RT}{\hat{V}} + \frac{BRT}{\hat{V}^2} + \frac{CRT}{\hat{V}^3}\right)^3$$

$$= 1 + B'\frac{RT}{\hat{V}} + B'\frac{BRT}{\hat{V}^2} + B'\frac{CRT}{\hat{V}^3} + C'\left[\left(\frac{RT}{\hat{V}}\right)^2 + \left(\frac{BRT}{\hat{V}^2}\right)^2 + \left(\frac{CRT}{\hat{V}^3}\right)^2 + \right.$$

$$\left. 2\frac{RT}{\hat{V}}\frac{BRT}{\hat{V}^2} + 2\frac{BRT}{\hat{V}^2}\frac{CRT}{\hat{V}^3} + 2\frac{CRT}{\hat{V}^3}\frac{RT}{\hat{V}}\right] + D'\left(\frac{RT}{\hat{V}} + \frac{BRT}{\hat{V}^2} + \frac{CRT}{\hat{V}^3}\right)^3$$

和 $\dfrac{P\hat{V}}{RT} = 1 + \dfrac{B}{\hat{V}} + \dfrac{C}{\hat{V}^2} + \dfrac{D}{\hat{V}^3}$ 比較係數：

● $B'RT = B$ ➔ $B' = \dfrac{B}{RT}$

● $C = B'BRT + C'(RT)^2$ ➔ $C = \dfrac{B}{RT}BRT + C'(RT)^2$

$$C = B^2 + C'(RT)^2$$

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

(3)Figure 4-5 shows a compressibility-factor graph for methane by using Virial Equations.

All isotherms originate at the value Z = 1 for P = 0. In addition the isotherms are nearly straight lines at low pressures.

(4)∵ $\left(\dfrac{\partial Z}{\partial P}\right)_T = B' + 2C'P + 3D'P^2 + \cdots$

$\left(\dfrac{\partial Z}{\partial P}\right)_{T\ (\text{at } P = 0)} = B'$　　∴ $Z = \dfrac{P\hat{V}}{RT} = 1 + B'P = 1 + \dfrac{BP}{RT}$

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●此呼應前面所說的 Virial equation 的第二項較重要→ B 值便較受注意。

(3)同理，以 $Z=\dfrac{P\hat{V}}{RT} = 1 + \dfrac{B}{\hat{V}} + \dfrac{C}{\hat{V}^2} + \dfrac{D}{\hat{V}^3} + ----$ 來看

$$Z = \dfrac{P\hat{V}}{RT} = 1 + \dfrac{B}{\hat{V}}$$

Figure 4-5
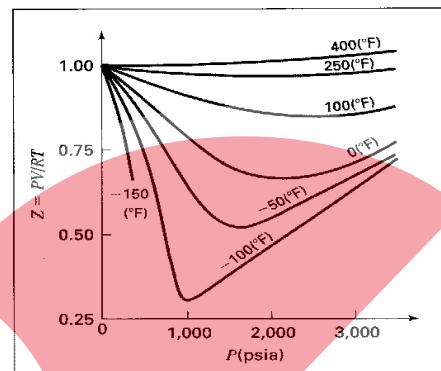
Example 4-4:

Reported values for the virial coefficients of isopropanol vapor at 200℃ are:

$$B = -388 \text{ cm}^3 \text{ mol}^{-1}$$

Calculate V and Z for isopropanol vapor at 200℃ and 10 bar by:

(a)The ideal gas equation

(b) $Z = \dfrac{P\hat{V}}{RT} = 1 + B'P = 1 + \dfrac{BP}{RT}$

Example 4-5:

For a gas of pressure low enough so that the virial expansion may be truncated to Z = 1 + B'P, show that the equation for isothermal work in a reversible compression is

$$W = -RT\, ln(\dfrac{P_1}{P_2})$$ the same as for an ideal gas.

Example 4-6:

Gas X enters a reversible, isothermal compressor at T_1 and P_1 and it is continuously compressed to P_2. Please calculate the work per mole of X required to run the compressor if X follows the equation of state $PV = RT + BP$, where V is the molar volume of X and B is a constant.

○使用 virial equation 或 corresponding states 都利用到 $Z = \dfrac{P\hat{V}}{RT}$，若求出的 Z 夠

正確，real gas 的 P, V, T 關係便搞定！但隨著 P, T 的條件不同，Z 值會產生偏移，因此便產生再次的修正：

$Z = Z^0 + \omega Z^1$

$Br = B^0 + \omega B^1$ 且 $Z = 1 + BrPr/Tr$ ---- 這些再修正就不再介紹了！

3. Cubic equation of state：

  (1)尋求一個廣用於整個氣相範圍但又不太複雜(太複雜則難以計算)的狀態方程式一直是一些學者的目標。Tab.4-2 是較常見的 real gas 之方程式，除了少部分是修正 Virial equations 外，目前以三次方的多項式狀態方程式較能滿足簡單與適用性廣泛的要求。

  (2)最早提出此類方程式的是諾貝爾物理獎得主(1910 年) J. D. van der Waals 在1873 年提出的 van der Waals equation：

$$P = \frac{nRT}{V-b} - \frac{an^2}{V^2} \quad \text{or} \quad P = \frac{RT}{\hat{V}-b} - \frac{a}{\hat{V}^2}$$

Table 4-2 較常見的 real gas 之方程式

Van der Waals:

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

Macleod:

$$n(\hat{V} - b') = RT$$

$$\pi = p + \frac{a}{\hat{V}_2}$$

$$b' = b_0(1 - B\pi + C\pi^2)$$

Clausius:

$$p = \frac{RT}{(\hat{V} - b)} - \frac{a}{T(\hat{V} + c)^2}$$

Lorentz:

$$p = \frac{RT}{\hat{V}^2}(\hat{V} + b) - \frac{a}{\hat{V}^2}$$

Dieterici:

$$p = \frac{RT}{(\hat{V} - b)}e^{-a/\hat{V}RT}$$

Berthelot:

$$p = \frac{R'T}{(\hat{V} - b)} - \frac{a}{T\hat{V}^2}$$

Wohl:

$$p = \frac{RT}{(\hat{V} - b)} - \frac{a}{\hat{V}(\hat{V} - b)} + \frac{c}{T\hat{V}^3}$$

Keyes:

$$p = \frac{RT}{(\hat{V} - \delta)} - \frac{A}{(\hat{V} - l)^2}$$

$$\delta = \beta e^{-\alpha/\hat{V}}$$

Redlich-Kwong:

$$\left[p + \frac{a}{T^{1/2}\hat{V}(\hat{V} + b)}\right](\hat{V} - b) = RT$$

$$a = 0.4278 \frac{R^2 T_c^{2.5}}{p_c}$$

$$b = 0.0867 \frac{RT_c}{p_c}$$

Beattie-Bridgeman:

$$p\hat{V} = RT + \frac{\beta}{\hat{V}} + \frac{\gamma}{\hat{V}^2} + \frac{\delta}{\hat{V}^3}$$

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2}$$

$$\gamma = -RTB_0 b + \omega A_0 - \frac{RB_0 c}{T^2}$$

$$\delta = \frac{RB_0 bc}{T^2}$$

Benedict-Webb-Rubin:

$$p\hat{V} = RT + \frac{\beta}{\hat{V}} + \frac{\sigma}{\hat{V}^2} + \frac{\eta}{\hat{V}^4} + \frac{w}{\hat{V}^5}$$

$$\beta = RTB_0 - A_0 - \frac{C_0}{T^2}$$

$$\sigma = bRT - a + \frac{c}{T^2}exp - \frac{\gamma}{\hat{V}^2}$$

$$\eta = c\gamma exp - \frac{\gamma}{\hat{V}^2}$$

$$w = a\alpha$$
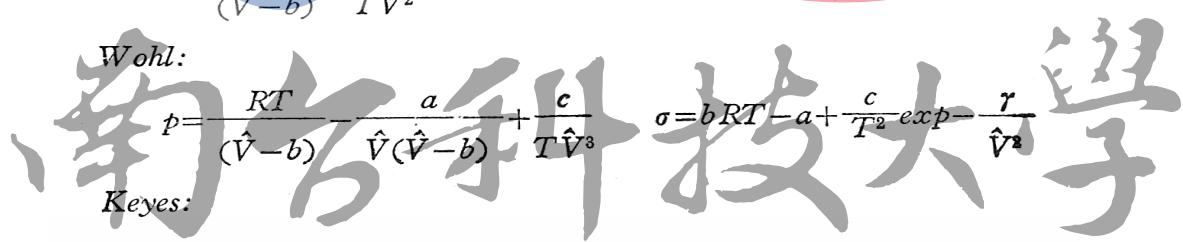
(3)隨後，許多 Cubic equation of state 也被提出來，但基本上大多是下列方程式的特別式。雖然多數方程式是由理論推導而得，但式中部分常數需以實驗方法確定。所以這些方程式應屬於半實驗式！

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

✴顯然的，當 $\eta = b$，$\theta = a$ 且 $\kappa=\lambda= 0$ ➔ 上式變成 $P = \dfrac{RT}{\hat{V}-b} - \dfrac{a}{\hat{V}^2}$

✴經過一些參數設定，可再簡化成： $P = \dfrac{RT}{\hat{V}-b} - \dfrac{a(T)}{(\hat{V}+\varepsilon b)(\hat{V}+\sigma b)}$

4. The van der Waals equation of state:

● $(P + \dfrac{an^2}{V^2})(V-nb) = nRT$ ➔ ◆ $P = \dfrac{nRT}{V-b} - \dfrac{an^2}{V^2}$

◆ $V^3 - (nb+\dfrac{nRT}{P})V^2 + \dfrac{an^2}{P}V - \dfrac{abn^3}{P} = 0$

● $(P + \dfrac{a}{\hat{V}^2})(\hat{V}-b) = RT$ ➔ $P = \dfrac{RT}{\hat{V}-b} - \dfrac{a}{\hat{V}^2}$

(1) The constants, a and b, are the van der Waals constants for a particular gas.

(2) "*a*" represents the pressure correction and is related to the magnitude of the interactions between gas particles.

❶real gas 分子間具吸引力 ➔ 此吸引力使氣體分子撞擊容器壁的力道減小 ➔ ∴ 使 real gas 的壓力變小

❷今有 real gas 的壓力為 P，若轉而以 ideal gas 來看，則

$P_{ideal} = P_{real} + \boxed{\text{因吸引力所造成的壓力減少量}}$

➔ ●與單位體積內的分子數目(mole 數)的平方成正比。

∴修正後的壓力應為 $(P + an^2/V^2)$，而 a 為修正壓力的比例常數。

❸◆ real gas 分子具有體積

➔ ∴氣體分子在體積為 V 的容器內的活動體積不再是 V。

◆若 1 mol 的氣體有"excluded volume"為 b，則 n mol 氣體分子的"excluded

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volume"應是 nb → 體積修正為 (V-nb)

※※每一個氣體分子的 excluded volume 為其體積的 4 倍。

分子體積 $V_m = \dfrac{4}{3}\pi(\dfrac{d}{2})^3$

excluded volume $= 4 V_m$
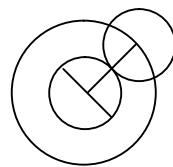
(3)一般而言，

- 已知 P, V 求 T 或已知 T, V 求 P → 找到 a, b 值，則可利用 the van der Waals equation 輕易解出。
- 已知 P, T 求 V → 找到 a, b 值，欲利用 the van der Waals equation 解題，將面臨解 3 次方的方程式。所以，一般並不鼓勵用 the van der Waals equation 求 V。

氣體	a $l^2\text{-}atm/mole^2$	b $l/mole$	氣體	a $l^2\text{-}atm/mole^2$	b $l/mole$
H_2	0.2444	0.02661	CH_4	2.253	0.04278
He	0.03412	0.02370	C_2H_6	5.489	0.06380
N_2	1.390	0.03913	C_3H_8	8.664	0.08445
O_2	1.360	0.03183	$C_4H_{10}(n)$	14.47	0.1226
Cl_2	6.493	0.05622	$C_4H_{10}(iso)$	12.87	0.1142
NH_3	4.170	0.0371	$C_5H_{12}(n)$	19.01	0.1460
NO_2	5.284	0.04424	CO	1.485	0.03985
H_2O	5.464	0.03049	CO_2	3.592	0.04267

Example 4-7:

Consider a 1.2 mole sample of CO_2, that has a pressure of 5 atm and a volume of 10.0 L. Predict the temperature of this sample of gas using the van der Waals equation.
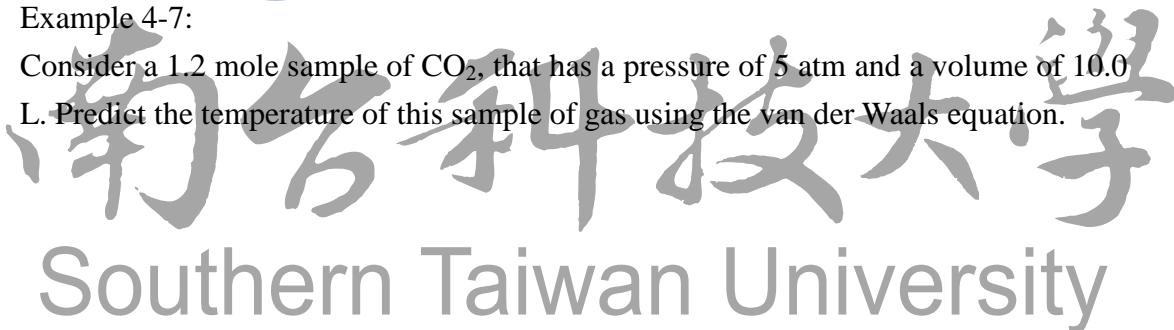
Example 4-8:

Consider a 5.0 mole sample of ammonia, NH_3, that has a pressure of 5 atm and a temperature of 500 K. Predict the volume of this sample of gas using the van der Waals equation.

5. Determination of the van der Waals constants：

  ●請注意！我們在這小段中，以 V 來代替 $\hat{V_c}$ ，因為要打 $\hat{V_c}$ 這個字是辛苦的！

(1)The van der Waals constants can be derived from T_c, P_c and $\hat{V_c}$.

(2)Since the critical isotherm exhibits a horizontal inflection at the critical point ➔

$$(\frac{\partial P}{\partial V})_{T;Cr} = (\frac{\partial^2 P}{\partial V^2})_{T;Cr} = 0$$

  ●"Cr" denotes the critical point.   That is, $T = T_c$, $V=V_c$, $P =P_c$.

  When n = 1, the van der Waals equation of state ➔ $P = \dfrac{RT}{V-b} - \dfrac{a}{V^2}$

(3) $\therefore (\frac{\partial P}{\partial V})_{T=Tc} = 0 = \dfrac{-RT_c}{(V_c - b)^2} + \dfrac{2a}{V_c^3}$

  $(\frac{\partial^2 P}{\partial V^2})_{T=Tc} = 0 = \dfrac{2RT_c}{(V_c - b)^3} - \dfrac{6a}{V_c^4}$

  $\therefore$ 聯立上三式可得 $a = 3P_c V_c^2$ ； $b = \dfrac{V_c}{3}$ ； $R = \dfrac{8P_c V_c}{3T_c}$

  但 V_c 不易精確測得

  $\therefore V_c = \dfrac{3RT_c}{8P_c}$ ➔ $a = \dfrac{27(RT_c)^2}{64P_c}$ ； $b = \dfrac{RT_c}{8P_c}$

  or $V_c = 3b$ ； $P_c = \dfrac{a}{27b^2}$ ； $T_c = \dfrac{8a}{27bR}$

(4)An equivalent, but more straightforward, procedure is illustrated for the van der
  Waals equation. Since $V = V_c$ for each of the three roots at the critical point,
  $\therefore (V-V_c)^3 = 0$ or $V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0$

  The van der Waals eq. at critical point: $V^3 - (b + \dfrac{RT_c}{P_c})V^2 + \dfrac{a}{P_c}V - \dfrac{ab}{P_c} = 0$

  $\therefore 3V_c = b + \dfrac{RT_c}{P_c}$ ； $3V_c^2 = \dfrac{a}{P_c}$ ； $V_c^3 = \dfrac{ab}{P_c}$

  $\therefore a = 3P_c V_c^2$ ； $b = \dfrac{V_c}{3}$

  $\therefore V_c = \dfrac{3RT_c}{8P_c}$ ； $a = \dfrac{27(RT_c)^2}{64P_c}$ ； $b = \dfrac{RT_c}{8P_c}$

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8}$$

- The Z_c values can be calculated when the critical states have been found (即 P_c, T_c,V_c 已求出)
- 實際上，由實驗所得的 Z_c 值，略小於由 P_c, T_c,V_c 所計算之值。

Example 4-9:

以氣體的臨界性質(properties at the critical point)來表示 1 mole 氣體知凡得瓦方程式(van der Waals equation)中的參數及氣體常數。

Example 4-10:

Eqn. Of state: $\left[P + \dfrac{a}{V^2 T^{0.5}} \right] (V - b) = RT$

(a) express a,b in terms of the critical property.   (b) reduced eqn. of state = ?

(c) at T=150℃ , V=5 cm^3/g , Z=$\dfrac{PV}{RT}$ = ?

    data given

        M_w = 28.013 P_c = 33.9 bar

        T_c = -146.95℃ V_c = 89.8 cm^3/gmole

        R = 83.1439 bar·cm^3/moleK

(d) K = $-\dfrac{1}{V} \left(\dfrac{\partial V}{\partial P} \right)_T$, Derive K, from eqn of state.