ch 2 Equation of State

2.1 Introduction

In thermodynamics, 在原有 mass, length, time 3個基本量外，又加上一個基本量 temperature.

The concept of temperature 源自於 systems in thermal equilibri...

Simplest thermodynamic system perhaps is a homogeneous flu... — say, a gas or vapor.

$$\boxed{P.V.T} \qquad f(P.V.T) = 0.$$
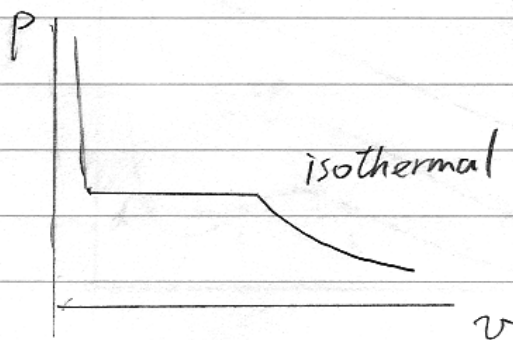
Three state variables, only two are independent.

注意 The equation of state does not involve time.
Systems are in thermal, mechanical, and chemical equilib...
that is thermodynamic equilibrium.

Canonically conjugate pairs : extensive 出 intensive 成對
且乘積為能量
$$PdV = W.$$

T 的對應量將在 ch 6 中討論。

2.2 Equation of State of an Ideal Gas

$$P V = \frac{m}{M} RT$$

$\triangle$ → 公斤 ° k

Pa →
$\left(N/m^2\right)$

立方公尺

kmole 質量
單位公斤

$$R = 8.314 \times 10^3 \ \frac{J}{kmore \cdot K}$$

$\triangle$
$$P V = n RT$$

kilomole

$\triangle$ Specific volume $\upsilon = \dfrac{V}{n} \quad \left(\dfrac{m^3}{kilomole}\right)$

$\triangle$
$$P \upsilon = RT$$

Fig 2.1 (a)   (b)   (c)

2.3 Van der Waal's Equation for a Real Gas

When the gas is near condensation, equation of state of an ideal gas 不適用.

P 图 (isothermal curve)

很多 equations of state 被 提出 來 敘述 此 real gas 現象
在此介紹 Van der Waal's eq. of state
因它 ① 簡單, ② 有 物理意義. ③ 適用 於 很大的 溫度, 压力 範圍.

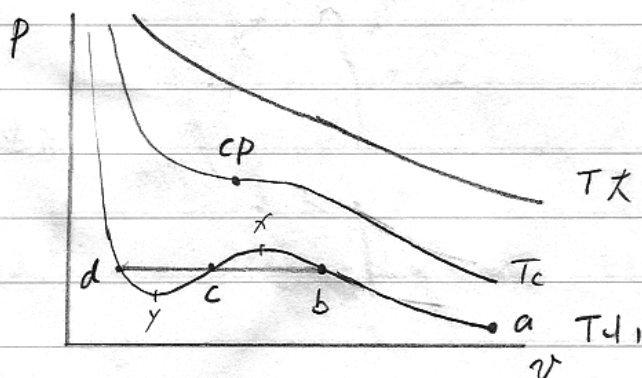$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \qquad (2.5)$$

a 和 b 是 特性常數, 隨氣体本質而定.

b 反應氣体分子實際佔有的体積.

a 反應氣体分子間的交互作用力 cohesive force.
来自於 the overlap of electron clouds.

(2.5) 乘開為：$P\upsilon^3 - (Pb + RT)\upsilon^2 + a\upsilon - ab = 0$ (2.6)

Isothermal process：P 是 υ 的 3 次方程式，其解如下：

$T \rightarrow$ 大：行為近似理想氣体。

$T = T_c$：有一個水平点，稱作 critical point CP，此線為 critical curve。

$T < T_c$：有二個水平点，此類曲線並不合理。
　　在 x 松 y 間 P, υ 同時增大或減小，顯然不符現實。
　　實際上 a→b 是 vapor，b→d 的水平直線是 液氣共存。
　　d 以下完全液化。

2.4 P-v-T surfaces for Real Substances

P25, Fig 2.3 : 實際物質的 state surface in P-v-T space.
水的不一樣.

注意固, 液, 氣三種 phases 的區域.

注意 triple line, where all three phases can coexist.

物理定義: Solid: 体積, 形狀固定

Liquid: 体積固定, 形狀不定

Gas: 体積, 形狀均不固定, 加壓不液化.

Vapor: 等溫線似於 Critical curve, 加壓會液化者

沸点: boiling-point, saturated vapor.
水燒開時, 飽和蒸氣圧 = 外界大氣圧、why?

P26, Fig 2.4: 觀察三相變化及邊界.

液氣間溫度 or 圧力高於 CP 点時, 液氣不分.
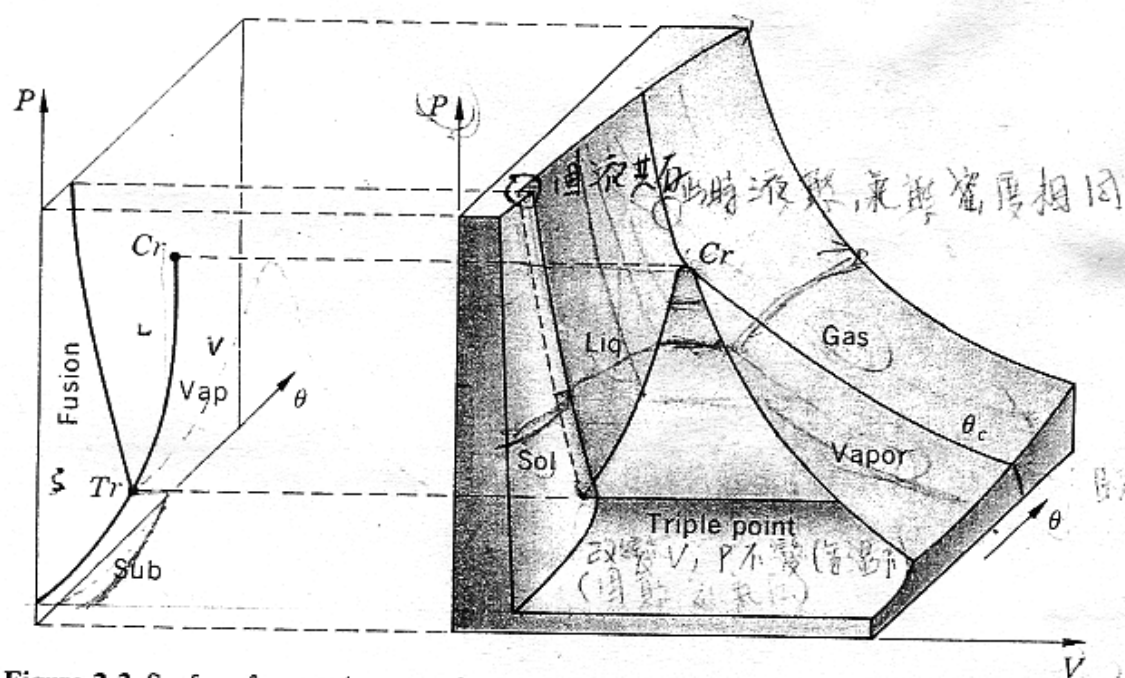
固, 液相變無臨界点, 因兩種相的对稱性不同.

P26 - P27 : 舉例.

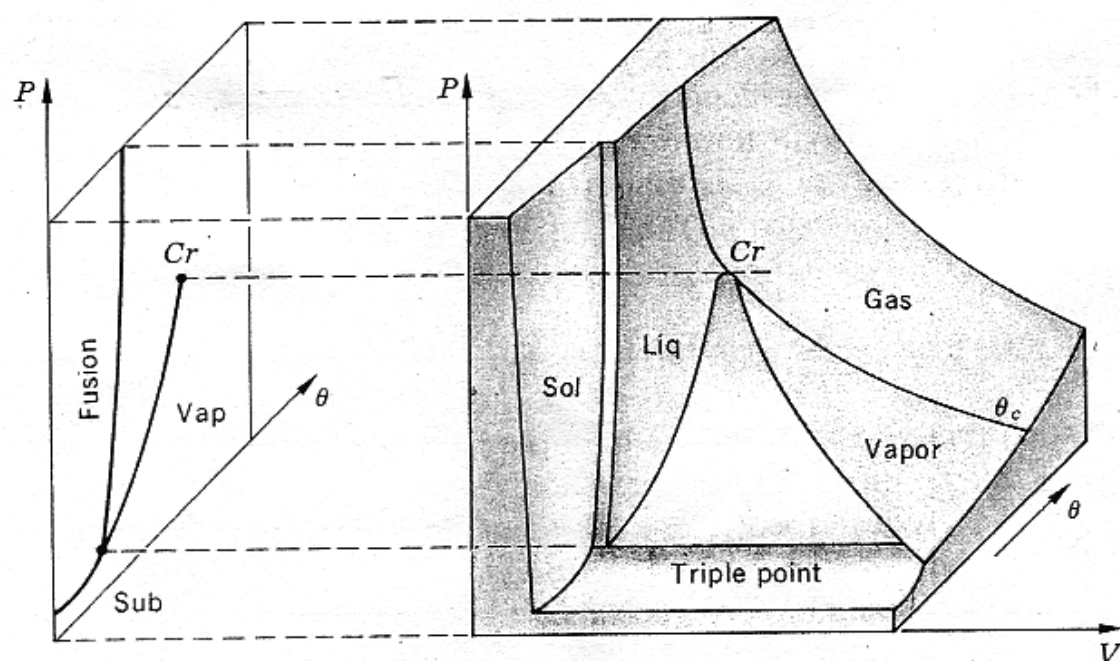**Figure 2-3** Surface for a substance that contracts on melting.

Figure 2-4 Surface for a substance that expands on melting.

2.5 Expansivity and Compressibility

System : state variables P, v, T, 獨立變數 2 個.

$\boxed{PVT}$ equation of state:

$$v = v(T, P)$$

$$\Rightarrow \quad dv = \underbrace{\left(\frac{\partial v}{\partial T}\right)_P}_{} dT + \underbrace{\left(\frac{\partial v}{\partial P}\right)_T}_{} dP$$

定義 $v\beta$ $-vK$

$$\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P : \text{expansivity or coefficient of volume expansion}$$

$$K \equiv \frac{-1}{v}\left(\frac{\partial v}{\partial P}\right)_T : \text{isothermal compressibility}.$$

因 $\left(\frac{\partial v}{\partial P}\right)_T < 0$, 故 加 "$-$" 便 $K > 0$.

For ideal gas $v = \dfrac{RT}{P}$. $\Rightarrow \begin{cases} \beta = \dfrac{R}{Pv} = \dfrac{1}{T} \\[2mm] K = \dfrac{-1}{v}\left(\dfrac{-RT}{P^2}\right) = \dfrac{1}{P} \end{cases}$

$\Rightarrow$ 高溫氣体 β 很小, 高压氣体 K 很小。

For a liquid or a solid, β and K are near constant over a wide range of T and P.

$$\Rightarrow \quad dv = \beta v \, dT - K v \, dP$$

因 v 變化極小, 可視為常數 $\Rightarrow dv \fallingdotseq \beta v_0 \, dT - K v_0 \, dP$.

因 v_0, β, K 均是常數 (固流)

$$\int_{v_0}^{v} dv = \beta v_0 \int_{T_0}^{T} dT - K v_0 \int_{P_0}^{P} dP$$

$$\Rightarrow v = v_0 \left[1 + \beta(T - T_0) - K(P - P_0) \right]$$

固流體的近似方程式, v 於 T, P 的變化是線性關係.

Appendix A

A1 Partial Derivatives

x, y, z 3個變數, 有一個關係式: $f(x, y, z) = 0$.

可任取 2個為獨立變數, $\Rightarrow \begin{cases} x(y, z) \\ y(x, z) \end{cases}$

$$\Rightarrow \begin{cases} dx = \left(\dfrac{\partial x}{\partial y}\right)_z dy + \left(\dfrac{\partial x}{\partial z}\right)_y dz \quad\text{------- (A 2)} \\[4mm] dy = \left(\dfrac{\partial y}{\partial x}\right)_z dx + \left(\dfrac{\partial y}{\partial z}\right)_x dz \quad\text{------- (A 3)} \end{cases}$$

(A3) 代入 (A2) $\Rightarrow dx = \left(\dfrac{\partial x}{\partial y}\right)_z \left[\left(\dfrac{\partial y}{\partial x}\right)_z dx + \left(\dfrac{\partial y}{\partial z}\right)_x dz \right] + \left(\dfrac{\partial x}{\partial z}\right)_y dz$

$$\Rightarrow dx = \left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial x}\right)_z dx + \left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial z}\right)_x dz + \left(\dfrac{\partial x}{\partial z}\right)_y dz$$

$$\text{(A 4)}$$

因有 2 個獨立變數, 取 x, z.

若 $dz = 0$ $\Rightarrow$ $\left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial x}\right)_z = 1$ $\qquad$ (A.5)

若 $dx = 0$ $\Rightarrow$ $\left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial z}\right)_x = -\left(\dfrac{\partial x}{\partial z}\right)_y$ $\qquad$ (A.6)

(A.5) $\Rightarrow$ $\left(\dfrac{\partial x}{\partial y}\right)_z = \dfrac{1}{\left(\dfrac{\partial y}{\partial x}\right)_z}$ $\Rightarrow$ $\boxed{\left(\dfrac{\partial x}{\partial z}\right)_y = \dfrac{1}{\left(\dfrac{\partial z}{\partial x}\right)_y}}$ reciprocal relation

再代入 (A.6) $\Rightarrow$ $\left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial z}\right)_x = \dfrac{-1}{\left(\dfrac{\partial z}{\partial x}\right)_y}$

$\Rightarrow$ $\boxed{\left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial z}\right)_x \left(\dfrac{\partial z}{\partial x}\right)_y = -1}$ $\qquad$ (A.7)

cyclical rule
cyclical relation

Show chain rule $\left(\dfrac{\partial x}{\partial z}\right)_u = \left(\dfrac{\partial x}{\partial y}\right)_u \left(\dfrac{\partial y}{\partial z}\right)_u$ $\qquad$ (A.11)

$\boxed{\text{system}}$ 有變數 x, y, z, u, 獨立變數 2 個 (可任取, 有 6 種取法)

$\Rightarrow$ $\begin{bmatrix} u(x,y), & x(u,y), & \text{---} \\ z(x,y), & z(u,y), & \text{---} \end{bmatrix}$

由 $x = x(u,y)$ $\Rightarrow$ $dx = \left(\dfrac{\partial x}{\partial u}\right)_y du + \left(\dfrac{\partial x}{\partial y}\right)_u dy$

使 u 不變, 將 dx 除以 dz $\Rightarrow$ $\left(\dfrac{\partial x}{\partial z}\right)_z = \left(\dfrac{\partial x}{\partial y}\right)_u \left(\dfrac{\partial y}{\partial z}\right)_u$

2.6 An Application

計算流体 (fluid) 溫度由 T_1 cool down to T_2 時壓力變化 ($T_2 < T_1$)

$\boxed{\text{system}}$ P, v, T , 2 個獨立變數。

$$f(P, v, T) = 0.$$

設 cooling process 是 quasi-static process, 是 reversible, 是 isochoric 每点都是平衡態。

$$\Rightarrow \quad P = P(v, T)$$

$$\Rightarrow \quad dP = \left(\frac{\partial P}{\partial v}\right)_T dv + \left(\frac{\partial P}{\partial T}\right)_v dT$$

0 because it is isochoric

$$\Rightarrow \quad \int_{P_1}^{P_2} dP = \int_{T_1}^{T_2} \left(\frac{\partial P}{\partial T}\right)_v dT$$

因 $\left(\dfrac{\partial P}{\partial T}\right)_v \left(\dfrac{\partial T}{\partial v}\right)_P \left(\dfrac{\partial v}{\partial P}\right)_T = -1$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_v = \frac{-1}{\left(\dfrac{\partial T}{\partial v}\right)_P \left(\dfrac{\partial v}{\partial P}\right)_T} = \frac{-\left(\dfrac{\partial v}{\partial T}\right)_P}{\left(\dfrac{\partial v}{\partial P}\right)_T} = \frac{\beta}{K}$$

If β, K are independent of T $\Rightarrow$ $P_2 - P_1 = \dfrac{\beta}{K}(T_2 - T_1)$

結果和 P29, (2.18) 的結果相同

實際上的 cooling 不可能是 reversible，因加熱會造成系統內的
溫度梯度。熱源與系統間亦有溫度梯度。

不過上述討論與 path 無關，只與起點與終點有關。
故可任意選擇路徑，方便上選 reversible process。

That is, $\int_{P_1}^{P_2} dP = \frac{P}{K} \int_{T_1}^{T_2} dT$

$(P_2 - P_1) = \frac{P}{K} (T_2 - T_1)$ 與路徑無關。