Review:

Unknowns
n
$Vol.$
p
T
U
S
δQ_{in}
δW

	Equations		
(1)	$N = nVol.$		
(2)	$p = nk_B T$	(2a)	$pVol. = Nk_B T$
(3)	$U = (3/2)pVol.$	(3a)	$U = (3/2)Nk_B T$
(4)	$\Delta U = \delta Q_{in} + \delta W$	(4a)	$\Delta U = T\Delta S - p\Delta Vol.$
(5)	$\Delta S = \delta Q_{in} / T$		
(6)	$\delta W = -p\Delta Vol.$		

The First Law of Thermodynamics

(4) $\Delta U = \delta Q_{in} + \delta W$ 外對內

Since

(3a) $U = (3/2)Nk_B T$,

it yields

(3b) $\Delta U = (3/2)Nk_B \Delta T$

Substituting equation (3b) and equation

(6) δW 外對內 $= -p\Delta Vol.$

into equation (4) to eliminate ΔU and δW , it yields

(4b) $(3/2)Nk_B \Delta T = \delta Q_{in} - p\Delta Vol.$

Case 1: Isochoric Process

For isochoric process (constant-volume process), we have $\Delta Vol. = 0$.

Substituting $\Delta Vol. = 0$ into equation

(4b) $(3/2)Nk_B \Delta T = \delta Q_{in} - p\Delta Vol.$

it yields

(4c) $\delta Q_{in}\big|_{Vol.=\text{constant}} = (3/2)Nk_B \Delta T\big|_{Vol.=\text{constant}} = C_V \Delta T\big|_{Vol.=\text{constant}}$

where C_V is the heat capacity at constant volume 等容熱容.

Case 2: Isobaric Process

For isobaric process (constant-pressure process), we have $\Delta p = 0$.

Differentiating equation (2a) once, it yields

(2b) $Vol.\Delta p + p\Delta Vol. = Nk_B \Delta T$

Substituting $\Delta p = 0$ into equation (2b), then substituting the resulting equation into equation

(4b) $(3/2)Nk_B \Delta T = \delta Q_{in} - p\Delta Vol.$

to eliminate $p\Delta Vol.$, it yields

(4d) $\delta Q_{in}\big|_{p=\text{constant}} = (5/2)Nk_B \Delta T\big|_{p=\text{constant}} = C_P \Delta T\big|_{p=\text{constant}}$

where C_P is the heat capacity at constant pressure 等壓熱容

In summary, we have

(4c) $\delta Q_{in}\big|_{Vol.=\text{constant}} = (3/2)Nk_B \Delta T\big|_{Vol.=\text{constant}} = C_V \Delta T\big|_{Vol.=\text{constant}}$

(4d) $\delta Q_{in}\big|_{p=\text{constant}} = (5/2)Nk_B \Delta T\big|_{p=\text{constant}} = C_P \Delta T\big|_{p=\text{constant}}$

where

(4c) $C_V = (3/2)Nk_B$

(4d) $C_P = (5/2)Nk_B$

Now, let us consider the entropy S as a function of pressure p and volume $Vol.$, it yields

$$\Delta S = \Delta p \left.\frac{\partial S}{\partial p}\right|_{Vol.=\text{constant}} + \Delta Vol. \left.\frac{\partial S}{\partial Vol.}\right|_{p=\text{constant}}$$

$$= \Delta S|_{Vol.=\text{constant}} + \Delta S|_{p=\text{constant}}$$

$$= \left.\frac{\delta Q_{in}}{T}\right|_{Vol.=\text{constant}} + \left.\frac{\delta Q_{in}}{T}\right|_{p=\text{constant}}$$

$$= C_V \left.\frac{\Delta T}{T}\right|_{Vol.=\text{constant}} + C_P \left.\frac{\Delta T}{T}\right|_{p=\text{constant}}$$

Now, we need to determine $(\Delta T / T)_{Vol.=\text{constant}}$ & $(\Delta T / T)_{p=\text{constant}}$.

Since the ideal gas law, equation (2*a*), can be rewritten as

(2*c*) $\ln p + \ln Vol. = \ln(Nk_B) + \ln T$

Differentiating equation (2*c*) once, it yields

(2*d*) $\frac{\Delta p}{p} + \frac{\Delta Vol.}{Vol.} = \frac{\Delta T}{T}$

Equation (2*d*) yields

(2*e*) $\left.\frac{\Delta T}{T}\right|_{Vol.=\text{constant}} = \left.\frac{\Delta p}{p}\right|_{Vol.=\text{constant}}$ and

(2*f*) $\left.\frac{\Delta T}{T}\right|_{p=\text{constant}} = \left.\frac{\Delta Vol.}{Vol.}\right|_{p=\text{constant}}$

Substituting equations (2*e*) and (2*f*) into

$$\Delta S = C_V \left.\frac{\Delta T}{T}\right|_{Vol.=\text{constant}} + C_P \left.\frac{\Delta T}{T}\right|_{p=\text{constant}}$$

it yields

$$\Delta S(p,Vol.) = C_V \left.\frac{\Delta p}{p}\right|_{Vol.=\text{constant}} + C_P \left.\frac{\Delta Vol.}{Vol.}\right|_{p=\text{constant}}$$

or

$$\Delta S(p,Vol.) = C_V \left\{ \Delta \ln p|_{Vol.=\text{constant}} + \frac{C_P}{C_V} \Delta \ln Vol.|_{p=\text{constant}} \right\}$$

Thus,

$$S(p,Vol.) = C_V \ln[p(Vol.)^{C_P/C_V}] + \text{constant}$$

is a solution of the above differential equation.

Since

$$\Delta S|_{Vol.=\text{constant}} = \Delta p \left.\frac{\partial S}{\partial p}\right|_{Vol.=\text{constant}} = C_V \left.\frac{\Delta p}{p}\right|_{Vol.=\text{constant}}$$

$$\Delta S|_{p=\text{constant}} = \Delta Vol. \left.\frac{\partial S}{\partial Vol.}\right|_{p=\text{constant}} = C_P \left.\frac{\Delta Vol.}{Vol.}\right|_{p=\text{constant}}$$

it yields

$$\left.\frac{\partial S}{\partial p}\right|_{Vol.=\text{constant}} = \frac{C_V}{p} = \frac{3}{2}\frac{Nk_B}{p} \quad \text{and} \quad \left.\frac{\partial S}{\partial Vol.}\right|_{p=\text{constant}} = \frac{C_P}{Vol.} = \frac{5}{2}\frac{Nk_B}{Vol.}$$

Exercise:

Write down the entropy S as a function of pressure p and temperature T.

Please show that

$$\left.\frac{\partial S}{\partial p}\right|_{T=\text{constant}} = -\frac{Nk_B}{p} \quad \text{and} \quad \left.\frac{\partial S}{\partial T}\right|_{p=\text{constant}} = \frac{5}{2}\frac{Nk_B}{T}$$

Exercise:

Write down the entropy S as a function of volume $Vol.$ and temperature T.

Please show that

$$\left.\frac{\partial S}{\partial Vol.}\right|_{T=\text{constant}} = \frac{Nk_B}{Vol.} \quad \text{and} \quad \left.\frac{\partial S}{\partial T}\right|_{Vol.=\text{constant}} = \frac{3}{2}\frac{Nk_B}{T}$$

Namely,

$$\left.\frac{\partial S}{\partial p}\right|_{T=\text{constant}} \neq \left.\frac{\partial S}{\partial p}\right|_{Vol.=\text{constant}} \quad \text{and} \quad \left.\frac{\partial S}{\partial Vol.}\right|_{T=\text{constant}} \neq \left.\frac{\partial S}{\partial Vol.}\right|_{p=\text{constant}}$$

In summary, the entropy S can be written as

$$S(p,Vol.) = \frac{3}{2}Nk_B \ln[p(Vol.)^{5/3}] + \text{constant}$$

or

$$S(p,T) = Nk_B \ln[T^{5/2}/p] + \text{constant}$$

or

$$S(Vol.,T) = Nk_B \ln[(Vol.)T^{3/2}] + \text{constant}$$

or

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這段熱力學教材，主要在闡述以下這個重要結論：

在寫偏微分時，一定要說清楚，是在什麼變數 keep constant 的情況下，所求的偏微分。

例如：

$$\left.\frac{\partial S}{\partial p}\right|_{Vol.=\text{constant}} \text{或簡寫為} \left.\frac{\partial S}{\partial p}\right|_{Vol.}$$

或清楚標明函數中的自變數。例如：$\dfrac{\partial S(p,Vol.)}{\partial p}$

如果單寫 $\dfrac{\partial S}{\partial p}$，是沒有意義的！