推导： $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$ 麦克斯韦关系式之一

$dU = đQ + đW = đQ - p \cdot dV = T \cdot dS - p \cdot dV$ ……①

另外： $U = U(S, V)$ —— PVT系统选两独立态函数 (S, V)

做全微分 $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S \cdot dV$ ……②

①式②式比较，对应系数相等

$T = \left(\frac{\partial U}{\partial S}\right)_V$ 和 $-p = \left(\frac{\partial U}{\partial V}\right)_S$

作用 $\left(\frac{\partial}{\partial V}\right)_S$ $\left(\frac{\partial}{\partial S}\right)_V$

得： $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial \left(\frac{\partial U}{\partial S}\right)_V}{\partial V}\right)_S$ 和 $-\left(\frac{\partial p}{\partial S}\right)_V = \left(\frac{\partial \left(\frac{\partial U}{\partial V}\right)_S}{\partial S}\right)_V$

推广 $y=f(x_1, x_2)$

$$\frac{\partial^2 y}{\partial x_1 \partial x_2} = \frac{\partial^2 y}{\partial x_2 \partial x_1}$$

微分先后次序可换

有：$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

其余 Maxwell 关系均可通过选择不同

$$\begin{matrix} U & F & H \\ S \rightarrow & \vdots & \vdots & \cdots \text{推导出来} \\ V & \vdots & \vdots \end{matrix}$$

关于焓的微分方程

$H = U + pV$

$H = H(S, p)$

$$dH = d(U + pV) = dU + d(pV)$$

$$= T \cdot dS - \cancel{p\,dV} + \cancel{p\,dV} + V \cdot dp$$

$$= T \cdot dS + V \cdot dp$$

数学知识.

$$f(x, y) = \underbrace{x}_{x} \cdot \underbrace{\sin(x+y)}_{u(x,y)}$$

$$\left(\frac{\partial f}{\partial x}\right)_y = \sin(x+y) + x \cdot \cos(x+y)$$

$$\left(\frac{\partial f}{\partial y}\right)_x = x \cdot \cos(x+y)$$

$f(x, u(x,y))$. 有 $\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial x}\right)_u + \left(\frac{\partial f}{\partial u}\right)_x \left(\frac{\partial u}{\partial x}\right)_y$

求 $C_p - C_v = T\cdot\left(\frac{\partial p}{\partial T}\right)_v\cdot\left(\frac{\partial v}{\partial T}\right)_p$ 均可测量

$$C_v \equiv \left(\frac{dQ}{dT}\right)_v = \left(\frac{dU + \cancel{p\,dv}}{dT}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v$$

等容过程 $dv = 0$

$$C_p \equiv \left(\frac{dQ}{dT}\right)_p = \left(\frac{dU + p\,dv}{dT}\right)_p$$

利用 $dH = dU + V\,dp + p\cdot dV$

$$C_p = \left(\frac{dH - \cancel{V\cdot dp}}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

等压过程 $dp = 0$

对 $\left(\frac{\partial U}{\partial T}\right)_V$ 操作.

引入 $U=U(V,T)$

做全微分 $dU=\left(\frac{\partial U}{\partial T}\right)_V \cdot dT+\left(\frac{\partial U}{\partial V}\right)_T \cdot dV$ ……①

另外. 热力学基本微分方程 $dU=T\cdot dS-p\cdot dV$

下一步应有 $dS \to dT$. 引入 $S=S(T,V)$

代入

全微分 $dS=\left(\frac{\partial S}{\partial T}\right)_V \cdot dT+\left(\frac{\partial S}{\partial V}\right)_T \cdot dV$

代入得 $dU=T\left(\frac{\partial S}{\partial T}\right)_V dT+\left[T\cdot\left(\frac{\partial S}{\partial V}\right)_T-p\right]\cdot dV$ ……②

①式②式对应系数相等得

$\left(\frac{\partial U}{\partial T}\right)_V=T\cdot\left(\frac{\partial S}{\partial T}\right)_V$ 和 $\left(\frac{\partial U}{\partial V}\right)_T=T\cdot\left(\frac{\partial S}{\partial V}\right)_T-p$

和前一页非常类似

对 $\left(\frac{\partial H}{\partial T}\right)_p$ 操作，引入 $H=H(T,p)$

做全微分 $dH=\left(\frac{\partial H}{\partial T}\right)_p\cdot dT+\left(\frac{\partial H}{\partial p}\right)_T\cdot dp$ ……③

之前有 $dH=T\cdot dS+V\cdot dp$

代入

再引入 $S=S(T,p)$

全微分有 $dS=\left(\frac{\partial S}{\partial T}\right)_p\cdot dT+\left(\frac{\partial S}{\partial p}\right)_T\cdot dp$

得 $dH=T\cdot\left(\frac{\partial S}{\partial T}\right)_p\cdot dT+\left[T\left(\frac{\partial S}{\partial p}\right)_T+V\right]dp$ ……④

③④对应系数相等得

$\left(\frac{\partial H}{\partial T}\right)_p=T\cdot\left(\frac{\partial S}{\partial T}\right)_p$ 和 $\left(\frac{\partial H}{\partial p}\right)_T=T\left(\frac{\partial S}{\partial p}\right)_T+V$

即 $C_p - C_v = T\left(\frac{\partial S}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial T}\right)_v$ ······ ⑤

PVT系统仅有两个独立变量 ~~$S=S(p,V,T)$~~

而是 $S=S(T,V(T,p))$

$\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial x}\right)_u + \left(\frac{\partial f}{\partial u}\right)_x \left(\frac{\partial u}{\partial x}\right)_y$

利用之前数学知识

$$\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_p$$

代入⑤式得 $C_p - C_v = T\cdot\left(\frac{\partial S}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_p$

查 Maxwell 关系式 $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

即 $C_p - C_v = T\cdot\left(\frac{\partial p}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_p$

对前面公式，做一个检验：

对理想气体 $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial\left(\frac{nRT}{V}\right)}{\partial T}\right)_V = \frac{nR}{V}$

$pV = nRT$

$$\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial\left(\frac{nRT}{p}\right)}{\partial T}\right)_p = \frac{nR}{p}$$

$$C_p - C_V = T \cdot \frac{nR}{V} \cdot \frac{nR}{p} = nR$$

和之前一致