五、证明题

（一）利用热力学基本方程

1、理想气体的内能是温度的函数。

（或理想气体 $\left(\frac{\partial U}{\partial V}\right)_T=0$ ）。

证明：热力学基本方程 $\mathrm{d}U=T\mathrm{d}S-p\mathrm{d}V$，在恒温下两边除以 $\mathrm{d}V$，有

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

利用麦克斯韦关系式 $\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial p}{\partial T}\right)_V$，

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

对理想气体，因 $p=\frac{nRT}{V}$，有 $\left(\frac{\partial p}{\partial T}\right)_V=\frac{nR}{V}$，代入上式得

$$\left(\frac{\partial U}{\partial V}\right)_T=T\times\frac{nR}{V}-p=p-p=0$$

拓展练习：对范德华气体 $\left(\frac{\partial U}{\partial V}\right)_T=\frac{n^2a}{V^2}$。

（范德华气体的状态方程为 $\left(p+\frac{n^2a}{V^2}\right)(V-nb)=nRT$，$a$、$b$ 为范德华常数。）

证明：热力学基本方程 $\mathrm{d}U=T\mathrm{d}S-p\mathrm{d}V$，在恒温下两边除以 $\mathrm{d}V$，有

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

利用麦克斯韦关系式 $\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial p}{\partial T}\right)_V$，

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

对范德华气体，因 $p=\frac{nRT}{V-nb}-\frac{n^2a}{V^2}$，有 $\left(\frac{\partial p}{\partial T}\right)_V=\frac{nR}{V-nb}$，代入上式得 $\left(\frac{\partial U}{\partial V}\right)_T=T\times\frac{nR}{V-nb}-p=\frac{n^2a}{V^2}$。

（二）状态函数法

2、$\mathrm{d}U=nC_{V,\mathrm{m}}\mathrm{d}T+\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]\mathrm{d}V$

证明：设 U 是 T、V 的函数，即 $U=U(T，V)$，则其全微分

$$\mathrm{d}U=\left(\frac{\partial U}{\partial T}\right)_V\mathrm{d}T+\left(\frac{\partial U}{\partial V}\right)_T\mathrm{d}V=nC_{V,\mathrm{m}}\mathrm{d}T+\left(\frac{\partial U}{\partial V}\right)_T\mathrm{d}V$$

热力学基本方程 $\mathrm{d}U=T\mathrm{d}S-p\mathrm{d}V$，在恒温下两边除以 $\mathrm{d}V$，有

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

利用麦克斯韦关系式 $\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial p}{\partial T}\right)_V$，

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

代入前面的全微分式，得

$$\mathrm{d}U=nC_{V,\mathrm{m}}\mathrm{d}T+\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]\mathrm{d}V$$

3、$\mathrm{d}H=nC_{p,\mathrm{m}}\mathrm{d}T+\left[V-T\left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}p$

证明：设 H 是 T、p 的函数，即 $H=H(T，p)$，则其全微分

$$\mathrm{d}H=\left(\frac{\partial H}{\partial T}\right)_p\mathrm{d}T+\left(\frac{\partial H}{\partial p}\right)_T\mathrm{d}p=nC_{p,\mathrm{m}}\mathrm{d}T+\left(\frac{\partial H}{\partial p}\right)_T\mathrm{d}p$$

热力学基本方程 $\mathrm{d}H=T\mathrm{d}S+V\mathrm{d}p$，在恒温下两边除以 $\mathrm{d}p$，有

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

利用麦克斯韦关系式 $\left(\frac{\partial S}{\partial p}\right)_T=-\left(\frac{\partial V}{\partial T}\right)_p$，

有 $\left(\frac{\partial H}{\partial p}\right)_T=-T\left(\frac{\partial V}{\partial T}\right)_p+V$

代入前面的全微分式，得

$$\mathrm{d}H = nC_{p,\mathrm{m}}\mathrm{d}T + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}p$$

4、$\mathrm{d}S = \frac{nC_{p,\mathrm{m}}}{T}\mathrm{d}T - \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p$

证明：设 S 是 T、p 的函数，即 $S = S(T, p)$，则其全微分

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p \quad ①$$

热力学基本方程 $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$，

在恒压下两边除以 $\mathrm{d}T$，

有 $\left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$，$\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p$。

将 $\mathrm{d}H = nC_{p,\mathrm{m}}\mathrm{d}T$ 代入得

$\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p = \frac{nC_{p,\mathrm{m}}}{T}$ ②

麦克斯韦关系式 $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$ ③

将 ②、③ 代入 ① 中得

$$\mathrm{d}S = \frac{nC_{p,\mathrm{m}}}{T}\mathrm{d}T - \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p$$

5、$\mathrm{d}S = \frac{nC_{V,\mathrm{m}}}{T}\left(\frac{\partial T}{\partial p}\right)_V \mathrm{d}p + \frac{nC_{p,\mathrm{m}}}{T}\left(\frac{\partial T}{\partial V}\right)_p \mathrm{d}V$

证明：设 S 是 p、V 的函数，即 $S = S(p, V)$，则其全微分

$$\mathrm{d}S = \left(\frac{\partial S}{\partial p}\right)_V \mathrm{d}p + \left(\frac{\partial S}{\partial V}\right)_p \mathrm{d}V \quad ①$$

热力学基本方程 $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$，

在恒容下两边除以 $\mathrm{d}p$，

有 $\left(\frac{\partial U}{\partial p}\right)_V = T\left(\frac{\partial S}{\partial p}\right)_V$，$\left(\frac{\partial S}{\partial p}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial p}\right)_V$。

将 $\mathrm{d}U = nC_{V,\mathrm{m}}\mathrm{d}T$ 代入得

$\left(\frac{\partial S}{\partial p}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial p}\right)_V = \frac{nC_{V,\mathrm{m}}}{T}\left(\frac{\partial T}{\partial p}\right)_V$ ②

同理热力学基本方程 $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$，在恒压下两边除以 $\mathrm{d}V$，

有 $\left(\frac{\partial H}{\partial V}\right)_p = T\left(\frac{\partial S}{\partial V}\right)_p$，$\left(\frac{\partial S}{\partial V}\right)_p = \frac{1}{T}\left(\frac{\partial H}{\partial V}\right)_p$。将 $\mathrm{d}H = nC_{p,\mathrm{m}}\mathrm{d}T$ 代入得 $\left(\frac{\partial S}{\partial V}\right)_p = \frac{1}{T}\left(\frac{\partial H}{\partial V}\right)_p = \frac{nC_{p,\mathrm{m}}}{T}\left(\frac{\partial T}{\partial V}\right)_p$ ③

将 ②、③ 代入 ① 中得

$\mathrm{d}S = \frac{nC_{V,\mathrm{m}}}{T}\left(\frac{\partial T}{\partial p}\right)_V \mathrm{d}p + \frac{nC_{p,\mathrm{m}}}{T}\left(\frac{\partial T}{\partial V}\right)_p \mathrm{d}V$。

6、$\left(\frac{\partial C_{p,\mathrm{m}}}{\partial p}\right)_T = -T\left(\frac{\partial^2 V_\mathrm{m}}{\partial T^2}\right)_p$

证明：$\mathrm{d}H = nC_{p,\mathrm{m}}\mathrm{d}T$，$C_{p,\mathrm{m}} = \frac{1}{n}\left(\frac{\partial H}{\partial T}\right)_p$。

热力学基本方程 $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$，

在恒压下两边除以 $\mathrm{d}T$，有

$$\left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

$$C_{p,\mathrm{m}} = \frac{1}{n}\left(\frac{\partial H}{\partial T}\right)_p = \frac{T}{n}\left(\frac{\partial S}{\partial T}\right)_p$$

$$\left(\frac{\partial C_{p,\mathrm{m}}}{\partial p}\right)_T = \frac{T}{n} \times \frac{\partial^2 S}{\partial T \partial p} = \frac{T}{n} \times \frac{\partial^2 S}{\partial p \partial T}$$

利用麦克斯韦关系式 $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$，

$$\left(\frac{\partial C_{p,\mathrm{m}}}{\partial p}\right)_T = \frac{T}{n} \times \frac{\partial^2 S}{\partial T \partial p} = \frac{T}{n} \times \frac{\partial^2 S}{\partial p \partial T}$$

$$= -\frac{T}{n} \times \frac{\partial^2 V}{\partial T \partial T} = -T\left(\frac{\partial^2 V_\mathrm{m}}{\partial T^2}\right)_p$$