1

解

$$F = U - TS$$

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V$$

故

$$\frac{\partial \frac{\partial F}{\partial T}}{\partial V} = \frac{\partial \frac{\partial F}{\partial V}}{\partial T}$$

$$(\frac{\partial S}{\partial V})_T = (\frac{\partial p}{\partial T})_p$$

又 $(\frac{\partial p}{\partial T})_p > 0$，故 $(\frac{\partial S}{\partial V})_T > 0$，即温度不变时，气体的熵随体积增加。

2

解　以 V, T 为参数有

$$= T\,\mathrm{d}S - p\,\mathrm{d}V$$

$$= T(\frac{\partial S}{\partial T})_V\,\mathrm{d}T + (T(\frac{\partial S}{\partial V})_T - p)\,\mathrm{d}V$$

故

$$(\frac{\partial U}{\partial V})_T = T(\frac{\partial S}{\partial V})_T - p = 0$$

以 p, T 为参数

$$= T\,\mathrm{d}S - p\,\mathrm{d}V$$

$$= T(\frac{\partial S}{\partial p})_T\,\mathrm{d}p + T(\frac{\partial S}{\partial T})_p\,\mathrm{d}T - p(\frac{\partial V}{\partial p})_T\,\mathrm{d}p - p(\frac{\partial V}{\partial T})_p\,\mathrm{d}T$$

故

$$\begin{aligned}(\frac{\partial U}{\partial p})_T &= T(\frac{\partial S}{\partial p})_T - p(\frac{\partial V}{\partial p})_T \\ &= T(\frac{\partial S}{\partial p})_T - T(\frac{\partial S}{\partial V})_T(\frac{\partial V}{\partial p})_T \\ &= T(\frac{\partial S}{\partial p})_T - T(\frac{\partial S}{\partial p})_T \\ &= 0\end{aligned}$$

3

解

$$
\begin{aligned}
\mathrm{d}S &= (\frac{\partial S}{\partial p})_T \,\mathrm{d}p + (\frac{\partial S}{\partial T})_p \,\mathrm{d}T \\
&= (\frac{\partial S}{\partial p})_T \,\mathrm{d}p + (\frac{\partial S}{\partial T})_p (\frac{\partial T}{\partial p})_V \,\mathrm{d}p + (\frac{\partial S}{\partial T})_p (\frac{\partial T}{\partial V})_p \,\mathrm{d}V
\end{aligned}
$$

故

$$
\begin{aligned}
(\frac{\partial S}{\partial V})_p &= (\frac{\partial S}{\partial T})_p (\frac{\partial T}{\partial V})_p \\
&= \frac{C_p}{T} (\frac{\partial T}{\partial V})_p
\end{aligned}
$$

$T > 0$ 又由稳定性要求 $C_p > 0$ 故 $(\frac{\partial S}{\partial V})_p$ 与 $\frac{C_p}{T}(\frac{\partial T}{\partial V})_p$ 正负性相同,题目得证。

4

解

$$
\begin{aligned}
\mathrm{d}U &= (\frac{\partial U}{\partial V})_T \,\mathrm{d}V + (\frac{\partial U}{\partial T})_V \,\mathrm{d}T \\
&= (T(\frac{\partial S}{\partial V})_T - p) \,\mathrm{d}V + C_V \,\mathrm{d}T
\end{aligned}
$$

代入

$$
\mathrm{d}U = T \,\mathrm{d}S - p \,\mathrm{d}V
$$

得

$$
\begin{aligned}
T \,\mathrm{d}S &= T(\frac{\partial S}{\partial V})_T \,\mathrm{d}V + C_V \,\mathrm{d}T \\
&= T(\frac{\partial p}{\partial T})_V \,\mathrm{d}V + C_V \,\mathrm{d}T
\end{aligned}
$$

又因为

$$
\begin{aligned}
(\frac{\partial p}{\partial T})_T (\frac{\partial V}{\partial p})_T (\frac{\partial T}{\partial V})_p &= -1 \\
(\frac{\partial p}{\partial T})_T &= -\frac{(\frac{\partial V}{\partial T})_p}{(\frac{\partial V}{\partial p})_T} \\
(\frac{\partial p}{\partial T})_T &= \frac{\alpha}{k_T}
\end{aligned}
$$

$$
T \,\mathrm{d}S = T(\frac{\partial S}{\partial V})_T \,\mathrm{d}V + C_V \,\mathrm{d}T
$$

又绝热过程中 $\mathrm{d}S = 0$,故

$$
T(\frac{\partial S}{\partial V})_T \,\mathrm{d}V + C_V \,\mathrm{d}T = 0
$$

$$T\frac{\alpha}{k_T}\,\mathrm{d}V + C_V\,\mathrm{d}T = 0$$
$$(\frac{\partial T}{\partial V})_S = -\frac{T\alpha}{C_V k_T}$$

因为 $T > 0, \alpha < 0, C_V > 0, T > 0$ 故

$$(\frac{\partial T}{\partial V})_S > 0$$

5

解

$$\mathrm{d}S = (\frac{\partial S}{\partial T})_p\,\mathrm{d}T + (\frac{\partial S}{\partial p})_T\,\mathrm{d}p$$

在绝热过程中 $\mathrm{d}S = 0$,即

$$(\frac{\partial S}{\partial T})_p\,\mathrm{d}T + (\frac{\partial S}{\partial p})_T\,\mathrm{d}p = 0$$

故

$$(\frac{\partial T}{\partial p})_S = -\frac{(\frac{\partial S}{\partial p})_T}{(\frac{\partial S}{\partial T})_p} = \frac{T(\frac{\partial V}{\partial T})_p}{C_p}$$

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

在节流过程中 $\mathrm{d}H = 0$,即

$$(\frac{\partial H}{\partial T})_p\,\mathrm{d}T + (\frac{\partial H}{\partial p})_T\,\mathrm{d}p = 0$$

故

$$\begin{aligned}(\frac{\partial T}{\partial p})_H &= -\frac{(\frac{\partial H}{\partial p})_T}{(\frac{\partial H}{\partial T})_p}\\ &= \frac{-(\frac{\partial S}{\partial p})_T + V}{T(\frac{\partial S}{\partial T})_p}\\ &= \frac{-T(\frac{\partial V}{\partial T})_p + V}{C_p}\end{aligned}$$

故

$$(\frac{\partial T}{\partial p})_S - (\frac{\partial T}{\partial p})_H = \frac{V}{C_p} > 0$$

6

解

$$
\begin{aligned}
(\frac{\partial U}{\partial V})_T &= T(\frac{\partial S}{\partial V})_T - p \\
&= T(\frac{\partial p}{\partial T})_V - p \\
&= 0
\end{aligned}
$$

$$
\begin{aligned}
pV &= f(T) \\
p\,\mathrm{d}V + V\,\mathrm{d}p &= \frac{\mathrm{d}f}{\mathrm{d}T}\,\mathrm{d}T \\
(\frac{\partial p}{\partial T})_V &= \frac{\frac{\mathrm{d}f}{\mathrm{d}T}}{V}
\end{aligned}
$$

故

$$
\begin{aligned}
\frac{\frac{\mathrm{d}f}{\mathrm{d}T}}{V} - p = 0 \\
pV = T\frac{\mathrm{d}f}{\mathrm{d}T} = f(T)
\end{aligned}
$$

$$
\begin{aligned}
T\frac{\mathrm{d}f}{\mathrm{d}T} &= f \\
\ln f &= \ln T + C \\
f &= CT
\end{aligned}
$$

故得

$$
pV = CT
$$

7

解

$$
\begin{aligned}
C_V &= T(\frac{\partial S}{\partial T})_V \\
(\frac{\partial C_V}{\partial V})_T &= T\frac{\partial^2 S}{\partial T \partial V} \\
&= T\frac{\partial^2 S}{\partial V \partial T} \\
&= T\frac{(\frac{\partial p}{\partial T})_V}{\partial T} \\
&= T(\frac{\partial^2 p}{\partial T^2})_V
\end{aligned}
$$

又由范德瓦尔斯气体状态方程可以知道

$$(\frac{\partial p}{\partial T})_V = \frac{nR}{V}$$
$$(\frac{\partial^2 p}{\partial T^2})_V = \frac{-nR}{V^2}(\frac{\partial V}{\partial T})_V = 0$$

故

$$(\frac{\partial C_V}{\partial V})_T = 0$$

7

解　1mol 范德瓦尔斯气体的物态方程为

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

由此可得

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$
$$(\frac{\partial p}{\partial T})_V = \frac{R}{V_m - b}$$
$$T(\frac{\partial p}{\partial T})_V - p = \frac{a}{V_m^2}$$

故

$$S_m = \int \frac{C_{V,m}}{T}\,\mathrm{d}T + R\ln(V_m - b) + S_{m0}$$

故

$$(\frac{\partial F_m}{\partial T})_V = -S_m = -(\int \frac{C_{V,m}}{T}\,\mathrm{d}T + R\ln(V_m - b) + S_{m0})$$
$$(\frac{\partial F_m}{\partial V})_T = -p = -(\frac{RT}{V_m - b} - \frac{a}{V_m^2})$$

故

$$\begin{aligned} F_m &= -\int S_m\,\mathrm{d}T - \int p\,\mathrm{d}V \\ &= -\int(\int \frac{C_{V,m}}{T}\,\mathrm{d}T + R\ln(V_m - b) + S_{m0})\,\mathrm{d}T - \int(\frac{RT}{V_m - b} - \frac{a}{V_m^2})\,\mathrm{d}V \\ &= -\int(\int \frac{C_{V,m}}{T}\,\mathrm{d}T)\,\mathrm{d}T - RT\ln(V_m - b) + S_{m0}T - \frac{a}{V_m} + U_{m0} \end{aligned}$$

故

$$U_m = F_m + TS_m$$

$$= -\int(\int \frac{C_{V,m}}{T}\,\mathrm{d}T)\,\mathrm{d}T + \int \frac{C_{V,m}}{T}\,\mathrm{d}T - \frac{a}{V_m} + U_{m0}$$

8

解

$$\mathrm{d}U = \bar{\mathrm{d}}Q - p\,\mathrm{d}V$$
$$3(p\,\mathrm{d}V + V\,\mathrm{d}p) = \bar{\mathrm{d}}Q - p\,\mathrm{d}V$$
$$\bar{\mathrm{d}} = 4p\,\mathrm{d}V + 3V\,\mathrm{d}p$$

又因为 $u = 3p = aT^4$，故等温过程中 $\mathrm{d}p = 0$，故

$$\begin{aligned} Q &= \int_{V_1}^{V_2} 4p\,\mathrm{d}V \\ &= \frac{4}{3}aT^4 \ln\frac{V_2}{V_1}\,\mathrm{d}V \\ &= \frac{4}{3}aT^4(V_2 - V_1) \end{aligned}$$

9

解　等温过程中 $\mathrm{d}p = 0$，故 p 为定值。绝热过程满足

$$3(p\,\mathrm{d}V + V\,\mathrm{d}p) = -p\,\mathrm{d}V$$
$$4p\,\mathrm{d}V + 3V\,\mathrm{d}p = 0$$
$$4\frac{\mathrm{d}V}{V} + 3\frac{\mathrm{d}p}{p} = 0$$
$$(\ln(p^3V^4)) = 0$$

故绝热过程满足

$$p = CV^{-\frac{4}{3}}$$

设卡诺循环为 $1 \to 2 \to 3 \to 4 \to 1$ 等温过程吸热为

$$Q = \frac{4}{3}aT_1^4(V_2 - V_1)$$

整个循环对外做功为

$$\begin{aligned} W &= \int_{V_1}^{V_2} p_1\,\mathrm{d}V + \int_{V_2}^{V_3} p_1V_2^{\frac{4}{3}}V^{-\frac{4}{3}}\,\mathrm{d}V + \int_{V_3}^{V_4} p_3\,\mathrm{d}V + \int_{V_4}^{V_1} p_3V_4^{\frac{4}{3}}V^{-\frac{4}{3}}\,\mathrm{d}V \\ &= p_1(V_2 - V_1) + 3p_1V_2^{\frac{4}{3}}(\frac{1}{\sqrt[3]{V_2}} - \frac{1}{\sqrt[3]{V_3}}) + p_3(V_4 - V_3) + 3p_3V_4^{\frac{4}{3}}(\frac{1}{\sqrt[3]{V_3}} - \frac{1}{\sqrt[3]{V_4}}) \end{aligned}$$

又因为

$$p_1 = \frac{aT_1^4}{3}$$

$$p_3 = \frac{aT_2^4}{3}$$

故

$$W = \frac{4T_1^4(T_1 - T_2)}{3T_1}a(V_2 - V_1)$$

所以效率

$$\begin{aligned}\eta &= \frac{W}{Q} \\ &= 1 - \frac{T_2}{T_1}\end{aligned}$$

10

解 当介质电位移有 $\mathrm{d}D$ 的改变时,外界做功为

$$\bar{\mathrm{d}}W = VE\,\mathrm{d}D$$

做代换

$$p \to -E$$

$$V \to VD$$

由于

$$C_p - C_V = T(\frac{\partial p}{\partial T})_V(\frac{\partial V}{\partial T})_p$$

故有

$$C_E - C_D = -VT(\frac{\partial E}{\partial T})_D(\frac{\partial D}{\partial T})_E$$

又

$$\begin{aligned}(\frac{\partial D}{\partial T})_E &= E\frac{\mathrm{d}\varepsilon}{\mathrm{d}T} \\ (\frac{\partial E}{\partial T})_D &= -\frac{D}{\varepsilon^2}\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}\end{aligned}$$

故有

$$\begin{aligned}C_E - C_D &= -VT(E\frac{\mathrm{d}\varepsilon}{\mathrm{d}T})(-\frac{D}{\varepsilon^2}\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}) \\ &= VT\frac{D^2}{\varepsilon^3}(\frac{\mathrm{d}\varepsilon}{\mathrm{d}T})^2\end{aligned}$$