2.4 求证：(1) $\left(\frac{\partial S}{\partial p}\right)_H < 0$；(2) $\left(\frac{\partial S}{\partial V}\right)_U > 0$.

解：

(1) 由 $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$ 得 $\mathrm{d}S = \frac{1}{T}\mathrm{d}H - \frac{V}{T}\mathrm{d}p$，故 $\left(\frac{\partial S}{\partial p}\right)_H = -\frac{V}{T} < 0$.

(2) 由 $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$ 得 $\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{p}{T}\mathrm{d}V$，故 $\left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T} > 0$.

2.7 试证明在相同的压强降落下，气体在准静态绝热膨胀中的温度降落大于在节流过程中的温度降落.

解：

由 $\mathrm{d}S = \frac{C_p}{T}\mathrm{d}T - \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p$ 得 $\left(\frac{\partial T}{\partial p}\right)_S = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p$.

由 $\mathrm{d}H = C_p\mathrm{d}T - \left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]\mathrm{d}p$ 得 $\left(\frac{\partial T}{\partial p}\right)_H = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p - \frac{V}{C_p}$.

$\left(\frac{\partial T}{\partial p}\right)_S - \left(\frac{\partial T}{\partial p}\right)_H = \frac{V}{C_p} > 0$，因为平衡稳定性要求 $C_p > 0$. 命题得证.

2.8 实验发现，一气体的压强 p 与比体积 v（单位质量物质的体积）的乘积及比内能 u（单位质量物质的内能）都只是温度的函数，即 $pv = f(T)$，$u = u(T)$. 试根据热力学理论，讨论该气体物态方程的形式.

解：

对单位质量气体，$\mathrm{d}u = c_V\mathrm{d}T + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]\mathrm{d}v$，故有

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p. \qquad (2.1)$$

由 $p = \frac{f(T)}{v}$ 可得

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = \frac{1}{v}\left(T\frac{\mathrm{d}f}{\mathrm{d}T} - f\right). \qquad (2.2)$$

由 $u = u(T)$ 可得

$$\left(\frac{\partial u}{\partial v}\right)_T = 0. \qquad (2.3)$$

根据以上三式，$T\frac{\mathrm{d}f}{\mathrm{d}T} - f = 0$. 解之得 $f = CT$，所以 $pv = CT$.