热统习题的部分答案

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1 第一章

1.1 习题 1.6

$$\begin{split} \alpha &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{\nu R}{p V} \quad \Rightarrow \quad \left(\frac{\partial V}{\partial T} \right)_p = \frac{\nu R}{p} \\ &\Rightarrow \quad V = \frac{\nu R T}{p} + g(p) \quad \text{代入 } \kappa = \frac{1}{p} + \frac{a}{V} = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \\ &\Rightarrow \quad \mathrm{d}(p g(p)) = -\frac{a}{2} \mathrm{d}(p^2) \\ &\Rightarrow \quad p g(p) = -\frac{a}{2} p^2 + \mathrm{const} \quad \text{代入第二行式子并整理} \\ &\Rightarrow \quad p V = \nu R T - \frac{a}{2} p^2 + \mathrm{const}. \end{split}$$

1.2 习题 1.8

1) 利用广延量假设,

$$S = Ns, V = Nv, U = Nu \Rightarrow s = A(vu)^{1/3}$$

$$\Rightarrow Tds = TA \frac{vdu + udv}{3(vu)^{2/3}} = du + pdv$$

$$du, dv 前的系数对应相等并恢复广延量 \Rightarrow \begin{cases} T = \frac{3u^{2/3}}{Av^{1/3}} = \frac{3U^{2/3}}{A(NV)^{1/3}} & 易得: U \sim T^{3/2} \\ p = \left(\frac{N}{V}\right)^{1/2} \left(\frac{AT}{3}\right)^{3/2} \end{cases}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{2}\sqrt{\frac{A^3NVT}{3}}$$
 利用了前面的温度表达式.

2) 对于每个热源而言, 我们有:

$$dQ = dU \sim T^{1/2} dT$$
,

由于高温热源放出热量 $(\Delta Q_h < 0)$ 必定大于等于低温热源吸热 $(\Delta Q_c > 0)$,不失一般性,我们假设 $T_1 > T_2$,

$$\Delta Q_h + \Delta Q_c \le 0 \quad \Rightarrow \quad \left(\int_{T_1}^{T_f} + \int_{T_2}^{T_f} \right) T^{1/2} dT \le 0$$

$$\Rightarrow \quad T_f \le \left(\frac{T_1^{3/2} + T_2^{3/2}}{2} \right)^{2/3};$$

另一方面, 由热力学第二定律: $\Delta S \geq 0$,

$$\begin{split} \Delta S &= \left(\int_{T_1}^{T_f} + \int_{T_2}^{T_f}\right) \frac{\mathrm{d}Q}{T} \sim \left(\int_{T_1}^{T_f} + \int_{T_2}^{T_f}\right) \frac{1}{T^{1/2}} \mathrm{d}T \geq 0 \\ \Rightarrow \quad T_f \geq \left(\frac{T_1^{1/2} + T_2^{1/2}}{2}\right)^2. \end{split}$$

由第一题的温度表达式, 我们得到:

$$U = \left(\frac{AT(NV)^{1/3}}{3}\right)^{3/2} = CT^{3/2}.$$

对于整个系统而言,

$$W = -\Delta U_{\text{dis}} = C \left(T_1^{3/2} + T_2^{3/2} - 2T_f^{3/2} \right) \leq \sqrt{\frac{A^3 NV}{27}} \left[T_1^{3/2} + T_2^{3/2} - 2 \left(\frac{T_1^{1/2} + T_2^{1/2}}{2} \right)^3 \right].$$

1.3 习题 1.11

首先,我们需要求出范氏气体的内能表达式,

由范氏气体的状态方程
$$\Rightarrow$$
 $\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V - b}$ 代人书上式子 (1.9.16) \Rightarrow $\left(\frac{\partial U}{\partial V}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_V = \frac{a}{V^2}$ \Rightarrow $\mathrm{d}U = C_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V = C_V \mathrm{d}T + \frac{a}{V^2} \mathrm{d}V$ \Rightarrow $U = C_V T - \frac{a}{V} + U_0$.

1) 对于等温过程,

$$\begin{split} \Delta U &= -\frac{a}{V_f} + \frac{a}{V_i} \\ W &= \int_{V_i}^{V_f} p \mathrm{d}V = \int_{V_i}^{V_f} \left(\frac{RT_i}{V - b} - \frac{a}{V^2} \right) \mathrm{d}V = RT_i \ln \left(\frac{V_f - b}{V_i - b} \right) + \frac{a}{V_f} - \frac{a}{V_i} \\ \Delta S &= \frac{\Delta U + W}{T_i} = R \ln \frac{V_f - b}{V_i - b}; \end{split}$$

2) 对于等压过程,

$$W = p_i(V_f - V_i) = \left(\frac{RT_i}{V_i - b} - \frac{a}{V_i^2}\right)(V_f - V_i)$$
利用状态方程 $\Rightarrow T_f = \left(p_i + \frac{a}{V_f^2}\right)(V_f - b)/R = \left(\frac{RT_i}{V_i - b} - \frac{a}{V_i^2} + \frac{a}{V_f^2}\right)(V_f - b)/R$

$$\Rightarrow \Delta U = C_V(T_f - T_i) - \frac{a}{V_f} + \frac{a}{V_i} = C_V\left[\left(\frac{RT_i}{V_i - b} - \frac{a}{V_i^2} + \frac{a}{V_f^2}\right)(V_f - b)/R - T_i\right] - \frac{a}{V_f} + \frac{a}{V_i}$$
由等压条件 $\Rightarrow TdS = dQ = C_pdT$

$$\Rightarrow dS = C_p d(\ln T)$$

$$\Rightarrow \Delta S = C_p \ln \frac{T_f}{T_i} = C_p \ln \left[\frac{V_f - b}{V_i - b} - a\left(\frac{1}{V_i^2} - \frac{1}{V_f^2}\right)\frac{V_f - b}{RT_i}\right];$$

3) 对于绝热过程,

$$dQ = dU + pdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV = C_V dT + \left(\frac{a}{V^2} + p\right) dV = 0,$$
 结合状态方程 $\Rightarrow C_V dT + \frac{RT}{V - b} dV = 0$ $\Rightarrow C_V \ln T + R \ln(V - b) = 0$ $\Rightarrow T^{C_V} (V - b)^R = \text{const}$ $\Rightarrow T_f = T_i \left(\frac{V_i - b}{V_f - b}\right)^{R/C_V}$

因此, 我们容易得到:

$$\Delta U = C_V T_i \left[\left(\frac{V_i - b}{V_f - b} \right)^{R/C_V} - 1 \right] - \frac{a}{V_f} + \frac{a}{V_i}$$

$$W = -\Delta U$$

$$\Delta S = 0.$$

1.4 习题 1.13

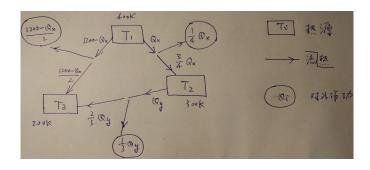
其中一个物体降温 (放热): $T_1 \to T_2$, 另一个物体升温 (吸热): $T_1 \to T_x$. 考虑整个体系, 由热力学第二定律,

$$\Delta S = \left(\int_{T_1}^{T_2} + \int_{T_1}^{T_x} \right) \frac{C_p dT}{T} \ge 0 \quad \Rightarrow \quad T_x \ge \frac{T_1^2}{T_2}.$$

因此,

$$W \ge \Delta U = C_p(T_x + T_2 - 2T_1) \ge C_p\left(\frac{T_1^2}{T_2} + T_2 - 2T_1\right) = C_p\frac{(T_1 - T_2)^2}{T_2}.$$

1.5 习题 1.22



由图, 我们有以下关系:

$$\frac{1200 - Q_x}{2} + \frac{Q_y}{3} + \frac{Q_x}{4} = 200 \implies \frac{3}{4}Q_x - Q_y = 1200$$

$$\Rightarrow \begin{cases} Q_2 = \frac{3}{4}Q_x - Q_y = 1200J \\ Q_3 = \frac{1200 - Q_x}{2} + \frac{2Q_y}{3} = -200J \end{cases}$$

$$\Rightarrow \begin{cases} \Delta S_1 = \frac{Q_1}{T_1} = \frac{-1200}{400} = -3J/K \\ \Delta S_2 = \frac{Q_2}{T_2} = \frac{1200}{300} = 4J/K \\ \Delta S_3 = \frac{Q_3}{Q_3}T_3 = \frac{-200}{200} = -1J/K \end{cases}$$

$$\Delta S_{\mathbb{H}} = \sum_{i=1}^3 \Delta S_i = 0J/K.$$

1.6 习题 1.23

考虑等熵过程 $(S = S_0)$,

$$W_{S_0} = \int_{V_0}^{V} p(S_0, V') dV' = RS_0 \ln \frac{V}{V_0} \quad \Rightarrow \quad p(S_0, V) = \frac{dW_{S_0}}{dV} = \frac{RS_0}{V}$$
$$U(S_0, V) - U(S_0, V_0) = -W_{S_0} \quad \Rightarrow \quad U(S_0, V) = U_0 - RS_0 \ln \frac{V}{V_0}.$$

现在考虑一个等体过程 $(V, S_0 \rightarrow V, S)$,

$$U(S, V) - U(S_0, V) = \int_{T(S_0, V)}^{T(S, V)} T(S', V) dS'$$
$$= \int_{S_0}^{S} \frac{RV_0}{V} \left(\frac{S'}{S_0}\right)^a dS'$$
$$= \frac{RV_0 S_0}{(a+1)V} \left[\left(\frac{S}{S_0}\right)^{a+1} - 1\right]$$

因此,

$$U(S,V) = \frac{RV_0S_0}{(a+1)V} \left[\left(\frac{S}{S_0} \right)^{a+1} - 1 \right] - RS_0 \ln \frac{V}{V_0} + U_0$$

又由:

$$\left(\frac{\partial p}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S = \frac{RV_0}{V^2} \left(\frac{S}{S_0}\right)^a$$

$$\Rightarrow \quad p(S,V) = \frac{RV_0S_0}{(a+1)V^2} \left[\left(\frac{S}{S_0}\right)^{a+1} - 1\right] + \frac{RS_0}{V}$$

$$W(S,V_0 \to V) = \int_{V_0}^V p(S,V') \mathrm{d}V' = \frac{RV_0S_0}{a+1} \left[\left(\frac{S}{S_0}\right)^{a+1} - 1\right] \left(\frac{1}{V_0} - \frac{1}{V}\right) + RS_0 \ln \frac{V}{V_0}.$$