热力学统计物理第二次作业

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2021.09.26

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记 p_i 为状态 i 的压强，V_i 为状态 i 的体积。
考虑绝热过程 $1 \to 2$，则有:

$$Q_{12} = 0,\ \ pV^\gamma = C_1$$

其中 C_1 为常数。
系统对外界做功为:

$$W_{12} = \int_{V_1}^{V_2} p\,dV = \int_{V_1}^{V_2} \frac{C_1}{V^\gamma}\,dV = \frac{C_1}{1-\gamma}\left(V_2^{1-\gamma} - V_1^{1-\gamma}\right) = \frac{p_1V_1 - p_2V_2}{\gamma - 1}$$

考虑等容过程 $2 \to 3$，则有:

$$W_{23} = 0,\ \ pV = nRT$$

系统放热为:

$$Q_{23} = C_V(T_2 - T_3) = \frac{p_2V_2 - p_3V_2}{\gamma - 1}$$

考虑绝热过程 $3 \to 4$，则有:

$$Q_{34} = 0,\ \ pV^\gamma = C_2$$

其中 C_2 为常数。
系统对外界做功为:

$$W_{34} = -\int_{V_4}^{V_3} p\,dV = \int_{V_3}^{V_4} \frac{C_2}{V^\gamma}\,dV = \frac{C_2}{1-\gamma}\left(V_4^{1-\gamma} - V_3^{1-\gamma}\right) = \frac{p_3V_2 - p_4V_1}{\gamma - 1}$$

考虑等容过程 $4 \to 1$，则有:

$$W_{41} = 0,\ \ pV = nRT$$

系统吸热为:

$$Q_{41} = C_V(T_1 - T_4) = \frac{p_1V_1 - p_4V_1}{\gamma - 1}$$

则此循环的效率为:

$$\eta = \frac{W_{12} + W_{34}}{Q_{41}} = 1 - \frac{p_2 - p_3}{p_1 - p_4}\frac{V_2}{V_1}$$

由于:

$$p_1V_1^\gamma = p_2V_2^\gamma, \quad p_4V_1^\gamma = p_3V_2^\gamma$$

则有:

$$\frac{p_1}{p_4} = \frac{p_2}{p_3}, \quad 1 - \frac{p_1}{p_4} = 1 - \frac{p_2}{p_3}$$

则有:

$$\eta = 1 - \frac{p_2}{p_1}\frac{1 - \frac{p_3}{p_2}}{1 - \frac{p_4}{p_1}}\frac{V_2}{V_1} = 1 - \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

其中，$\gamma = \frac{C_p}{C_V}$。

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在等压条件下有:

$$dH = C_p\,dT$$

对两侧定积分得焓变为

$$\Delta H = \int_{300}^{1200} (a + bT)\,dT = 3984570\ J/mol$$

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对于范德瓦尔斯气体，状态方程为:

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

设内能可以表示为: $U = U(V, T)$。对内能函数全微分得:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

其中，$\left(\frac{\partial U}{\partial T}\right)_V = C_V$，利用麦克斯韦关系有：$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$。
由状态方程可计算得:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{an^2}{V^2}$$

则有:

$$dU = C_V\,dT + \frac{an^2}{V^2}\,dV$$

当等压热容为常数时，两侧积分可得范德瓦尔斯气体内能为:

$$U = C_V T - \frac{an^2}{V} + U_0$$

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对于范德瓦尔斯气体，状态方程为:

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

在绝热过程中由热力学第一定律，有:

$$dU = dW + dQ = -p\,dV$$

当 C_V 为常数时，有

$$dU = C_V\,dT + \frac{an^2}{V^2}\,dV$$

则有

$$\left(p + \frac{an^2}{V^2}\right)dV + C_V\,dT = \frac{nRT}{V - nb}\,dV + C_V\,dT = 0$$

即范德瓦尔斯气体绝热方程为:

$$T\,(V - nb)^{nR/C_V} = C = constant$$

则有当范德瓦尔斯气体绝热膨胀时对外做功为:

$$\begin{aligned} W &= \int_{V_1}^{V_2} p\,dV = \int_{V_1}^{V_2}\left[nRC\,(V - nb)^{-(1+nR/C_V)} - \frac{an^2}{V^2}\right]dV \\ &= CC_V\left[(V_1 - nb)^{-nR/C_V} - (V_2 - nb)^{-nR/C_V}\right] - \left(\frac{an^2}{V_1} - \frac{an^2}{V_2}\right) \end{aligned}$$

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由热力学基本微分方程可知:

$$dH = T\,dS + V\,dp$$
$$dG = -S\,dT + V\,dp$$

则有:

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

设 $G = G(T, p)$，对其做全微分则有:

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

则有:

$$-S = \left(\frac{\partial G}{\partial T}\right)_p, \quad V = \left(\frac{\partial G}{\partial p}\right)_T$$

再次偏微分可得:

$$\frac{\partial^2 G}{\partial T \partial p} = -\left(\frac{\partial S}{\partial p}\right)_T = \frac{\partial^2 G}{\partial p \partial T} = \left(\frac{\partial V}{\partial T}\right)_p$$

则有:

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