高等热力学与统计物理第一次作业

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(1) *Proof.* 设 $w = w(x, y)$，两侧微分可得:

$$dw = \left(\frac{\partial w}{\partial x}\right)_y dx + \left(\frac{\partial w}{\partial y}\right)_x dy$$

则有:

$$\left(\frac{\partial x}{\partial y}\right)_w = -\frac{\left(\frac{\partial w}{\partial y}\right)_x}{\left(\frac{\partial w}{\partial x}\right)_y}.$$

对 $f(x, y, z) = 0$ 全微分可知:

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{z,x} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz = 0.$$

有:

$$dx = -\frac{\left(\frac{\partial f}{\partial y}\right)_{z,x} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz}{\left(\frac{\partial f}{\partial x}\right)_{y,z}},$$

$$dy = -\frac{\left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz}{\left(\frac{\partial f}{\partial y}\right)_{z,x}}.$$

带入 $w = w(x, y)$ 的全微分式，有:

$$dw = \frac{\left(\frac{\partial w}{\partial y}\right)_x \left(\frac{\partial f}{\partial x}\right)_{y,z} - \left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial f}{\partial y}\right)_{z,x}}{\left(\frac{\partial f}{\partial x}\right)_{y,z}} dy - \frac{\left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial f}{\partial z}\right)_{x,y}}{\left(\frac{\partial f}{\partial x}\right)_{y,z}} dz$$

$$dw = \frac{\left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial f}{\partial y}\right)_{z,x} - \left(\frac{\partial w}{\partial y}\right)_x \left(\frac{\partial f}{\partial x}\right)_{y,z}}{\left(\frac{\partial f}{\partial y}\right)_{z,x}} dx - \frac{\left(\frac{\partial w}{\partial y}\right)_x \left(\frac{\partial f}{\partial z}\right)_{x,y}}{\left(\frac{\partial f}{\partial y}\right)_{z,x}} dz$$

则有:

$$\left(\frac{\partial y}{\partial z}\right)_w = \frac{\left(\frac{\partial f}{\partial z}\right)_{x,y} \left(\frac{\partial w}{\partial x}\right)_y}{\left(\frac{\partial w}{\partial y}\right)_x \left(\frac{\partial f}{\partial x}\right)_{y,z} - \left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial f}{\partial y}\right)_{z,x}}$$

$$\left(\frac{\partial x}{\partial z}\right)_w = \frac{\left(\frac{\partial f}{\partial z}\right)_{x,y} \left(\frac{\partial w}{\partial y}\right)_x}{\left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial f}{\partial y}\right)_{z,x} - \left(\frac{\partial w}{\partial y}\right)_x \left(\frac{\partial f}{\partial x}\right)_{y,z}}$$

$$\left(\frac{\partial x}{\partial y}\right)_w\left(\frac{\partial y}{\partial z}\right)_w=\frac{\left(\frac{\partial f}{\partial z}\right)_{x,y}\left(\frac{\partial w}{\partial y}\right)_x}{\left(\frac{\partial w}{\partial x}\right)_y\left(\frac{\partial f}{\partial y}\right)_{z,x}-\left(\frac{\partial w}{\partial y}\right)_x\left(\frac{\partial f}{\partial x}\right)_{y,z}}=\left(\frac{\partial x}{\partial z}\right)_w.$$

□

(2) *Proof.* 由于 x,y,z 满足 $f(x,y,z)=0$, 则有 $z=z(x,y)$。两侧微分可得:

$$dz=\left(\frac{\partial z}{\partial x}\right)_y dx+\left(\frac{\partial z}{\partial y}\right)_x dy$$

则有:

$$\left(\frac{\partial x}{\partial y}\right)_z=-\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y},\ \left(\frac{\partial y}{\partial x}\right)_z=-\frac{\left(\frac{\partial z}{\partial x}\right)_y}{\left(\frac{\partial z}{\partial y}\right)_x}.$$

则有:

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial x}\right)_z=1.$$

□

(3) *Proof.* 由 (2) 中 $z=z(x,y)$ 微分式可知:

$$\left(\frac{\partial y}{\partial z}\right)_x=\frac{1}{\left(\frac{\partial z}{\partial y}\right)_x}$$

则有:

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y=-\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y}\frac{1}{\left(\frac{\partial z}{\partial y}\right)_x}\left(\frac{\partial z}{\partial x}\right)_y=-1.$$

□

(4) (check) 令 $x=P$, $y=T$, $z=V$ 由理想气体状态方程 $PV=nRT$ 得知:

$$\left(\frac{\partial P}{\partial T}\right)_V=\frac{nR}{V},\ \left(\frac{\partial T}{\partial P}\right)_V=\frac{V}{nR}.$$

则有:

$$\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial P}\right)_V=1.$$

即 (2) 式成立。

$$\left(\frac{\partial T}{\partial V}\right)_P=\frac{P}{nR},\ \left(\frac{\partial V}{\partial P}\right)_T=-\frac{nRT}{P^2}.$$

则有:

$$\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T=-\frac{nRT}{PV}=-1.$$

即 (3) 式成立。

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(1) *Proof.* 对于理想气体，在绝热过程中，由热力学第一定律可知:

$$dU = C_V\,dT = -p\,dV.$$

对理想气体状态方程微分可得:

$$nR\,dT = p\,dV + V\,dp.$$

两式联立可得:

$$\frac{C_p}{C_V}p\,dV + V\,dp = 0.$$

令 $\gamma = \frac{C_p}{C_V}$，则有

$$d\left(pV^\gamma\right) = 0.$$

则有

$$pV^\gamma = C_1,$$

C_1 为常数。 □

(2) *Proof.* 由理想气体状态方程与 (1) 结果可知

$$TV^{\gamma-1} = \frac{C_1}{nR} = C_2$$

C_2 为常数。 □

(3) *Proof.* 由理想气体状态方程 $pV = nRT$ 可知

$$p^{1-\gamma}T^\gamma = \frac{C_1}{(nR)^\gamma}$$

两侧同时开 $1-\gamma$ 次方，则有:

$$pT^{\frac{\gamma}{1-\gamma}} = \left(\frac{C_1}{(nR)^\gamma}\right)^{\frac{1}{1-\gamma}} = C_3$$

C_3 为常数。 □

(4) 在绝热过程中理想气体从 (P_1, V_1) 到 (P_2, V_2) 做功为:

$$W = \int_{V_1}^{V_2} P\,dV = \int_{V_1}^{V_2} \frac{C_1}{V^\gamma}\,dV = \frac{C_1}{1-\gamma}\left(V_2^{1-\gamma} - V_1^{1-\gamma}\right) = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

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(1) *Proof.* 设 $A \to B$ 过程吸热 Q_2,$C \to D$ 过程放热 Q_1，则循环效率为:

$$\eta = 1 - \frac{Q_1}{Q_2}.$$

等温过程 $A \to B$ 过程中，理想气体的内能不变，则吸热为:

$$Q_2 = \int_{V_A}^{V_B} \frac{nRT_2}{V}\,dV = nRT_2 \ln\frac{V_B}{V_A}.$$

等温过程 $C \to D$ 过程中，理想气体内能不变，则放热为:

$$Q_1 = \int_{V_D}^{V_C} \frac{nRT_1}{V} \, dV = nRT_1 \ln \frac{V_C}{V_D}.$$

绝热过程 $B \to C$ 与 $D \to A$ 过程中，有:

$$T_2 V_B^{\gamma-1} = T_1 V_C^{\gamma-1}, \; T_1 V_D^{\gamma-1} = T_2 V_A^{\gamma-1}.$$

即有:

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}, \; \frac{Q_1}{Q_2} = \frac{T_1}{T_2}.$$

则 Carnot 循环效率为:

$$\eta = 1 - \frac{T_1}{T_2}.$$

□