习题 I

截止时间：2021. .（周二）

姓名：陈 稼 霖
学号：45875852
成绩：________

第 1 题 得分: ________. 令变量 x, y, z 满足方程 $f(x,y,z)=0$，w 为 x, y, z 中任意两个变量的函数. 证明：

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

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

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

并用理想气体的状态方程验证 2) 和 3)，其中 $x=P$, $y=T$, $z=V$.

证: 1) 将 w 写作 x, y 的函数

$$w=w(x,y) \tag{1}$$

并取微分，有

$$\mathrm{d}w=\left(\frac{\partial w}{\partial x}\right)_y\mathrm{d}x+\left(\frac{\partial w}{\partial y}\right)_x\mathrm{d}y. \tag{2}$$

令上式中 $\mathrm{d}w=0$，得

$$\left(\frac{\partial x}{\partial y}\right)_w=-\frac{\left(\frac{\partial w}{\partial y}\right)_x}{\left(\frac{\partial w}{\partial x}\right)_y}. \tag{3}$$

对式 $f(x,y,z)=0$ 取微分，有

$$\mathrm{d}f=\left(\frac{\partial f}{\partial x}\right)_{y,z}\mathrm{d}x+\left(\frac{\partial f}{\partial y}\right)_{x,z}\mathrm{d}y+\left(\frac{\partial f}{\partial z}\right)_{x,y}\mathrm{d}z=0, \tag{4}$$

从而可将 $\mathrm{d}x$ 表示为

$$\mathrm{d}x=-\frac{\left(\frac{\partial f}{\partial y}\right)_{x,z}\mathrm{d}y+\left(\frac{\partial f}{\partial z}\right)_{x,y}\mathrm{d}z}{\left(\frac{\partial f}{\partial x}\right)_{y,z}}. \tag{5}$$

将上式代入式 (2)，得

$$\mathrm{d}w=-\left(\frac{\partial w}{\partial x}\right)_y\frac{\left(\frac{\partial f}{\partial y}\right)_{x,z}\mathrm{d}y+\left(\frac{\partial f}{\partial z}\right)_{x,y}\mathrm{d}z}{\left(\frac{\partial f}{\partial x}\right)_{y,z}}+\left(\frac{\partial w}{\partial y}\right)_x\mathrm{d}y. \tag{6}$$

令上式中 $\mathrm{d}w=0$，得

$$\left(\frac{\partial y}{\partial z}\right)_w=\frac{-\left(\frac{\partial w}{\partial x}\right)_y\left(\frac{\partial f}{\partial z}\right)_{x,y}}{\left(\frac{\partial w}{\partial x}\right)_y\left(\frac{\partial f}{\partial y}\right)_{x,z}-\left(\frac{\partial w}{\partial y}\right)_x\left(\frac{\partial f}{\partial x}\right)_{y,z}}. \tag{7}$$

由式 (4)，也可将 $\mathrm{d}y$ 表为

$$\mathrm{d}y=-\frac{\left(\frac{\partial f}{\partial x}\right)_{y,z}\mathrm{d}x+\left(\frac{\partial f}{\partial z}\right)_{x,y}\mathrm{d}z}{\left(\frac{\partial f}{\partial y}\right)_{x,z}}. \tag{8}$$

将上式代入式 (2)，得

$$\mathrm{d}w=\left(\frac{\partial w}{\partial x}\right)_y\mathrm{d}x-\left(\frac{\partial w}{\partial y}\right)_x\frac{\left(\frac{\partial f}{\partial x}\right)_{y,z}\mathrm{d}x+\left(\frac{\partial f}{\partial z}\right)_{x,y}\mathrm{d}z}{\left(\frac{\partial f}{\partial y}\right)_{x,z}}. \tag{9}$$

令上式中 $\mathrm{d}w=0$ 得

$$\left(\frac{\partial x}{\partial z}\right)_w=\frac{\left(\frac{\partial w}{\partial y}\right)_x\left(\frac{\partial f}{\partial z}\right)_{x,y}}{\left(\frac{\partial w}{\partial x}\right)_y\left(\frac{\partial f}{\partial y}\right)_{x,z}-\left(\frac{\partial w}{\partial y}\right)_x\left(\frac{\partial f}{\partial x}\right)_{y,z}} \tag{10}$$

式 (3) 与 (7) 相乘恰好等于式 (10)，

$$\left(\frac{\partial x}{\partial y}\right)_w\left(\frac{\partial y}{\partial z}\right)_w=\frac{\left(\frac{\partial w}{\partial y}\right)_x\left(\frac{\partial f}{\partial z}\right)_{x,y}}{\left(\frac{\partial w}{\partial x}\right)_y\left(\frac{\partial f}{\partial y}\right)_{x,z}-\left(\frac{\partial w}{\partial y}\right)_x\left(\frac{\partial f}{\partial x}\right)_{y,z}}=\left(\frac{\partial x}{\partial z}\right)_w, \tag{11}$$

得证.

2) 令 z 保持不变，即在式 (4) 中令 $\mathrm{d}z=0$，得

$$\mathrm{d}f=\left(\frac{\partial f}{\partial x}\right)_{y,z}\mathrm{d}x+\left(\frac{\partial f}{\partial y}\right)_{x,z}\mathrm{d}y=0, \tag{12}$$

从而

$$\left(\frac{\partial x}{\partial y}\right)_z=-\frac{\left(\frac{\partial f}{\partial y}\right)_{x,z}}{\left(\frac{\partial f}{\partial x}\right)_{y,z}}, \tag{13}$$

$$\left(\frac{\partial y}{\partial x}\right)_z=-\frac{\left(\frac{\partial f}{\partial x}\right)_{y,z}}{\left(\frac{\partial f}{\partial y}\right)_{x,z}}. \tag{14}$$

上面两式相乘，得

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial x}\right)_z=1. \tag{15}$$

3) 令式 (4) 中的 $\mathrm{d}x=0$ ，得

$$\left(\frac{\partial y}{\partial z}\right)_x=-\frac{\left(\frac{\partial f}{\partial z}\right)_{x,y}}{\left(\frac{\partial f}{\partial y}\right)_{x,z}}. \tag{16}$$

令式 (4) 中的 $\mathrm{d}y=0$，得

$$\left(\frac{\partial z}{\partial x}\right)_y=-\frac{\left(\frac{\partial f}{\partial x}\right)_{y,z}}{\left(\frac{\partial f}{\partial z}\right)_{x,y}}. \tag{17}$$

式 (13), (16) 和 (17) 相乘，得

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y=-1. \tag{18}$$

理想气体的状态方程为

$$PV=nRT. \tag{19}$$

验证 *2)*：

$$\begin{cases}\left(\frac{\partial P}{\partial T}\right)_V=\frac{nR}{V},\\ \left(\frac{\partial T}{\partial P}\right)_V=\frac{V}{nR},\end{cases} \tag{20}$$

$$\Longrightarrow \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V = 1. \tag{21}$$

验证 *3)*：

$$\begin{cases} \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}, \\ \left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{nR}, \\ \left(\frac{\partial V}{\partial P}\right)_T = -\frac{nRT}{P^2}, \end{cases} \tag{22}$$

$$\Longrightarrow \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -\frac{nRT}{VP} = -1. \tag{23}$$

□

第 2 题 得分: ________. 假设热容量 C_V 为常数，证明理想气体绝热过程中的下列关系：

1) $PV^\gamma =$常数

2) $TV^{\gamma-1} =$常数

3) $PT^{\frac{\gamma}{1-\gamma}} =$常数

其中 $\gamma \equiv C_P/C_V$，并计算理想气体从初态 (P_1, V_1) 到末态 (P_2, V_2) 所做的功.

解: 1) 由热力学第一定律，

$$\mathrm{d}U = \delta W + \delta Q \tag{24}$$

在绝热过程中，气体与外界无热量交换，$\delta Q = 0$，而外界对气体所做的功为 $\delta W = -P\mathrm{d}V$. 对于理想气体，由焦耳定律知，内能的微分可表为 $\mathrm{d}U = C_V\,\mathrm{d}T$. 从而式 (24) 可化为

$$C_V\mathrm{d}T + P\,\mathrm{d}V = 0. \tag{25}$$

将理想气体的物态方程 $PV = nRT$ 全式进行微分，得

$$P\,\mathrm{d}V + V\,\mathrm{d}P = nR\,\mathrm{d}T. \tag{26}$$

由于定压热容 C_P 和定容热容 C_V 之差为 $C_P - C_V = nR$，上式可化为

$$P\,\mathrm{d}V + V\,\mathrm{d}p = (C_P - C_V)\,\mathrm{d}T = (\gamma - 1)C_V\,\mathrm{d}T, \tag{27}$$

其中 $\gamma = C_P/C_V$. 联立式 (25) 和 (27)，消去 C_V，得

$$V\,\mathrm{d}P + \gamma P\,\mathrm{d}V = 0, \tag{28}$$

即

$$\frac{\mathrm{d}P}{P} = -\gamma\frac{\mathrm{d}V}{V}. \tag{29}$$

在温度变化范围较小的情况下，可将 γ 视为常数，对上式积分，得

$$PV^\gamma = \text{常数}. \tag{30}$$

2) 由理想气体的状态方程 $pV = nRT$，P 可表为

$$P = \frac{nRT}{V}. \tag{31}$$

将上式代入式 (30)，得

$$TV^{\gamma-1} = \text{常数}. \tag{32}$$

3) 由理想气体的状态方程 $pV=nRT$，V 可表为

$$V=\frac{nRT}{P}. \tag{33}$$

将上式代入式 (30)，得

$$P^{1-\gamma}T^{\gamma}=\text{常数}. \tag{34}$$

取上式的 $\frac{1}{1-\gamma}$ 次方，得

$$pT^{\frac{\gamma}{1-\gamma}}=\text{常数}. \tag{35}$$

理想气体从初态 (P_1,V_1) 到末态 (P_2,V_2) 对外界所做的功为

$$W=\int_{V_1}^{V_2}P\,\mathrm{d}V=C\int_{V_1}^{V_2}\frac{\mathrm{d}V}{V^{\gamma}}=\frac{C}{\gamma-1}\left(\frac{1}{V_2^{\gamma-1}}-\frac{1}{V_1^{\gamma-1}}\right) \tag{36}$$

其中 C 为常数，

$$P_1V_1^{\gamma}=P_2V_2^{\gamma}=C. \tag{37}$$

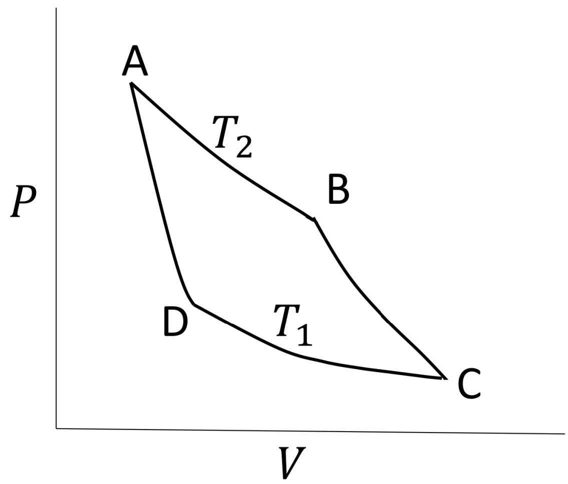
故上式可化为

$$W=\frac{P_2V_2-P_1V_1}{\gamma-1}. \tag{38}$$

□

第 3 题 得分: ________. 理想气体的 Carnot 循环：$A\to B\to C\to D\to A$
— 等温过程：$A\to B$（与高温热源接触）$C\to D$（与低温热源接触）
— 绝热过程：$B\to C$, $D\to A$.
假设热容量为常数，证明循环效率为

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



证: 等温过程 $A\to B$ 中，外界对气体做的功为

$$W_{A\to B}=-\int_{V_A}^{V_B}P\,\mathrm{d}V=-RT_1\int_{V_A}^{V_B}\frac{\mathrm{d}V}{V}=-RT_1\ln\frac{V_B}{V_A}. \tag{39}$$

等温过程中理想气体的内能不变，故由热力学第一定律可知，气体从高温热源吸收的热量为

$$Q_1 = -W_{A\to B} = RT_1 \ln \frac{V_B}{V_A}. \tag{40}$$

同理，等温过程 $C \to D$ 中，气体向低温热源释放的热量为

$$Q_2 = RT_2 \ln \frac{V_C}{V_D}. \tag{41}$$

绝热过程 $B \to C$ 和 $D \to A$ 中，气体与外界均无热量交换，因此，在一个 Carnot 循环中，气体净吸收的热量为

$$Q = Q_1 - Q_2 = RT_1 \ln \frac{V_B}{V_A} - RT_2 \ln \frac{V_C}{V_D}. \tag{42}$$

一个 Carnot 循环后，气体回到原来的状态，故内能变化为零，由热力学第一定律知，在整个循环中，气体对外做的净功为

$$W = Q = RT_1 \ln \frac{V_B}{V_A} - RT_2 \ln \frac{V_C}{V_D}. \tag{43}$$

因为过程 $B \to C$ 和 $D \to A$ 绝热，故有

$$T_1 V_B^{\gamma-1} = T_2 V_C^{\gamma-1}, \tag{44}$$

$$T_2 V_D^{\gamma-1} = T_1 V_A^{\gamma-1}. \tag{45}$$

上面两式联立消去 T_1 和 T_2，得

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}. \tag{46}$$

因此，

$$W = R(T_1 - T_2) \ln \frac{V_B}{V_A}. \tag{47}$$

在整个循环中，气体从高温热源吸收了热量 Q_1，对外做功 W，故循环效率为

$$\eta = \frac{W}{Q_1} = \frac{R(T_1 - T_2)\ln \frac{V_B}{V_A}}{RT_1 \ln \frac{V_B}{V_A}} = 1 - \frac{T_2}{T_1}. \tag{48}$$

$\square$