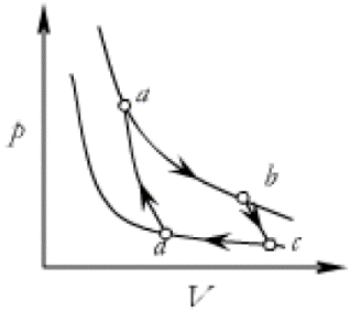
第二章作业参考答案

1. 解：如图所示：Carnot 循环由 a→b（等温可逆膨胀）、b→c（绝热可逆膨胀）、c→d（等温可逆压缩）和 d→a（绝热可逆压缩）构成。

	ΔU	ΔH	ΔS
a→b	0	0	$nR\ln\frac{V_b}{V_a}$
b→c	$\int_{T_H}^{T_L} C_V \mathrm{d}T$	$\int_{T_H}^{T_L} C_p \mathrm{d}T$	0
c→d	0	0	$nR\ln\frac{V_d}{V_c}$
d→a	$\int_{T_\mathrm{L}}^{T_\mathrm{H}} C_V \mathrm{d}T$	$\int_{T_\mathrm{L}}^{T_\mathrm{H}} C_p \mathrm{d}T$	0

$\Delta U(\mathrm{a}\rightarrow\mathrm{b}) = \Delta H(\mathrm{a}\rightarrow\mathrm{b}) = 0$

$\Delta S(\mathrm{a}\rightarrow\mathrm{b}) = nR\ln\frac{V_b}{V_a}$



$\Delta U(\mathrm{b}\rightarrow\mathrm{c}) = \int_{T_H}^{T_L} C_V \mathrm{d}T \approx C_V(T_L - T_H)$

$\Delta H(\mathrm{b}\rightarrow\mathrm{c}) = \int_{T_H}^{T_L} C_p \mathrm{d}T \approx C_p(T_L - T_H)$

$\Delta S(\mathrm{b}\rightarrow\mathrm{c}) = \Delta S(\mathrm{d}\rightarrow\mathrm{a}) = 0$

$\Delta U(\mathrm{c}\rightarrow\mathrm{d}) = \Delta H(\mathrm{c}\rightarrow\mathrm{d}) = 0$

$\Delta S(\mathrm{c}\rightarrow\mathrm{d}) = nR\ln\frac{V_d}{V_c} = -\Delta S(\mathrm{a}\rightarrow\mathrm{b}) = -nR\ln\frac{V_b}{V_a}$

$\Delta U(\mathrm{d}\rightarrow\mathrm{a}) = \int_{T_\mathrm{L}}^{T_\mathrm{H}} C_V \mathrm{d}T = -\int_{T_\mathrm{H}}^{T_\mathrm{L}} C_V \mathrm{d}T = -\Delta U(\mathrm{b}\rightarrow\mathrm{c}) \approx C_V(T_H - T_L)$

$\Delta H(\mathrm{d}\rightarrow\mathrm{a}) = \int_{T_\mathrm{L}}^{T_\mathrm{H}} C_p \mathrm{d}T = -\int_{T_\mathrm{H}}^{T_\mathrm{L}} C_p \mathrm{d}T = -\Delta H(\mathrm{b}\rightarrow\mathrm{c}) \approx C_p(T_H - T_L)$

2. 解：设计可逆过程 273 K, 100 kPa → 298 K, 100 kPa → 298 K, 1000 kPa

等压升温：$\Delta S_1 = \int_{T_1}^{T_2} \frac{C_p}{T}\mathrm{d}T = n\left(C_{V,\mathrm{m}} + R\right)\ln\frac{T_2}{T_1} = 5 \times \frac{5}{2} \times 8.314 \times \ln\frac{298}{273}\ \mathrm{J\cdot K^{-1}} = 9.11\ \mathrm{J\cdot K^{-1}}$

等温压缩：$\Delta S_2 = \frac{Q_2}{T_2} = nR\ln\frac{p_1}{p_2} = 5 \times 8.314 \times \ln\frac{100}{1000}\ \mathrm{J\cdot K^{-1}} = -95.72\ \mathrm{J\cdot K^{-1}}$

$\Delta S = \Delta S_1 + \Delta S_2 = -86.61\ \mathrm{J\cdot K^{-1}}$

另解：$\Delta S = \int_1^2 \frac{\delta Q}{T} = \int_1^2 \frac{dU-\delta W}{T} = \int_1^2 \left(\frac{nC_{V,\mathrm{m}}dT}{T} + \frac{pdV}{T}\right)$

$= nC_{V,\mathrm{m}} \ln\frac{T_2}{T_1} + \int_1^2 \frac{nRdV}{V}$

$= nC_{V,\mathrm{m}} \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1}$

$= nC_{V,\mathrm{m}} \ln\frac{T_2}{T_1} + nR \ln\frac{T_2 p_1}{T_1 p_2}$

$= \left(5 \times \frac{3}{2} \times 8.314 \times \ln\frac{298}{273} + 5 \times 8.314 \times \ln\frac{298\times100\times10^3}{273\times10^6}\right)\ \mathrm{J\cdot K^{-1}}$

$= -86.61\ \mathrm{J\cdot K^{-1}}$

3. 解：设混合后水温为 T_3，有：

$4.184 \times 100 \times (T_3/\mathrm{K} - 283) = 4.184 \times 200 \times (313 - T_3/\mathrm{K})$　　解得：$T_3 = 303\ \mathrm{K}$

$$\Delta S = \Delta S_1 + \Delta S_2 = \int_{T_1}^{T_3} \frac{C_p}{T}\mathrm{d}T + \int_{T_2}^{T_3} \frac{C_p}{T}\mathrm{d}T$$

$$= \left(100 \times 4.184 \times \ln\frac{303}{283} + 200 \times 4.184 \times \ln\frac{303}{313}\right)\mathrm{J\cdot K^{-1}}$$

$$= (28.57 - 27.17)\ \mathrm{J\cdot K^{-1}}$$

$$= 1.40\ \mathrm{J\cdot K^{-1}}$$

4. 解：设计恒压 p^θ 下的可逆过程

H_2O (g, 473 K) → H_2O (g, 373 K) → H_2O (l, 373K) → H_2O (l, 298 K)

等压降温：$\Delta S_1 = \int_{T_1}^{T_2} \frac{nC_{p,\mathrm{m}}(\mathrm{g})}{T}\mathrm{d}T = \int_{473\ \mathrm{K}}^{373\ \mathrm{K}} \frac{1\times(30.21+9.92\times10^{-3}T)}{T}\mathrm{d}T = -8.17\ \mathrm{J\cdot K^{-1}}$

可逆相变：$\Delta S_2 = \frac{Q_2}{T_2} = \frac{-2255\times18}{373}\ \mathrm{J\cdot K^{-1}} = -108.8\ \mathrm{J\cdot K^{-1}}$

等压降温：$\Delta S_3 = \int_{T_2}^{T_3} \frac{nC_{p,\mathrm{m}}(\mathrm{l})}{T}\mathrm{d}T = nC_{p,\mathrm{m}}(\mathrm{l})\ln\frac{T_3}{T_2} = 4.184 \times 18 \times \ln\frac{298}{373}\ \mathrm{J\cdot K^{-1}} = -16.90\ \mathrm{J\cdot K^{-1}}$

$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -133.9\ \mathrm{J\cdot K^{-1}}$

5. 解：因为是理想气体等温变化，所以 $\Delta U = \Delta H = 0$

$$W = -nRT\ln\frac{p_1}{p_2} = -8.314 \times 298 \times \ln\frac{101.325}{607.95}\ \mathrm{J} = 4439.2\ \mathrm{J}$$

$Q = -W = -4439.2\ \mathrm{J}$

等温下：$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V = -p\mathrm{d}V$，$\Delta F = -\int_{V_1}^{V_2} p\mathrm{d}V = -nRT\ln\frac{p_1}{p_2} = 4439.2\ \mathrm{J}$

或 $\Delta F = \Delta U - \mathrm{T}\Delta S_{\text{体系}} = 4439.2\ \mathrm{J}$

或根据过程为等温可逆且无非体积功得 $\Delta F = W_{\text{体积}} = 4439.2\ \text{J}$

等温下：$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p = V\mathrm{d}p$，$\Delta G = \int_{p_1}^{p_2} V\mathrm{d}p = nRT\ln\frac{p_2}{p_1} = 4439.2\ \text{J}$

或 $\Delta G = \Delta H - \mathrm{T}\Delta S_{\text{体系}} = 4439.2\ \text{J}$

等温过程 $\Delta S_{\text{体系}} = \frac{Q}{T} = \frac{-4439.2}{298}\ \text{J}\cdot\text{K}^{-1} = -14.9\ \text{J}\cdot\text{K}^{-1}$

$\Delta S_{\text{环境}} = \frac{Q_{\text{环}}}{T_{\text{环}}} = \frac{4439.2}{298}\ \text{J}\cdot\text{K}^{-1} = 14.9\ \text{J}\cdot\text{K}^{-1}$

$\Delta S_{\text{孤立}} = \Delta S_{\text{体系}} + \Delta S_{\text{环境}} = 0$

6. 解：此过程为可逆过程

$W = -p^{\theta}\Delta V = -p^{\theta}V_{\text{g}} = -nRT = -1 \times 8.314 \times 383\ \text{J} = -3184\ \text{J}$

$Q = nM_{\text{toluene}}\Delta H_0 = 1\ \text{mol}^{-1} \times 92.14\ \text{g}\cdot\text{mol}^{-1} \times 361.9\ \text{J}\cdot\text{g}^{-1} = 33345\ \text{J}$

等压过程 $\Delta H = Q = 33345\ \text{J}$

$\Delta U = Q + W = 30161\ \text{J}$

等温过程 $\Delta S = Q/T = 87.06\ \text{J}\cdot\text{K}^{-1}$

$\Delta G = \Delta H - T\Delta S = \Delta H - Q = 0$（可逆相变过程规律）

（书后答案带入的甲苯摩尔质量 M_{toluene} 似乎有问题）

9. 解：293 K，100 kPa 下，1 mol 乙醇体积 $V_1 = m/\rho = 1 \times 46.07/0.789\ \text{cm}^3 = 58.390\ \text{cm}^3$

由此可知 $V_0 = \frac{V_1}{1-\beta p} = \frac{58.390\times10^{-6}}{1-1.04\times10^{-6}\times100}\ \text{m}^3 = 58.396\times10^{-6}\ \text{m}^3$

$$\Delta G = \int_{p_1}^{p_2} V\mathrm{d}p = \int_{p_1}^{p_2} V_0(1-\beta p)\mathrm{d}p = V_0(p_2 - p_1) - \frac{1}{2}V_0\beta({p_2}^2 - {p_1}^2)$$

$$= 58.396\times10^{-6}\ \text{m}^3 \times (2533\ \text{kPa} - 100\ \text{kPa})$$

$$-\frac{1}{2}\times 58.396\times10^{-6}\ \text{m}^3 \times 1.04\times10^{-6}\times(\text{kPa})^{-1}\times\left[(2533\ \text{kPa})^2 - (100\ \text{kPa})^2\right]$$

$$= 141.88\ \text{J}$$