

## 第2章 热力学定律和热力学基本方程

## 基本概念

1. 过程的方向和限度问题。
2. 热从低温物体传给高温物体而不产生其他变化是不可能的；从一个热源吸热，使之完全转化为功，而不产生其他变化是不可能的。
3. 不违背开尔文说法，因为理想气体的状态发生了变化。

$$4. \quad dS - \frac{dQ}{T_{\text{环}}} \geq 0$$

$$5. \quad \Delta S \stackrel{\text{def}}{=} \int_A^B \frac{dQ_R}{T}; \text{ 系统混乱程度的度量。}$$

$$6. \quad dS \geq 0, \text{ 孤立系统或绝热过程。}$$

$$7. \quad =$$

$$8. (1) 2; (2) \quad W = - \int_{V_A}^{V_B} \frac{C}{V^\nu} dV \quad C = pV^\nu, \quad W = - \int_{V_A}^{V_B} \frac{nRT}{V} dV。$$

$$9. \quad 1.15 \text{ J} \cdot \text{K}^{-1}; \quad 2.74 \text{ J} \cdot \text{K}^{-1}。$$

$$10. \quad =, <, >。$$

$$11. (2), (4)。$$

$$12. \text{ 证明: } dU = TdS - pdV$$

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

$$\text{由麦克斯韦关系式 } \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V \text{ 和 } pV = nRT$$

$$\text{得 } \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p = T \frac{nR}{V} - p = 0$$

13. 理想气体恒温过程；恒压变温过程；可逆相变化；恒温过程；纯组分系统， $L \rightarrow V$ ,  $V_m(l) \approx 0$ ，气体为理想气体， $\Delta_{\text{vap}} H_m = C$ ；纯组分系统的两相平衡。

$$14. \text{ 根据克-克方程 } \frac{dp}{dT} = \frac{\Delta_{\text{相变}} H_m}{T \Delta_{\text{相变}} V_m}$$

由于  $\text{H}_2\text{O}$  的  $V_m(l) < V_m(s)$ ，而  $\text{C}_6\text{H}_6$  的  $V_m(l) > V_m(s)$

所以水的相图中液固平衡线的斜率是负值，而苯的相图中液固平衡线的斜率是正值。

15. 当温度趋于  $0\text{K}$  时，凝聚系统中恒温过程的熵变趋于零。

16. 当温度趋于 0K, 系统中所有处于内部平衡的状态之间, 熵变趋于零。  
 17. 在积分的温度范围内无相变化。  
 18. 恒温, 恒容, 非体积功为零的封闭系统。  
 19. 恒温, 恒压, 非体积功为零的封闭系统。

### 计算题

1. 解: (1)  $W = -nRT \ln \frac{V_2}{V_1} = \left( -2 \times 8.3145 \times 298.2 \times \ln \frac{40.00}{15.00} \right) \text{J} = -4864 \text{J};$

$$\Delta U = 0; \quad \Delta H = 0。$$

(2)  $W = -p_{\text{外}}(V_2 - V_1) = -101325 \times (40.00 - 15.00) \times 10^{-3} \text{J} = -2533 \text{J}; \Delta U = 0; \Delta H = 0。$

(3)  $W = -p(V_2 - V_1) = -nR(T_2 - T_1) = -2 \times 8.3145 \times (795.2 - 298.2) \text{J} = -8265 \text{J}$

$$\Delta U = nC_{V,m}(T_2 - T_1) = 2 \times \frac{3}{2} \times 8.3145 \times (795.2 - 298.2) \text{J} = 12.40 \text{kJ}$$

$$\Delta H = nC_{p,m}(T_2 - T_1) = 2 \times \frac{5}{2} \times 8.3145 \times (795.2 - 298.2) \text{J} = 20.66 \text{kJ}$$

2. 解: (1) 取 He, O<sub>2</sub> 为系统, 经历恒容绝热过程。

$$\Delta U = \Delta U_1 + \Delta U_2 = 0, \quad n_1 C_{V,m,1}(t - t_1) + n_2 C_{V,m,2}(t - t_2) = 0$$

$$1 \times \frac{3}{2} R(x - 100) + 0.5 \times \frac{5}{2} R(x - 0) = 0,$$

解得  $x = 54.55$ , 即  $t = 54.55^\circ\text{C}$ 。

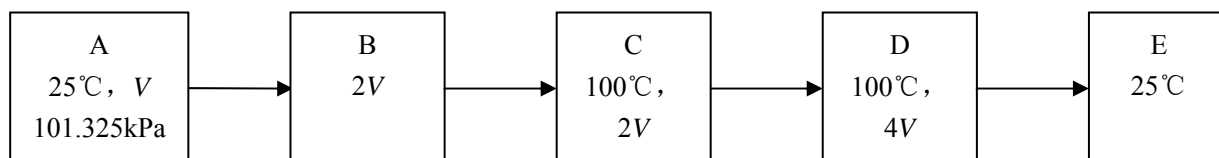
- (2) 取 He, O<sub>2</sub> 为系统, 经历恒压绝热过程。

$$\Delta H = \Delta H_1 + \Delta H_2 = 0, \quad n_1 C_{p,m,1}(t - t_1) + n_2 C_{p,m,2}(t - t_2) = 0$$

$$1 \times \frac{5}{2} R(x - 100) + 0.5 \times \frac{7}{2} R(x - 0) = 0,$$

解得  $x = 58.82$ , 即  $t = 58.82^\circ\text{C}$ 。

3. 解:



$$\Delta U = 0, \quad \Delta H = 0;$$

$$W_1 = 0, \quad W_2 = 0,$$

$$W_3 = -nRT \ln \frac{V_D}{V_C} = -[1 \times 8.3145 \times (100 + 273.15) \times \ln 2] \text{J} = -2151 \text{J}$$

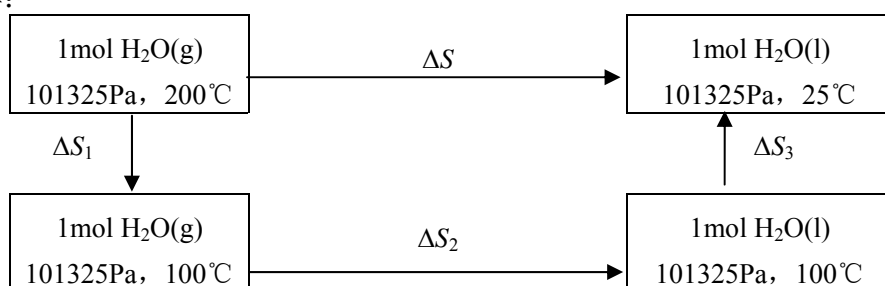
$$W_4 = \Delta U_4 = nC_{V,m}(T_E - T_D) = \left[ 1 \times \frac{3}{2} \times 8.3145 \times (25 - 100) \right] \text{J} = -935 \text{J}$$

$$\therefore W = -3086 \text{J}, \quad Q = \Delta U - W = 3086 \text{J},$$

$$\begin{aligned} \Delta S &= \Delta S_{A-D} + \Delta S_{D-E} = \Delta S_{A-D} = nC_{V,m} \ln \frac{T_D}{T_A} + nR \ln \frac{V_D}{V_A} \\ &= \left( 1 \times \frac{3}{2} \times 8.3145 \ln \frac{100 + 273.15}{25 + 273.15} + 1 \times 8.3145 \ln \frac{4}{1} \right) \text{J} \cdot \text{K}^{-1} = 14.32 \text{J} \cdot \text{K}^{-1} \end{aligned}$$

$$\Delta A = \Delta U - T\Delta S = (0 - 298.15 \times 14.32) \text{J} = -4270 \text{J}, \quad \Delta G = \Delta A = -4270 \text{J}.$$

4. 解:



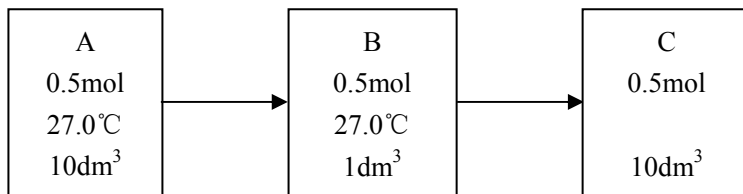
$$\begin{aligned} \Delta S_1 &= \int_{T_1}^{T_2} \frac{nC_{p,m(g)}}{T} dT \\ &= \left[ 30.21 \ln \frac{100 + 273.15}{200 + 273.15} + 9.92 \times 10^{-3} \times (100 - 200) \right] \text{J} \cdot \text{K}^{-1} = -8.165 \text{J} \cdot \text{K}^{-1} \end{aligned}$$

$$\Delta S_2 = \frac{\Delta H}{T_2} = -\frac{18.02 \times 2256}{373.15} \text{J} \cdot \text{K}^{-1} = -108.95 \text{J} \cdot \text{K}^{-1}$$

$$\Delta S_3 = \int_{T_2}^{T_3} \frac{nC_{p,m(l)}}{T} dT = \left( 18.02 \times 4.18 \ln \frac{25 + 273.15}{100 + 273.15} \right) \text{J} \cdot \text{K}^{-1} = -16.90 \text{J} \cdot \text{K}^{-1}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -134.02 \text{J} \cdot \text{K}^{-1}$$

5. 解:



$$\gamma = \frac{C_{p,m}}{C_{v,m}} = \frac{7}{2} R / \frac{5}{2} R = \frac{7}{5}, \quad \gamma - 1 = \frac{2}{5}$$

$$T_C = \left( \frac{V_B}{V_C} \right)^{\gamma-1} T_B = \left( \frac{1}{10.0} \right)^{\frac{2}{5}} \times (27.0 + 273.15) \text{K} = 119.5 \text{K}$$

$$\Delta U = nC_{V,m}(T_C - T_A) = 0.5 \times \frac{5}{2} \times 8.3145(119.5 - 300.15)\text{J} = -1878\text{J}$$

$$\Delta H = nC_{p,m}(T_C - T_A) = 0.5 \times \frac{7}{2} \times 8.3145(119.5 - 300.15)\text{J} = -2629\text{J}$$

$$\Delta S = nC_{V,m} \ln \frac{T_C}{T_A} = \left( 0.5 \times \frac{5}{2} \times 8.3145 \ln \frac{119.5}{300.15} \right) \text{J} \cdot \text{K}^{-1} = -9.57\text{J} \cdot \text{K}^{-1}$$

$$Q = Q_1 + Q_2 = -W_1 = nRT \ln \frac{V_B}{V_A} = \left( 0.5 \times 8.3145 \times 300.15 \ln \frac{1}{10.0} \right) \text{J} = -2873\text{J}$$

$$W = \Delta U - Q = [-1878 - (-2873)]\text{J} = 995\text{J}$$

6. 解: (1)  $\ln \frac{p_2^*}{p_1^*} = -\frac{\Delta_{\text{vap}} H_m}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right),$

$$\text{即 } \ln \frac{101.325}{37.60} = -\frac{35.27 \times 10^3}{8.3145} \left( \frac{1}{T_2/\text{K}} - \frac{1}{40 + 273.15} \right), \quad T_2 = 337.88\text{K}。$$

$$\Delta H = n\Delta_{\text{vap}} H_m = (1.50 \times 35.27)\text{kJ} = 52.91\text{kJ}$$

$$\begin{aligned} \Delta U &= \Delta H - \Delta(pV) \approx \Delta H - (nRT - 0) = (52.91 - 1.50 \times 8.3145 \times 337.88 \times 10^{-3})\text{kJ} \\ &= 48.70\text{kJ} \end{aligned}$$

$$\Delta S = \frac{\Delta H}{T} = \left( \frac{52.91 \times 10^3}{337.88} \right) \text{J} \cdot \text{K}^{-1} = 156.6\text{J} \cdot \text{K}^{-1}$$

$$\Delta A = \Delta U - T\Delta S = -4.21\text{kJ} \quad (\Delta A = W_R \approx -nRT = -4.21)\text{kJ}$$

$$\Delta G = \Delta H - T\Delta S = 0, \quad W = 0$$

$$Q = \Delta U - W = \Delta U = 48.70\text{kJ}$$

$$(2) \quad \Delta S - \frac{Q}{T_{\text{环}}} = \left( 156.6 - \frac{48.70 \times 10^3}{337.88} \right) \text{J} \cdot \text{K}^{-1} = 12.5\text{J} \cdot \text{K}^{-1} > 0,$$

或  $-\Delta A > -W$ , 为不可逆过程。

7. 解:  $\Delta G = \int_{p_1}^{p_2} V dp = V(p_2 - p_1) = \frac{nM}{\rho}(p_2 - p_1)$

$$= \left[ \frac{1 \times 200.61}{13.534} \times 10^{-6} \times (10 - 0.1) \times 10^6 \right] \text{J} = 146.7\text{J}$$

$$\Delta S = \int_{p_1}^{p_2} \left( \frac{\partial S}{\partial p} \right)_T dp = - \int_{p_1}^{p_2} \left( \frac{\partial V}{\partial T} \right)_p dp = - \int_{p_1}^{p_2} \alpha V dp = -\alpha V(p_2 - p_1)$$

$$= - \left[ 1.82 \times 10^{-4} \times \frac{1 \times 200.61}{13.534} \times 10^{-6} \times (10 - 0.1) \times 10^6 \right] \text{J} \cdot \text{K}^{-1} = -0.0267 \text{J} \cdot \text{K}^{-1}$$