

1. 如果一个系统从环境吸收了 40 J 的热,而系统的热力学能却增加了 200 J,问系统从环境得到了多少功? 如果该系统在膨胀过程中对环境做了 10 kJ 的功,同时吸收了 28 kJ 的热,求系统的热力学能变化值。

解: (1)  $\Delta U = Q + W$

$$W = \Delta U - Q = 200 \text{ J} - 40 \text{ J} = 160 \text{ J}$$

$$(2) \Delta U' = Q' + W' = 28 \text{ kJ} - 10 \text{ kJ} = 18 \text{ kJ}$$

2. 有 10 mol 的气体(设为理想气体),压力为 1 000 kPa,温度为 300 K,分别求出等温时下列过程的功:

(1) 在空气压力为 100 kPa 时,体积胀大  $1 \text{ dm}^3$ ;

(2) 在空气压力为 100 kPa 时,膨胀到气体压力也是 100 kPa;

(3) 等温可逆膨胀至气体的压力为 100 kPa。

解: (1)  $W = -p_{\text{外}} \Delta V = -1\,000 \text{ kPa} \times 1 \times 10^{-3} \text{ m}^3 = -1 \text{ kJ}$

$$(2) W = -p_{\text{外}}(V_2 - V_1) = -p_2 \left( \frac{nRT}{p_2} - \frac{nRT}{p_1} \right) = -nRT \left( 1 - \frac{p_2}{p_1} \right)$$

$$\begin{aligned}
 &= -10 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 300 \text{ K} \times \left(1 - \frac{100 \text{ kPa}}{1\,000 \text{ kPa}}\right) \\
 &= -24\,942 \text{ J} \times 0.9 \\
 &= -22\,447.8 \text{ J}
 \end{aligned}$$

$$\begin{aligned}
 (3) \quad W_{\text{R}} &= nRT \ln \frac{p_1}{p_2} \\
 &= 10 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 300 \text{ K} \times \ln \frac{1\,000 \text{ kPa}}{100 \text{ kPa}} \\
 &= -57\,431 \text{ J}
 \end{aligned}$$

结论:等温过程中可逆功最大。

3. 1 mol 单原子理想气体,  $C_{V,m} = \frac{3}{2}R$ , 始态(1)的温度为 273 K, 体积为 22.4 dm<sup>3</sup>, 经历如下三步, 又回到始态, 请计算每步过程的  $Q$ ,  $W$  和  $\Delta U$ 。

(1) 等容可逆升温, 由始态(1)到 546 K 的状态(2);

(2) 等温(546 K)可逆膨胀, 由状态(2)到 44.8 dm<sup>3</sup> 的状态(3);

(3) 经等压过程由状态(3)回到始态(1)。

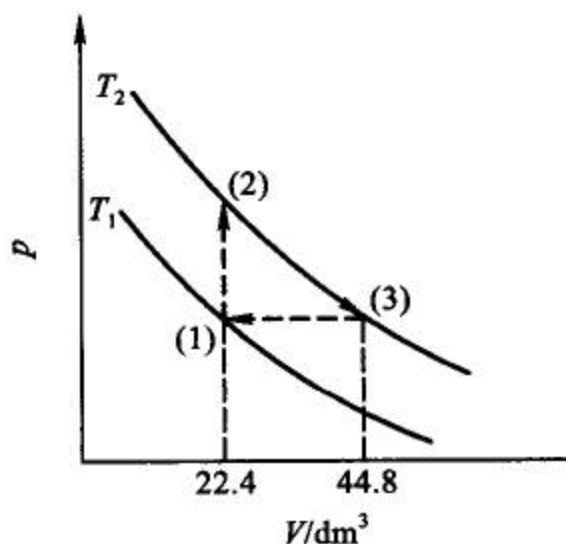


图 2-11

解: 题中三步过程如图 2-11 所示。

(1) 等容可逆升温:

$$\begin{aligned}
 W &= - \int p dV = 0 \\
 \Delta U &= \int_{T_1}^{T_2} C_V dT = nC_{V,m}(T_2 - T_1) \\
 &= n \frac{3}{2} R (T_2 - T_1) \\
 &= 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (546 \text{ K} - 273 \text{ K}) \\
 &= 3\,404.6 \text{ J} \\
 Q &= \Delta U - W = \Delta U = 3\,404.6 \text{ J}
 \end{aligned}$$

$$\begin{aligned}
 (2) \quad W_{\text{R}} &= -nRT \ln \frac{V_2}{V_1} = -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 546 \text{ K} \\
 &\quad \times \ln \frac{44.8 \text{ dm}^3}{22.4 \text{ dm}^3} \\
 &= -3\,146.5 \text{ J}
 \end{aligned}$$

$$\Delta U = f(T) = 0$$

$$Q \approx -W_R = 3\,146.5\text{ J}$$

$$\begin{aligned} (3) \quad W &= -p\Delta V = -\frac{nRT_1}{V_1}(V_1 - V_3) \\ &= -\frac{1\text{ mol} \times 8.314\text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 273\text{ K}}{22.4 \times 10^{-3}\text{ m}^3} \times (22.4 - 44.8) \times 10^{-3}\text{ m}^3 \\ &= 2\,269.7\text{ J} \end{aligned}$$

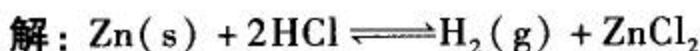
$$\begin{aligned} \Delta U &= nC_{V,m}(T_2 - T_1) \\ &= 1\text{ mol} \times \frac{3}{2} \times 8.314\text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (273\text{ K} - 546\text{ K}) \\ &= -3\,404.6\text{ J} \end{aligned}$$

$$Q = \Delta U - W = -3\,404.6\text{ J} - 2\,269.7\text{ J} = -5\,674.3\text{ J}$$

或

$$\begin{aligned} Q &= Q_p = \int_{T_1}^{T_2} C_p dT = n(C_{V,m} + R)(T_2 - T_1) \\ &= 1\text{ mol} \times \frac{5}{2} \times 8.314\text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (273\text{ K} - 546\text{ K}) \\ &= -5\,674.3\text{ J} \end{aligned}$$

4. 在 291 K 和 100 kPa 下, 1 mol Zn(s) 溶于足量稀盐酸中, 置换出 1 mol H<sub>2</sub>(g), 并放热 152 kJ。若以 Zn 和盐酸为系统, 求该反应所做的功及系统热力学能的变化。



$$\begin{aligned} W &= -p\Delta V = -pV_m(\text{H}_2) = -nRT \\ &= -1\text{ mol} \times 8.314\text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 291\text{ K} \\ &= -2\,419.4\text{ J} \end{aligned}$$

$$\Delta U = Q + W = -152\,000\text{ J} - 2\,419.4\text{ J} = -154\,419\text{ J}$$

5. 在 298 K 时, 有 2 mol N<sub>2</sub>(g), 始态体积为 15 dm<sup>3</sup>, 保持温度不变, 经下列三个过程膨胀到终态体积为 50 dm<sup>3</sup>, 计算各过程的  $\Delta U$ ,  $\Delta H$ ,  $W$  和  $Q$  的值。设气体为理想气体。

- (1) 自由膨胀;
- (2) 反抗恒定外压 100 kPa 膨胀;
- (3) 可逆膨胀。

$$\text{解: 始态 } n = 2\text{ mol}, \quad V_1 = 15\text{ dm}^3, \quad T_1 = 298\text{ K}$$

$$\text{终态 } V_2 = 50\text{ dm}^3$$

- (1) 自由膨胀:

$$W = -p_{\text{外}} \Delta V = 0$$

$$\cancel{\Delta U} = \cancel{\Delta H} = f(T) = 0$$

$$Q = \Delta U - W = 0$$

(2) 反抗恒定外压 100 kPa 膨胀:

$$W = -p_{\text{外}} \Delta V = -100 \times 10^3 \text{ Pa} \times (50 - 15) \times 10^{-3} \text{ m}^3 = -3500 \text{ J}$$

$$\cancel{\Delta U} = \cancel{\Delta H} = f(T) = 0$$

$$Q = \Delta U - W = 3500 \text{ J}$$

(3) 可逆膨胀:

$$W = -nRT \ln \frac{V_2}{V_1}$$

$$= -2 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K} \times \ln \frac{50 \text{ dm}^3}{15 \text{ dm}^3}$$

$$= -5965.9 \text{ J}$$

$$\cancel{\Delta U} = \cancel{\Delta H} = f(T) = 0$$

$$Q = \Delta U - W = 5965.9 \text{ J}$$

6. 在水的正常沸点 (373.15 K, 101.325 kPa), 有 1 mol  $\text{H}_2\text{O}(\text{l})$  变为同温、同压的  $\text{H}_2\text{O}(\text{g})$ , 已知水的摩尔汽化焓变值为  $\Delta_{\text{vap}} H_{\text{m}} = 40.69 \text{ kJ} \cdot \text{mol}^{-1}$ , 请计算该变化的  $Q, \Delta U, \Delta H$  的值各为多少。



$$Q_p = n\Delta_{\text{vap}} H_{\text{m}} = 1 \text{ mol} \times 40.69 \text{ kJ} \cdot \text{mol}^{-1} = 40.69 \text{ kJ}$$

$$W = -p_{\text{外}} \Delta V = -p_{\text{外}} (V_{\text{g}} - V_{\text{l}}) = -nRT$$

$$= -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 373.15 \text{ K} = -3102.4 \text{ J}$$

$$\Delta U = Q_p + W = 40.69 \times 10^3 \text{ J} - 3102.4 \text{ J} = 37588 \text{ J}$$

7. 理想气体等温可逆膨胀, 体积从  $V_1$  膨胀到  $10V_1$ , 对外做了 41.85 kJ 的功, 系统的起始压力为 202.65 kPa。

(1) 求始态体积  $V_1$ ;

(2) 若气体的量为 2 mol, 试求系统的温度。

解: (1)  $W = -nRT \ln \frac{V_2}{V_1}$

$$-41.85 \times 10^3 \text{ J} = -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times T \times \ln \frac{10V_1}{V_1}$$

$$T = 2186 \text{ K}$$

$$V_1 = \frac{nRT}{p_1} = \frac{1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 2186 \text{ K}}{202.65 \times 10^3 \text{ Pa}} = 0.08968 \text{ m}^3$$

(2)  $p_1 V_1 = nRT_1$



$$T_1 = \frac{p_1 V_1}{nR} = \frac{202.65 \times 10^3 \text{ Pa} \times 0.08968 \text{ m}^3}{2 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}} = 1093 \text{ K}$$

$$p_1 V_1 = n_1 R T_1 \quad (1)$$

$$p_1 V_1 = n_2 R T_2 \quad (2)$$

式(1)除以式(2)得

$$T_2 = \frac{n_1}{n_2} T_1 = \frac{1 \text{ mol}}{2 \text{ mol}} \times 2186 \text{ K} = 1093 \text{ K}$$

8. 在 101.325 kPa 及 423 K 时, 将 1 mol  $\text{NH}_3(\text{g})$  等温压缩到体积等于  $10 \text{ dm}^3$ , 求最少需做多少功?

(1) 假定是理想气体。

(2) 假定符合 van der Waals 方程。已知 van der Waals 常数  $a = 0.417 \text{ Pa} \cdot \text{m}^6 \cdot \text{mol}^{-2}$ ,  $b = 3.71 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$ 。

$$\begin{aligned} \text{解: (1) } V_1 &= \frac{nRT}{p_1} = \frac{1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 423 \text{ K}}{101325 \text{ Pa}} \\ &= 0.03471 \text{ m}^3 \end{aligned}$$

$$W = -nRT \ln \frac{V_2}{V_1}$$

$$= -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 423 \text{ K} \times \ln \frac{0.01 \text{ m}^3}{0.03471 \text{ m}^3}$$

$$= -4376 \text{ J}$$

$$(2) \left( p + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

$$\left( 101325 \text{ Pa} + \frac{0.417 \text{ Pa} \cdot \text{m}^6 \cdot \text{mol}^{-2}}{V_m^2} \right) \times (V_m - 3.71 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1})$$

$$= 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 423 \text{ K}$$

$$V_m^3 - 3.475 \times 10^{-2} V_m^2 + 4.115 \times 10^{-6} V_m - 1.547 \times 10^{-10} = 0$$

$$V_m = 0.03464 \text{ m}^3$$

$$W = - \int_{V_1}^{V_2} p dV = - \int_{V_1}^{V_2} \left( \frac{nRT}{V - nb} - \frac{an^2}{V^2} \right) dV$$

$$= -nRT \ln \frac{V_2 - nb}{V_1 - nb} - an^2 \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$$

$$= -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 423 \text{ K}$$

$$\times \ln \frac{0.01 \text{ m}^3 - 1 \text{ mol} \times 3.71 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}}{0.03469 \text{ m}^3 - 1 \text{ mol} \times 3.71 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}}$$

$$- 0.417 \text{ Pa} \cdot \text{m}^6 \cdot \text{mol}^{-2} \times (1 \text{ mol})^2 \times \left( \frac{1}{0.01 \text{ m}^3} - \frac{1}{0.03469 \text{ m}^3} \right)$$

$$= 4\,345\text{ J}$$

9. 已知在 373 K 和 101.325 kPa 压力时, 1 kg  $\text{H}_2\text{O}(\text{l})$  的体积为  $1.043\text{ dm}^3$ , 1 kg  $\text{H}_2\text{O}(\text{g})$  的体积为  $1\,677\text{ dm}^3$ ,  $\text{H}_2\text{O}(\text{l})$  的摩尔汽化焓变值  $\Delta_{\text{vap}}H_{\text{m}} = 40.66\text{ kJ} \cdot \text{mol}^{-1}$ 。当 1 mol  $\text{H}_2\text{O}(\text{l})$  在 373 K 和外压为 101.325 kPa 时完全蒸发成  $\text{H}_2\text{O}(\text{g})$ , 试求:

(1) 蒸发过程中系统对环境所做的功;

(2) 假定液态水的体积可忽略不计, 试求蒸发过程中系统对环境所做的功, 并计算所得结果的相对误差;

(3) 假定把蒸汽看作理想气体, 且略去液态水的体积, 求系统所做的功;

(4) 求(1)中变化的  $\Delta_{\text{vap}}U_{\text{m}}$  和  $\Delta_{\text{vap}}H_{\text{m}}$ ;

(5) 解释何故蒸发的焓变大于系统所做的功。

解: (1)  $W = -p(V_{\text{g}} - V_{\text{l}})$

$$\begin{aligned} &= -101\,325\text{ Pa} \times (1.677 - 1.043 \times 10^{-3})\text{ m}^3 \cdot \text{kg}^{-1} \times 18.0 \times 10^{-3}\text{ kg} \\ &= -3.057\text{ kJ} \end{aligned}$$

$$\begin{aligned} (2) \quad W &= -pV_{\text{g}} = -101\,325\text{ Pa} \times 18.0 \times 10^{-3}\text{ kg} \times 1.677\text{ m}^3 \cdot \text{kg}^{-1} \\ &= -3.059\text{ kJ} \end{aligned}$$

$$x = [(3\,059 - 3\,057)/3\,057] \times 100\% = 0.065\%$$

$$\begin{aligned} (3) \quad W &= -pV_{\text{g}} = -nRT = -1\text{ mol} \times 8.314\text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 373\text{ K} \\ &= -3.101\text{ kJ} \end{aligned}$$

$$(4) \quad \Delta_{\text{vap}}H_{\text{m}} = Q_p = 40.66\text{ kJ} \cdot \text{mol}^{-1}$$

$$\begin{aligned} \Delta_{\text{vap}}U_{\text{m}} &= \frac{Q_p + W}{n} = (40.66\text{ kJ} - 3.057\text{ kJ})/1\text{ mol} \\ &= 37.60\text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

(5) 水在蒸发过程中吸收的热量一部分用于胀大自身体积对外做功。另一部分用于克服分子间引力, 增加分子间距离, 提高分子热力学能(因为  $\Delta U > 0$ ,  $\Delta U = Q + W > 0$ , 所以  $Q > |W|$ )。

10. 1 mol 单原子理想气体, 从始态 273 K, 200 kPa, 到终态 323 K, 100 kPa, 通过两种途径:

(1) 先等压加热至 323 K, 再等温可逆膨胀至 100 kPa;

(2) 先等温可逆膨胀至 100 kPa, 再等压加热至 323 K。

请分别计算两种途径的  $Q, W, \Delta U$  和  $\Delta H$ , 试比较两种结果有何不同, 说明为什么。

解: 题中两种途径如图 2-12 所示。

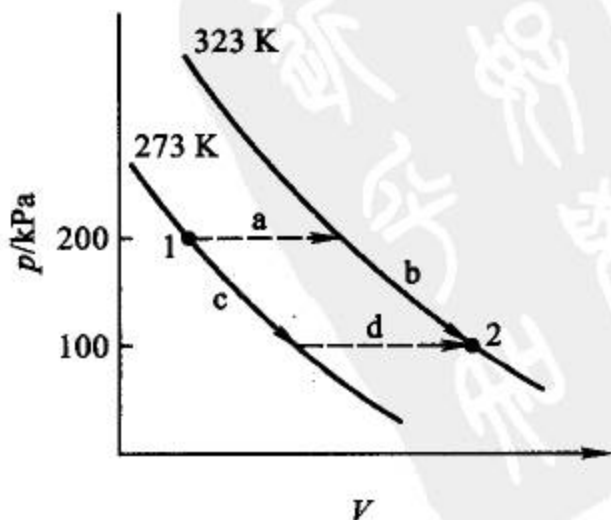


图 2-12

(1) 先等压加热至 323 K, 再等温可逆膨胀

$$(a) Q_a = Q_p = \Delta H_a = nC_{p,m}(T_2 - T_1)$$

$$= 1 \text{ mol} \times \frac{5}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (323 \text{ K} - 273 \text{ K})$$

$$= 1\,039.25 \text{ J}$$

$$\Delta U_a = nC_{v,m}(T_2 - T_1)$$

$$= 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (323 \text{ K} - 273 \text{ K})$$

$$= 623.55 \text{ J}$$

$$W_a = \Delta U_a - Q_p = 623.55 \text{ J} - 1\,039.25 \text{ J} = -415.7 \text{ J}$$

$$(b) \Delta U_b = \Delta H_b = J(T) = 0$$

$$W_b = -nRT \ln \frac{p_1}{p_2}$$

$$= -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 323 \text{ K} \times \ln \frac{200 \text{ kPa}}{100 \text{ kPa}}$$

$$= -1\,861.4 \text{ J}$$

$$Q_b = -W_b = 1\,861.4 \text{ J}$$

过程(1)总和:

$$\Delta U_1 = \Delta U_a + \Delta U_b = 623.55 \text{ J} + 0 = 623.55 \text{ J}$$

$$\Delta H_1 = \Delta H_a + \Delta H_b = 1\,039.25 \text{ J} + 0 = 1\,039.25 \text{ J}$$

$$Q_1 = Q_a + Q_b = 1\,039.25 \text{ J} + 1\,861.4 \text{ J} = 2\,900.65 \text{ J}$$

$$W_1 = W_a + W_b = -415.7 \text{ J} - 1\,861.4 \text{ J} = -2\,277.1 \text{ J}$$

(2) 先等温可逆膨胀至 100 kPa, 再等压加热至 323 K。

$$(c) \Delta U_c = \Delta H_c = J(T) = 0$$

$$W_c = -nRT \ln \frac{p_1}{p_2}$$

$$= -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 273 \text{ K} \times \ln \frac{200 \text{ kPa}}{100 \text{ kPa}}$$

$$= -1\,573.3 \text{ J}$$

$$Q_c = -W_c = 1\,573.3 \text{ J}$$

$$(d) Q_d = Q_p = \Delta H = nC_{p,m}(T_2 - T_1)$$

$$= 1 \text{ mol} \times \frac{5}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (323 \text{ K} - 273 \text{ K})$$

$$= 1\,039.25 \text{ J}$$

$$\Delta U_d = nC_{v,m}(T_2 - T_1)$$



$$= 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (323 \text{ K} - 273 \text{ K})$$

$$= 623.55 \text{ J}$$

$$\Delta H_d = nC_{p,m}(T_2 - T_1) = 1039.25 \text{ J}$$

$$W_d = \Delta U_d - Q_d = -415.7 \text{ J}$$

过程(2)的总和:

$$\Delta U_2 = \Delta U_c + \Delta U_d = 0 + 623.55 \text{ J} = 623.55 \text{ J}$$

$$\Delta H_2 = \Delta H_c + \Delta H_d = 0 + 1039.25 \text{ J} = 1039.25 \text{ J}$$

$$Q_2 = Q_c + Q_d = 1573.3 \text{ J} + 1039.25 \text{ J} = 2612.55 \text{ J}$$

$$W_2 = W_c + W_d = 1573.3 \text{ J} - 415.7 \text{ J} = -1989 \text{ J}$$

小结:(1)  $\Delta U_1 = \Delta U_2$ ,  $\Delta H_1 = \Delta H_2$ , 说明状态函数的变化只与始终态的状态有关, 而与变化过程无关。

(2)  $Q_1 \neq Q_2$ ,  $W_1 \neq W_2$ , 说明热和功与过程有关。

11. 273 K, 压力为  $5 \times 10^5 \text{ Pa}$  时,  $\text{N}_2(\text{g})$  的体积为  $2.0 \text{ dm}^3$ , 在外压为  $100 \text{ kPa}$  压力下等温膨胀, 直到  $\text{N}_2(\text{g})$  的压力也等于  $100 \text{ kPa}$  为止。求过程中的  $W$ ,  $\Delta U$ ,  $\Delta H$  和  $Q$ 。假定气体为理想气体。

解: 始态  $p_1 = 5 \times 10^5 \text{ Pa}$ ,  $T_1 = 273 \text{ K}$ ,  $V_1 = 2.0 \text{ dm}^3$

过程 等温等外压( $100 \text{ kPa}$ )膨胀

终态  $p_2 = 100 \text{ kPa}$

$$\begin{aligned} W &= -p_{\text{外}}(V_2 - V_1) = -p_2 \left( \frac{nRT_1}{p_2} - \frac{nRT_1}{p_1} \right) = -nRT_1 \left( 1 - \frac{p_2}{p_1} \right) = -p_1 V_1 \left( 1 - \frac{p_2}{p_1} \right) \\ &= -5 \times 10^5 \text{ Pa} \times 2.0 \times 10^{-3} \text{ m}^3 \times \left( 1 - \frac{100 \times 10^3 \text{ Pa}}{5 \times 10^5 \text{ Pa}} \right) = -800 \text{ J} \end{aligned}$$

或者:

$$n = \frac{p_1 V_1}{RT_1} = \frac{5 \times 10^5 \text{ Pa} \times 2.0 \times 10^{-3} \text{ m}^3}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 273 \text{ K}} = 0.4406 \text{ mol}$$

$$V_2 = \frac{nRT_2}{p_2} = \frac{0.4406 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 273 \text{ K}}{100 \times 1000 \text{ Pa}} = 0.0100 \text{ m}^3$$

$$\begin{aligned} W &= -p_{\text{外}}(V_2 - V_1) = -100 \times 1000 \text{ Pa} \times (0.0100 \text{ m}^3 - 2.0 \times 10^{-3} \text{ m}^3) \\ &= -800 \text{ J} \end{aligned}$$

$$\Delta U = \Delta H = f(T) = 0$$

$$Q = \Delta U - W = 0 - (-800 \text{ J}) = 800 \text{ J}$$

12.  $0.02 \text{ kg}$  乙醇在其沸点时蒸发为气体。已知蒸发热为  $858 \text{ kJ} \cdot \text{kg}^{-1}$ , 蒸气的比容为  $0.607 \text{ m}^3 \cdot \text{kg}^{-1}$ 。试求过程的  $\Delta U$ ,  $\Delta H$ ,  $W$  和  $Q$  (计算时略去液体的体积)。



解：乙醇在沸点时蒸发是等温等压可逆过程，则

$$Q_p = 0.02 \text{ kg} \times 858 \text{ kJ} \cdot \text{kg}^{-1} = 17.16 \text{ kJ}$$

$$\begin{aligned} W &= -p\Delta V \approx -pV_g = -101\,325 \text{ Pa} \times 0.02 \text{ kg} \times 0.607 \text{ m}^3 \cdot \text{kg}^{-1} \\ &= -1\,230 \text{ J} \end{aligned}$$

$$\Delta U = Q + W = (17.16 - 1.23) \text{ kJ} = 15.93 \text{ kJ}$$

$$\Delta H = Q_p = 17.16 \text{ kJ}$$

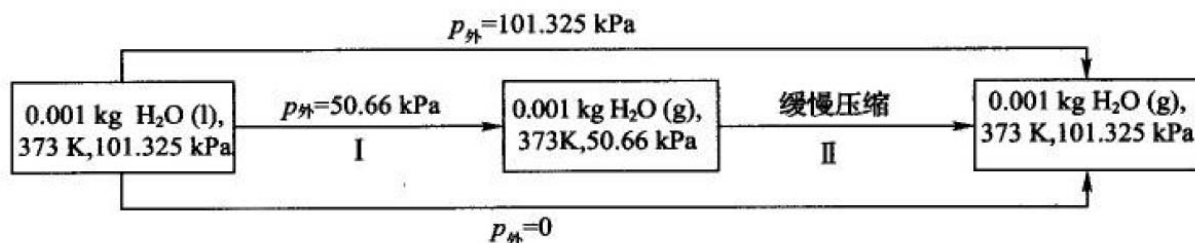
13. 373 K, 压力为 101.325 kPa 时, 1.0 g  $\text{H}_2\text{O}(\text{l})$  经下列不同的过程变为 373 K, 101.325 kPa 的  $\text{H}_2\text{O}(\text{g})$ , 请分别求出各过程的  $\Delta U, \Delta H, W$  和  $Q$  值。

(1) 在 373 K, 101.325 kPa 压力下  $\text{H}_2\text{O}(\text{l})$  变成同温、同压的  $\text{H}_2\text{O}(\text{g})$ 。

(2) 先在 373 K, 外压为 50.66 kPa 下变成  $\text{H}_2\text{O}(\text{g})$ , 然后加压成 373 K, 101.325 kPa 的  $\text{H}_2\text{O}(\text{g})$ 。

(3) 把这个  $\text{H}_2\text{O}(\text{l})$  突然放进恒温 373 K 的真空箱中, 控制容积使终态压力为 101.325 kPa 的汽。已知水的汽化热为  $2\,259\text{ kJ} \cdot \text{kg}^{-1}$ 。

解: (1) 三种不同过程图示如下。



$$(a) \Delta H = Q_p = 2\,259\text{ kJ} \cdot \text{kg}^{-1} \times 1 \times 10^{-3}\text{ kg} = 2.259\text{ kJ}$$

$$W = -p(V_g - V_l) \approx -pV_g = -nRT$$

$$= -\frac{1 \times 10^{-3}\text{ kg}}{18.0 \times 10^{-3}\text{ kg} \cdot \text{mol}^{-1}} \times 8.314\text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 373\text{ K}$$

$$= -172.3\text{ J}$$

$$\Delta U = Q + W = 2\,087\text{ J}$$

$$(b) W_I = -p(V_g - V_l) \approx -pV_g$$

$$= -nRT = -172.3\text{ J}$$

$$W_{II} = -nRT \ln \frac{p_1}{p_2}$$

$$= -\frac{1 \times 10^{-3}\text{ kg}}{18.0 \times 10^{-3}\text{ kg} \cdot \text{mol}^{-1}} \times 8.314\text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\times 373\text{ K} \times \ln \frac{50.66\text{ kPa}}{101.325\text{ kPa}}$$

$$= 119.4\text{ J}$$

$$W = W_I + W_{II} = -52.9\text{ J}$$

~~$\Delta U, \Delta H$~~  是状态函数, 其值同(a)中的  $\Delta U, \Delta H$ 。

$$Q = \Delta U - W = (2\,087 + 52.9)\text{ J} = 2\,140\text{ J}$$

$$(c) W = -p\Delta V = 0$$

$\Delta U, \Delta H$  值同(a)中的  $\Delta U, \Delta H$ 。

$$Q = \Delta U = 2\,087\text{ J}$$

比较上述计算结果可见  $|W_a| > |W_b| > |W_c|$ ,  $Q_a > Q_b > Q_c$ 。说明不可逆程度愈大时, 过程中的  $Q$  和  $|W|$  的值愈小。

14. 1 mol 单原子理想气体, 始态为  $2 \times 101.325 \text{ kPa}$ ,  $11.2 \text{ dm}^3$ , 经  $pT = \text{常数}$  的可逆过程 (即过程中  $pT = \text{常数}$ ), 压缩到终态为  $4 \times 101.325 \text{ kPa}$ , 已知气体的  $C_{V,m} = \frac{3}{2}R$ 。试求:

(1) 终态的体积和温度;

(2)  $\Delta U$  和  $\Delta H$ ;

(3) 所做的功。

解: (1)  $T_1 = \frac{p_1 V_1}{nR}$

$$= \frac{2 \times 101.325 \text{ Pa} \times 0.0112 \text{ m}^3}{1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}$$
$$= 273 \text{ K}$$

$pT = \text{常数}$ ,  $p_1 T_1 = p_2 T_2$

$$T_2 = \frac{p_1 T_1}{p_2} = \frac{2 \times 101.325 \text{ Pa} \times 273 \text{ K}}{4 \times 101.325 \text{ Pa}}$$
$$= 136.5 \text{ K}$$

$$V_2 = \frac{nRT_2}{p_2} = \frac{1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 136.5 \text{ K}}{4 \times 101.325 \text{ Pa}}$$
$$= 2.8 \times 10^{-3} \text{ m}^3$$

(2) 理想气体任何过程:

$$\Delta U = \int_{T_1}^{T_2} C_V dT, \quad \Delta H = \int_{T_1}^{T_2} C_p dT$$



$$\Delta U = C_V(T_2 - T_1)$$

$$= 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (136.5 \text{ K} - 273 \text{ K})$$

$$= -1702 \text{ J}$$

$$\Delta H = C_p(T_2 - T_1)$$

$$= 1 \text{ mol} \times \frac{5}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (136.5 \text{ K} - 273 \text{ K})$$

$$= -2837 \text{ J}$$

$$(3) W = - \int p dV$$

$$pT = C, \quad V = \frac{nRT}{p} = \frac{nRT^2}{C}$$

$$dV = \frac{2nRT}{C} dT$$

$$W = - \int_{V_1}^{V_2} p dV = - \int_{T_1}^{T_2} \frac{C}{T} \frac{2nRT}{C} dT$$

$$= - \int_{T_1}^{T_2} 2nR dT = -2nR(T_2 - T_1)$$

$$= -2 \times 1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (136.5 \text{ K} - 273 \text{ K})$$

$$= 2270 \text{ J}$$

另解

$$pT = C, \quad pV = nRT \Rightarrow pV^{0.5} = \text{常数}$$

$$W = - \frac{nR}{\delta - 1} (T_1 - T_2)$$

$$= - \frac{1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}{0.5 - 1} (273 \text{ K} - 136.5 \text{ K})$$

$$= 2270 \text{ J}$$

15. 设有压力为 101.325 kPa, 温度为 293 K 的理想气体 3.0 dm<sup>3</sup>, 在等压下加热, 直到最后的温度为 353 K 为止。计算过程中的  $W, \Delta U, \Delta H$  和  $Q$ 。已知该气体的等压摩尔热容为  $C_{p,m} = (27.28 + 3.26 \times 10^{-3} T/\text{K}) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ 。

$$\text{解: } n = \frac{p_1 V_1}{RT_1} = \frac{101.325 \text{ Pa} \times 0.003 \text{ m}^3}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 293 \text{ K}}$$

$$= 0.125 \text{ mol}$$

$$V_2 = \frac{nRT_2}{p_2}$$

$$= \frac{0.125 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 353 \text{ K}}{101.325 \text{ Pa}}$$

$$= 3.62 \times 10^{-3} \text{ m}^3$$

$$W = -p(V_2 - V_1)$$

$$= -101\,325 \text{ Pa} \times (3.62 \times 10^{-3} \text{ m}^3 - 0.003 \text{ m}^3)$$

$$= -61.8 \text{ J}$$

$$\Delta H = Q_p = \int_{T_1}^{T_2} C_p dT = n \int_{T_1}^{T_2} C_{p,m} dT$$

$$= n \int_{293 \text{ K}}^{353 \text{ K}} [(27.28 + 3.26 \times 10^{-3} T/\text{K}) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}] dT$$

$$= 0.125 \text{ mol} \times [27.28 \times (353 - 293) + \frac{1}{2} \times 3.26 \times$$

$$10^{-3} \times (353^2 - 293^2)] \text{ J} \cdot \text{mol}^{-1}$$

$$= 212.5 \text{ J}$$

$$\Delta U = Q + W = 212.5 \text{ J} - 61.8 \text{ J} = 150.7 \text{ J}$$

16. 在 1 200 K, 100 kPa 压力下, 有 1 mol  $\text{CaCO}_3(\text{s})$  完全分解为  $\text{CaO}(\text{s})$  和  $\text{CO}_2(\text{g})$ , 吸热 180 kJ。计算过程的  $W$ ,  $\Delta U$ ,  $\Delta H$  和  $Q$ 。设气体为理想气体。

解:  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

$$W = -p(V_2 - V_1) = -pV_2 = -n_{\text{CO}_2}RT$$

$$= -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 1\,200 \text{ K}$$

$$= -9\,976.8 \text{ J}$$

$$Q = Q_p = \Delta_r H_m^\ominus = 180 \text{ kJ}$$

$$\Delta U = Q + W = 180 \text{ kJ} - 9.9768 \text{ kJ}$$

$$= 170.023 \text{ kJ}$$

17. 证明:  $\left(\frac{\partial U}{\partial T}\right)_p = C_p - p\left(\frac{\partial V}{\partial T}\right)_p$ , 并证明对于理想气体有  $\left(\frac{\partial H}{\partial V}\right)_T = 0$ ,  $\left(\frac{\partial C_p}{\partial V}\right)_T = 0$ 。

解: (1)  $U = H - pV$

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial T}\right)_p = C_p - p\left(\frac{\partial V}{\partial T}\right)_p$$

(2) 理想气体的热力学能和焓只是温度的函数, 若温度不变焓也不变。令

$$H = f(T, V)$$

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

若  $dT = 0$ , 则

$$dH = \left(\frac{\partial H}{\partial V}\right)_T dV = 0$$

因为  $dV \neq 0$ , 所以  $\left(\frac{\partial H}{\partial V}\right)_T = 0$ 。

$$(3) \left( \frac{\partial C_v}{\partial V} \right)_T = \left[ \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial T} \right)_v \right]_T = \left[ \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right)_T \right]_v$$

对理想气体  $\left( \frac{\partial U}{\partial V} \right)_T = 0$ , 所以  $\left( \frac{\partial C_v}{\partial V} \right)_T = 0$ 。

18. 证明:

$$\begin{aligned} \left( \frac{\partial U}{\partial V} \right)_p &= C_p \left( \frac{\partial T}{\partial V} \right)_p - p \\ C_p - C_v &= - \left( \frac{\partial p}{\partial T} \right)_v \left[ \left( \frac{\partial H}{\partial p} \right)_T - V \right] \end{aligned}$$

解: (1)  $U = H - pV$

$$\begin{aligned} \left( \frac{\partial U}{\partial V} \right)_p &= \left( \frac{\partial H}{\partial V} \right)_p - p \\ &= \left( \frac{\partial H}{\partial T} \right)_p \left( \frac{\partial T}{\partial V} \right)_p - p \\ &= C_p \left( \frac{\partial T}{\partial V} \right)_p - p \end{aligned}$$

$$\begin{aligned} (2) \quad C_p - C_v &= \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_v \\ &= \left( \frac{\partial H}{\partial T} \right)_p - \left[ \frac{\partial (H - pV)}{\partial T} \right]_v \\ &= \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial H}{\partial T} \right)_v + V \left( \frac{\partial p}{\partial T} \right)_v \end{aligned} \quad (1)$$

令

$$H = f(T, p)$$

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

$$\left( \frac{\partial H}{\partial T} \right)_v = \left( \frac{\partial H}{\partial T} \right)_p + \left( \frac{\partial H}{\partial p} \right)_T \left( \frac{\partial p}{\partial T} \right)_v \quad (2)$$

将(2)式代入(1)式得

$$\begin{aligned} C_p - C_v &= \left( \frac{\partial H}{\partial T} \right)_p - \left[ \left( \frac{\partial H}{\partial T} \right)_p + \left( \frac{\partial H}{\partial p} \right)_T \left( \frac{\partial p}{\partial T} \right)_v \right] + V \left( \frac{\partial p}{\partial T} \right)_v \\ &= - \left( \frac{\partial p}{\partial T} \right)_v \left[ \left( \frac{\partial H}{\partial p} \right)_T - V \right] \end{aligned}$$

19. 在标准大气压力下, 把一个极小的冰块投入 0.1 kg, 268 K 的水中, 结果使系统的温度变为 273 K, 并有一定数量的水凝结成冰。由于过程进行得很快, 可以看作是绝热的。已知冰的溶解热为  $333.5 \text{ kJ} \cdot \text{kg}^{-1}$ , 在 268 ~ 273 K 水的比热容为  $4.21 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$ 。

(1) 写出系统物态的变化, 并求出  $\Delta H$ ;

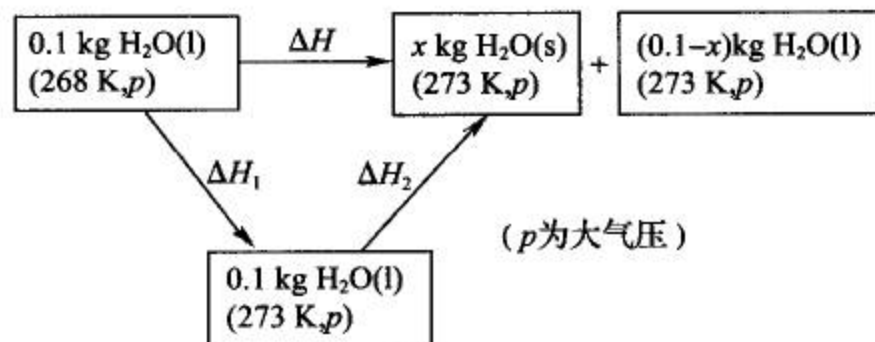


(2) 求析出冰的质量。

解: (1) 这是绝热等压过程:

$$\Delta H = Q_p = 0$$

(2) 极微小冰块作为晶体, 不计质量不计热效应。



$$\Delta H = \Delta H_1 + \Delta H_2 = 0$$

$$0.1 \text{ kg} \times 4.21 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{kg}^{-1} \times (273 \text{ K} - 268 \text{ K}) + (-333.5 \text{ kJ} \cdot \text{kg}^{-1})x = 0$$

$$x = 6.31 \times 10^{-3} \text{ kg}$$

20. 1 mol  $\text{N}_2(\text{g})$ , 在 298.2 K 和 101.325 kPa 压力下, 经可逆绝热过程压缩到 5 dm<sup>3</sup>。试计算(设气体为理想气体):

(1)  $\text{N}_2(\text{g})$  的最后温度;

(2)  $\text{N}_2(\text{g})$  的最后压力;

(3) 需做多少功。

解: (1) 设  $\text{N}_2(\text{g})$  为理想气体, 则有

$$V_1 = \frac{nRT_1}{p} = \frac{1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298.2 \text{ K}}{101325 \text{ Pa}} = 0.02447 \text{ m}^3$$

$$\gamma = \frac{C_{p,m}}{C_{v,m}} = \frac{\frac{5}{2}R + R}{\frac{5}{2}R} = \frac{7}{5} = 1.4$$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1} = 298.2 \text{ K} \times \left( \frac{0.02447 \text{ m}^3}{0.005 \text{ m}^3} \right)^{1.4-1} = 562.8 \text{ K}$$

$$(2) p_2 = \frac{nRT_2}{V_2} = \frac{1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 562.8 \text{ K}}{0.005 \text{ m}^3} = 935.8 \text{ kPa}$$

$$(3) W = -C_v(T_1 - T_2) = -\frac{5}{2}nR(T_1 - T_2)$$

$$= -\frac{5}{2} \times 1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (298.2 \text{ K} - 562.8 \text{ K})$$

$$= 5500 \text{ J}$$

21. 理想气体经可逆多方过程膨胀, 过程方程为  $pV^n = C$ , 式中  $C, n$  均为常数,  $n > 1$ 。

(1) 若  $n = 2$ , 1 mol 气体从  $V_1$  膨胀到  $V_2$ , 温度由  $T_1 = 573 \text{ K}$  到  $T_2 = 473 \text{ K}$ , 求过程的功  $W$ ;

(2) 如果气体的  $C_{V,m} = 20.9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , 求过程的  $Q, \Delta U$  和  $\Delta H$ 。

解: (1)  $pV^n = C, n = 2, p = \frac{C}{V^2}$ , 则

$$W = - \int_{V_1}^{V_2} p dV = - \int_{V_1}^{V_2} \frac{C}{V^2} dV = -C \left( \frac{1}{V_1} - \frac{1}{V_2} \right)$$

$$= -(p_1 V_1 - p_2 V_2) = -nR(T_1 - T_2)$$

$$= -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (573 \text{ K} - 473 \text{ K})$$

$$= -831.4 \text{ J}$$

(2) 对于理想气体:

$$\Delta U = \int_{T_1}^{T_2} C_V dT = nC_{V,m}(T_2 - T_1)$$

$$= 1 \text{ mol} \times 20.9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (473 \text{ K} - 573 \text{ K})$$

$$= -2090 \text{ J}$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT = nC_{p,m}(T_2 - T_1)$$

$$= 1 \text{ mol} \times (20.9 + 8.314) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (473 \text{ K} - 573 \text{ K})$$

$$= -2921.4 \text{ J}$$

$$Q = \Delta U - W = -2090 \text{ J} + 831.4 \text{ J} = -1258.6 \text{ J}$$

22. 在 298 K 时, 有一定量的单原子理想气体 ( $C_{V,m} = 1.5R$ ), 从始态  $20 \times 101.325 \text{ kPa}$  及  $20 \text{ dm}^3$  经下列不同过程, 膨胀到终态压力为  $101.325 \text{ kPa}$ , 求各过程的  $\Delta U, \Delta H, Q$  及  $W$ 。

(1) 等温可逆膨胀;

(2) 绝热可逆膨胀;

(3) 以  $\delta = 1.3$  的多方过程可逆膨胀。

试在  $p-V$  图上画出三种膨胀功的示意图, 并比较三种功的大小。

解: (1) 等温可逆过程, 则

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

$$n = \frac{p_1 V_1}{RT_1} = \frac{20 \times 101.325 \text{ Pa} \times 0.020 \text{ m}^3}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K}}$$

$$= 16.36 \text{ mol}$$

$$Q = -W = nRT \ln \frac{p_1}{p_2}$$

$$= 16.36 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K} \times \ln \frac{20p}{p}$$

$$= 1.214 \times 10^5 \text{ J} = 121.4 \text{ kJ}$$

(2) 绝热可逆过程:

$$Q = 0$$

$$\gamma = \frac{C_{p,m}}{C_{v,m}} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.667$$

$$p_1^{\gamma-1} T_1^{\gamma} = p_2^{\gamma-1} T_2^{\gamma}$$

$$T_2 = \left( \frac{p_1}{p_2} \right)^{\frac{1-\gamma}{\gamma}} T_1 = \left( \frac{20p}{p} \right)^{\frac{1-1.667}{1.667}} \times 298 \text{ K} = \underline{89.9 \text{ K}}$$

$$\Delta U = nC_{v,m}(T_2 - T_1) = n \frac{3}{2} R(T_2 - T_1)$$

$$= 16.36 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (89.9 \text{ K} - 298 \text{ K})$$

$$= -4.246 \times 10^4 \text{ J}$$

$$= -42.46 \text{ kJ}$$

$$W = \Delta U = -42.46 \text{ kJ}$$

$$\Delta H = nC_{p,m}(T_2 - T_1) = n \frac{5}{2} R(T_2 - T_1)$$

$$= 16.36 \text{ mol} \times \frac{5}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (89.9 \text{ K} - 298 \text{ K})$$

$$= -70.76 \text{ kJ}$$

(3) 多方可逆过程:

$$pV^{\delta} = C, \quad pV = nRT$$

联立上两式得

$$p^{1-\delta} T^{\delta} = C'$$

$$T_2 = \left( \frac{p_1}{p_2} \right)^{\frac{1-\delta}{\delta}} T_1 = \left( \frac{20p}{p} \right)^{\frac{1-1.3}{1.3}} \times 298 \text{ K}$$

$$= \underline{149.3 \text{ K}}$$

$$\Delta U = nC_{v,m}(T_2 - T_1) = n \frac{3}{2} R(T_2 - T_1)$$



$$= 16.36 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (149.3 \text{ K} - 298 \text{ K})$$

$$= -3.034 \times 10^4 \text{ J}$$

$$= -30.34 \text{ kJ}$$

$$\Delta H = nC_{p,m}(T_2 - T_1) = n \frac{5}{2} R(T_2 - T_1)$$

$$= 16.36 \text{ mol} \times \frac{5}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (149.3 \text{ K} - 298 \text{ K})$$

$$= -5.056 \times 10^4 \text{ J}$$

$$= -50.56 \text{ kJ}$$

$$W = -\frac{nR}{1-\delta}(T_2 - T_1)$$

$$= -\frac{16.36 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}{1-1.3} \times (149.3 \text{ K} - 298 \text{ K})$$

$$= -6.742 \times 10^4 \text{ J}$$

$$= -67.42 \text{ kJ}$$

$$Q = \Delta U - W = -30.34 \text{ kJ} + 67.42 \text{ kJ} = 37.08 \text{ kJ}$$

上述三种不同过程的膨胀功示于图

2-13。

始态  $p_1 = 20 \times p$  ( $p = 101325 \text{ Pa}$ ),

$$V_1 = 0.02 \text{ m}^3$$

终态  $p_2 = p$

(1) 等温可逆过程:

$$pV = C$$

$$V_2 = \frac{p_1 V_1}{p_2} = 0.4 \text{ m}^3$$

(2) 绝热可逆过程:

$$pV^{1.67} = C$$

$$V_2 = \left( \frac{p_1}{p_2} \right)^{\frac{1}{1.67}} V_1 = 0.12 \text{ m}^3$$

(3) 多方可逆过程:

$$pV^{1.3} = C$$

$$V_2 = \left( \frac{p_1}{p_2} \right)^{\frac{1}{1.3}} V_1 = 0.2 \text{ m}^3$$

曲线下的面积就是功值,由此可见功的大小次序与计算值相同:

$$|W_{(1)}| > |W_{(3)}| > |W_{(2)}|$$

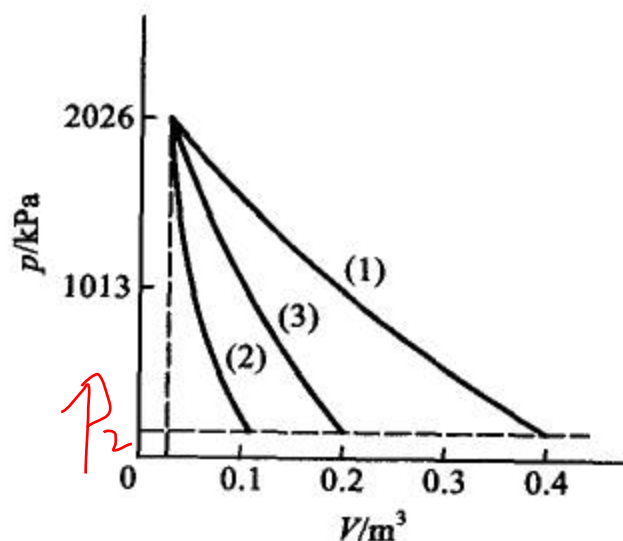


图 2-13

23. 1 mol 单原子理想气体从始态 298 K, 202.65 kPa, 经下列途径使体积加倍, 试计算每种途径的终态压力及各过程的  $Q$ ,  $W$  及  $\Delta U$  的值, 画出  $p-V$  示意图, 并把  $\Delta U$  和  $W$  的值按大小次序排列。

- (1) 等温可逆膨胀;
- (2) 绝热可逆膨胀;
- (3) 沿着  $p/\text{Pa} = 10\ 132.5\ V_{\text{m}}/(\text{dm}^3 \cdot \text{mol}^{-1}) + b$  的途径可逆变化。

解: 始态

$$p_1 = 202.65\ \text{kPa}, \quad T_1 = 298\ \text{K}, \quad n = 1\ \text{mol}$$

$$V_{\text{m},1} = \frac{RT_1}{p_1} = 12.23\ \text{dm}^3 \cdot \text{mol}^{-1}$$

$$V_{\text{m},2} = 2V_{\text{m},1} = 24.46\ \text{dm}^3 \cdot \text{mol}^{-1}$$

- (1) 等温可逆膨胀:

$$p_2 = \frac{p_1 V_1}{V_2} = \frac{p_1}{2} = 101.325\ \text{kPa}$$

$$\Delta U = 0$$

$$\begin{aligned} Q &= -W = nRT \ln \frac{V_2}{V_1} \\ &= 1\ \text{mol} \times 8.314\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298\ \text{K} \times \ln 2 \\ &= 1\ 717\ \text{J} \end{aligned}$$

- (2) 绝热可逆过程:

$$Q = 0$$

单原子理想气体:

$$C_{V,\text{m}} = \frac{3}{2}R, \quad C_{p,\text{m}} = \frac{5}{2}R, \quad \gamma = \frac{C_p}{C_v} = \frac{5}{3}$$

$$p_1 V_1^\gamma = p_2 V_2^\gamma, \quad p_2 = 63.83\ \text{kPa}$$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}, \quad T_2 = 187.7\ \text{K}$$

$$\Delta U = C_V(T_1 - T_2)$$

$$= 1\ \text{mol} \times \frac{3}{2} \times 8.314\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (187.7 - 298)\ \text{K}$$

$$= -1\ 376\ \text{J}$$

$$W = \Delta U - Q = -1\ 376\ \text{J}$$

- (3) 沿着  $p/\text{Pa} = 10\ 132.5\ V_{\text{m}}/(\text{dm}^3 \cdot \text{mol}^{-1}) + b$  的途径:

$$202\ 650 = 10\ 132.5 \times 12.23 + b$$

$$b = 78\ 730$$

$$p_2/\text{Pa} = 10\ 132.5 \times 24.46 + 78\ 730 = 326\ 571$$

$$T_2 = \frac{p_2 V_2}{nR} = 961.8 \text{ K}$$

$$\Delta U = nC_{V,m}(T_2 - T_1)$$

$$= 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (961.8 \text{ K} - 298 \text{ K})$$

$$= 8278 \text{ J}$$

$$W = - \int_{V_1}^{V_2} p dV$$

$$= - \int_{V_1}^{V_2} \{ [10132.5 V_m / (\text{dm}^3 \cdot \text{mol}^{-1}) + b] \text{ Pa} \} dV$$

$$= - \left[ \frac{1}{2} \times 10132.5 \text{ Pa} \cdot \text{mol} \cdot \text{dm}^{-3} (V_2^2 - V_1^2) + b(V_2 - V_1) \text{ Pa} \right]$$

$$= - \frac{1}{2} \{ 10132.5 \text{ Pa} \cdot \text{mol} \cdot \text{dm}^{-3} [ (24.46 \text{ dm}^3)^2 - (12.23 \text{ dm}^3)^2 ]$$

$$\times 10^{-3} + 78730 \text{ Pa} \times (24.46 \text{ dm}^3 - 12.23 \text{ dm}^3) \times 10^{-3} \}$$

$$= -3239 \text{ J}$$

$$Q = \Delta U - W = (8278 + 3239) \times 10^{-3} \text{ kJ}$$

$$= 11.52 \text{ kJ}$$

上述三条不同途径的  $p-V$  图如图 2-14 所示。

在  $p-V$  图中, 由  $a, b, c$  三条线下的面积大小次序可得功的大小为

$$|W_b| < |W_a| < |W_c|$$

由于终态体积相同,  $p$  大  $T$  也大, 从图中得

$$p_b < p_a < p_c$$

则  $T_b < T_a < T_c$ , 理想气体的热力学能是温度的函数, 则

$$\Delta U_b < \Delta U_a < \Delta U_c$$

24. 某一热机的低温热源为 313 K, 若高温热源分别为

(1) 373 K (在大气压力下水的沸点);

(2) 538 K (是压力为 50 大气压力下的沸点)。

试分别计算热机的理论转换系数。

$$\text{解: (1) } \eta = \frac{T_2 - T_1}{T_2} = \frac{373 \text{ K} - 313 \text{ K}}{373 \text{ K}} \times 100\% = 16.1\%$$

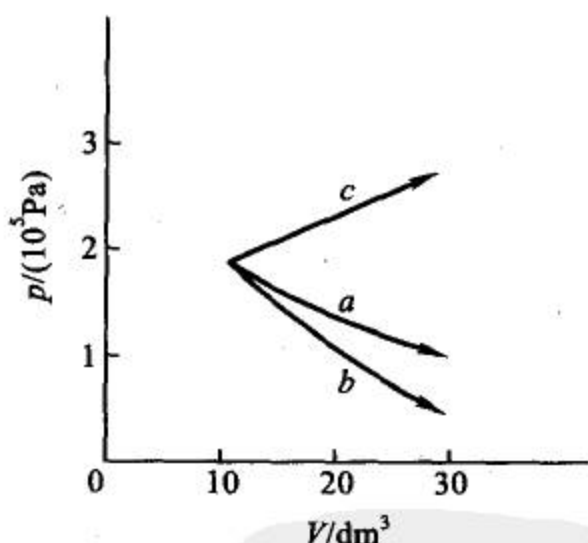


图 2-14



$$(2) \eta = \frac{T_2 - T_1}{T_2} = \frac{538 \text{ K} - 313 \text{ K}}{538 \text{ K}} \times 100\% = 41.8\%$$

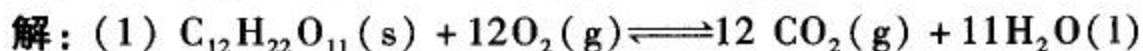
25. 某电冰箱内的温度为 273 K, 室温为 298 K, 今欲使 1 kg 273 K 的水变成冰, 问最少需做多少功? 已知 273 K 时的冰的融化热为  $335 \text{ kJ} \cdot \text{kg}^{-1}$ 。

$$\text{解: } \beta = \frac{Q_1}{W} = \frac{T_1}{T_2 - T_1}$$

$$\begin{aligned} W &= Q_1 \frac{T_2 - T_1}{T_1} \\ &= 335 \text{ kJ} \cdot \text{kg}^{-1} \times 1 \text{ kg} \times \frac{298 \text{ K} - 273 \text{ K}}{273 \text{ K}} \\ &= 30.68 \text{ kJ} \end{aligned}$$

26. 有如下反应, 设都在 298 K 和标准大气压力下进行, 请比较各个反应的  $\Delta U$  与  $\Delta H$  的大小, 并说明这差别主要是由什么因素造成的。

- (1)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  (蔗糖) 完全燃烧;
- (2)  $\text{C}_{10}\text{H}_8$  (萘, s) 完全氧化为苯二甲酸  $\text{C}_6\text{H}_4(\text{COOH})_2$  (s);
- (3) 乙醇的完全燃烧;
- (4)  $\text{PbS}$  (s) 完全氧化为  $\text{PbO}$  (s) 和  $\text{SO}_2$  (g)。



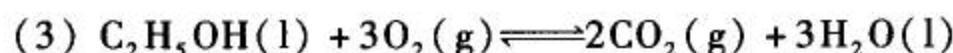
$$\Delta_r H_m = \Delta_r U_m + \sum \nu_B RT, \quad \sum \nu_B = 12 - 12 = 0$$

$$\Delta_r H_m = \Delta_r U_m$$



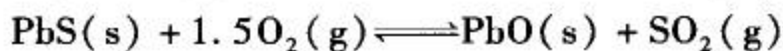
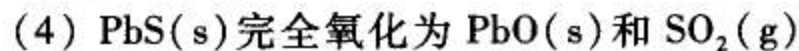
$$\sum \nu_B = -21 < 0$$

$$\Delta_r H_m < \Delta_r U_m$$



$$\sum \nu_B = 2 - 3 = -1 < 0$$

$$\Delta_r H_m < \Delta_r U_m$$



$$\sum \nu_B = 1 - 1.5 = -0.5 < 0$$

$$\Delta_r H_m < \Delta_r U_m$$

差别的原因是由反应式中气体的化学计量数之和  $\sum \nu_B$  的符号不同而造成的, 当  $\sum \nu_B = 0$  时,  $\Delta_r H_m = \Delta_r U_m$ ; 当  $\sum \nu_B > 0$  时,  $\Delta_r H_m > \Delta_r U_m$ ; 当  $\sum \nu_B < 0$  时,  $\Delta_r H_m < \Delta_r U_m$ 。

27. 0.500 g 正庚烷放在弹式热量计中, 燃烧后温度升高 2.94 K。若热量计本身及其附件的热容为  $8.177 \text{ kJ} \cdot \text{K}^{-1}$ , 计算 298 K 时正庚烷的摩尔燃烧焓(热

量计的平均温度为 298 K)。

解: 0.500 g 正庚烷燃烧后放出的恒容热效应为

$$Q_v = 8.177 \text{ kJ} \cdot \text{K}^{-1} \times (-2.94 \text{ K}) = -24.04 \text{ kJ}$$

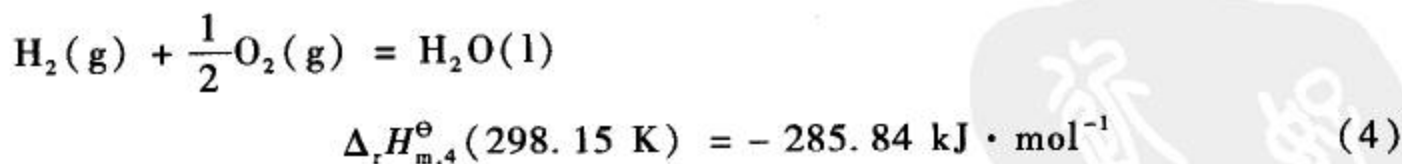
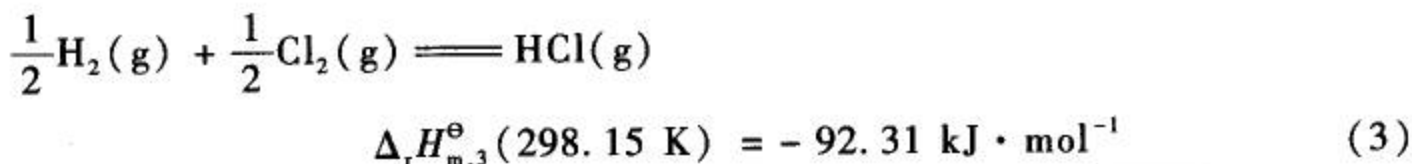
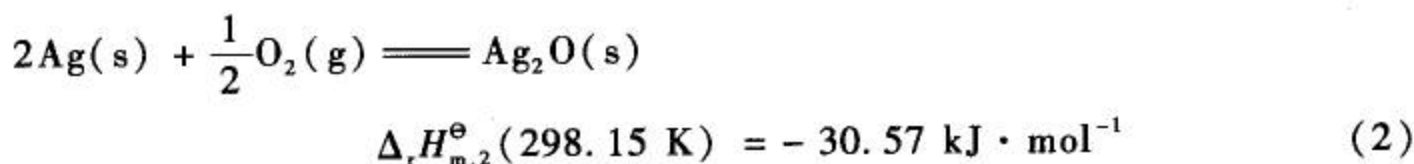
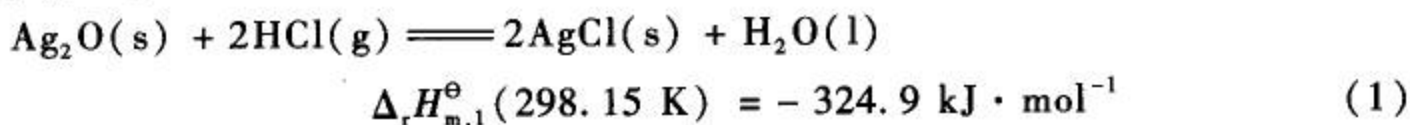
1 mol 正庚烷燃烧后放出的等容热效应为

$$\begin{aligned}\Delta_c U_m &= \frac{Q_v}{m/M} \\ &= -\frac{24.04 \text{ kJ}}{0.500 \text{ g} / (100.2 \text{ g} \cdot \text{mol}^{-1})} \\ &= -4818 \text{ kJ} \cdot \text{mol}^{-1} \\ \text{C}_7\text{H}_{16}(\text{l}) + 11\text{O}_2(\text{g}) &= 7\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\text{l})\end{aligned}$$

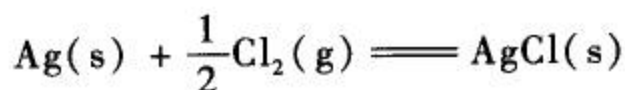
正庚烷的燃烧焓为

$$\begin{aligned}\Delta_c H_m^\ominus(\text{C}_7\text{H}_{16}, 298 \text{ K}) &= \Delta_c U_m + \sum \nu_B RT \\ &= -4818 \text{ kJ} \cdot \text{mol}^{-1} + (7 - 11) \times 8.314 \\ &\quad \times 10^{-3} \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 298 \text{ K} \\ &= -4828 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

28. 根据下列反应在 298.15 K 时的焓变值, 计算  $\text{AgCl}(\text{s})$  的标准摩尔生成焓  $\Delta_f H_m^\ominus(\text{AgCl}, \text{s}, 298.15 \text{ K})$ 。



解:  $(1) \times \frac{1}{2} + (2) \times \frac{1}{2} + (3) - (4) \times \frac{1}{2}$  得



$$\begin{aligned}\Delta_f H_m^\ominus(\text{AgCl}, T) &= \frac{1}{2}\Delta_r H_m^\ominus(1) + \frac{1}{2}\Delta_r H_m^\ominus(2) + \Delta_r H_m^\ominus(3) - \frac{1}{2}\Delta_r H_m^\ominus(4) \\ &= \frac{1}{2} \times (-324.9 \text{ kJ} \cdot \text{mol}^{-1}) + \frac{1}{2} \times (-30.57 \text{ kJ} \cdot \text{mol}^{-1})\end{aligned}$$

$$+ (-92.31 \text{ kJ} \cdot \text{mol}^{-1}) - \frac{1}{2} \times (-285.84 \text{ kJ} \cdot \text{mol}^{-1})$$

$$= -127.13 \text{ kJ} \cdot \text{mol}^{-1}$$

29. 在 298.15 K 及 100 kPa 压力时, 设环丙烷、石墨及氢气的燃烧焓  $\Delta_c H_m^\ominus$  (298.15 K) 分别为  $-2092 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $-393.8 \text{ kJ} \cdot \text{mol}^{-1}$  及  $-285.84 \text{ kJ} \cdot \text{mol}^{-1}$ 。若已知环丙烷  $\text{C}_3\text{H}_6(\text{g})$  的标准摩尔生成焓  $\Delta_f H_m^\ominus$  (298.15 K)  $= 20.50 \text{ kJ} \cdot \text{mol}^{-1}$ 。试求:

(1) 环丙烷的标准摩尔生成焓  $\Delta_f H_m^\ominus$  (298.15 K);

(2) 环丙烷异构化变为丙烯的摩尔反应焓变值  $\Delta_r H_m^\ominus$  (298.15 K)。

解: (1)  $3\text{C}(\text{s}) + 3\text{H}_2(\text{g}) \longrightarrow \text{C}_3\text{H}_6(\text{环丙烷})$

该反应的反应热就是环丙烷的生成焓, 即

$$\begin{aligned}\Delta_f H_m^\ominus(\text{C}_3\text{H}_6) &= \Delta_r H_m^\ominus(T) = -\sum \nu_B \Delta_c H_m^\ominus(B) \\ &= 3\Delta_c H_m^\ominus\{\text{C}(\text{s})\} + 3\Delta_c H_m^\ominus\{\text{H}_2(\text{g})\} - \Delta_c H_m^\ominus\{\text{C}_3\text{H}_6(\text{g})\} \\ &= 3 \times (-393.8 \text{ kJ} \cdot \text{mol}^{-1}) + 3 \times (-285.84 \text{ kJ} \cdot \text{mol}^{-1}) \\ &\quad - (-2092 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= 53.08 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

(2)  $\text{C}_3\text{H}_6(\text{环丙烷}) \longrightarrow \text{CH}_3\text{CH}=\text{CH}_2$

$$\begin{aligned}\Delta_r H_m^\ominus(T) &= \Delta_f H_m^\ominus(\text{丙烯}, T) - \Delta_f H_m^\ominus(\text{环丙烷}, T) \\ &= 20.50 \text{ kJ} \cdot \text{mol}^{-1} - 53.08 \text{ kJ} \cdot \text{mol}^{-1} \\ &= -32.58 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

30. 根据以下数据, 计算乙酸乙酯的标准摩尔生成焓  $\Delta_f H_m^\ominus$  ( $\text{CH}_3\text{COOC}_2\text{H}_5$ , 1, 298.15 K)



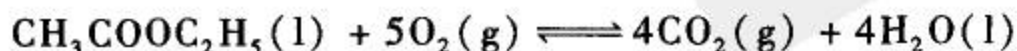
$$\Delta_r H_m^\ominus(298.15 \text{ K}) = -9.20 \text{ kJ} \cdot \text{mol}^{-1}$$

乙酸和乙醇的标准摩尔燃烧焓  $\Delta_c H_m^\ominus$  (298.15 K) 分别为  $-874.54 \text{ kJ} \cdot \text{mol}^{-1}$  和  $-1366 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$  的标准摩尔生成焓分别为  $-393.51 \text{ kJ} \cdot \text{mol}^{-1}$  和  $-285.83 \text{ kJ} \cdot \text{mol}^{-1}$ 。

解:  $\text{CH}_3\text{COOH}(\text{l}) + \text{C}_2\text{H}_5\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l})$

$$\begin{aligned}\Delta_r H_m^\ominus &= \Delta_c H_m^\ominus(\text{CH}_3\text{COOH}, \text{l}) + \Delta_c H_m^\ominus(\text{C}_2\text{H}_5\text{OH}, \text{l}) - \Delta_c H_m^\ominus(\text{CH}_3\text{COOC}_2\text{H}_5, \text{l}) \\ &\quad - \Delta_c H_m^\ominus(\text{H}_2\text{O}, \text{l}) \\ -9.20 \text{ kJ} \cdot \text{mol}^{-1} &= -874.54 \text{ kJ} \cdot \text{mol}^{-1} - 1366 \text{ kJ} \cdot \text{mol}^{-1} - \Delta_c H_m^\ominus(\text{CH}_3\text{COOC}_2\text{H}_5, \text{l}) - 0 \\ \Delta_c H_m^\ominus(\text{CH}_3\text{COOC}_2\text{H}_5, \text{l}) &= -2231.3 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

乙酸乙酯的燃烧反应如下:

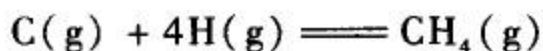




该反应的反应焓变就是乙酸乙酯的燃烧焓,即

$$\begin{aligned}\Delta_c H_m^\ominus(\text{CH}_3\text{COOC}_2\text{H}_5, \text{l}) &= \Delta_r H_m^\ominus = 4\Delta_f H_m^\ominus(\text{CO}_2) + 4\Delta_f H_m^\ominus(\text{H}_2\text{O}, \text{l}) \\ &- \Delta_f H_m^\ominus(\text{CH}_3\text{COOC}_2\text{H}_5, \text{l}) - 5\Delta_f H_m^\ominus(\text{O}_2) \\ &- 2231.3 \text{ kJ} \cdot \text{mol}^{-1} = 4 \times (-393.51 \text{ kJ} \cdot \text{mol}^{-1}) + 4 \times (-285.83 \text{ kJ} \cdot \text{mol}^{-1}) \\ &- \Delta_f H_m^\ominus(\text{CH}_3\text{COOC}_2\text{H}_5, \text{l}) - 0 \\ \Delta_f H_m^\ominus(\text{CH}_3\text{COOC}_2\text{H}_5, \text{l}) &= -486.06 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

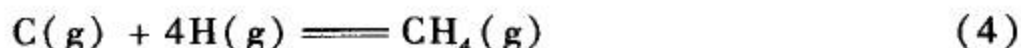
31. 请计算 298 K 和标准压力下, 如下反应的标准摩尔焓变  $\Delta_r H_m^\ominus(298.15 \text{ K})$ , 这个数值的 1/4 称为 C—H 键的“键焓”(平均值)。



已知: 石墨升华为碳原子的焓变估计为  $\Delta_{\text{sub}} H_m^\ominus = 711.1 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\text{H}_2(\text{g}) \rightleftharpoons 2\text{H}(\text{g})$  的标准解离焓为  $431.7 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\text{CH}_4(\text{g})$  的标准摩尔生成焓为  $\Delta_f H_m^\ominus(298.15 \text{ K}) = -74.78 \text{ kJ} \cdot \text{mol}^{-1}$ 。



反应(3) - 2 × (2) - (1) 得



$$\begin{aligned}\Delta_r H_m^\ominus(4) &= \Delta_r H_m^\ominus(3) - 2\Delta_r H_m^\ominus(2) - \Delta_r H_m^\ominus(1) \\ &= -74.78 \text{ kJ} \cdot \text{mol}^{-1} - 2 \times 431.7 \text{ kJ} \cdot \text{mol}^{-1} \\ &\quad - 711.1 \text{ kJ} \cdot \text{mol}^{-1} \\ &= -1649.28 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\varepsilon(\text{C—H}) &\approx -\frac{1}{4}\Delta_r H_m^\ominus(4) = -\frac{1}{4} \times (-1649.28 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= 412.32 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

32. 反应  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$ , 在 298 K 和标准压力下的摩尔反应焓变为  $\Delta_r H_m^\ominus(298.15 \text{ K}) = -285.84 \text{ kJ} \cdot \text{mol}^{-1}$ 。试计算该反应在 800 K 时进行的摩尔反应焓变。已知  $\text{H}_2\text{O}(\text{l})$  在 373 K 和标准压力下的摩尔蒸发焓为  $\Delta_{\text{vap}} H_m^\ominus(373 \text{ K}) = 40.65 \text{ kJ} \cdot \text{mol}^{-1}$ 。

$$C_{p,m}(\text{H}_2, \text{g}) = 29.07 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + (8.36 \times 10^{-4} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2})T$$

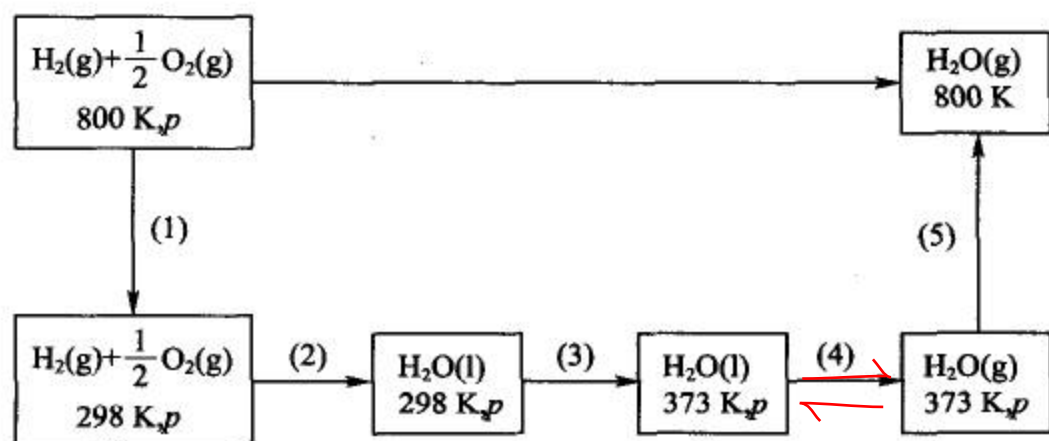
$$C_{p,m}(\text{O}_2, \text{g}) = 36.16 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + (8.45 \times 10^{-4} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2})T$$

$$C_{p,m}(\text{H}_2\text{O}, \text{g}) = 30.00 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + (10.7 \times 10^{-3} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2})T$$

$$C_{p,m}(\text{H}_2\text{O}, \text{l}) = 75.26 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

解: 设计如下过程,





$$\begin{aligned}\Delta_r H_m(1) &= \int_{800\text{ K}}^{298\text{ K}} \left[ C_{p,m}(\text{H}_2) + \frac{1}{2} C_{p,m}(\text{O}_2) \right] dT \\ &= \int_{800\text{ K}}^{298\text{ K}} [47.15 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} - (4.14 \times 10^{-4} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}) T] dT \\ &= (47.15 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \times (298 \text{ K} - 800 \text{ K}) - \left( \frac{1}{2} \times 4.14 \right. \\ &\quad \times 10^{-4} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}) \times [(298 \text{ K})^2 - (800 \text{ K})^2] \\ &= -23\,555.2 \text{ J} \cdot \text{mol}^{-1}\end{aligned}$$

$$\Delta_r H_m(2) = -285.84 \text{ kJ} \cdot \text{mol}^{-1} \text{ (题意)}$$

$$\begin{aligned}\Delta_r H_m(3) &= \int_{298\text{ K}}^{373\text{ K}} C_{p,m} \{ \text{H}_2\text{O}(\text{l}) \} dT = \int_{298\text{ K}}^{373\text{ K}} (75.26 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) dT \\ &= 5\,644.5 \text{ J} \cdot \text{mol}^{-1}\end{aligned}$$

$$\Delta_r H_m(4) = 40.65 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\begin{aligned}\Delta_r H_m(5) &= \int_{373\text{ K}}^{800\text{ K}} C_{p,m} \{ \text{H}_2\text{O}(\text{g}) \} dT \\ &= \int_{373\text{ K}}^{800\text{ K}} [30.00 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + (10.7 \times 10^{-3} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}) T] dT \\ &= 15\,531.7 \text{ J} \cdot \text{mol}^{-1}\end{aligned}$$

$$\Delta_r H_m = \Delta_r H_m(1) + \Delta_r H_m(2) + \Delta_r H_m(3) + \Delta_r H_m(4) + \Delta_r H_m(5) = -247.6 \text{ kJ} \cdot \text{mol}^{-1}$$

33. 某高压容器中含有未知气体,可能是氮气或氩气。今在 298 K 时,取出一些样品,从 5 dm<sup>3</sup> 绝热可逆膨胀到 6 dm<sup>3</sup>,温度降低了 21 K,试判断容器中是何种气体。设振动的贡献可忽略不计。

解: 忽略振动能对  $C_v$  的贡献,单原子理想气体的  $C_{v,m} = \frac{3}{2}R$ ,  $\gamma = \frac{C_{p,m}}{C_{v,m}} = \frac{\frac{5}{2}R}{\frac{3}{2}R} =$

1.67。

双原子理想气体的  $C_{v,m} = \frac{5}{2}R$ ,  $\gamma = \frac{C_{p,m}}{C_{v,m}} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.4$ 。

绝热可逆过程:

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\frac{T_1}{T_2} = \left( \frac{V_2}{V_1} \right)^{\gamma-1}$$

$$\frac{298 \text{ K}}{298 \text{ K} - 21 \text{ K}} = \left( \frac{6 \text{ dm}^3}{5 \text{ dm}^3} \right)^{\gamma-1}$$

$$\gamma = 1.4$$

故容器中的气体应该是氮气。

34. 将  $\text{H}_2\text{O}$  看作刚体非线性分子, 用经典理论来估计其气体的  $C_{p,m}(\text{H}_2\text{O}, \text{g})$  值。

(1) 在温度不太高时, 忽略振动自由度项的贡献;

(2) 在温度很高时, 将所有的振动贡献都考虑进去。

解: (1) 经典理论将分子视为刚体, 无振动能, 每个分子的平动自由度为 3, 非线性分子的转动自由度为 3。每个平动自由度和每个转动自由度对能量的贡献为  $\frac{1}{2}kT$ 。

$$\varepsilon = \varepsilon_t + \varepsilon_r = 3 \times \left( \frac{1}{2}kT \right) + 3 \times \left( \frac{1}{2}kT \right) = 3kT$$

$$E_m = L \cdot \varepsilon = L \cdot 3kT = 3RT$$

$$C_{V,m} = \left( \frac{\partial E_m}{\partial T} \right)_V = \left[ \frac{\partial(3RT)}{\partial T} \right]_V = 3R$$

$$\begin{aligned} C_{p,m} &= C_{V,m} + R = 4R = 4 \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ &= 33.26 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

(2) 如果温度升高, 振动能全部释放出来。非线性分子的振动自由度为  $(3n-6)$ , 每个振动自由度对能量的贡献为  $kT$ 。

$$\varepsilon = \varepsilon_t + \varepsilon_r + \varepsilon_v$$

$$= 3 \times \left( \frac{1}{2}kT \right) + 3 \times \left( \frac{1}{2}kT \right) + (3 \times 3 - 6)kT = 6kT$$

$$E_m = L \cdot \varepsilon = 6RT$$

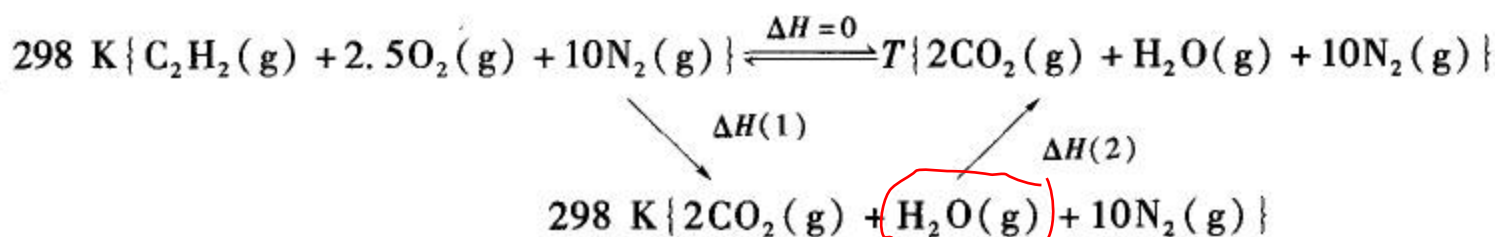
$$C_{V,m} = \left( \frac{\partial E_m}{\partial T} \right)_V = 6R$$

$$\begin{aligned} C_{p,m} &= C_{V,m} + R = 7R = 7 \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ &= 58.20 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

35. 在环境温度为 298 K、压力为 100 kPa 的条件下, 用乙炔与压缩空气混合, 燃烧后用来切割金属, 试粗略计算这种火焰可能达到的最高温度, 设空气中氧的含量为 20%。已知 298 K 时的热力学数据如下:

物质	$\Delta_f H_m^\ominus / (\text{kJ} \cdot \text{mol}^{-1})$	$\bar{C}_{p,m} / (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$
$\text{CO}_2(\text{g})$	-393.51	37.1
$\text{H}_2\text{O}(\text{g})$	-241.82	33.58
$\text{C}_2\text{H}_2(\text{g})$	226.7	43.93
$\text{N}_2(\text{g})$	0	29.12

解:



燃烧反应在瞬间进行, 视为绝热过程, 所以  $\Delta_r H_m^\ominus = 0$ 。

$$\begin{aligned}
 \Delta H(1) &= [2\Delta_f H_m^\ominus(\text{CO}_2) + \Delta_f H_m^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_f H_m^\ominus(\text{C}_2\text{H}_2) - 2.5\Delta_f H_m^\ominus(\text{O}_2)] \times 1 \text{ mol} \\
 &= 2 \text{ mol} \times (-393.51 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol} \times (-241.82 \text{ kJ} \cdot \text{mol}^{-1}) \\
 &\quad - 1 \text{ mol} \times 226.7 \text{ kJ} \cdot \text{mol}^{-1} - 0 \\
 &= -1255.54 \text{ kJ}
 \end{aligned}$$

$$\begin{aligned}
 \Delta H(2) &= \int \sum C_p(\text{生成物}) dT \\
 &= \int \{ [2C_{p,m}(\text{CO}_2) + C_{p,m}(\text{H}_2\text{O}, \text{g}) + 10C_{p,m}(\text{N}_2, \text{g})] \times 1 \text{ mol} \} dT \\
 &= \int_{T_1}^{T_2} [(2 \times 37.1 + 33.58 + 10 \times 29.12) \text{ J} \cdot \text{K}^{-1}] dT \\
 &= 398.98 \text{ J} \cdot \text{K}^{-1} \times (T_2 - T_1)
 \end{aligned}$$

$$\Delta H = \Delta H(1) + \Delta H(2)$$

$$0 = -1255.54 \times 10^3 \text{ J} + 398.98 \text{ J} \cdot \text{K}^{-1} \times (T_2 - 298 \text{ K})$$

$$T_2 = 3445 \text{ K}$$