

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 dm³;

(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) $W = -p_{\text{外}} \Delta V = -1000 \text{ kPa} \times 1 \times 10^{-3} \text{ m}^3 = -1 \text{ kJ}$

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

$$\begin{aligned}
 &= -10 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 300 \text{ K} \times \left(1 - \frac{100 \text{ kPa}}{1000 \text{ kPa}}\right) \\
 &= -24942 \text{ J} \times 0.9 \\
 &= -22447.8 \text{ J}
 \end{aligned}$$

$$\begin{aligned}
 (3) \quad W_R &= nRT \ln \frac{p_1}{p_2} \\
 &= 10 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 300 \text{ K} \times \ln \frac{1000 \text{ kPa}}{100 \text{ kPa}} \\
 &= -57431 \text{ J}
 \end{aligned}$$

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 dm³，经历如下三步，又回到始态，请计算每步过程的 Q , W 和 ΔU 。

- (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 dm³ 的状态(3)；
- (3) 经等压过程由状态(3)回到始态(1)。

解：题中三步过程如图 2-11 所示。

(1) 等容可逆升温：

$$W = - \int p dV = 0$$

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

$$= n \frac{3}{2}R(T_2 - T_1)$$

$$= 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (546 \text{ K} - 273 \text{ K})$$

$$= 3404.6 \text{ J}$$

$$Q = \Delta U - W = \Delta U = 3404.6 \text{ J}$$

$$\begin{aligned}
 (2) \quad W_R &= -nRT \ln \frac{V_2}{V_1} = -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 546 \text{ K} \\
 &\quad \times \ln \frac{44.8 \text{ dm}^3}{22.4 \text{ dm}^3} \\
 &= -3146.5 \text{ J}
 \end{aligned}$$

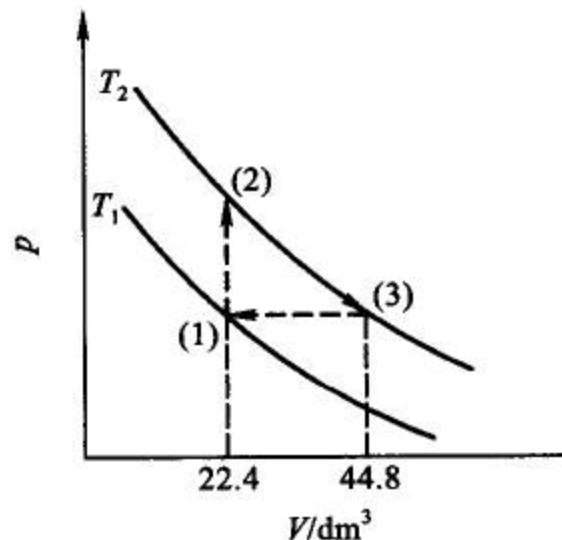


图 2-11

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

$$Q \approx -W_R = 3146.5 \text{ J}$$

$$(3) W = -p\Delta V = -\frac{nRT_1}{V_1}(V_1 - V_3)$$

$$= -\frac{1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 273 \text{ K}}{22.4 \times 10^{-3} \text{ m}^3} \times (22.4 - 44.8) \times 10^{-3} \text{ m}^3$$

$$= 2269.7 \text{ J}$$

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

$$= 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (273 \text{ K} - 546 \text{ K})$$

$$= -3404.6 \text{ J}$$

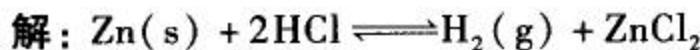
$$Q = \Delta U - W = -3404.6 \text{ J} - 2269.7 \text{ J} = -5674.3 \text{ J}$$

或 $Q = Q_p = \int_{T_1}^{T_2} C_p dT = n(C_{V,m} + R)(T_2 - T_1)$

$$= 1 \text{ mol} \times \frac{5}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (273 \text{ K} - 546 \text{ K})$$

$$= -5674.3 \text{ J}$$

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 H₂(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。



$$W = -p\Delta V = -pV_m(H_2) \doteq -nRT$$

$$= -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 291 \text{ K}$$

$$= -2419.4 \text{ J}$$

$$\Delta U = Q + W = -152000 \text{ J} - 2419.4 \text{ J} = -154419 \text{ J}$$

5. 在 298 K 时, 有 2 mol N₂(g), 始态体积为 15 dm³, 保持温度不变, 经下列三个过程膨胀到终态体积为 50 dm³, 计算各过程的 ΔU , ΔH , 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。

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

终态 $V_2 = 50 \text{ dm}^3$

(1) 自由膨胀:

$$W = -p_{\text{外}} \Delta V = 0$$

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

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

(2) 反抗恒定外压 100 kPa 膨胀:

$$W = -p_{\text{外}} \Delta V = -100 \times 10^3 \text{ Pa} \times (50 - 15) \times 10^{-3} \text{ m}^3 = -3500 \text{ J}$$
~~$$\Delta U = \Delta H = f(T) = 0$$~~

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

(3) 可逆膨胀:

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

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

$$= -5965.9 \text{ J}$$
~~$$\Delta U = \Delta H = f(T) = 0$$~~

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

6. 在水的正常沸点(373.15 K, 101.325 kPa), 有 1 mol H₂O(l) 变为同温、同压的 H₂O(g), 已知水的摩尔汽化焓变值为 Δ_{vap}H_m = 40.69 kJ · mol⁻¹, 请计算该变化的 Q, ΔU, ΔH 的值各为多少。



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

$$W = -p_{\text{外}} \Delta V = -p_{\text{外}}(V_g - V_l) = -nRT$$

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

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

7. 理想气体等温可逆膨胀, 体积从 V₁ 膨胀到 10V₁, 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 V₁;

(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 NH₃(g) 等温压缩到体积等于 10 dm³, 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 $a = 0.417 \text{ Pa} \cdot \text{m}^6 \cdot \text{mol}^{-2}$, $b = 3.71 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$ 。

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

$$W = -nRT \ln \frac{V_2}{V_1} \\ = -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 423 \text{ K} \times \ln \frac{0.01 \text{ m}^3}{0.03471 \text{ m}^3} \\ = 4376 \text{ J}$$

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

$$\left(101325 \text{ Pa} + \frac{0.417 \text{ Pa} \cdot \text{m}^6 \cdot \text{mol}^{-2}}{V_m^2} \right) \times (V_m - 3.71 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}) \\ = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 423 \text{ K}$$

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

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

$$W = - \int_{V_1}^{V_2} p dV = - \int_{V_1}^{V_2} \left(\frac{nRT}{V - nb} - \frac{an^2}{V^2} \right) dV \\ = -nRT \ln \frac{V_2 - nb}{V_1 - nb} - an^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \\ = -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 423 \text{ K} \\ \times \ln \frac{0.01 \text{ m}^3 - 1 \text{ mol} \times 3.71 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}}{0.03469 \text{ m}^3 - 1 \text{ mol} \times 3.71 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}} \\ - 0.417 \text{ Pa} \cdot \text{m}^6 \cdot \text{mol}^{-2} \times (1 \text{ mol})^2 \times \left(\frac{1}{0.01 \text{ m}^3} - \frac{1}{0.03469 \text{ m}^3} \right)$$

$$= 4345 \text{ J}$$

9. 已知在 373 K 和 101.325 kPa 压力时, $1 \text{ kg H}_2\text{O(l)}$ 的体积为 1.043 dm^3 , $1 \text{ kg H}_2\text{O(g)}$ 的体积为 1.677 dm^3 , $\text{H}_2\text{O(l)}$ 的摩尔汽化焓变值 $\Delta_{\text{vap}}H_m = 40.66 \text{ kJ} \cdot \text{mol}^{-1}$ 。当 $1 \text{ mol H}_2\text{O(l)}$ 在 373 K 和外压为 101.325 kPa 时完全蒸发成 $\text{H}_2\text{O(g)}$, 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 $\Delta_{\text{vap}}U_m$ 和 $\Delta_{\text{vap}}H_m$;
- (5) 解释何故蒸发的焓变大于系统所做的功。

$$\text{解: (1)} \quad W = -p(V_g - V_l)$$

$$= -101.325 \text{ Pa} \times (1.677 - 1.043 \times 10^{-3}) \text{ m}^3 \cdot \text{kg}^{-1} \times 18.0 \times 10^{-3} \text{ kg}$$

$$= -3.057 \text{ kJ}$$

$$\text{(2)} \quad W = -pV_g = -101.325 \text{ Pa} \times 18.0 \times 10^{-3} \text{ kg} \times 1.677 \text{ m}^3 \cdot \text{kg}^{-1}$$

$$= -3.059 \text{ kJ}$$

$$x = [(3.059 - 3.057)/3.057] \times 100\% = 0.065\%$$

$$\text{(3)} \quad W = -pV_g = -nRT = -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 373 \text{ K}$$

$$= -3.101 \text{ kJ}$$

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

$$\Delta_{\text{vap}}U_m = \frac{Q_p + W}{n} = (40.66 \text{ kJ} - 3.057 \text{ kJ})/1 \text{ mol}$$

$$= 37.60 \text{ kJ} \cdot \text{mol}^{-1}$$

(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 , ΔU 和 ΔH , 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。

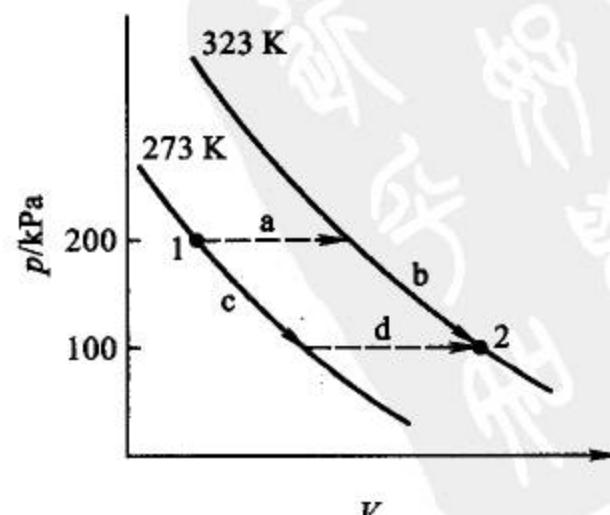


图 2-12

(1) 先等压加热至 323 K, 再等温可逆膨胀

$$\begin{aligned} \text{(a)} \quad Q_a &= Q_p = \Delta H_a = nC_{p,m}(T_2 - T_1) \\ &= 1 \text{ mol} \times \frac{5}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (323 \text{ K} - 273 \text{ K}) \\ &= 1039.25 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta U_a &= nC_{v,m}(T_2 - T_1) \\ &= 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (323 \text{ K} - 273 \text{ K}) \\ &= 623.55 \text{ J} \end{aligned}$$

$$W_a = \Delta U_a - Q_p = 623.55 \text{ J} - 1039.25 \text{ J} = -415.7 \text{ J}$$

$$\text{(b)} \quad \cancel{\Delta U_b} = \cancel{\Delta H_b} = \cancel{f(T)} = 0$$

$$\begin{aligned} W_b &= -nRT \ln \frac{p_1}{p_2} \\ &= -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 323 \text{ K} \times \ln \frac{200 \text{ kPa}}{100 \text{ kPa}} \\ &= -1861.4 \text{ J} \end{aligned}$$

$$Q_b = -W_b = 1861.4 \text{ J}$$

过程(1)总和:

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

$$\Delta H_1 = \Delta H_a + \Delta H_b = 1039.25 \text{ J} + 0 = 1039.25 \text{ J}$$

$$Q_1 = Q_a + Q_b = 1039.25 \text{ J} + 1861.4 \text{ J} = 2900.65 \text{ J}$$

$$W_1 = W_a + W_b = -415.7 \text{ J} - 1861.4 \text{ J} = -2277.1 \text{ J}$$

(2) 先等温可逆膨胀至 100 kPa, 再等压加热至 323 K。

$$\text{(c)} \quad \cancel{\Delta U_c} = \cancel{\Delta H_c} = \cancel{f(T)} = 0$$

$$\begin{aligned} W_c &= -nRT \ln \frac{p_1}{p_2} \\ &= -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 273 \text{ K} \times \ln \frac{200 \text{ kPa}}{100 \text{ kPa}} \\ &= -1573.3 \text{ J} \end{aligned}$$

$$Q_c = -W_c = 1573.3 \text{ J}$$

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

$$\begin{aligned} &= 1 \text{ mol} \times \frac{5}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (323 \text{ K} - 273 \text{ K}) \\ &= 1039.25 \text{ J} \end{aligned}$$

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

$$= 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (323 \text{ K} - 273 \text{ K}) \\ = 623.55 \text{ J}$$

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

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

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末态的状态有关, 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 dm^3 , 在外压为 100 kPa 压力下等温膨胀, 直到 $\text{N}_2(\text{g})$ 的压力也等于 100 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 kPa)膨胀

终态 $p_2 = 100 \text{ kPa}$

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

或者：

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

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

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

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

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

12. 0.02 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

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

$$\begin{aligned}W &= -p\Delta V \approx -pV_g = -101325 \text{ Pa} \times 0.02 \text{ kg} \times 0.607 \text{ m}^3 \cdot \text{kg}^{-1} \\&= -1230 \text{ J}\end{aligned}$$

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

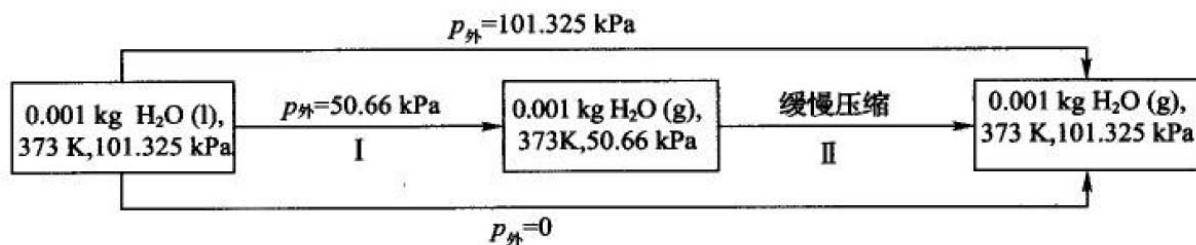
$$\Delta H = Q_p = 17.16 \text{ kJ}$$

13. 373 K, 压力为 101.325 kPa 时, 1.0 g H₂O(l) 经下列不同的过程变为 373K, 101.325 kPa 的 H₂O(g), 请分别求出各过程的 ΔU , ΔH , W 和 Q 值。

- (1) 在 373 K, 101.325 kPa 压力下 H₂O(l) 变成同温、同压的 H₂O(g)。
- (2) 先在 373 K, 外压为 50.66 kPa 下变成 H₂O(g), 然后加压成 373 K, 101.325 kPa 的 H₂O(g)。

(3) 把这个 H₂O(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 kJ · kg⁻¹。

解: (1) 三种不同过程图示如下。



$$(a) \underline{\Delta H} = Q_p = 2259 \text{ kJ} \cdot \text{kg}^{-1} \times 1 \times 10^{-3} \text{ kg} = \underline{2.259 \text{ kJ}}$$

$$\begin{aligned} W &= -p(V_g - V_l) \approx -pV_g = -nRT \\ &= -\frac{1 \times 10^{-3} \text{ kg}}{18.0 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1}} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 373 \text{ K} \\ &= -172.3 \text{ J} \end{aligned}$$

$$\underline{\Delta U} = Q + W = \underline{2087 \text{ J}}$$

$$\begin{aligned} (b) W_1 &= -p(V_g - V_l) \approx -pV_g \\ &= -nRT = -172.3 \text{ J} \end{aligned}$$

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

$$\begin{aligned} &= -\frac{1 \times 10^{-3} \text{ kg}}{18.0 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1}} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ &\quad \times 373 \text{ K} \times \ln \frac{50.66 \text{ kPa}}{101.325 \text{ kPa}} \\ &= 119.4 \text{ J} \end{aligned}$$

$$W = W_1 + W_{II} = -52.9 \text{ J}$$

~~ΔU, ΔH~~ 是状态函数, 其值同(a) 中的 ΔU , ΔH 。

$$Q = \Delta U - W = (2087 + 52.9) \text{ J} = 2140 \text{ J}$$

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

ΔU , ΔH 值同(a) 中的 ΔU , ΔH 。

$$\underline{Q = \Delta U = 2087 \text{ J}}$$

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) ΔU 和 ΔH ;
- (3) 所做的功。

$$\text{解: (1)} \quad T_1 = \frac{p_1 V_1}{nR}$$

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

$$= 273 \text{ K}$$

$pT = \text{常数}$, $p_1 T_1 = p_2 T_2$

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

$$= 136.5 \text{ K}$$

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

$$= 2.8 \times 10^{-3} \text{ m}^3$$

(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 dm³, 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, ΔU, ΔH 和 Q。已知该气体的等压摩尔热容为 $C_{p,m} = (27.28 + 3.26 \times 10^{-3} T/K) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ 。

$$\text{解: } n = \frac{p_1 V_1}{RT_1} = \frac{101.325 \text{ Pa} \times 0.003 \text{ m}^3}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 293 \text{ K}} \\ = 0.125 \text{ mol}$$

$$V_2 = \frac{nRT_2}{p_2} \\ = \frac{0.125 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 353 \text{ K}}{101.325 \text{ Pa}}$$

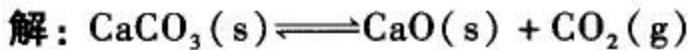
$$= 3.62 \times 10^{-3} \text{ m}^3$$

$$\begin{aligned} W &= -p(V_2 - V_1) \\ &= -101325 \text{ Pa} \times (3.62 \times 10^{-3} \text{ m}^3 - 0.003 \text{ m}^3) \\ &= -61.8 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta H &= Q_p = \int_{T_1}^{T_2} C_p dT = n \int_{T_1}^{T_2} C_{p,m} dT \\ &= n \int_{293 \text{ K}}^{353 \text{ K}} [(27.28 + 3.26 \times 10^{-3} T/\text{K}) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}] dT \\ &= 0.125 \text{ mol} \times [27.28 \times (353 - 293) + \frac{1}{2} \times 3.26 \times \\ &\quad 10^{-3} \times (353^2 - 293^2)] \text{ J} \cdot \text{mol}^{-1} \\ &= 212.5 \text{ J} \end{aligned}$$

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

16. 在 1200 K, 100 kPa 压力下, 有 1 mol CaCO₃(s) 完全分解为 CaO(s) 和 CO₂(g), 吸热 180 kJ。计算过程的 W, ΔU, ΔH 和 Q。设气体为理想气体。



$$\begin{aligned} W &= -p(V_2 - V_1) = -pV_2 = -n_{\text{CO}_2}RT \\ &= -1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 1200 \text{ K} \\ &= -9976.8 \text{ J} \end{aligned}$$

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

$$\begin{aligned} \Delta U &= Q + W = 180 \text{ kJ} - 9976.8 \text{ J} \\ &= 170.023 \text{ kJ} \end{aligned}$$

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 $\left(\frac{\partial H}{\partial V}\right)_T = 0$, $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$ 。

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) $U = H - pV$

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

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

令

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

$$\begin{aligned} dH &= \left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp \\ \left(\frac{\partial H}{\partial T} \right)_V &= \left(\frac{\partial H}{\partial T} \right)_p + \left(\frac{\partial H}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V \end{aligned} \tag{2}$$

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 $4.21 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$ 。

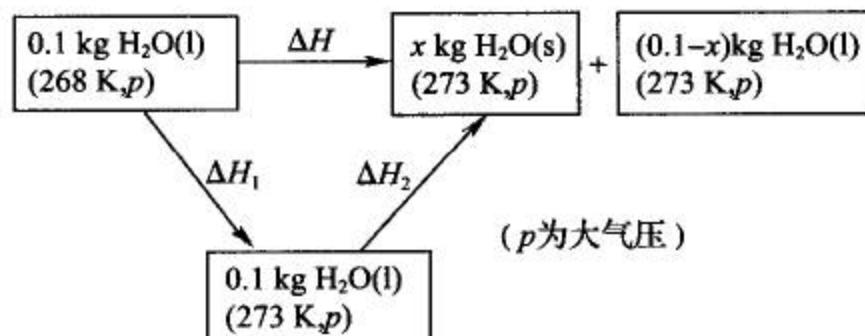
(1) 写出系统物态的变化, 并求出 ΔH ;

(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 N₂(g), 在 298.2 K 和 101.325 kPa 压力下, 经可逆绝热过程压缩到 5 dm³。试计算(设气体为理想气体)：

- (1) N₂(g) 的最后温度；
- (2) N₂(g) 的最后压力；
- (3) 需做多少功。

解：(1) 设 N₂(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 ΔH 。

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:

$$\Delta U = \int_{T_1}^{T_2} C_V dT = n C_{V,m} (T_2 - T_1) \\ = 1 \text{ mol} \times 20.9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (473 \text{ K} - 573 \text{ K}) \\ = -2090 \text{ J}$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT = n C_{p,m} (T_2 - T_1) \\ = 1 \text{ mol} \times (20.9 + 8.314) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (473 \text{ K} - 573 \text{ K}) \\ = -2921.4 \text{ J}$$

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

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 dm^3 经下列不同过程, 膨胀到终态压力为 101.325 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

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

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

$$= 16.36 \text{ mol}$$

$$\begin{aligned} Q &= -W = nRT \ln \frac{p_1}{p_2} \\ &= 16.36 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K} \times \ln \frac{20p}{p} \\ &= 1.214 \times 10^5 \text{ J} = 121.4 \text{ kJ} \end{aligned}$$

(2) 绝热可逆过程:

$$Q = 0$$

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

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

$$\begin{aligned} \Delta U &= nC_{V,m}(T_2 - T_1) = n \frac{3}{2}R(T_2 - T_1) \\ &= 16.36 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (89.9 \text{ K} - 298 \text{ K}) \\ &= -4.246 \times 10^4 \text{ J} \\ &= -42.46 \text{ kJ} \end{aligned}$$

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

$$\begin{aligned} \Delta H &= nC_{p,m}(T_2 - T_1) = n \frac{5}{2}R(T_2 - T_1) \\ &= 16.36 \text{ mol} \times \frac{5}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (89.9 \text{ K} - 298 \text{ K}) \\ &= -70.76 \text{ kJ} \end{aligned}$$

(3) 多方可逆过程:

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

联立上两式得

$$\begin{aligned} p^{1-\delta} T^\delta &= C' \\ T_2 &= \left(\frac{p_1}{p_2} \right)^{\frac{1-\delta}{\delta}} T_1 = \left(\frac{20p}{p} \right)^{\frac{1-1.3}{1.3}} \times 298 \text{ K} \\ &= 149.3 \text{ K} \\ \Delta U &= nC_{V,m}(T_2 - T_1) = n \frac{3}{2}R(T_2 - T_1) \end{aligned}$$

$$\begin{aligned}
 &= 16.36 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (149.3 \text{ K} - 298 \text{ K}) \\
 &= -3.034 \times 10^4 \text{ J} \\
 &= -30.34 \text{ kJ}
 \end{aligned}$$

$$\begin{aligned}
 \Delta H = nC_{p,m}(T_2 - T_1) &= n \frac{5}{2}R(T_2 - T_1) \\
 &= 16.36 \text{ mol} \times \frac{5}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (149.3 \text{ K} - 298 \text{ K}) \\
 &= -5.056 \times 10^4 \text{ J} \\
 &= -50.56 \text{ kJ}
 \end{aligned}$$

$$\begin{aligned}
 W &= -\frac{nR}{1-\delta}(T_2 - T_1) \\
 &= -\frac{16.36 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}{1-1.3} \times (149.3 \text{ K} - 298 \text{ K}) \\
 &= -6.742 \times 10^4 \text{ J} \\
 &= -67.42 \text{ kJ}
 \end{aligned}$$

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

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:

$$\begin{aligned}
 pV &= C \\
 V_2 &= \frac{p_1 V_1}{p_2} = 0.4 \text{ m}^3
 \end{aligned}$$

(2) 绝热可逆过程:

$$\begin{aligned}
 pV^{1.67} &= C \\
 V_2 &= \left(\frac{p_1}{p_2}\right)^{\frac{1}{1.67}} V_1 = 0.12 \text{ m}^3
 \end{aligned}$$

(3) 多方可逆过程:

$$\begin{aligned}
 pV^{1.3} &= C \\
 V_2 &= \left(\frac{p_1}{p_2}\right)^{\frac{1}{1.3}} V_1 = 0.2 \text{ m}^3
 \end{aligned}$$

曲线下面积就是功值,由此可见功的大小次序与计算值相同:

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

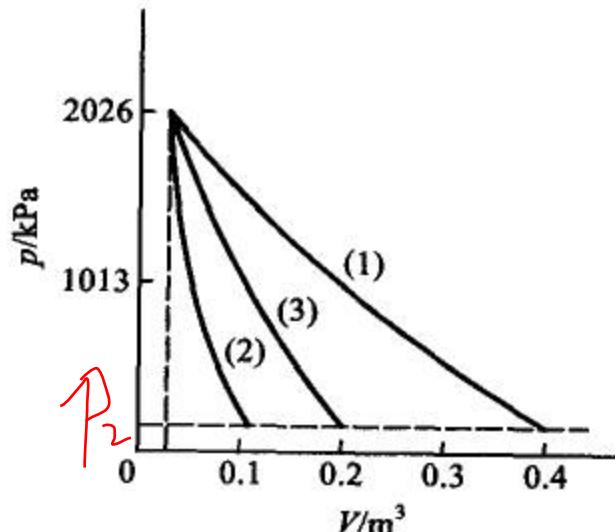


图 2-13

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 ΔU 的值, 画出 p - V 示意图, 并把 ΔU 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 $p/\text{Pa} = 10\ 132.5 V_m / (\text{dm}^3 \cdot \text{mol}^{-1}) + b$ 的途径可逆变化。

解: 始态

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

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

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

- (1) 等温可逆膨胀:

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

$$\Delta U = 0$$

$$\begin{aligned} Q &= -W = nRT \ln \frac{V_2}{V_1} \\ &= 1 \text{ mol} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K} \times \ln 2 \\ &= 1717 \text{ J} \end{aligned}$$

- (2) 绝热可逆过程:

$$Q = 0$$

单原子理想气体:

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

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

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

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

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

$$= -1376 \text{ J}$$

$$W = \Delta U - Q = -1376 \text{ J}$$

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

$$202.650 = 10\ 132.5 \times 12.23 + b$$

$$b = 78730$$

$$p_2/\text{Pa} = 10\ 132.5 \times 24.46 + 78730 = 326571$$

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

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

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

$$= 8278 \text{ J}$$

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

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

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

$$= - \frac{1}{2} \{ 10132.5 \text{ Pa} \cdot \text{mol} \cdot \text{dm}^{-3} [(24.46 \text{ dm}^3)^2 - (12.23 \text{ dm}^3)^2] \times 10^{-3} + 78730 \text{ Pa} \times (24.46 \text{ dm}^3 - 12.23 \text{ dm}^3) \times 10^{-3} \}$$

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

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

$$= 11.52 \text{ kJ}$$

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。

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

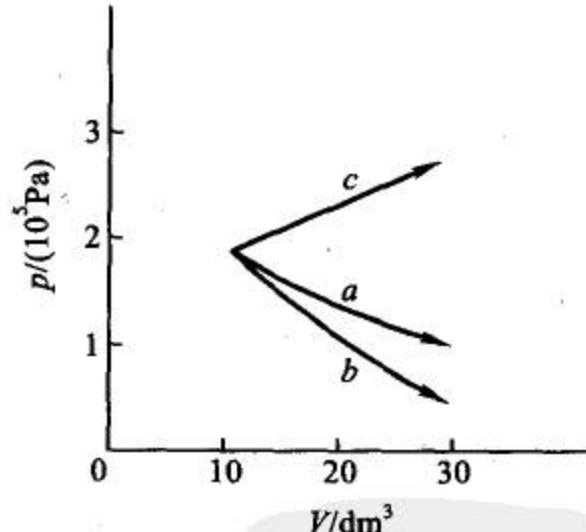


图 2-14

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

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 $335 \text{ kJ} \cdot \text{kg}^{-1}$ 。

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

$$W = Q_1 \frac{T_2 - T_1}{T_1}$$

$$= 335 \text{ kJ} \cdot \text{kg}^{-1} \times 1 \text{ kg} \times \frac{298 \text{ K} - 273 \text{ K}}{273 \text{ K}}$$

$$= 30.68 \text{ kJ}$$

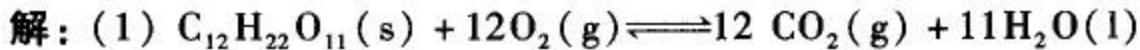
26. 有如下反应, 设都在 298 K 和标准大气压力下进行, 请比较各个反应的 ΔU 与 ΔH 的大小, 并说明这差别主要是什么因素造成的。

(1) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (蔗糖) 完全燃烧;

(2) C_{10}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) PbS (s) 完全氧化为 PbO (s) 和 SO_2 (g)。



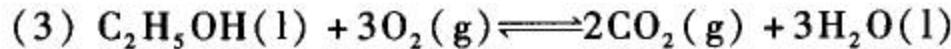
$$\Delta_r H_m = \Delta_r U_m + \sum \nu_B RT, \quad \sum \nu_B = 12 - 12 = 0$$

$$\Delta_r H_m = \Delta_r U_m$$



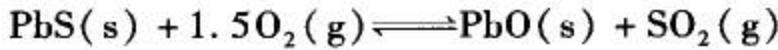
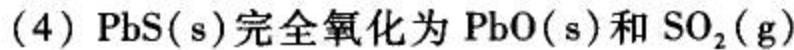
$$\sum \nu_B = -21 < 0$$

$$\Delta_r H_m < \Delta_r U_m$$



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

$$\Delta_r H_m < \Delta_r U_m$$



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

$$\Delta_r H_m < \Delta_r U_m$$

差别的原因是由于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

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

1 mol 正庚烷燃烧后放出的等容热效应为

$$\begin{aligned}\Delta_c U_m &= \frac{Q_v}{m/M} \\ &= -\frac{24.04 \text{ kJ}}{0.500 \text{ g}/(100.2 \text{ g} \cdot \text{mol}^{-1})} \\ &= -4818 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$



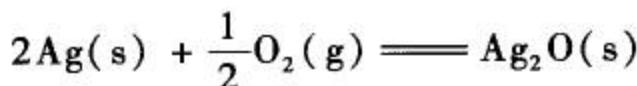
正庚烷的燃烧焓为

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

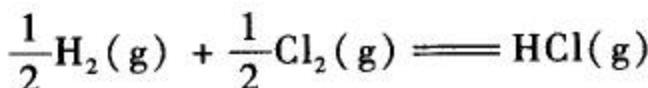
28. 根据下列反应在 298.15 K 时的焓变值, 计算 AgCl(s) 的标准摩尔生成焓 $\Delta_f H_m^\ominus(\text{AgCl}, s, 298.15 \text{ K})$ 。



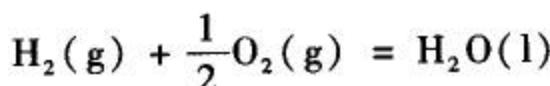
$$\Delta_r H_{m,1}^\ominus(298.15 \text{ K}) = -324.9 \text{ kJ} \cdot \text{mol}^{-1} \quad (1)$$



$$\Delta_r H_{m,2}^\ominus(298.15 \text{ K}) = -30.57 \text{ kJ} \cdot \text{mol}^{-1} \quad (2)$$

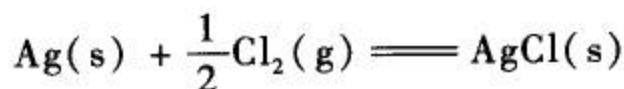


$$\Delta_r H_{m,3}^\ominus(298.15 \text{ K}) = -92.31 \text{ kJ} \cdot \text{mol}^{-1} \quad (3)$$



$$\Delta_r H_{m,4}^\ominus(298.15 \text{ K}) = -285.84 \text{ kJ} \cdot \text{mol}^{-1} \quad (4)$$

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



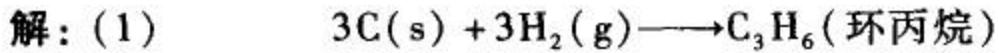
$$\Delta_f H_m^\ominus(\text{AgCl}, T) = \frac{1}{2}\Delta_r H_m^\ominus(1) + \frac{1}{2}\Delta_r H_m^\ominus(2) + \Delta_r H_m^\ominus(3) - \frac{1}{2}\Delta_r H_m^\ominus(4)$$

$$= \frac{1}{2} \times (-324.9 \text{ kJ} \cdot \text{mol}^{-1}) + \frac{1}{2} \times (-30.57 \text{ kJ} \cdot \text{mol}^{-1})$$

$$\begin{aligned}
 & + (-92.31 \text{ kJ} \cdot \text{mol}^{-1}) - \frac{1}{2} \times (-285.84 \text{ kJ} \cdot \text{mol}^{-1}) \\
 & = -127.13 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

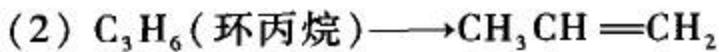
29. 在 298.15 K 及 100 kPa 压力时, 设环丙烷、石墨及氢气的燃烧焓 $\Delta_c H_m^\ominus$ (298.15 K) 分别为 $-2092 \text{ kJ} \cdot \text{mol}^{-1}$, $-393.8 \text{ kJ} \cdot \text{mol}^{-1}$ 及 $-285.84 \text{ kJ} \cdot \text{mol}^{-1}$ 。若已知环丙烷 $C_3H_6(g)$ 的标准摩尔生成焓 $\Delta_f H_m^\ominus(298.15 \text{ K}) = 20.50 \text{ kJ} \cdot \text{mol}^{-1}$ 。试求:

- (1) 环丙烷的标准摩尔生成焓 $\Delta_f H_m^\ominus(298.15 \text{ K})$;
- (2) 环丙烷异构化变为丙烯的摩尔反应焓变值 $\Delta_r H_m^\ominus(298.15 \text{ K})$ 。



该反应的反应热就是环丙烷的生成焓, 即

$$\begin{aligned}
 \Delta_f H_m^\ominus(C_3H_6) &= \Delta_r H_m^\ominus(T) = -\sum \nu_B \Delta_c H_m^\ominus(B) \\
 &= 3\Delta_c H_m^\ominus(C(s)) + 3\Delta_c H_m^\ominus(H_2(g)) - \Delta_c H_m^\ominus(C_3H_6(g)) \\
 &= 3 \times (-393.8 \text{ kJ} \cdot \text{mol}^{-1}) + 3 \times (-285.84 \text{ kJ} \cdot \text{mol}^{-1}) \\
 &\quad - (-2092 \text{ kJ} \cdot \text{mol}^{-1}) \\
 &= 53.08 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$



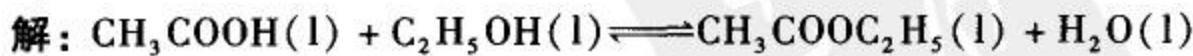
$$\begin{aligned}
 \Delta_r H_m^\ominus(T) &= \Delta_f H_m^\ominus(\text{丙烯}, T) - \Delta_f H_m^\ominus(\text{环丙烷}, T) \\
 &= 20.50 \text{ kJ} \cdot \text{mol}^{-1} - 53.08 \text{ kJ} \cdot \text{mol}^{-1} \\
 &= -32.58 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

30. 根据以下数据, 计算乙酸乙酯的标准摩尔生成焓 $\Delta_f H_m^\ominus(CH_3COOC_2H_5, 1, 298.15 \text{ K})$



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

乙酸和乙醇的标准摩尔燃烧焓 $\Delta_c H_m^\ominus(298.15 \text{ K})$ 分别为 $-874.54 \text{ kJ} \cdot \text{mol}^{-1}$ 和 $-1366 \text{ kJ} \cdot \text{mol}^{-1}$, $CO_2(g)$, $H_2O(l)$ 的标准摩尔生成焓分别为 $-393.51 \text{ kJ} \cdot \text{mol}^{-1}$ 和 $-285.83 \text{ kJ} \cdot \text{mol}^{-1}$ 。

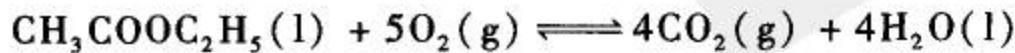


$$\begin{aligned}
 \Delta_r H_m^\ominus &= \Delta_c H_m^\ominus(CH_3COOH, l) + \Delta_c H_m^\ominus(C_2H_5OH, l) - \Delta_c H_m^\ominus(CH_3COOC_2H_5, l) \\
 &\quad - \Delta_c H_m^\ominus(H_2O, l)
 \end{aligned}$$

$$-9.20 \text{ kJ} \cdot \text{mol}^{-1} = -874.54 \text{ kJ} \cdot \text{mol}^{-1} - 1366 \text{ kJ} \cdot \text{mol}^{-1} - \Delta_c H_m^\ominus(CH_3COOC_2H_5, l) - 0$$

$$\Delta_c H_m^\ominus(CH_3COOC_2H_5, l) = -2231.3 \text{ kJ} \cdot \text{mol}^{-1}$$

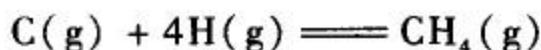
乙酸乙酯的燃烧反应如下:



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）。

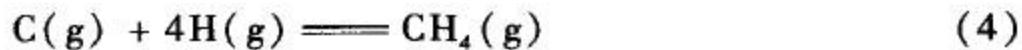


已知：石墨升华为碳原子的标准摩尔焓变 $\Delta_{\text{sub}} H_m^\ominus = 711.1 \text{ kJ} \cdot \text{mol}^{-1}$ ， $\text{H}_2\text{(g)} = 2\text{H(g)}$ 的标准解离焓为 $431.7 \text{ kJ} \cdot \text{mol}^{-1}$ ， $\text{CH}_4\text{(g)}$ 的标准摩尔生成焓为 $\Delta_f H_m^\ominus(298.15 \text{ K}) = -74.78 \text{ kJ} \cdot \text{mol}^{-1}$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

解：



反应 (3) $- 2 \times (2) - (1)$ 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 $\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightleftharpoons \text{H}_2\text{O(l)}$ 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 $\text{H}_2\text{O(l)}$ 在 373 K 和标准压力下的摩尔蒸发焓为 $\Delta_{\text{vap}} H_m^\ominus(373 \text{ K}) = 40.65 \text{ kJ} \cdot \text{mol}^{-1}$ 。

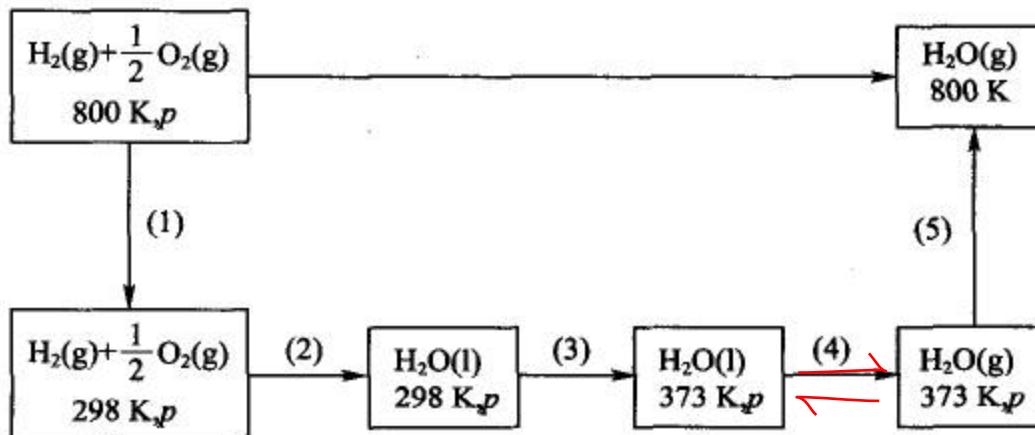
$$C_{p,m}(\text{H}_2, \text{g}) = 29.07 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + (8.36 \times 10^{-4} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2})T$$

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

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

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

解：设计如下过程，



$$\begin{aligned}\Delta_r H_m(1) &= \int_{800 \text{ K}}^{298 \text{ K}} \left[C_{p,m}(\text{H}_2) + \frac{1}{2} C_{p,m}(\text{O}_2) \right] dT \\ &= \int_{800 \text{ K}}^{298 \text{ K}} [47.15 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} - (4.14 \times 10^{-4} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}) T] dT \\ &= (47.15 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \times (298 \text{ K} - 800 \text{ K}) - \left(\frac{1}{2} \times 4.14 \right. \\ &\quad \left. \times 10^{-4} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2} \right) \times [(298 \text{ K})^2 - (800 \text{ K})^2] \\ &= -23555.2 \text{ J} \cdot \text{mol}^{-1}\end{aligned}$$

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

$$\begin{aligned}\Delta_r H_m(3) &= \int_{298 \text{ K}}^{373 \text{ K}} C_{p,m} \{ \text{H}_2\text{O(l)} \} dT = \int_{298 \text{ K}}^{373 \text{ K}} (75.26 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) dT \\ &= 5644.5 \text{ J} \cdot \text{mol}^{-1}\end{aligned}$$

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

$$\begin{aligned}\Delta_r H_m(5) &= \int_{373 \text{ K}}^{800 \text{ K}} C_{p,m} \{ \text{H}_2\text{O(g)} \} dT \\ &= \int_{373 \text{ K}}^{800 \text{ K}} [30.00 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + (10.7 \times 10^{-3} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}) T] dT \\ &= 15531.7 \text{ J} \cdot \text{mol}^{-1}\end{aligned}$$

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

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 dm³ 绝热可逆膨胀到 6 dm³, 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 $C_{V,m} = \frac{3}{2}R$, $\gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$

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 H_2O 看作刚体非线性分子, 用经典理论来估计其气体的 $C_{p,m}(\text{H}_2\text{O}, g)$ 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 $\frac{1}{2}kT$ 。

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

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

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

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

(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 。

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

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

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

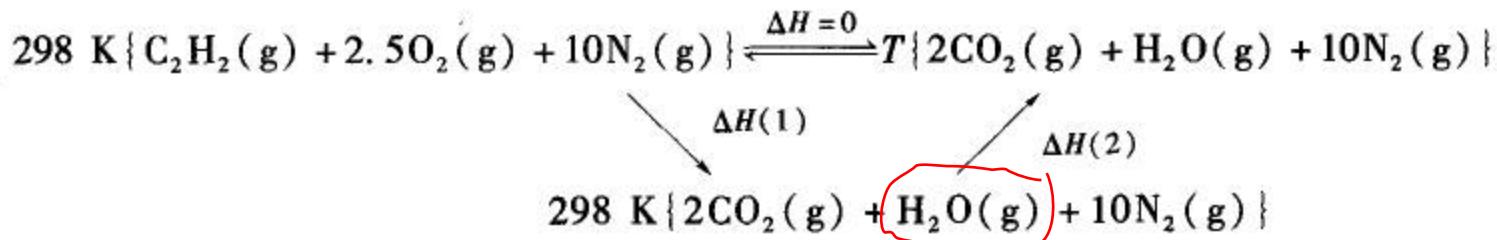
$$C_{V,m} = \left(\frac{\partial E_m}{\partial T} \right)_V = 6R$$

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

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 $\Delta_r H_m^\ominus = 0$ 。

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

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

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

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

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