

第2章 热力学定律和热力学基本方程

习题解答

1. 27℃时, 5 mol $\text{NH}_3(\text{g})$ 由 5 dm^3 恒温可逆膨胀至 50 dm^3 , 试计算体积功。假设 $\text{NH}_3(\text{g})$ 服从范德华方程。

解: 由表 1-6 查得, $\text{NH}_3(\text{g})$ 的 $a = 0.423 \text{ Pa} \cdot \text{m}^6 \cdot \text{mol}^{-2}$, $b = 0.0371 \times 10^{-3} \text{ m}^3 \cdot \text{mol}^{-1}$ 。对于 1 mol $\text{NH}_3(\text{g})$

$$\begin{aligned} W_{\text{R}} &= -\int_{V_{\text{m},1}}^{V_{\text{m},2}} p dV_{\text{m}} = -\int_{V_{\text{m},1}}^{V_{\text{m},2}} \left(\frac{RT}{V_{\text{m}} - b} - \frac{a}{V_{\text{m}}^2} \right) dV_{\text{m}} \\ &= -RT \ln \frac{V_{\text{m},2} - b}{V_{\text{m},1} - b} - a \left(\frac{1}{V_{\text{m},2}} - \frac{1}{V_{\text{m},1}} \right) \\ &= \left\{ -8.3145 \times (27 + 273.15) \times \ln \frac{(50/5) - 0.0371}{(5/5) - 0.0371} \right. \\ &\quad \left. - 0.423 \times \left[\frac{1}{(50/5)} - \frac{1}{(5/5)} \right] \times 10^3 \right\} \text{ J} \\ &= -5446 \text{ J} \cdot \text{mol}^{-1} \end{aligned}$$

对于 5 mol $\text{NH}_3(\text{g})$

$$W_{\text{R}} = 5 \times (-5446) \text{ J} = -27.23 \times 10^3 \text{ J} = -27.23 \text{ kJ}$$

2. 某一热机的低温热源温度为 40℃, 若高温热源温度为: (1) 100℃ (101325 Pa 下水的沸点); (2) 265℃ (5 MPa 下水的沸点); 试分别计算卡诺循环的热机效率。

$$\text{解: (1) } \eta_{\text{R}} = \frac{T_1 - T_2}{T_1} = \frac{100 - 40}{100 + 273.15} = 0.161 = 16.1 \%$$

$$(2) \eta_{\text{R}} = \frac{265 - 40}{265 + 273.15} = 0.418 = 41.8 \%$$

3. 某电冰箱内的温度为 0℃, 室温为 25℃, 今欲使 1000g 温度为 0℃ 的水变成冰, 问最少需做功多少? 已知 0℃ 时冰的熔化焓为 $333.4 \text{ J} \cdot \text{g}^{-1}$ 。

$$\begin{aligned}\text{解: } W'_R &= \frac{T_1 - T_2}{T_2} Q'_{R_2} \\ &= \left[\frac{25 - 0}{0 + 273.15} \times (333.4 \times 1000) \right] \text{J} = 30.51 \times 10^3 \text{J} = 30.51 \text{kJ}\end{aligned}$$

4. 某系统与环境的温度均为 300 K, 设系统经历了一个恒温不可逆过程, 从状态 A 变化到状态 B, 对环境做功, $W = -4 \text{ kJ}$ 。已知该过程的不可逆程度为 $\int_A^B (\mathrm{d}Q_R / T) - \int_A^B (\mathrm{d}Q / T_{\text{环}}) = 20 \text{ J} \cdot \text{K}^{-1}$ 。试计算欲使系统复原, 环境至少需做多少功。

$$\begin{aligned}\text{解: } \int_A^B \frac{\mathrm{d}Q_R}{T} - \int_A^B \frac{\mathrm{d}Q_R}{T_{\text{环}}} &= \frac{Q_R}{T} - \frac{Q}{T_{\text{环}}} = \frac{Q_R - Q}{T} = \frac{(\Delta U - W_R) - (\Delta U - W)}{T} \\ &= \frac{-W_R + W}{T} = 20 \text{ J} \cdot \text{K}^{-1}\end{aligned}$$

$$-W_R + W = (20 \times 300) \text{J} = 6 \text{ kJ}$$

$$-W_R = -W + 6 \text{ kJ} = (4 + 6) \text{ kJ} = 10 \text{ kJ}$$

即环境至少需作功 10 kJ。

5. 10 A 的电流通过一个 10Ω 的电阻, 时间为 10 s, 此电阻放在流动的水中而保持在 10°C 。假设水的数量很大, 水温也保持在 10°C 。求这个电阻的熵变及水的熵变。

解: 电阻 $\Delta S = 0$

$$\text{水} \quad \Delta S = \frac{Q_R}{T} = \frac{I^2 R \tau}{T} = \left(\frac{10^2 \times 10 \times 10}{10 + 273.15} \right) \text{J} \cdot \text{K}^{-1} = 35.32 \text{ J} \cdot \text{K}^{-1}$$

6. 10 A 的电流通过一个 10Ω 的电阻, 时间为 1 s, 此电阻被绝热的物质包住。电阻的初始温度为 10°C , 质量为 10 g, 比热容为 $1 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$, 求电阻的熵变及绝热物质的熵变。

$$\text{解: 电阻} \quad \Delta T = \frac{I^2 R \tau}{cm} = \left(\frac{10^2 \times 10 \times 1}{1 \times 10} \right) \text{K} = 100 \text{ K}$$

$$\begin{aligned}\Delta S &= cm \ln \frac{T_2}{T_1} \\ &= \left(1 \times 10 \times \ln \frac{110 + 273.15}{10 + 273.15} \right) \text{J} \cdot \text{K}^{-1} = 3.02 \text{ J} \cdot \text{K}^{-1}\end{aligned}$$

绝热物质 $\Delta S = 0$

7. 有一反应器, 其温度恒定在 373 K, 环境温度为 300 K。反应器向环境散热 5000 J。试通过计算判断过程的可逆性。

$$\text{解: } \Delta S = \frac{Q_R}{T} = \left(\frac{-5000}{373} \right) \text{J} \cdot \text{K}^{-1} = -13.4 \text{J} \cdot \text{K}^{-1}$$

$$\Delta S_{\text{环}} = \frac{Q}{T_{\text{环}}} = \left(\frac{5000}{300} \right) \text{J} \cdot \text{K}^{-1} = 16.7 \text{J} \cdot \text{K}^{-1}$$

$$\Delta S_{\text{总}} = \Delta S + \Delta S_{\text{环}} = (-13.4 + 16.7) \text{J} \cdot \text{K}^{-1} = 3.3 \text{J} \cdot \text{K}^{-1}$$

$\therefore \Delta S_{\text{总}} > 0$, \therefore 散热过程是一个不可逆过程。

8. 在 0.1 MPa 下, 1 mol 气态 NH_3 由 -25°C 变为 0°C , 试计算此过程中 NH_3 的熵变。已知 NH_3 的 $C_{p,m}^\circ / (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 24.77 + 37.49 \times 10^{-3} (T/\text{K})$ 。若热源的温度为 0°C , 试判断此过程的可逆性。

$$\begin{aligned} \text{解: } \Delta S &= \int_{T_1}^{T_2} n C_{p,m}^\circ \frac{dT}{T} = \int_{T_1}^{T_2} \left[1 \times \left(24.77 + 37.49 \times 10^{-3} \frac{T}{\text{K}} \right) \text{J} \cdot \text{K}^{-1} \right] \frac{dT}{T} \\ &= \left\{ 1 \times 24.77 \times \ln \frac{0 + 273.15}{-25 + 273.15} + 1 \times 37.49 \times 10^{-3} [0 - (-25)] \right\} \text{J} \cdot \text{K}^{-1} \end{aligned}$$

$$= 3.315 \text{J} \cdot \text{K}^{-1}$$

$$\begin{aligned} Q &= \int_{T_1}^{T_2} n C_{p,m}^\circ dT = \int_{T_1}^{T_2} \left[1 \times \left(24.77 + 37.49 \times 10^{-3} \frac{T}{\text{K}} \right) \text{J} \cdot \text{K}^{-1} \right] dT \\ &= \left[1 \times 24.77 \times (273.15 - 248.15) + \frac{1}{2} \times 1 \times 37.49 \times 10^{-3} \right. \\ &\quad \left. \times (273.15^2 - 248.15^2) \right] \text{J} = 863.6 \text{J} \end{aligned}$$

$$\frac{Q}{T_{\text{环}}} = \frac{863.6}{273.15} \text{J} \cdot \text{K}^{-1} = 3.162 \text{J} \cdot \text{K}^{-1}$$

$$\Delta S - \frac{Q}{T_{\text{环}}} = (3.315 - 3.162) \text{J} \cdot \text{K}^{-1} = 0.153 \text{J} \cdot \text{K}^{-1} > 0$$

\therefore 这是一个不可逆过程。

9. 证明下列各式:

$$(1) \left(\frac{\partial U}{\partial T} \right)_p = C_p - p \left(\frac{\partial V}{\partial T} \right)_p; \quad (2) \left(\frac{\partial U}{\partial V} \right)_p = C_p \left(\frac{\partial T}{\partial V} \right)_p - p;$$

$$(3) \left(\frac{\partial U}{\partial p} \right)_V = C_V \left(\frac{\partial T}{\partial p} \right)_V; \quad (4) \left(\frac{\partial H}{\partial V} \right)_p = C_p \left(\frac{\partial T}{\partial V} \right)_p;$$

$$(5) \left(\frac{\partial U}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p - p \left(\frac{\partial V}{\partial p} \right)_T;$$

$$(6) \left(\frac{\partial H}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V + V \left(\frac{\partial p}{\partial V} \right)_T.$$

证: (1) $\left(\frac{\partial U}{\partial T} \right)_p = \left[\frac{\partial(H - pV)}{\partial T} \right]_p = \left(\frac{\partial H}{\partial T} \right)_p - p \left(\frac{\partial V}{\partial T} \right)_p$

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

$$(2) \left(\frac{\partial U}{\partial V} \right)_p = \left[\frac{\partial(H - pV)}{\partial V} \right]_p = \left(\frac{\partial H}{\partial V} \right)_p - p$$

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

$$(3) \left(\frac{\partial U}{\partial p} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V \left(\frac{\partial T}{\partial p} \right)_V = C_V \left(\frac{\partial T}{\partial p} \right)_V$$

$$(4) \left(\frac{\partial H}{\partial V} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p \left(\frac{\partial T}{\partial V} \right)_p = C_p \left(\frac{\partial T}{\partial V} \right)_p$$

$$(5) dU = TdS - pdV$$

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

$$(6) dH = TdS + Vdp$$

$$\left(\frac{\partial H}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T + V \left(\frac{\partial p}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V + V \left(\frac{\partial p}{\partial V} \right)_T$$

10. 证明下列各式:

$$(1) C_p - C_V = \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p; \quad (2) C_p - C_V = T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p;$$

$$(3) C_p - C_V = - \left[\left(\frac{\partial H}{\partial p} \right)_T - V \right] \left(\frac{\partial p}{\partial T} \right)_V;$$

$$(4) \quad C_p - C_v = \frac{\alpha^2 VT}{\kappa}; \quad \text{式中 } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p, \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T.$$

$$\begin{aligned} \text{证: (1)} \quad C_p - C_v &= \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_v \\ &= \left[\frac{\partial(U + pV)}{\partial T} \right]_p - \left(\frac{\partial U}{\partial T} \right)_v \\ &= \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_v \\ dU &= \left(\frac{\partial U}{\partial T} \right)_v dT + \left(\frac{\partial U}{\partial V} \right)_T dV \\ \left(\frac{\partial U}{\partial T} \right)_p &= \left(\frac{\partial U}{\partial T} \right)_v + \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p \\ \therefore C_p - C_v &= \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p \\ &= \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p \end{aligned}$$

$$(2) \quad \text{以 } \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v - p \text{ 代入(1)的结果, 得}$$

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

$$\begin{aligned} (3) \quad C_p - C_v &= \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_v \\ &= \left(\frac{\partial H}{\partial T} \right)_p - \left[\frac{\partial(H - pV)}{\partial T} \right]_v \\ &= \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial H}{\partial T} \right)_v + V \left(\frac{\partial p}{\partial T} \right)_v \\ dH &= \left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp \\ \left(\frac{\partial H}{\partial T} \right)_v &= \left(\frac{\partial H}{\partial T} \right)_p + \left(\frac{\partial H}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_v \end{aligned}$$

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

(4) 由 $\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1$, 得

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

以此代入(2)的结果, 得

$$\begin{aligned}C_p - C_v &= T \left[-\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} \right] \left(\frac{\partial V}{\partial T}\right)_p = T \frac{\left[\left(\frac{\partial V}{\partial T}\right)_p\right]^2}{\left[-\left(\frac{\partial V}{\partial p}\right)_T\right]} \\ &= T \frac{\left[\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p\right]^2 V}{\left[-\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T\right]} = T \frac{\alpha^2 V}{\kappa} = \frac{\alpha^2 VT}{\kappa}\end{aligned}$$

11. 某实际气体的状态方程为 $pV_m = RT + \alpha p$, 其中 α 是常数。

1 mol 该气体在恒定的温度 T 下, 经可逆过程由 p_1 变到 p_2 。试用 T 、 p_1 、 p_2 表示过程的 W 、 Q 、 ΔU 、 ΔH 、 ΔS 、 ΔA 及 ΔG 。

解: $p = \frac{RT}{V_m - \alpha}$

$$\begin{aligned}W = W_R &= -\int_{V_{m1}}^{V_{m2}} p dV_m = \int_{V_{m2}}^{V_{m1}} \frac{RT}{V_m - \alpha} dV_m \\ &= RT \ln \frac{V_{m1} - \alpha}{V_{m2} - \alpha} = RT \ln \frac{p_2}{p_1}\end{aligned}$$

$$dU_m = TdS_m - pdV_m$$

$$\begin{aligned}\left(\frac{\partial U_m}{\partial V_m}\right)_T &= T\left(\frac{\partial S_m}{\partial V_m}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_{V_m} - \frac{RT}{V_m - \alpha} \\ &= T \cdot \frac{R}{V_m - \alpha} - \frac{RT}{V_m - \alpha} = 0\end{aligned}$$

$\therefore dU_m = 0$, 即 $\Delta U = 0$

$$Q = \Delta U - W = 0 - RT \ln \frac{p_2}{p_1} = RT \ln \frac{p_1}{p_2}$$

$$\Delta S = \frac{Q_R}{T} = R \ln \frac{p_1}{p_2}$$

$$\begin{aligned}\Delta H &= \Delta U + \Delta(pV) = 0 + (p_2 V_{m,2} - p_1 V_{m,1}) \\ &= (RT + \alpha p_2) - (RT + \alpha p_1) = \alpha(p_2 - p_1)\end{aligned}$$

$$\Delta A = W_R = RT \ln \frac{p_2}{p_1}$$

$$\Delta G = \Delta A + \Delta(pV) = RT \ln \frac{p_2}{p_1} + \alpha(p_2 - p_1)$$

12. 200 K 时, 固态 Hg 的 $\alpha = 1.43 \times 10^{-4} \text{ K}^{-1}$, $\kappa = 3.44 \times 10^{-11} \text{ Pa}^{-1}$, 摩尔体积为 $14.14 \text{ cm}^3 \cdot \text{mol}^{-1}$, $C_{p,m} = 27.11 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ 。试利用式 $C_{p,m} - C_{V,m} = \alpha^2 V_m T / \kappa$ 求 200K 时固态 Hg 的 $C_{V,m}$ 。

$$\begin{aligned}\text{解: } C_{p,m} - C_{V,m} &= \frac{\alpha^2 V_m T}{\kappa} \\ &= \left[\frac{(1.43 \times 10^{-4})^2 \times (14.14 \times 10^{-6}) \times 200}{3.44 \times 10^{-11}} \right] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &= 1.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

$$\therefore C_{V,m} = (27.11 - 1.68) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 25.43 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

13. 试证明对 1 mol 理想气体, 无论进行可逆过程或不可逆过程, 都有:

$$\begin{aligned}\Delta S &= C_{V,m}^\circ \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right) = C_{p,m}^\circ \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{p_1}{p_2} \right) \\ &= C_{p,m}^\circ \ln \left(\frac{V_2}{V_1} \right) + C_{V,m}^\circ \ln \left(\frac{p_2}{p_1} \right)\end{aligned}$$

证: 因为熵是状态函数, 故熵变只决定于初、终状态而与过程的可逆与否无关。设想由初态开始先进行恒压可逆的加热或冷却过程使温度

变为终态的, 然后进行恒温可逆的膨胀或压缩过程使压力变为终态的, 于是

$$\Delta S = \Delta S_1 + \Delta S_2 = C_{p,m}^\circ \ln \frac{T_2}{T_1} + R \ln \frac{p_1}{p_2}$$

$$\text{或 } \Delta S = C_{p,m}^\circ \ln \frac{T_2}{T_1} + R \ln \frac{T_1/V_1}{T_2/V_2} = C_{V,m}^\circ \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$$\text{或 } \Delta S = C_{p,m}^\circ \ln \frac{p_2 V_2}{p_1 V_1} + R \ln \frac{p_1}{p_2} = C_{p,m}^\circ \ln \frac{V_2}{V_1} + C_{V,m}^\circ \ln \frac{p_2}{p_1}$$

14. 12 g O_2 从 20°C 被冷却到 -40°C , 同时压力从 0.1 MPa 变为 6 MPa, 求其熵变。设 O_2 可作为理想气体, $C_{p,m}^\circ = 29.16 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ 。

$$\begin{aligned} \text{解: } \Delta S &= n \left(C_{p,m}^\circ \ln \frac{T_2}{T_1} + R \ln \frac{p_1}{p_2} \right) \\ &= \left[\frac{12}{32.00} \times \left(29.16 \times \ln \frac{-40 + 273.15}{20 + 273.15} + 8.3145 \times \ln \frac{0.1}{6} \right) \right] \text{ J} \cdot \text{K}^{-1} \\ &= -15.27 \text{ J} \cdot \text{K}^{-1} \end{aligned}$$

15. 把 1 mol He 在 127°C 和 0.5 MPa 下恒温压缩至 1 MPa, 试求其 Q 、 W 、 ΔU 、 ΔH 、 ΔS 、 ΔA 、 ΔG 。He 可作为理想气体。(1) 设为可逆过程; (2) 设压缩时外压自始至终为 1 MPa。

解: (1) $\Delta U = 0$, $\Delta H = 0$

$$\begin{aligned} W &= -nRT \ln \frac{p_1}{p_2} = \left[-1 \times 8.3145 \times (127 + 273.15) \times \ln \frac{0.5}{1} \right] \text{ J} \\ &= 2306 \text{ J} \end{aligned}$$

$$Q = \Delta U - W = -2306 \text{ J}$$

$$\Delta S = nR \ln \frac{p_1}{p_2} = \left(1 \times 8.3145 \times \ln \frac{0.5}{1} \right) \text{ J} \cdot \text{K}^{-1} = -5.763 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta A = W_R = 2306 \text{ J}$$

$$\Delta G = \Delta A = 2306 \text{ J}$$

(2) ΔU 、 ΔH 、 ΔS 、 ΔA 、 ΔG 同 (1)

$$\begin{aligned} W &= -p_{\text{外}} \Delta V = -p_2 \left(\frac{nRT}{p_2} - \frac{nRT}{p_1} \right) = -nRT \left(1 - \frac{p_2}{p_1} \right) \\ &= \left[-1 \times 8.3145 \times (127 + 273.15) \times \left(1 - \frac{1}{0.5} \right) \right] \text{ J} = 3327 \text{ J} \end{aligned}$$

$$Q = \Delta U - W = -3327 \text{ J}$$

16. 0°C 、 0.5 MPa 的 $\text{N}_2(\text{g})$ 2 dm^3 , 在外压为 0.1 MPa 下恒温膨胀, 直至氮气的压力等于 0.1 MPa , 求过程的 Q 、 W 、 ΔU 、 ΔH 、 ΔS 、 ΔG 和 ΔA 。假设氮气服从理想气体状态方程。

解: $\Delta U = 0$, $\Delta H = 0$

$$V_2 = \frac{p_1}{p_2} V_1 = \frac{0.5}{0.1} \times 2\text{ dm}^3 = 10\text{ dm}^3$$

$$W = -p_{\text{外}} \Delta V = \left[-(0.1 \times 10^6) \times (10 - 2) \times 10^{-3} \right] \text{ J} = -800\text{ J}$$

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

$$\begin{aligned} \Delta S &= nR \ln \left(\frac{p_1}{p_2} \right) = \frac{p_1 V_1}{T_1} \ln \left(\frac{p_1}{p_2} \right) \\ &= \left[\frac{0.5 \times 10^6 \times 2 \times 10^{-3}}{273.15} \times \ln \left(\frac{0.5}{0.1} \right) \right] \text{ J} \cdot \text{K}^{-1} \\ &= 5.892\text{ J} \cdot \text{K}^{-1} \end{aligned}$$

$$\Delta G = \Delta H - T \Delta S = 0 - 273.15 \times 5.892\text{ J} = -1609\text{ J} = -1.609\text{ kJ}$$

$$\Delta A = \Delta G = -1.609\text{ kJ}$$

17. $1\text{ mol H}_2(\text{g})$ 在 25°C 和 0.1 MPa 下可逆绝热压缩至体积为 5 dm^3 , 试求终态温度、压力及过程的 Q 、 W 、 ΔU 、 ΔH 、 ΔS 。假设氢气为理想气体, $C_{V,m}^{\ominus} = (5/2)R$ 。

$$\text{解: } \gamma = \frac{C_{p,m}^{\ominus}}{C_{V,m}^{\ominus}} = \frac{(7/2)R}{(5/2)R} = 1.4$$

$$\begin{aligned} V_1 &= \frac{nRT_1}{p_1} = \left[\frac{1 \times 8.3145 \times (25 + 273.15)}{0.1 \times 10^6} \right] \text{ m}^3 \\ &= 24.79 \times 10^{-3} \text{ m}^3 = 24.79\text{ dm}^3 \end{aligned}$$

$$\begin{aligned} p_2 &= \left(\frac{V_1}{V_2} \right)^{\gamma} p_1 = \left(\frac{24.79}{5} \right)^{1.4} \times 0.1\text{ MPa} \\ &= 0.941\text{ MPa} \end{aligned}$$

$$T_2 = \frac{p_2 V_2}{nR} = \left[\frac{(0.941 \times 10^6) \times (5 \times 10^{-3})}{1 \times 8.3145} \right] \text{ K} = 565.9\text{ K}$$

$$\Delta U = nC_{V,m}^{\ominus} \Delta T = \left[1 \times \frac{5}{2} \times 8.3145 \times (565.9 - 298.15) \right] \text{ J} = 5566\text{ J}$$

$$\Delta H = nC_{p,m}^{\ominus} \Delta T = \left[1 \times \frac{7}{2} \times 8.3145 \times (565.9 - 298.15) \right] \text{ J} = 7792\text{ J}$$

$$Q = 0$$

$$W = \Delta U = 5566 \text{ J}$$

$$\Delta S = \int \frac{dQ_R}{T} = 0$$

18. 1 mol 0°C、0.2 MPa 的理想气体沿着 $p/V = \text{常数}$ 的可逆途径到达压力为 0.4 MPa 的终态。已知 $C_{V,m}^\circ = (5/2)R$ ，求过程的 Q 、 W 、 ΔU 、 ΔH 、 ΔS 。

$$\begin{aligned} \text{解: } V_1 &= \frac{nRT_1}{p_1} = \left(\frac{1 \times 8.3145 \times 273.15}{0.2 \times 10^6} \right) \text{ m}^3 \\ &= 11.35 \times 10^{-3} \text{ m}^3 = 11.35 \text{ dm}^3 \end{aligned}$$

$$\frac{p_2}{V_2} = \frac{p_1}{V_1}$$

$$\therefore V_2 = \frac{p_1}{p_2} V_1 = \frac{0.2}{0.4} \times 11.35 \text{ dm}^3 = 5.675 \text{ dm}^3$$

$$T_2 = \frac{p_2 V_2}{nR} = \left[\frac{(0.4 \times 10^6) \times (5.675 \times 10^{-3})}{1 \times 8.3145} \right] \text{ K} = 1092 \text{ K}$$

$$\begin{aligned} W &= - \int_{V_1}^{V_2} p dV = - \int_{V_1}^{V_2} \left(\frac{p_1}{V_1} V \right) dV = - \frac{p_1}{V_1} \cdot \frac{1}{2} (V_2^2 - V_1^2) \\ &= - \frac{1}{2} (p_2 V_2 - p_1 V_1) \\ &= \left[- \frac{1}{2} \times (0.4 \times 22.70 - 0.2 \times 11.35) \times 10^3 \right] \text{ J} \\ &= -3.405 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta U &= nC_{V,m}^\circ \Delta T = \left[1 \times \frac{5}{2} \times 8.3145 \times (1092 - 273) \right] \text{ J} \\ &= 17.02 \times 10^3 \text{ J} = 17.02 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta H &= nC_{p,m}^\circ \Delta T = \left[1 \times \frac{7}{2} \times 8.3145 \times (1092 - 273) \right] \text{ J} \\ &= 23.83 \times 10^3 \text{ J} = 23.83 \text{ kJ} \end{aligned}$$

$$Q = \Delta U - W = [17.02 - (-3.405)] \text{ kJ} = 20.43 \text{ kJ}$$

$$\begin{aligned}
 \Delta S &= n \left(C_{p,m}^{\circ} \ln \frac{T_2}{T_1} + R \ln \frac{p_1}{p_2} \right) \\
 &= 1 \times \left[\left(\frac{5}{2} + 1 \right) \times 8.3145 \times \ln \frac{1092}{273.15} + 8.3145 \times \ln \frac{0.2}{0.4} \right] \text{J} \cdot \text{K}^{-1} \\
 &= 34.56 \text{J} \cdot \text{K}^{-1}
 \end{aligned}$$

19. 计算下列各恒温过程的熵变(气体为理想气体):

(1) 1 mol 体积为 V 的 N_2 与 1 mol 体积为 V 的 Ar 混合, 成为体积为 $2V$ 的混合气体;

(2) 1 mol 体积为 V 的 N_2 与 1 mol 体积为 V 的 Ar 混合, 成为体积为 V 的混合气体;

(3) 1 mol 体积为 V 的 N_2 与 1 mol 体积为 V 的 N_2 合并成 2 mol 体积为 $2V$ 的 N_2 ;

(4) 1 mol 体积为 V 的 N_2 与 1 mol 体积为 V 的 N_2 合并成 2 mol 体积为 V 的 N_2 。

$$\begin{aligned}
 \text{解: (1)} \quad \Delta S &= n_1 R \ln 2 + n_2 R \ln 2 = (2 \times 8.3145 \times \ln 2) \text{J} \cdot \text{K}^{-1} \\
 &= 11.53 \text{J} \cdot \text{K}^{-1}
 \end{aligned}$$

$$(2) \quad \Delta S = 0$$

$$(3) \quad \Delta S = 0$$

$$(4) \quad \Delta S = n R \ln \frac{p_1}{p_2} = \left(2 \times 8.3145 \times \ln \frac{1}{2} \right) \text{J} \cdot \text{K}^{-1} = -11.53 \text{J} \cdot \text{K}^{-1}$$

20. 一绝热容器被隔板分成体积相等的两部分, 左边有 1 mol 10°C 的 O_2 , 右边有 1 mol 20°C 的 H_2 。设两种气体均可当作理想气体, $C_{p,m}^{\circ} = (7/2)R$ 。求两边温度相等时总的熵变。若将隔板抽去, 求总的熵变。

解: 两边温度相等后, $Q = 0$, $W = 0$

$$\therefore \Delta U = 0$$

$$\Delta U = \Delta U_1 + \Delta U_2 = n_1 C_{V,m}^{\circ} (T - T_1) + n_2 C_{V,m}^{\circ} (T - T_2) = 0$$

$$T = \frac{1}{2} (T_1 + T_2) = \frac{1}{2} \times [(10 + 273.15) + (20 + 273.15)] \text{K} = 288.15 \text{K}$$

$$\begin{aligned}
 \Delta S &= \Delta S_1 + \Delta S_2 = n_1 C_{V,m}^{\circ} \ln \frac{T}{T_1} + n_2 C_{V,m}^{\circ} \ln \frac{T}{T_2} \\
 &= \left[1 \times \left(\frac{5}{2} \times 8.3145 \right) \times \ln \frac{288.15}{283.15} + 1 \times \left(\frac{5}{2} \times 8.3145 \right) \times \ln \frac{288.15}{293.15} \right] \text{J} \cdot \text{K}^{-1}
 \end{aligned}$$

$$= 0.0063 \text{ J} \cdot \text{K}^{-1}$$

抽去隔板后, 两气体在恒温下混合, 每一种气体的分压均变为原来压力的一半

$$\begin{aligned} \Delta S &= n_1 R \ln 2 + n_2 R \ln 2 = (n_1 + n_2) R \ln 2 = (2 \times 8.3145 \times \ln 2) \text{ J} \cdot \text{K}^{-1} \\ &= 11.53 \text{ J} \cdot \text{K}^{-1} \end{aligned}$$

故总的熵变为 $(0.0063 + 11.53) \text{ J} \cdot \text{K}^{-1} = 11.54 \text{ J} \cdot \text{K}^{-1}$

21. 以旋塞隔开而体积相等的两个玻璃球, 分别贮有 1 mol O_2 和 1 mol N_2 , 温度均为 25°C , 压力均为 0.1 MPa 。在绝热条件下, 打开旋塞使两种气体混合。取两种气体为系统, 试求混合过程的 Q 、 W 、 ΔU 、 ΔH 、 ΔS 、 ΔA 、 ΔG 。(设 O_2 和 N_2 均为理想气体)

解: 因为绝热, 故 $Q = 0$

因为系统的体积不变, 故 $W = 0$

则 $\Delta U = Q + W = 0$

而 $\Delta U = n C_{V,m}^\circ \Delta T$, 故 $\Delta T = 0$

于是 $\Delta H = n C_{p,m}^\circ \Delta T = 0$

两种气体的压力都从 0.1 MPa 变为 0.05 MPa

$$\begin{aligned} \therefore \Delta S &= \Delta S_1 + \Delta S_2 = n_1 R \ln 2 + n_2 R \ln 2 = (n_1 + n_2) R \ln 2 \\ &= (2 \times 8.3145 \times \ln 2) \text{ J} \cdot \text{K}^{-1} = 11.53 \text{ J} \cdot \text{K}^{-1} \\ \Delta A &= \Delta U - T \Delta S = [0 - (25 + 273.15) \times 11.53] \text{ J} = -3438 \text{ J} \\ \Delta G &= \Delta A = -3438 \text{ J} \end{aligned}$$

22. 1 mol CO_2 自 20°C 、 0.3040 MPa 、 7878 cm^3 反抗恒定的 0.101325 MPa 外压恒温膨胀至 0.101325 Pa 、 23920 cm^3 。试求此过程的 Q 、 W 、 ΔU 、 ΔH 。已知 CO_2 在 20°C 、 0.3040 MPa 下节流膨胀至 0.101325 MPa 时的温度为 17.72°C ; 在 0.101325 MPa 下及 20°C 附近其 $C_{p,m} = 37.07 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ 。

解: $W = -p_{\text{外}} \Delta V$

$$= [- (0.101325 \times 10^6) \times (23920 - 7878) \times 10^{-6}] \text{ J} = -1625 \text{ J}$$

$$\Delta H = \Delta H_1 + \Delta H_2 = 0 + n C_{p,m} \Delta T$$

$$= [1 \times 37.07 \times (20 - 17.72)] \text{ J} = 84.5 \text{ J}$$

$$\Delta U = \Delta H - \Delta(pV)$$

$$= [84.5 - (0.101325 \times 23920 - 0.3040 \times 7878)] \text{ J} = 55.7 \text{ J}$$

$$Q = \Delta U - W = [55.7 - (-1625)] \text{ J} = 1681 \text{ J}$$

23. 2 mol 液态 O_2 在正常沸点(-182.97°C)时蒸发成为 101325 Pa 的气体, 求其熵变。已知此时液态 O_2 的摩尔蒸发焓为 $6.820 \text{ kJ} \cdot \text{mol}^{-1}$ 。

$$\text{解: } \Delta S = \frac{\Delta H}{T} = \left(\frac{2 \times 6.820 \times 10^3}{-182.97 + 273.15} \right) \text{ J} \cdot \text{K}^{-1} = 151.3 \text{ J} \cdot \text{K}^{-1}$$

24. 100 g 10°C 的水与 200 g 40°C 的水在绝热条件下混合, 求此过程的熵变。已知水的比热容为 $4.184 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$ 。

解: 绝热条件下混合, $\Delta H = Q_p = 0$

$$\Delta H = \Delta H_1 + \Delta H_2 = cm_1(t - t_1) + cm_2(t - t_2) = 0$$

$$t = \frac{m_1 t_1 + m_2 t_2}{m_1 + m_2} = \left(\frac{100 \times 10 + 200 \times 40}{100 + 200} \right) ^\circ\text{C} = 30^\circ\text{C}$$

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 = cm_1 \ln \frac{T}{T_1} + cm_2 \ln \frac{T}{T_2} \\ &= \left(4.184 \times 100 \times \ln \frac{30 + 273.15}{10 + 273.15} + 4.184 \times 200 \times \ln \frac{30 + 273.15}{40 + 273.15} \right) \text{ J} \cdot \text{K}^{-1} \\ &= 1.40 \text{ J} \cdot \text{K}^{-1} \end{aligned}$$

25. 在一个绝热的容器中有 1000 g 25°C 的水, 投入 150 g 0°C 的冰, 计算总的熵变。已知冰的熔化焓为 $333.4 \text{ J} \cdot \text{g}^{-1}$, 水的比热容为 $4.184 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$ 。

解: 绝热过程, $\Delta H = Q_p = 0$

$$\Delta H = \Delta H_1 + \Delta H_2 = cm_1(t - t_1) + m_2 \Delta_{\text{fus}} H + cm_2(t - t_2)$$

$$\begin{aligned} &= \left[4.184 \times 1000 \left(\frac{t}{^\circ\text{C}} - 25 \right) + 150 \times 333.4 + 4.184 \times 150 \times \left(\frac{t}{^\circ\text{C}} - 0 \right) \right] \text{ J} \\ &= 0 \end{aligned}$$

$$t = 11.34^\circ\text{C}$$

$$\Delta S_1 = cm_1 \ln \frac{T}{T_1} = \left(4.184 \times 1000 \times \ln \frac{11.34 + 273.15}{25 + 273.15} \right) \text{ J} \cdot \text{K}^{-1}$$

$$= -196.2 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta S_2 = m_2 \frac{\Delta_{\text{fus}} H}{T_2} + cm_2 \ln \frac{T}{T_2}$$

$$= \left(150 \times \frac{333.4}{0 + 273.15} + 4.184 \times 150 \times \ln \frac{11.34 + 273.15}{0 + 273.15} \right) \text{ J} \cdot \text{K}^{-1}$$

$$= 208.6 \text{ J} \cdot \text{K}^{-1}$$

$$\therefore \Delta S = \Delta S_1 + \Delta S_2 = (-196.2 + 208.6) \text{ J} \cdot \text{K}^{-1} = 12.4 \text{ J} \cdot \text{K}^{-1}$$

26. 1 mol $\text{C}_6\text{H}_5\text{CH}_3$ 在其正常沸点 110.6°C 时蒸发为 101325 Pa 的气体, 求该过程的 Q 、 W 、 ΔU 、 ΔH 、 ΔS 、 ΔA 、 ΔG 。已知在该温度下 $\text{C}_6\text{H}_5\text{CH}_3$ 的摩尔蒸发焓为 $33.38 \text{ kJ} \cdot \text{mol}^{-1}$ 。与蒸气相比较, 液体的体积可略去, 蒸气可作为理想气体。(1) 设外压为 101325 Pa ; (2) 设外压为 10132.5 Pa 。

$$\begin{aligned} \text{解: (1)} \quad W &= -p_{\text{外}} \Delta V = -p[V(\text{g}) - V(\text{l})] \approx -pV(\text{g}) \approx -nRT \\ &= [-1 \times 8.3145 \times (110.6 + 273.15)] \text{ J} \\ &= -3190 \text{ J} = -3.190 \text{ kJ} \end{aligned}$$

$$Q = \Delta H = 33.38 \text{ kJ}$$

$$\Delta U = Q + W = (33.38 - 3.190) \text{ kJ} = 30.19 \text{ kJ}$$

$$\Delta S = \frac{\Delta H}{T} = \left(\frac{33.38 \times 10^3}{110.6 + 273.15} \right) \text{ J} \cdot \text{K}^{-1} = 87.0 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta A = W_{\text{R}} = -3.190 \text{ kJ}$$

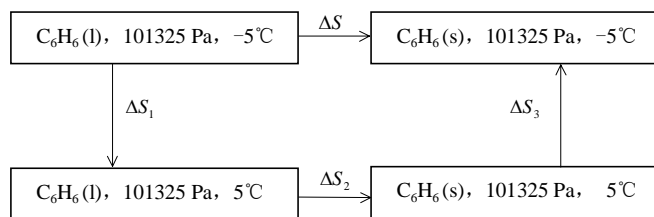
$$\Delta G = 0$$

(2) ΔU 、 ΔH 、 ΔS 、 ΔA 、 ΔG 同(1)

$$\begin{aligned} W &= -p_{\text{外}} \Delta V \approx -p_{\text{外}} V(\text{g}) \approx -p_{\text{外}} \cdot \frac{nRT}{p} = -\frac{p_{\text{外}}}{p} \cdot nRT \\ &= \left[-\frac{10132.5}{101325} \times 1 \times 8.3145 \times (110.6 + 273.15) \right] \text{ J} \\ &= -319 \text{ J} = -0.319 \text{ kJ} \\ Q &= \Delta U - W = [30.19 - (-0.319)] \text{ kJ} = 30.51 \text{ kJ} \end{aligned}$$

27. C_6H_6 的正常熔点为 5°C , 摩尔熔化焓为 $9916 \text{ J} \cdot \text{mol}^{-1}$, $C_{p,m}(\text{l}) = 126.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $C_{p,m}(\text{s}) = 122.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ 。求 101325 Pa 下 $1 \text{ mol } -5^\circ\text{C}$ 的过冷 C_6H_6 凝固成 -5°C 的固态 C_6H_6 的 Q 、 ΔU 、 ΔH 、 ΔS 、 ΔA 、 ΔG 。设凝固过程的体积功可略去不计。

解:



$$Q = \Delta H = \{-9916 + (122.6 - 126.8) \times [(-5) - 5]\} \text{ J} = -9874 \text{ J}$$

$$\Delta U = Q + W \approx Q = -9874 \text{ J}$$

$$\Delta S_1 = C_{p,m(l)} \ln \frac{T_2}{T_1} = \left(126.8 \times \ln \frac{5 + 273.15}{-5 + 273.15} \right) \text{ J} \cdot \text{K}^{-1} = 4.643 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta S_2 = \frac{\Delta H_2}{T_2} = \left(\frac{-9916}{5 + 273.15} \right) \text{ J} \cdot \text{K}^{-1} = -35.65 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta S_3 = C_{p,m(s)} \ln \frac{T_1}{T_2} = \left(122.6 \times \ln \frac{-5 + 273.15}{5 + 273.15} \right) \text{ J} \cdot \text{K}^{-1}$$

$$= -4.489 \text{ J} \cdot \text{K}^{-1}$$

$$\therefore \Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = (4.643 - 35.65 - 4.489) \text{ J} \cdot \text{K}^{-1}$$

$$= -35.50 \text{ J} \cdot \text{K}^{-1}$$

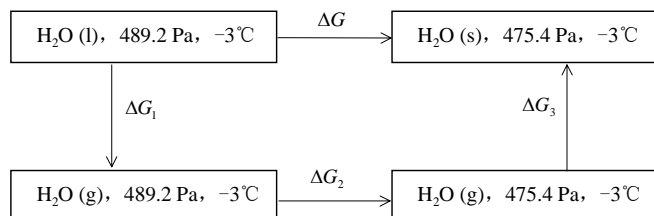
$$\Delta A = \Delta U - T\Delta S = [-9874 - (-5 + 273.15) \times (-35.50)] \text{ J}$$

$$= -355 \text{ J}$$

$$\Delta G = \Delta H - T\Delta S = -355 \text{ J}$$

28. 在 -3°C 时, 冰的蒸气压为 475.4 Pa , 过冷水的蒸气压为 489.2 Pa 。试求在 -3°C 时 1 mol 过冷 H_2O 转变为冰的 ΔG 。

解:



$$\Delta G_1 = 0$$

$$\Delta G_2 = nRT \ln \frac{p_2}{p_1} = \left[1 \times 8.3145 \times (-3 + 273.15) \times \ln \frac{475.4}{489.2} \right] \text{ J}$$

$$= -64.3 \text{ J}$$

$$\Delta G_3 = 0$$

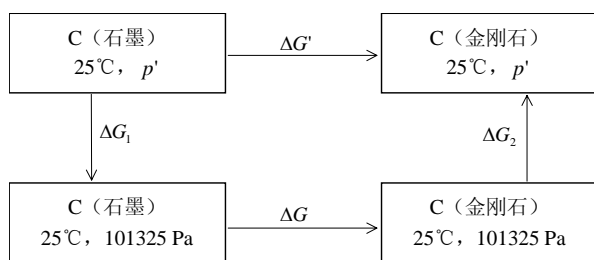
$$\therefore \Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 = 0 - 64.3 \text{ J} + 0 = -64.3 \text{ J}$$

29. 25°C 、 101325 Pa 时, 石墨转变为金刚石的 $\Delta H = 1895 \text{ J} \cdot \text{mol}^{-1}$, $\Delta S = -3.363 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ 。石墨的密度为 $2.260 \text{ g} \cdot \text{cm}^{-3}$, 金刚石的密度为 $3.513 \text{ g} \cdot \text{cm}^{-3}$ 。(1) 求 25°C 、 101325 Pa 下石墨转变为金刚石的 ΔG ; (2) 在这种情况下, 哪一种晶型比较稳定? (3) 增加压力能否使原来不稳定的晶型成为稳定的晶型? 如果可能, 所需的压力是多少? 假设密度不随压力而变。

解: (1) $\Delta G = \Delta H - T\Delta S = [1895 - (25 + 273.15) \times (-3.363)] \text{ J} = 2898 \text{ J}$

(2) $\Delta G > 0$, 表示石墨不可能转变成金刚石, 即石墨是稳定的。

(3)



设 25°C , 压力为 p' 时石墨与金刚石正好能平衡共存, 则 $\Delta G' = 0$

$$\Delta G_1 = \int_{p'}^p V_1 dp \approx V_1(p - p')$$

$$\Delta G_2 = \int_p^{p'} V_2 dp \approx V_2(p' - p)$$

$$\Delta G' = \Delta G_1 + \Delta G + \Delta G_2$$

即 $0 = V_1(p - p') + \Delta G + V_2(p' - p) = (V_2 - V_1)(p' - p) + \Delta G$

$$\begin{aligned} p' - p &= -\frac{\Delta G}{V_2 - V_1} = -\frac{\Delta G}{M[(1/\rho_2) - (1/\rho_1)]} \\ &= \left\{ -\frac{2898}{12.011 \times 10^{-3} \times [(1/3.515) - (1/2.260)] \times 10^{-3}} \right\} \text{ Pa} \\ &= 1527 \times 10^6 \text{ Pa} = 1527 \text{ MPa} \end{aligned}$$

$$\therefore p \approx 1527 \text{ MPa}$$

30. 将 1 mol Hg(l) 在 25°C 的恒定温度下, 从 0.1 MPa 压缩至 10 MPa , 试求其状态变化的 ΔS 和 ΔG 。已知 25°C 时 Hg(l) 的密度为 $13.534 \text{ g} \cdot \text{cm}^{-3}$, 密度随压力的变化可以略去, Hg(l) 的体积膨胀系数 $\alpha = 1.82 \times 10^{-4} \text{ K}^{-1}$, Hg 的摩尔质量为 $200.61 \text{ g} \cdot \text{mol}^{-1}$ 。

$$\begin{aligned}
 \text{解: } \Delta G &= \int_{p_1}^{p_2} V dp = V(p_2 - p_1) = \frac{nM}{\rho}(p_2 - p_1) \\
 &= \left[\left(\frac{1 \times 200.61}{13.534} \times 10^{-6} \right) \times (10 - 0.1) \times 10^6 \right] \text{ J} = 146.7 \text{ J} \\
 \Delta S &= \int_{p_1}^{p_2} \left(\frac{\partial S}{\partial p} \right)_T dp = - \int_{p_1}^{p_2} \left(\frac{\partial V}{\partial T} \right)_p dp = - \int_{p_1}^{p_2} \alpha V dp \\
 &= -\alpha V(p_2 - p_1) \\
 &= \left[-1.82 \times 10^{-4} \times \left(\frac{1 \times 200.61}{13.534} \times 10^{-6} \right) \times (10 - 0.1) \times 10^6 \right] \text{ J} \cdot \text{K}^{-1} \\
 &= -0.0267 \text{ J} \cdot \text{K}^{-1}
 \end{aligned}$$

31. 70℃时四氯化碳的蒸气压为82.81 kPa, 80℃时为112.43 kPa。试计算四氯化碳的摩尔蒸发焓及正常沸点。设四氯化碳的摩尔蒸发焓不随温度而变化。

$$\begin{aligned}
 \text{解: } \Delta_{\text{vap}} H_{\text{m}} &= \frac{RT_2 T_1}{T_2 - T_1} \ln \frac{p^*(T_2)}{p^*(T_1)} \\
 &= \left[\frac{8.3145 \times (80 + 273.15) \times (70 + 273.15)}{80 - 70} \times \ln \frac{112.43}{82.81} \right] \text{ J} \cdot \text{mol}^{-1} \\
 &= 30.81 \times 10^3 \text{ J} \cdot \text{mol}^{-1} = 30.81 \text{ kJ} \cdot \text{mol}^{-1} \\
 \frac{1}{T_2} &= \frac{1}{T_1} - \frac{R}{\Delta H} \ln \frac{p^*(T_2)}{p^*(T_1)} \\
 &= \left[\frac{1}{70 + 273.15} - \frac{8.3145}{30.81 \times 10^3} \times \ln \frac{101.325}{82.81} \right] \text{ K}^{-1} \\
 &= 2.8597 \times 10^{-3} \text{ K}^{-1} \\
 \therefore T_2 &= 349.69 \text{ K}, \quad t_2 = 76.54 \text{ } ^\circ\text{C}
 \end{aligned}$$

32. 卫生部门规定汞蒸气在 1 m^3 空气中的最高允许含量为 0.01 mg。已知汞在 20℃ 的饱和蒸气压为 0.160 Pa, 摩尔蒸发焓为 $60.7 \text{ kJ} \cdot \text{mol}^{-1}$ 。若在 30℃ 时汞蒸气在空气中达到饱和, 问此时空气中汞的含量是最高允许含量的多少倍。已知汞蒸气是单原子分子。

$$\begin{aligned}
 \text{解: } \ln \frac{p^*(T_2)}{p^*(T_1)} &= \frac{\Delta_{\text{vap}} H_{\text{m}}}{R} \cdot \frac{T_2 - T_1}{T_2 T_1} \\
 &= \frac{60.7 \times 10^3}{8.3145} \times \frac{30 - 20}{(30 + 273.15) \times (20 + 273.15)} = 0.821
 \end{aligned}$$

$$\frac{p^*(T_2)}{p^*(T_1)} = 2.27, \quad p^*(T_2) = 2.27 \times 0.160 \text{ Pa} = 0.363 \text{ Pa}$$

$$m = nM = \frac{pV}{RT} M = \left[\frac{0.363 \times 1}{8.3145 \times (30 + 273.15)} \times 200.6 \right] \text{ g}$$

$$= 28.9 \times 10^{-3} \text{ g} = 28.9 \text{ mg}$$

∴ 空气中汞的含量是最高允许含量的 $28.9 / 0.01 = 2.89 \times 10^3$ 倍。

33. 萘在其正常熔点 80°C 时的熔化焓为 $150.6 \text{ J} \cdot \text{g}^{-1}$ 。已知固态萘及液态萘的密度分别为 1.145 与 $0.981 \text{ g} \cdot \text{cm}^{-3}$ ，试计算压力增加 0.1 MPa 后熔点的变化。

解：对 1 g 萘，由固态变为液态

$$\Delta_{\text{fus}} V = V(\text{l}) - V(\text{s}) = \frac{1}{\rho(\text{l})} - \frac{1}{\rho(\text{s})} = \frac{\rho(\text{s}) - \rho(\text{l})}{\rho(\text{l})\rho(\text{s})}$$

$$\frac{dT}{dp} = \frac{T\Delta_{\text{fus}} V}{\Delta_{\text{fus}} H} = \frac{T}{\Delta_{\text{fus}} H} \cdot \frac{\rho(\text{s}) - \rho(\text{l})}{\rho(\text{l})\rho(\text{s})}$$

$$= \left[\frac{80.0 + 273.15}{150.6} \times \left(\frac{1.145 - 0.981}{0.981 \times 1.145} \times 10^{-6} \right) \right] \text{ K} \cdot \text{Pa}^{-1}$$

$$= 0.342 \times 10^{-6} \text{ K} \cdot \text{Pa}^{-1}$$

$$\frac{\Delta T}{\Delta p} \approx \frac{dT}{dp}$$

$$\therefore \Delta T = [0.342 \times 10^{-6} \times (0.1 \times 10^6)] \text{ K} = 0.0342 \text{ K}$$

34. 101325 Pa 下， HgI_2 的红、黄两种晶体的晶型转变温度为 127°C 。已知由红色 HgI_2 转变为黄色 HgI_2 时，转变焓为 $1250 \text{ J} \cdot \text{mol}^{-1}$ ，体积变化为 $-5.4 \text{ cm}^3 \cdot \text{mol}^{-1}$ ，试求压力为 10 MPa 时的晶型转变温度。

解：

$$\frac{dT}{dp} = \frac{T\Delta_{\text{trs}} V}{\Delta_{\text{trs}} H}, \quad \frac{dT}{T} = \frac{\Delta_{\text{trs}} V}{\Delta_{\text{trs}} H} dp$$

$$\ln \frac{T_2}{T_1} \approx \frac{\Delta_{\text{trs}} V}{\Delta_{\text{trs}} H} (p_2 - p_1)$$

$$= \frac{-5.4 \times 10^{-6}}{1250} \times [(10 - 101325 \times 10^{-6}) \times 10^6] = -0.0428$$

$$\frac{T_2}{T_1} = 0.958$$

$$\therefore T_2 = [0.958 \times (127 + 273.15)] \text{ K} = 383 \text{ K}, \quad t_2 = 110^\circ\text{C}$$

35. 在熔点附近的温度范围内, TaBr_5 固体的蒸气压与温度的关系为: $\lg(p^*/\text{Pa}) = 14.696 - 5650/(T/\text{K})$, 液体的蒸气压与温度的关系为: $\lg(p^*/\text{Pa}) = 10.296 - 3265/(T/\text{K})$ 。试求三相点的温度和压力, 并求三相点时的摩尔升华焓、摩尔蒸发焓及摩尔熔化焓。

$$\text{解: } 14.696 - \frac{5650}{T/\text{K}} = 10.296 - \frac{3265}{T/\text{K}}, \quad 4.400 = \frac{2385}{T/\text{K}}$$

$$\therefore T = \left(\frac{2385}{4.400} \right) \text{K} = 542.0 \text{K}$$

$$\lg\left(\frac{p^*}{\text{Pa}}\right) = 10.296 - \frac{3265}{542.0} = 4.272$$

$$p^* = 18.7 \times 10^3 \text{Pa} = 18.7 \text{kPa}$$

对固气平衡

$$\frac{\mathrm{d}\ln(p^*/\text{Pa})}{\mathrm{d}T} = \frac{\Delta_{\text{sub}}H_{\text{m}}}{RT^2} = \frac{\ln 10 \times 5650 \text{K}}{T^2}$$

$$\therefore \Delta_{\text{sub}}H_{\text{m}} = (8.3145 \times \ln 10 \times 5650) \text{J} \cdot \text{mol}^{-1} \\ = 108.17 \times 10^3 \text{J} \cdot \text{mol}^{-1} = 108.17 \text{kJ} \cdot \text{mol}^{-1}$$

对液气平衡

$$\frac{\mathrm{d}\ln(p^*/\text{Pa})}{\mathrm{d}T} = \frac{\Delta_{\text{vap}}H_{\text{m}}}{RT^2} = \frac{(\ln 10) \times 3265 \text{K}}{T^2},$$

$$\therefore \Delta_{\text{vap}}H_{\text{m}} = (8.3145 \times \ln 10 \times 3265) \text{J} \cdot \text{mol}^{-1} \\ = 62.51 \times 10^3 \text{J} \cdot \text{mol}^{-1} = 62.51 \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta_{\text{fus}}H_{\text{m}} = \Delta_{\text{sub}}H_{\text{m}} - \Delta_{\text{vap}}H_{\text{m}} = (108.17 - 62.51) \text{kJ} \cdot \text{mol}^{-1} \\ = 45.66 \text{kJ} \cdot \text{mol}^{-1}$$

36. 方程 $\ln\{p^*\} = -(\Delta_{\text{vap}}H_{\text{m}}/RT) + C$ 是在假设摩尔蒸发焓不随温度而变的条件下导出的。如假设蒸发过程的 $\Delta C_{p,m}$ 是常数, 试导出相应的方程式。此时 $\ln\{p^*\}$ 对 $(1/T)$ 作图是否仍为直线? 如何由所作之图求某一温度下的摩尔蒸发焓?

解:

$$\frac{\mathrm{d}\Delta_{\text{vap}}H_{\text{m}}}{\mathrm{d}T} = \Delta C_{p,m}$$

上式不定积分后得

$$\Delta_{\text{vap}}H_{\text{m}} = \Delta C_{p,m}T + A$$

式中 A 为积分常数。

$$\frac{d\ln\{p^*\}}{dT} = \frac{\Delta_{\text{vap}}H_m}{RT^2} = \frac{\Delta C_{p,m}T + A}{RT^2} = \frac{\Delta C_{p,m}}{R} \cdot \frac{1}{T} + \frac{A}{R} \cdot \frac{1}{T^2}$$

$$\therefore \ln\{p^*\} = \frac{\Delta C_{p,m}}{R} \ln\{T\} - \frac{A}{R} \cdot \frac{1}{T} + C$$

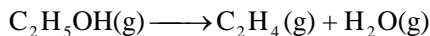
式中 C 为积分常数, 故 $\ln\{p^*\}$ 对 $1/T$ 作图不是直线。

$$\text{式 } \frac{d\ln\{p^*\}}{dT} = \frac{\Delta_{\text{vap}}H_m}{RT^2} \text{ 可写成}$$

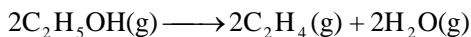
$$\frac{d\ln\{p^*\}}{d(1/T)} = -\frac{\Delta_{\text{vap}}H_m}{R}$$

故 $\ln\{p^*\} - 1/T$ 图中曲线上任一点切线的斜率即为 $-\Delta_{\text{vap}}H_m/R$ 。于是在图中相应于某一温度处作切线, 即可由切线的斜率求得该温度下的摩尔蒸发焓。

37. (1) 乙醇气相脱水制乙烯, 反应为:



试计算 25°C 的 $\Delta_r S_m^\circ$ 。(2) 若将反应写成:



则 25°C 时的 $\Delta_r S_m^\circ$ 又是多少?

解: (1) 由附录查得

物 质	$\text{C}_2\text{H}_5\text{OH}(\text{g})$	$\text{C}_2\text{H}_4(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$S_m^\circ(298.15\text{K})/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	282.70	219.56	188.825

$$\Delta_r S_m^\circ(298.15\text{K}) = [(219.56 + 188.825) - 282.70] \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$= 125.69 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$(2) \Delta_r S_m^\circ(298.15\text{K}) = 2 \times 125.69 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 251.38 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

38. 已知 25°C 时硝基甲烷 $\text{CH}_3\text{NO}_2(\text{l})$ 的标准摩尔熵为 $171.75 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, 摩尔蒸发焓为 $38.36 \text{kJ} \cdot \text{mol}^{-1}$, 饱和蒸气压为 4.887kPa 。求 $\text{CH}_3\text{NO}_2(\text{g})$ 在 25°C 时的标准摩尔熵。设蒸气服从理想气体状态方程。

$$\text{解: } \Delta S_1 = \frac{\Delta_{\text{vap}}H_m}{T} = \left(\frac{38.36 \times 10^3}{298.15} \right) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$= 128.66 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\begin{aligned}\Delta S_2 &= R \ln \frac{p_1}{p_2} = \left(8.3145 \times \ln \frac{4.887}{100} \right) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &= -25.10 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\therefore S_{\text{m}}^{\circ}(\text{g}, 298.15\text{K}) &= S_{\text{m}}^{\circ}(\text{l}, 298.15\text{K}) + \Delta S_1 + \Delta S_2 \\ &= (171.75 + 128.66 - 25.10) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &= 275.31 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

39. 已知 25 °C 时 $\text{C}_2\text{H}_5\text{OH}(\text{g})$ 的标准摩尔生成焓为 $-235.10 \text{kJ} \cdot \text{mol}^{-1}$ ，试利用附录所载的 C 、 H_2 、 O_2 、 $\text{C}_2\text{H}_5\text{OH}(\text{g})$ 的标准摩尔熵，计算 25 °C 时 $\text{C}_2\text{H}_5\text{OH}(\text{g})$ 的标准摩尔生成吉氏函数。

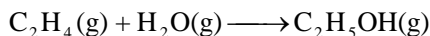
解：

$$\begin{aligned}2\text{C}(\text{s}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) &\longrightarrow \text{C}_2\text{H}_5\text{OH}(\text{g}) \\ \Delta_{\text{r}} S_{\text{m}}^{\circ} &= \sum_{\text{B}} \nu_{\text{B}} S_{\text{m}}^{\circ}(\text{B}) \\ &= \left[282.70 - \left(2 \times 5.740 + 3 \times 130.684 + \frac{1}{2} \times 205.138 \right) \right] \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &= -223.40 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ \Delta_{\text{r}} G_{\text{m}}^{\circ} &= \Delta_{\text{r}} H_{\text{m}}^{\circ} - T \Delta_{\text{r}} S_{\text{m}}^{\circ} \\ &= \left[-235.10 - 298.15 \times (-223.40) \times 10^{-3} \right] \text{kJ} \cdot \text{mol}^{-1} \\ &= -168.49 \text{kJ} \cdot \text{mol}^{-1}\end{aligned}$$

40. 已知 25 °C 时 $\text{H}_2\text{O}(\text{l})$ 的标准摩尔生成吉氏函数为 $-237.129 \text{kJ} \cdot \text{mol}^{-1}$ ，水的饱和蒸气压为 3.167 kPa，求 25 °C 时 $\text{H}_2\text{O}(\text{g})$ 的标准摩尔生成吉氏函数。

$$\begin{aligned}\text{解：} \Delta_{\text{r}} G_{\text{m}}^{\circ}(\text{g}, 298.15\text{K}) &= \Delta_{\text{r}} G_{\text{m}}^{\circ}(\text{l}, 298.15\text{K}) + RT \ln \frac{p_2}{p_1} \\ &= \left[-237.129 + 8.3145 \times 298.15 \times \left(\ln \frac{100}{3.167} \right) \times 10^{-3} \right] \text{kJ} \cdot \text{mol}^{-1} \\ &= -228.57 \text{kJ} \cdot \text{mol}^{-1}\end{aligned}$$

41. 乙烯水化为乙醇的反应为：



各物质 $C_{p,m}^{\circ}$ 的数据如下表所列。试计算 225 °C 时该反应的 $\Delta_{\text{r}} H_{\text{m}}^{\circ}$ 、 $\Delta_{\text{r}} S_{\text{m}}^{\circ}$ 和 $\Delta_{\text{r}} G_{\text{m}}^{\circ}$ 。所需其他数据可查附录。

物 质	$C_{p,m}^{\circ} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
$\text{C}_2\text{H}_5\text{OH}(\text{g})$	$9.04 + 207.9 \times 10^{-3}(T / \text{K})$
$\text{C}_2\text{H}_4(\text{g})$	$8.70 + 130.1 \times 10^{-3}(T / \text{K})$
$\text{H}_2\text{O}(\text{g})$	$31.59 + 5.9 \times 10^{-3}(T / \text{K})$

$$\begin{aligned} \text{解: } \Delta_r H_m^{\circ}(298\text{K}) &= [-235.10 - 52.26 - (-241.818)] \text{kJ} \cdot \text{mol}^{-1} \\ &= -45.54 \text{kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r a &= (9.04 - 8.70 - 31.59) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &= -31.25 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r b &= (207.9 - 130.1 - 5.9) \times 10^{-3} \text{J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1} \\ &= 71.9 \times 10^{-3} \text{J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1} \end{aligned}$$

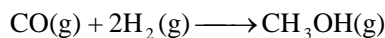
$$\begin{aligned} \Delta_r H_m^{\circ}(498\text{K}) &= \Delta_r H_m^{\circ}(298\text{K}) + \Delta_r a(T_2 - T_1) + \frac{\Delta_r b}{2}(T_2^2 - T_1^2) \\ &= \left\{ -45.54 + \left[(-31.25) \times (498 - 298) + \frac{71.9 \times 10^{-3}}{2} \times (498^2 - 298^2) \right] \right. \\ &\quad \left. \times 10^{-3} \right\} \text{kJ} \cdot \text{mol}^{-1} \\ &= -46.07 \text{kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r S_m^{\circ}(298\text{K}) &= (282.70 - 219.56 - 188.825) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &= -125.68 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r S_m^{\circ}(498\text{K}) &= \Delta_r S_m^{\circ}(298\text{K}) + \Delta_r a \ln \frac{T_2}{T_1} + \Delta_r b(T_2 - T_1) \\ &= \left[-125.68 + (-31.25) \ln \frac{498}{298} + 71.9 \times 10^{-3} (498 - 298) \right] \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &= -127.35 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r G_m^{\circ}(498\text{K}) &= \Delta_r H_m^{\circ}(498\text{K}) - 498\text{K} \cdot \Delta_r S_m^{\circ}(498\text{K}) \\ &= [-46.07 - 498 \times (-127.35) \times 10^{-3}] \text{kJ} \cdot \text{mol}^{-1} \\ &= 17.35 \text{kJ} \cdot \text{mol}^{-1} \end{aligned}$$

42. 求 400°C 时反应

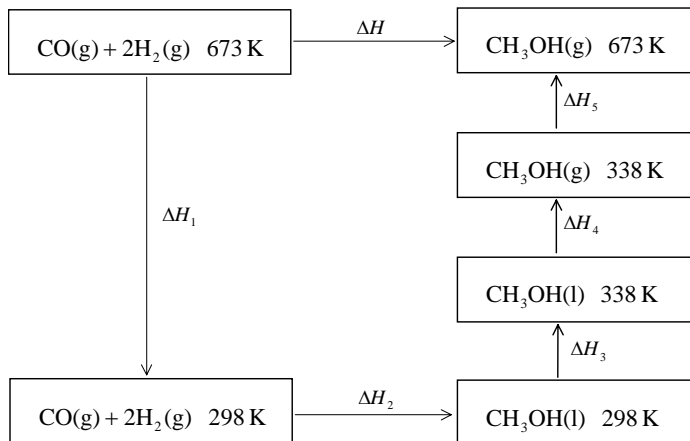


的 $\Delta_r H_m^{\circ}$ 、 $\Delta_r S_m^{\circ}$ 和 $\Delta_r G_m^{\circ}$ 。已知甲醇的正常沸点为 64.7°C，摩尔蒸发焓

为 $35.27 \text{ kJ} \cdot \text{mol}^{-1}$ ，其他所需数据可查附录，并见下表：

物 质	$\Delta_f H_m^\circ(298.15\text{K})/\text{kJ} \cdot \text{mol}^{-1}$	$\bar{C}_{p,m}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
CO(g)	-110.525	30.2 (25~400℃ 范围内)
H ₂ (g)	0	29.3 (25~400℃ 范围内)
CH ₃ OH(l)	-238.66	77.2 (25~64.7℃ 范围内)
CH ₃ OH(g)		59.2 (64.7~400℃ 范围内)

解：



$$\Delta H_1 = [(30.2 + 2 \times 29.3) \times (298 - 673)] \text{ J} \cdot \text{mol}^{-1} = -33.3 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_2 = [-238.66 - (-110.525)] \text{ kJ} \cdot \text{mol}^{-1} = -128.14 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_3 = [77.2 \times (338 - 298)] \text{ J} \cdot \text{mol}^{-1} = 3.09 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_4 = 35.27 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_5 = [59.2 \times (673 - 338)] \text{ J} \cdot \text{mol}^{-1} = 19.8 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\begin{aligned} \therefore \Delta_r H_m^\circ &\approx \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 \\ &= (-33.3 - 128.14 + 3.09 + 35.27 + 19.8) \text{ kJ} \cdot \text{mol}^{-1} \\ &= -103.3 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S_1 &= \left[(1 \times 30.2 + 2 \times 29.3) \ln \frac{298}{673} \right] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &= -72.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S_2 &= (126.8 - 197.674 - 2 \times 130.684) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &= -332.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\Delta S_3 = \left(77.2 \ln \frac{338}{298} \right) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 9.72 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta S_4 = \left(\frac{35.27 \times 10^3}{64.7 + 273.15} \right) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 104.40 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta S_5 = \left(59.2 \ln \frac{673}{338} \right) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 40.8 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

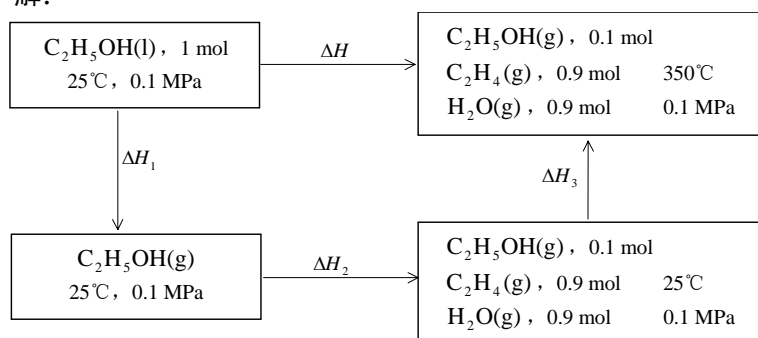
$$\begin{aligned} \Delta_r S_m^\circ(673\text{K}) &= \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 \\ &= (-72.3 - 332.2 + 9.72 + 104.40 + 40.8) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &= -249.6 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r G_m^\circ(673\text{K}) &= \Delta_r H_m^\circ(673\text{K}) - 673\text{K} \cdot \Delta_r S_m^\circ(673\text{K}) \\ &= [-103.3 - 673 \times (-249.6) \times 10^{-3}] \text{kJ} \cdot \text{mol}^{-1} \\ &= 64.7 \text{kJ} \cdot \text{mol}^{-1} \end{aligned}$$

43. 在 0.1 MPa 下, 1 mol 温度为 25°C 的 $\text{C}_2\text{H}_5\text{OH}(\text{l})$ 变为温度为 350°C 的 0.1mol $\text{C}_2\text{H}_5\text{OH}(\text{g})$ 、0.9mol $\text{C}_2\text{H}_4(\text{g})$ 及 0.9mol $\text{H}_2\text{O}(\text{g})$ 的混合物, 试求这个过程的热量。设气体服从理想气体状态方程, 已知数据为:

物 质	$\Delta_f H_m^\circ(298.15\text{K})/\text{kJ} \cdot \text{mol}^{-1}$	$C_{p,m}^\circ/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.69	
$\text{C}_2\text{H}_5\text{OH}(\text{g})$	-235.10	$9.04 + 207.9 \times 10^{-3}(T/\text{K})$
$\text{C}_2\text{H}_4(\text{g})$	52.26	$8.70 + 130.1 \times 10^{-3}(T/\text{K})$
$\text{H}_2\text{O}(\text{g})$	-241.818	$31.59 + 5.9 \times 10^{-3}(T/\text{K})$

解:



$$\Delta H_1 = 1 \times [-235.10 - (-277.69)] \text{kJ} = 42.59 \text{kJ}$$

$$\Delta H_2 = 0.9 \times [52.26 + (-241.818) - (-235.10)] \text{kJ} = 40.99 \text{kJ}$$

$$\begin{aligned}\Delta H_3 &= \int_{298\text{K}}^{623\text{K}} \left\{ 0.9 \times [8.70 + 31.59 + (130.1 + 5.9) \times 10^{-3} (T / \text{K})] \right. \\ &\quad \left. + 0.1 \times [9.04 + 207.9 \times 10^{-3} (T / \text{K})] \right\} \text{J} \cdot \text{K}^{-1} \text{d}T \\ &= \int_{298\text{K}}^{623\text{K}} [37.17 + 143.2 \times 10^{-3} (T / \text{K})] \text{J} \cdot \text{K}^{-1} \text{d}T \\ &= \left[37.17 \times (623 - 298) + \frac{143.2 \times 10^{-3}}{2} \times (623^2 - 298^2) \right] \text{J} \\ &= 33.51 \text{ kJ} \\ \Delta H &= \Delta H_1 + \Delta H_2 + \Delta H_3 = (42.59 + 40.99 + 33.51) \text{ kJ} = 117.09 \text{ kJ}\end{aligned}$$