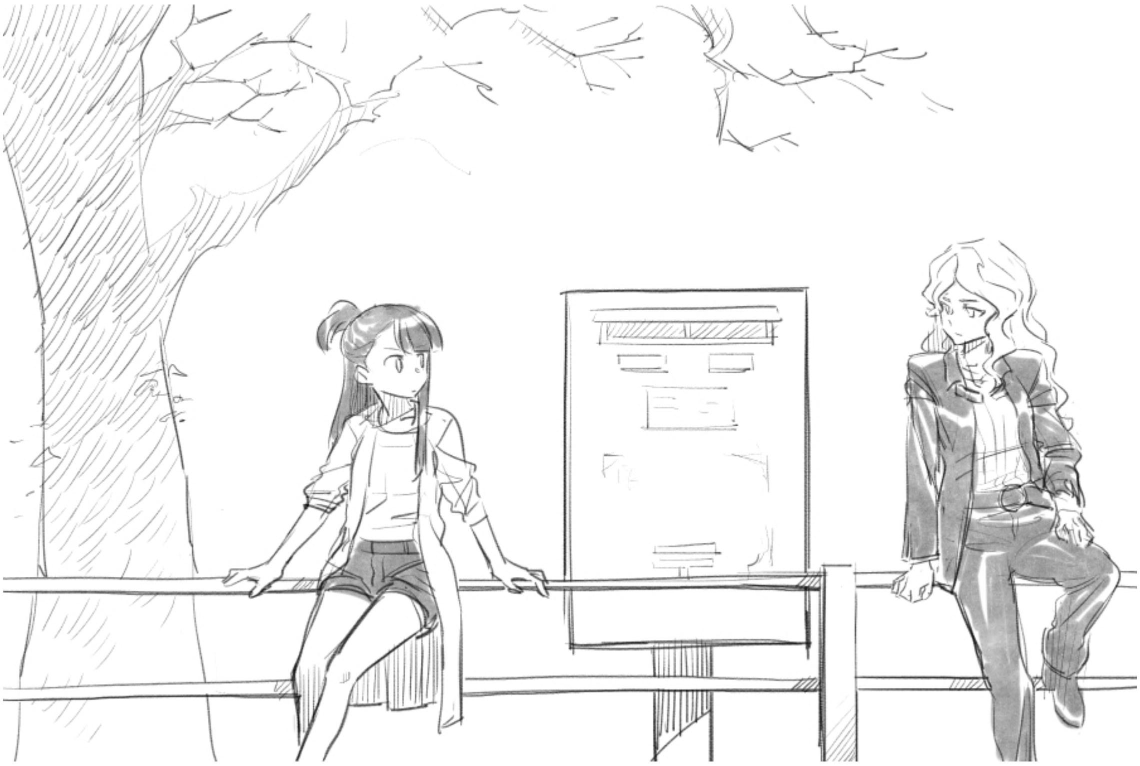

Op.149, No.1

Homework Collection

Walpurgis

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A Believing Heart is Your Magic!

1. 第一周作业

1.

(1)

$$pV = Nk_\mathrm{B}T \implies \tag{1.1.}$$

$$N = \frac{pV}{k_\mathrm{B}T} = 2.687\mathrm{e}+27. \tag{1.2.}$$

(2)

$$\langle v\rangle = \sqrt{\frac{3RT}{M}} = 484.7. \tag{1.3.}$$

(3)

$$n = \frac{p}{k_\mathrm{B}T} = 2.687\mathrm{e}+25, \tag{1.4.}$$

$$\mathit{\Gamma} = \frac{1}{6}n\langle v\rangle = 2.171\mathrm{e}+27. \tag{1.5.}$$

(4)

$$Z = \sqrt{2}\sigma n\langle v\rangle = 7.922\mathrm{e}+9. \tag{1.6.}$$

(5)

$$\lambda = \frac{\langle v\rangle}{Z} = \frac{1}{\sqrt{2}\sigma n} = 6.119\mathrm{e}-8. \tag{1.7.}$$

3.

本题即为求算质子在此环境中的平均自由程, 首先空气分子静止不动, 于是

$$Z = \sigma n\langle v\rangle, \tag{1.8.}$$

其中碰撞截面 σ 应是 $\pi(r_\mathrm{air}+r_\mathrm{proton})$ 而非 πd^2, 考虑不同的两种粒子 A, B, 其相互碰撞的截面应为 $\pi(r_\mathrm{A}+r_\mathrm{B})^2$, 其在 A = B 下退化至 πd^2.
此处质子半径为空气分子半径的小量, 于是

$$\lambda = \frac{\langle v\rangle}{Z} = \frac{1}{n\sigma} = \frac{1}{\frac{p}{k_\mathrm{B}T}\pi r^2}, \tag{1.9.}$$

$$p = \frac{k_\mathrm{B}T}{\lambda\pi r^2} = 5.581\mathrm{e}-7. \tag{1.10.}$$

5.

真空度即为体系压强, 原真空度是小量, 故其粒子数贡献可忽略, 于是

$$N = \frac{pV}{k_\mathrm{B}T} = 1.887\mathrm{e}+18. \tag{1.11.}$$

2.

(1) 考虑物态方程

$$V = V[T, p] \implies \tag{1.12.}$$

$$\mathrm{d}V = \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T \implies \tag{1.13.}$$

$$\frac{\mathrm{d}V}{V} = \alpha\,\mathrm{d}T - \beta\,\mathrm{d}p \implies \tag{1.14.}$$

$$\ln V = \int \alpha\,\mathrm{d}T - \beta\,\mathrm{d}p. \tag{1.15.}$$

(2)

法一:

代入微分表达式:

$$\mathrm{d}V = \alpha V\,\mathrm{d}p - \beta V\,\mathrm{d}p = \frac{nR}{p}\,\mathrm{d}T - (\frac{V}{p} + a)\,\mathrm{d}p, \tag{1.16.}$$

$$p\,\mathrm{d}V + V\,\mathrm{d}p + ap\,\mathrm{d}p - nR\,\mathrm{d}T = 0, \tag{1.17.}$$

$$\mathrm{d}(pV + \frac{a}{2}p^2 - nRT) = 0, \tag{1.18.}$$

$$pV + \frac{a}{2}p^2 = nRT + \mathrm{Const}. \tag{1.19.}$$

对于物质的量密度 $n/V \to 0$ 时,

$$p\frac{V}{n} + \frac{ap^2}{2n} = RT + \mathrm{Const} \tag{1.20.}$$

中等式右侧为有限值, 故 $p \to 0$, 此时 p^2 项为小量, 故

$$pV_\mathrm{m} = RT + \mathrm{Const}, \tag{1.21.}$$

此时其回归理想气体, 故 $\mathrm{Const} = 0$, 此时状态方程变为

$$pV + \frac{a}{2}p^2 = nRT. \tag{1.22.}$$

R 一个纯粹的数学推导如下:

$$pV_\mathrm{m} + \frac{ap^2}{2n} = RT + \frac{\mathrm{Const}}{n}, \tag{1.23.}$$

$$p = \frac{-V_\mathrm{m} + \sqrt{V_\mathrm{m}^2 + \frac{2a}{n}(RT + \frac{\mathrm{Const}}{n})}}{\frac{a}{n}}, \tag{1.24.}$$

$$Z = \frac{pV_\mathrm{m}}{RT} = \frac{\sqrt{\frac{1}{\rho^2} + \frac{2a}{n}(RT + \frac{\mathrm{Const}}{n})} - \frac{1}{\rho}}{a/n}\,\frac{1}{\rho RT}, \tag{1.25.}$$

关于 $\rho = 0$ 处 Taylor 展开:

$$Z = \frac{\mathrm{Const} + nRT}{nRT} - \frac{a(\mathrm{Const} + nRT)^2}{2n^3RT}r^2 + \frac{a^2(\mathrm{Const} + nRT)^3}{2n^5RT}r^4 + O(r^6), \tag{1.26.}$$

于是其在 $\rho \to 0$ 极限下回归理想气体, 即 $\mathrm{Const} = 0$.

法二:

微分方程固然是可以的, 但是在热力学系统, 建议仍使用带有括号的偏导数符号, 学了微分几何后, 你们可以随意不加那个括号.

$$V = V[p, T], \tag{1.27.}$$

$$\begin{cases} \dfrac{\partial V}{\partial T} = \dfrac{nR}{p}, \\ \dfrac{\partial V}{\partial p} = -(a + \dfrac{V}{p}), \end{cases} \tag{1.28.}$$

根据第一个方程:

$$V = \frac{nRT}{p} + f[p], \tag{1.29.}$$

代入第二个方程:

$$-\frac{nRT}{p^2} + \frac{\mathrm{d}f}{\mathrm{d}p} = -(a + \frac{V}{p}) = -(a + \frac{nRT}{p^2} + \frac{f}{p}), \tag{1.30.}$$

$$f + pf' + ap = 0, \tag{1.31.}$$

$$f[p] = -\frac{ap}{2} + \frac{\mathrm{Const}}{p}, \tag{1.32.}$$

之后回归法一.

4.

对于 Ar:

$$N = \frac{m}{M} N_{\mathrm{A}} = 4.974\mathrm{e} + 15, \tag{1.33.}$$

$$p = \frac{\sum N k_{\mathrm{B}} T}{V} = 0.0259. \tag{1.34.}$$

2. 第二周作业

6.

(1)

$$n = \frac{N}{V} = \frac{MNN_A}{MN_AV} = \frac{mN_A}{MV} = 2.002\mathrm{e}+19\ \mathrm{cm}^{-3}. \tag{2.1.}$$

P.S. 根据理想气体状态方程:

$$p = nk_\mathrm{B}T \Longrightarrow n = \frac{p}{k_\mathrm{B}T} = 1.967\mathrm{e}+19\ \mathrm{cm}^{-3}. \tag{2.2.}$$

(2)

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}, \Gamma = \frac{1}{4}n\bar{v} = 3.314\mathrm{e}+27\ \mathrm{s}^{-1}\cdot\mathrm{m}^{-2}. \tag{2.3.}$$

$$\mathit{\Gamma} = \frac{1}{4}n\sqrt{\frac{8k_\mathrm{B}T}{\pi m}} = \frac{1}{4}\frac{p}{k_\mathrm{B}T}\sqrt{\frac{8k_\mathrm{B}T}{\pi m}} = \frac{p}{\sqrt{2\pi mk_\mathrm{B}T}} \tag{2.4.}$$

(3)

$$\Gamma_{-1} = \Gamma = 3.314\mathrm{e}+27\mathrm{s}^{-1}\cdot\mathrm{m}^{-2}. \tag{2.5.}$$

(4)

$$\bar{\epsilon_k} = \frac{3}{2}k_\mathrm{B}T = 7.728\mathrm{e}-21\ \mathrm{J} \tag{2.6.}$$

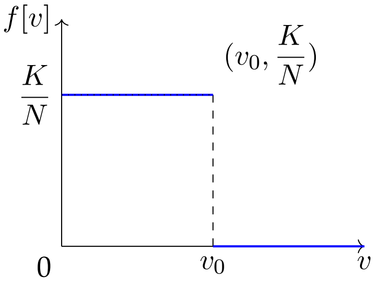
$$\epsilon_\mathrm{vap} = 6.731\mathrm{e}-20\ \mathrm{J} > \bar{\epsilon_k} \tag{2.7.}$$

液态水蒸发过程首先需克服表面能, 变成等体积气态水, 然后做等压可逆膨胀对外做功, 能量降低.

7.

(1)

$$f[v] = \frac{\mathrm{d}N}{N\,\mathrm{d}v} = \begin{cases} \dfrac{K}{N} & , 0 < v < v_0 \\ 0 & , v > v_0 \end{cases} \tag{2.8.}$$



(2)

$$\int f[v]\,\mathrm{d}v = 1 \Longrightarrow \tag{2.9.}$$
$$\frac{K}{N}v_0 = 1, K = \frac{N}{v_0}. \tag{2.10.}$$

(3)

$$\langle v\rangle = \int vf[v]\,\mathrm{d}v = \frac{1}{v_0}\int_0^{v_0} v\,\mathrm{d}v = \frac{v_0}{2}. \tag{2.11.}$$
$$v_{\mathrm{rms}} = \sqrt{\int v^2 f[v]\,\mathrm{d}v} = \frac{v_0}{\sqrt{3}}. \tag{2.12.}$$

8.

$$f[v] = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}\frac{v^2}{\mathrm{e}^{\frac{mv^2}{2kT}}} \tag{2.13.}$$
$$\langle\frac{1}{v}\rangle = \int \frac{1}{v}f[v]\,\mathrm{d}v = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}\int \frac{v}{\mathrm{e}^{\frac{mv^2}{2kT}}}\,\mathrm{d}v = \sqrt{\frac{2m}{\pi kT}}. \tag{2.14.}$$
$$\frac{1}{\langle v\rangle} = \sqrt{\frac{\pi m}{8kT}}. \tag{2.15.}$$

9.

$$f[\epsilon]\,\mathrm{d}\epsilon = f[v]\,\mathrm{d}v \tag{2.16.}$$
$$f[\epsilon]\,\mathrm{d}\left(\frac{1}{2}mv^2\right) = f[v]\,\mathrm{d}v \tag{2.17.}$$
$$f[\epsilon] = \sqrt{\frac{2m}{\pi}}\left(\frac{1}{kT}\right)^{3/2}\frac{v}{\mathrm{e}^{\frac{mv^2}{2kT}}} = \frac{2\sqrt{\epsilon}}{\sqrt{\pi}}\left(\frac{1}{kT}\right)^{3/2}\mathrm{e}^{-\frac{\epsilon}{kT}} \tag{2.18.}$$
$$\frac{\mathrm{d}f[\epsilon]}{\mathrm{d}\epsilon} = 0 \tag{2.19.}$$
$$\epsilon = \frac{kT}{2} \tag{2.20.}$$

10.

$$Z = \mathcal{Z}[p, V_m, T] = \mathcal{Z}[p, V_m[p, T], T] \quad \text{「2.21.」}$$

$$Z = \frac{pV_m}{RT} = \frac{RT + Bp + Cp^2 + \cdots}{RT} = 1 + \frac{Bp + Cp^2 + \cdots}{RT} \quad \text{「2.22.」}$$

$$\left(\frac{\partial Z}{\partial p}\right)_T = \frac{B + 2Cp + o(p^2)}{RT} \quad \text{「2.23.」}$$

$$\lim_{p\to 0}\left(\frac{\partial Z}{\partial p}\right)_T = \frac{B}{RT}. \quad \text{「2.24.」}$$

11.

$$pV_\mathrm{m} = \frac{RTV_\mathrm{m}}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}}, \quad \text{「2.25.」}$$

$$\left(\frac{\partial(pV_\mathrm{m})}{\partial p}\right)_T = \left(\frac{RT(V_\mathrm{m} - b) - RTV_\mathrm{m}}{(V_\mathrm{m} - b)^2} + \frac{a}{V_\mathrm{m}^2}\right)\left(\frac{\partial V_\mathrm{m}}{\partial p}\right)_T, \quad \text{「2.26.」}$$

$$\lim_{p\to 0}\left(\frac{\partial(pV_\mathrm{m})}{\partial p}\right)_T = \lim_{p\to 0}\left(\frac{-bRT}{(V_\mathrm{m} - b)^2} + \frac{a}{V_\mathrm{m}^2}\right)\left(\frac{\partial V_\mathrm{m}}{\partial p}\right)_T = 0 \implies \quad \text{「2.27.」}$$

$$\lim_{p\to 0}\left(\frac{-bRT}{(V_\mathrm{m} - b)^2} + \frac{a}{V_\mathrm{m}^2}\right) = 0, \quad \text{「2.28.」}$$

$$T_\mathrm{B} = \lim_{p\to 0}\frac{a}{bR}(V_\mathrm{m} - b)^2 V_\mathrm{m}^2 = \frac{a}{bR}. \quad \text{「2.29.」}$$

3. 第三周作业

3.

(1)

$$p_1 = 101333, \tag{3.1.}$$
$$\frac{p_1}{T_1} = \frac{p_2}{T_2} \implies \tag{3.2.}$$
$$p_2 = 202666, \tag{3.3.}$$
$$W = 0, \tag{3.4.}$$
$$\Delta U = C_V \Delta T = 3404.8, \tag{3.5.}$$
$$Q = 3404.8. \tag{3.6.}$$

(2)

$$p_2 V_2 = p_3 V_3 \implies \tag{3.7.}$$
$$p_3 = 101333, \tag{3.8.}$$
$$W = \int -p \,\mathrm{d}V = \int -\frac{nRT}{V} \,\mathrm{d}V = -3146.7, \tag{3.9.}$$
$$\Delta U = 0, \tag{3.10.}$$
$$Q = 3146.7. \tag{3.11.}$$

(3)

$$W = -p\Delta V = 2269.9, \tag{3.12.}$$
$$\Delta U = C_V \Delta T = -3404.8, \tag{3.13.}$$
$$Q = -5674.3. \tag{3.14.}$$

5.

(1)

$$\Delta U = 0 \tag{3.15.}$$
$$W = 0 \tag{3.16.}$$
$$Q = 0 \tag{3.17.}$$

(2)

$$\Delta U = 0 \tag{3.18.}$$
$$W = -p\Delta V = -3500 \text{ J} \tag{3.19.}$$
$$Q = 3500 \text{ J} \tag{3.20.}$$

(3)

$$\Delta U = 0 \qquad 「3.21.」$$

$$W = -\int p\,\mathrm{d}V = -\int_{V_1}^{V_2} \frac{nRT}{V}\,\mathrm{d}V = -5965.9\ \mathrm{J} \qquad 「3.22.」$$

$$Q = 5965.9\ \mathrm{J} \qquad 「3.23.」$$

6.

(1)

$$-W = nRT\ln\frac{V_2}{V_1} = p_1V_1\ln\frac{V_2}{V_1} \Longrightarrow \qquad 「3.24.」$$

$$V_1 = 0.08969\ \mathrm{m}^3 \qquad 「3.25.」$$

(2)

$$-W = nRT\ln\frac{V_2}{V_1} \Longrightarrow \qquad 「3.26.」$$

$$T = 1093.0\ \mathrm{K} \qquad 「3.27.」$$

8.

(1)

$$W = p\Delta V = p(V - V_0) = 3019.4\ \mathrm{J} \qquad 「3.28.」$$

(2)

$$W' = pV = 3021.3\ \mathrm{J} \qquad 「3.29.」$$

$$E_W = 0.062\%. \qquad 「3.30.」$$

(3)

$$W = nRT = 3101.1\ \mathrm{J} \qquad 「3.31.」$$

(4)

$$\Delta_{\mathrm{vap}}H_{\mathrm{m}} = 40.69\ \mathrm{kJ\cdot mol^{-1}} \qquad 「3.32.」$$

$$\Delta_{\mathrm{vap}}U_{\mathrm{m}} = \Delta_{\mathrm{vap}}H_{\mathrm{m}} - p\Delta V_{\mathrm{m}} = 37.67\ \mathrm{kJ\cdot mol^{-1}} \qquad 「3.33.」$$

(5) 膨胀过程处对外做功外还有克服内部引力所需能量, 该能量由热量提供.

(6) 该系统初末状态与蒸发焓所需的初末状态相等, 由焓的状态函数特性可知

$$\Delta H = n\Delta_{\mathrm{vap}}H_{\mathrm{m}} = 2258.5\ \mathrm{J} \qquad 「3.34.」$$

$$\Delta U = \Delta H - \Delta(pV) = 2090.9\ \mathrm{J} \qquad 「3.35.」$$

$$W = 0 \qquad 「3.36.」$$

$$Q = \Delta U = 2090.9\ \mathrm{J} \qquad 「3.37.」$$

9.

$$C_{p,\mathrm{m}} = \frac{5}{2}R,\ C_{V,\mathrm{m}} = \frac{3}{2}R \tag{3.38.}$$

(1)

$$\mathrm{d}H = đQ + V\,\mathrm{d}p = đQ_p = C_p\,\mathrm{d}T \implies \tag{3.39.}$$
$$\Delta H = nC_{p,\mathrm{m}}\Delta T = 1039.2\ \mathrm{J} \tag{3.40.}$$
$$\Delta U = nC_{V,\mathrm{m}}\Delta T = 623.6\ \mathrm{J} \tag{3.41.}$$
$$W_1 = -nR\Delta T = -415.7\ \mathrm{J} \tag{3.42.}$$
$$W_2 = -nRT\ln\frac{V_2}{V_1} = -1861.4\ \mathrm{J} \tag{3.43.}$$
$$W = W_1 + W_2 = -2277.1\ \mathrm{J} \tag{3.44.}$$
$$Q = \Delta U - W = 2900.7\ \mathrm{J} \tag{3.45.}$$

(2)

$$\mathrm{d}H = đQ + V\,\mathrm{d}p = đQ_p = C_p\,\mathrm{d}T \implies \tag{3.46.}$$
$$\Delta H = nC_{p,\mathrm{m}}\Delta T = 1039.2\ \mathrm{J} \tag{3.47.}$$
$$\Delta U = nC_{V,\mathrm{m}}\Delta T = 623.6\ \mathrm{J} \tag{3.48.}$$
$$W_1 = -nRT\ln\frac{V_2}{V_1} = 2 - 1573.3\ \mathrm{J} \tag{3.49.}$$
$$W_2 = -nR\Delta T = -415.7\ \mathrm{J} \tag{3.50.}$$
$$W = W_1 + W_2 = -1989.0\ \mathrm{J} \tag{3.51.}$$
$$Q = \Delta U - W = 2612.2\ \mathrm{J} \tag{3.52.}$$

状态函数无关过程, 功不一样画个 $p - V$ 图就行了.

14.

$$(pV = nRT) \wedge (pT = \mathrm{Cosnt}) \implies \tag{3.53.}$$
$$T_1 = 269.4\ \mathrm{K},\ T_2 = 134.7\ \mathrm{K}. \tag{3.54.}$$
$$V_2 = 2.80\ \mathrm{dm}^3 \tag{3.55.}$$
$$\Delta U = C_V\Delta T = -1679.8\ \mathrm{J} \tag{3.56.}$$
$$\Delta H = \Delta U - \Delta(pV) = -2799.7\ \mathrm{J} \tag{3.57.}$$
$$W = -\int p\,\mathrm{d}V = -\int \mathrm{d}(pV) + \int V\,\mathrm{d}p = -\Delta(pV) - \int \frac{V}{T}p\,\mathrm{d}T = -nR\Delta T - nR\Delta T = 2239.7\ \mathrm{J} \tag{3.58.}$$

15.

$$V' = 3.614\text{e} - 3, \quad (3.59.)$$
$$W = -p\Delta V = -61.4. \quad (3.60.)$$
$$\Delta H = \int C_p \, \mathrm{d}T = 209.3. \quad (3.61.)$$
$$Q = \Delta U - W = \Delta H - p\Delta V + p\Delta V = \Delta H = 209.3. \quad (3.62.)$$

17.

$$
\begin{aligned}
(\frac{\partial U}{\partial V})_p &= (\frac{\partial (H - pV)}{\partial V})_p && (3.63.)\\
&= (\frac{\partial H}{\partial V})_p - (\frac{p\partial V + V\partial p}{\partial V})_p && (3.64.)\\
&= \frac{\partial (H,p)}{\partial (V,p)} \frac{\partial (T,p)}{\partial (T,p)} - p && (3.65.)\\
&= C_p(\frac{\partial T}{\partial V})_p - p. && (3.66.)
\end{aligned}
$$

$$
\begin{aligned}
C_p - C_V &= (\partial_T H)_p - (\partial_T U)_V && (3.67.)\\
&= (\partial_T H)_p - (\partial_T (H - pV))_V && (3.68.)\\
&= (\partial_T H)_p - (\partial_T H)_V + V(\partial_T p)_V && (3.69.)\\
&= (\partial_T H)_p - ((\partial_p H)_T(\partial_T p)_V + (\partial_T H)_p(\partial_T T)_v) + V(\partial_T p)_V && (3.70.)\\
&= -(\partial_T p)_V((\partial_p H)_T - V). && (3.71.)
\end{aligned}
$$

20.

$$pV^\gamma = \text{Const} \Longrightarrow \quad (3.72.)$$
$$p_1 = 10^5,\ T_1 = 298,\ V_1 = 0.02478. \quad (3.73.)$$
$$V_2 = 0.005,\ p_2 = 940121,\ T_2 = 565. \quad (3.74.)$$
$$W = \Delta U = C_V \Delta T = 5550. \quad (3.75.)$$

22.

考虑一般情况的任意 δ:

$$pV^\delta = \text{Const},\ pV = nRT. \quad (3.76.)$$
$$p_2 = p_1(V_1/V_2)^\delta = \frac{p_1}{2^\delta} \quad (3.77.)$$

$$T_2 = \frac{T_1}{2^{\delta-1}} \tag{3.78.}$$

$$\Delta U = C_V \Delta T = 3nRT_1(\frac{1}{2^\delta} - \frac{1}{2}). \tag{3.79.}$$

$$\mathrm{d}(pV) = nR\,\mathrm{d}T,\ \mathrm{d}(pV^\delta) = 0 \Longrightarrow \tag{3.80.}$$

$$V\,\mathrm{d}p = -\delta p\,\mathrm{d}V \Longrightarrow \tag{3.81.}$$

$$W = -\int p\,\mathrm{d}V = \int \frac{nR\,\mathrm{d}T}{\delta - 1} = \frac{nR\Delta T}{\delta - 1} = \frac{2nRT_1}{\delta - 1}(\frac{1}{2^\delta} - \frac{1}{2}) \tag{3.82.}$$

$$Q = \Delta U - W = (3 - \frac{2}{\delta - 1})nRT_1(\frac{1}{2^\delta} - \frac{1}{2}) \tag{3.83.}$$

(1)

$$\delta = 1 \tag{3.84.}$$

$$\Delta U = 0 \tag{3.85.}$$

$$W = \lim_{\delta \to 1} \frac{2nRT_1}{\delta - 1}(\frac{1}{2^\delta} - \frac{1}{2}) = nRT_1 \lim_{\delta \to 1} \frac{1 - 2^{\delta-1}}{\delta - 1} = nRT_1 \ln 2 = -1717.3 \tag{3.86.}$$

$$Q = -W = 1717.3 \tag{3.87.}$$

(2)

$$\delta = 5/3 \tag{3.88.}$$

$$\Delta U = -1375.2 \tag{3.89.}$$

$$W = -1375.2 \tag{3.90.}$$

$$Q = 0 \tag{3.91.}$$

(3)

$$\delta = 1.3 \tag{3.92.}$$

$$\Delta U = -697.7 \tag{3.93.}$$

$$W = -1550.5 \tag{3.94.}$$

$$Q = 852.8 \tag{3.95.}$$

(4) 考虑 SI 单位制, 则

$$p = 10^7 V/n + b = 10^7 V + b \tag{3.96.}$$

$$\mathrm{d}p = 10^7\,\mathrm{d}V \tag{3.97.}$$

$$\Delta V = V_1 = 0.01239 \tag{3.98.}$$

$$\Delta p = 123878.6,\ p_2 = 323878.6 \tag{3.99.}$$

$$b = 76100 \tag{3.100.}$$

$$T_1 = 298,\ T_2 = 965 \tag{3.101.}$$

$$\Delta U = C_V \Delta T = 8322.2 \tag{3.102.}$$

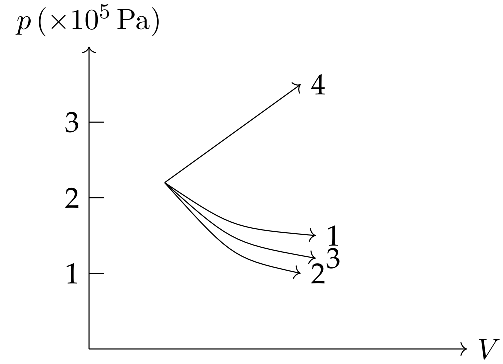
$$\mathrm{d}(10^7V^2 + bV) = (2p - b)\,\mathrm{d}V = nR\,\mathrm{d}T \Longrightarrow \tag{3.103.}$$

$$-\,p\,\mathrm{d}V = -\frac{1}{2}(nR\,\mathrm{d}T + b\,\mathrm{d}V) \Longrightarrow \tag{3.104.}$$

$$W = -\int p\,\mathrm{d}V = -\frac{1}{2}(nR\Delta T + b\Delta V) = -3244.2 \tag{3.105.}$$

$$Q = \Delta U - W = 11566.4 \tag{3.106.}$$

图随便画的, 仅作定性参考:



「3.107.」

顺序:

$$|W_2| < |W_3| < |W_1| < |W_4|, \tag{3.108.}$$

$$\Delta U_2 < \Delta U_3 < \Delta U_1 < \Delta U_4. \tag{3.109.}$$

4. 第四周作业

18.

$$\mu_{\mathrm{J-T}} = -\frac{V}{C_p}(\beta C_V \mu_{\mathrm{J}} - \beta p + 1) \iff \tag{4.1.}$$

$$-\partial_H T_p \partial_p H_T = -\frac{1}{\partial_T H_p}(-\partial_p V_T \partial_T U_V \partial_V T_U + p\partial_p V_T + V) \iff \tag{4.2.}$$

$$\partial_p H_T = -\partial_p V_T \partial_T U_V \partial_V T_U + p\partial_p V_T + V \iff \tag{4.3.}$$

$$\partial_p (U + pV)_T = \partial_p U_T + p\partial_p V_T + V \iff \tag{4.4.}$$

$$\partial_p U_T + p\partial_p V_T + V = \partial_p U_T + p\partial_p V_T + V. \tag{4.5.}$$

23.

(1)

$$\begin{aligned}
\mu_{\mathrm{J}} &= \partial_V T_U && (4.6.)\\
&= -\partial_V U_T \partial_U T_V && (4.7.)\\
&= -\frac{1}{C_V}\partial_V U_T && (4.8.)\\
&= -\frac{1}{C_V}(\partial_V U_S \partial_V V_T + \partial_S U_V \partial_V S_T) && (4.9.)\\
&= -\frac{1}{C_V}(-p + T\partial_T p_V) && (4.10.)
\end{aligned}$$

$$pV = nRT + bnp \implies \tag{4.11.}$$

$$\mu_{\mathrm{J}} = 0. \tag{4.12.}$$

故温度不变. (2)

$$\begin{aligned}
\mu_{\mathrm{J-K}} &= \partial_p T_H && (4.13.)\\
&= -\partial_p H_T \partial_H T_p && (4.14.)\\
&= -\frac{1}{C_p}\partial_p H_T && (4.15.)\\
&= -\frac{1}{C_p}(V + T\partial_p S_T) && (4.16.)\\
&= \frac{1}{C_p}(T\partial_T V_p - V) && (4.17.)
\end{aligned}$$

$$pV = nRT + bnp \implies \tag{4.18.}$$

$$\mu_{\mathrm{J-K}} = -\frac{bn}{C_p} < 0. \tag{4.19.}$$

故温度上升.

24.

$$
\begin{aligned}
\eta &= \frac{\text{给办公室的热量}}{\text{热源燃烧的热量}} && \text{「4.20.」} \\
&= \frac{\text{给办公室的热量}}{\text{热机对热泵所做的功}}\frac{\text{热机对热泵所做的功}}{\text{热源燃烧的热量}} && \text{「4.21.」} \\
&= \frac{293.15}{293.15-283.15}\frac{1273.15-293.15}{1273.15} && \text{「4.22.」} \\
&= 22.565 && \text{「4.23.」}
\end{aligned}
$$

25.

$$
\begin{aligned}
\eta &= \frac{T_c}{T_h-T_c} = 10.92 && \text{「4.24.」} \\
W &= \frac{333.5\mathrm{e}+3\cdot 1}{10.92} = 30540\ \mathrm{J} && \text{「4.25.」}
\end{aligned}
$$

37.

(1)

1→2

$$
\begin{aligned}
W &= \int -p\,\mathrm{d}V = -nRT_1\ln(V_2/V_1) && \text{「4.26.」} \\
Q &= nRT_1\ln(V_2/V_1) && \text{「4.27.」}
\end{aligned}
$$

$2 \to 3$

$$
\begin{aligned}
W &= C_V(T_2-T_1) && \text{「4.28.」} \\
Q &= 0 && \text{「4.29.」}
\end{aligned}
$$

$3 \to 4$

$$
\begin{aligned}
W &= \int -p\,\mathrm{d}V = -nRT_2\ln(V_4/V_3) && \text{「4.30.」} \\
Q &= nRT_2\ln(V_4/V_3) && \text{「4.31.」}
\end{aligned}
$$

$4 \to 1$

$$
\begin{aligned}
W &= C_V(T_1-T_2) && \text{「4.32.」} \\
Q &= 0 && \text{「4.33.」}
\end{aligned}
$$

loop:

$$
\begin{aligned}
W &= -nRT_1\ln(V_2/V_1) - nRT_2\ln(V_4/V_3) = nR(T_1-T_2)\ln\frac{V_1}{V_2} && \text{「4.34.」} \\
Q &= nR(T_2-T_1)\ln\frac{V_1}{V_2} && \text{「4.35.」}
\end{aligned}
$$

(2) 假设 $C_p - C_V = nR$, 则

$$\gamma = C_p/C_V = 1.396 \tag{4.36.}$$

$$pV^\gamma = \mathrm{Const},\ pV = nRT \Longrightarrow \tag{4.37.}$$

$$p_3 = p_2(T_1/T_2)^{\frac{\gamma}{1-\gamma}} = 22318 \tag{4.38.}$$

$$p_4 = p_1(T_1/T_2)^{\frac{\gamma}{1-\gamma}} = 223184 \tag{4.39.}$$

$$W = nR(T_1 - T_2)\ln\frac{V_1}{V_2} = nR(T_1 - T_2)\ln\frac{p_2}{p_1} = -3828.7 \tag{4.40.}$$

$$Q = 3828.7. \tag{4.41.}$$

4.

(1)

$$W = -p\Delta V = -RT\Delta n = -2419\ \mathrm{J} \tag{4.42.}$$

$$\Delta U = W + Q = -154419\ \mathrm{J} \tag{4.43.}$$

$$\Delta H = \Delta U + RT\Delta n = -152000\ \mathrm{J} \tag{4.44.}$$

(2)
考虑密封状态到开口状态, 等温膨胀对外做功, 则吸热.
故密闭容器放热较多, 差值是体积功 W.

27.

(1)

$$\Delta_\mathrm{r} H_\mathrm{m}^\ominus = -110.53 - -241.82 = 131.29 \tag{4.45.}$$

(2) 碳与水蒸气吸热量等于碳与氧气放热量, 设空气中氧气占比 21%, 体积比为 k:

$$131.29k = 2 \times 110.53 \times 21\% \times (1 - 20\%) \Longrightarrow \tag{4.46.}$$

$$k = 0.2829. \tag{4.47.}$$

31.

$$607 + 4 \times 413 + 2 \times 463 - (348 + 5 \times 413 + 351 + 463) = -42, \tag{4.48.}$$

$$-42 - 42 = -84. \tag{4.49.}$$

33.

$$p_1V_1^\gamma = p_2V_2^\gamma \tag{4.50.}$$
$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \tag{4.51.}$$
$$\gamma = \frac{\ln(T_2/T_1)}{\ln(V_1/V_2)} + 1 = 1.4008 = \frac{C_{V,\mathrm{m}}+R}{C_{V,\mathrm{m}}} \Longrightarrow \tag{4.52.}$$
$$C_{V,\mathrm{m}} = \frac{5}{2}R. \tag{4.53.}$$

这是双原子分子, 故为氮气.

35.

$$\mathrm{C_2H_2} + \frac{5}{2}\mathrm{O_2} \to 2\,\mathrm{CO_2} + \mathrm{H_2O} \tag{4.54.}$$
$$\Delta H_\mathrm{m} = -1256240 \tag{4.55.}$$

此时剩余气体:

$$\mathrm{N_2} : \frac{5}{2} \times \frac{1-20\%}{20\%} = 10. \tag{4.56.}$$
$$\mathrm{CO_2} : 2 \tag{4.57.}$$
$$\mathrm{H_2O} : 1 \tag{4.58.}$$
$$\Delta T = \frac{Q}{C_p} = 3148.5 \tag{4.59.}$$
$$T = 3446.5. \tag{4.60.}$$

36.

(1)

$$\Delta H_\mathrm{m}^\ominus = 2\times -277.6 - -393.51 - 3\times(-393.51 + 2\times -285.83 - -891) = 60.82 \tag{4.61.}$$
$$\Delta U_\mathrm{m}^\ominus = \Delta H_\mathrm{m}^\ominus - \Delta zRT = 70.73. \tag{4.62.}$$

(2)

$$\Delta(\Delta H) = \int_{298}^{173} \Delta C_p \,\mathrm{d}T = -10048.75. \tag{4.63.}$$

5. 第五周作业

PPT 反证法

考虑如下三步:
1. 从一高温热源取出 $Q_{\rm h}$, 全部转化为做功 W;
2. 这些功作用在一定倒开的 Carnot 热机上, 即从低温热源吸热 $Q_{\rm l}$, 经过功 W, 给予高温热源热 $Q'_{\rm h}$;
3. 考虑总的热效应: 低温热源给出热量 $Q_{\rm l}$, 高温热源获得热量 $Q'_{\rm h} - Q_{\rm h} = Q'_{\rm h} - W = Q_{\rm l}$, 即违背了 Clausius 表述.

复习题 4

(1) 等温可逆膨胀. (2) 中间连个可逆热机 (或者无数个温差无穷小的物体). (3) 等温降压至 p_s, 可逆相变, 再等温压缩. (4) 这随便设计, 先等压可逆到等温线, 再等温可逆. 无数条.

习题 1

(1) 显然温差大者效率高.
(2)

$$\eta = 1 - \frac{T_{\rm l}}{T_{\rm h}} = \frac{W}{Q_{\rm h}} \tag{5.1.}$$

$$p^{\ominus} : Q_{\rm h} = 6219 \tag{5.2.}$$

$$50p^{\ominus} : Q_{\rm h} = 2392 \tag{5.3.}$$

(3) 显然低温热源降低 t 的效果等价于高温热源升高大于 t 的某个温度, 故降低的影响更大.(求个偏导比一下也可以)

6. 第六周作业

2.

先求出绝热可逆压缩后的状态:

$$\gamma = \frac{3.5}{2.5} = 7/5 \tag{6.1.}$$

$$p_1 = 100000,\ T_1 = 300,\ V_1 = 0.049884 \tag{6.2.}$$

$$p_2 = 300000,\ V_2 = 0.022759,\ T_2 = 410.6 \tag{6.3.}$$

$$Q_1 = 0 \tag{6.4.}$$

$$W_1 = \int \frac{nR\,\mathrm{d}T}{\gamma - 1} = 4597.6 \tag{6.5.}$$

$$\Delta U_1 = 4597.6 \tag{6.6.}$$

$$\Delta H_1 = 6436.7 \tag{6.7.}$$

$$\Delta S_1 = 0 \tag{6.8.}$$

真空膨胀除了熵啥也不变, 故上述就是整个过程的, 对于熵, 设计等温可逆膨胀:

$$\Delta S_2 = nR\ln\frac{V_2}{V_1} = 18.27 \tag{6.9.}$$

$$\Delta S = 18.27. \tag{6.10.}$$

3.

初状态:

$$p_1 = 100000,\ T_1 = 273,\ V_1 = 0.22697. \tag{6.11.}$$

末状态:

$$p_3 = 1000000,\ T_3 = 398,\ V_3 = 0.033090. \tag{6.12.}$$

(1) 先绝热可逆至 $p_2 = 1000\ \mathrm{kPa}$, 此时

$$V_2 = V_1(\frac{p_1}{p_2})^{1/\gamma} = 0.057012 \tag{6.13.}$$

$$T_2 = \frac{p_2V_2}{nR} = 685.7 \tag{6.14.}$$

$$\Delta S = 0. \tag{6.15.}$$

再等压可逆压缩

$$\Delta S = \int \mathrm{d}S = \frac{đQ}{T} = \frac{C_p\,\mathrm{d}T}{T} = nC_{p,\mathrm{m}}\ln\frac{T_3}{T_2} = -113.07. \tag{6.16.}$$

(2) 先等温

$$V_2 = V_1 \frac{p_1}{p_2} = 0.022697 \tag{6.17.}$$

$$\Delta S_1 = \frac{Q}{T} = nR \ln \frac{V_2}{V_1} = -191.44 \tag{6.18.}$$

再等压

$$\Delta S_2 = nC_{p,\mathrm{m}} \ln \frac{T_3}{T_2} = 78.36 \tag{6.19.}$$

$$\Delta S = -113.08. \tag{6.20.}$$

(3) 先等容

$$T_2 = T_1 \frac{p_2}{p_1} = 2730 \tag{6.21.}$$

$$\Delta S_1 = nC_{V,\mathrm{m}} \ln \frac{T_2}{T_1} = 287.16 \tag{6.22.}$$

再等压

$$\Delta S_2 = nC_{p,\mathrm{m}} \ln \frac{T_3}{T_2} = -400.24 \tag{6.23.}$$

$$\Delta S = -113.08. \tag{6.24.}$$

如果算得准, 可逆过程的熵变与路径无关.

4.

设最终温度为 T :

$$Q = 0.50 \times 4184 \times (353 - T) \tag{6.25.}$$

$$Q = 0.1 \times 333000 + 0.1 \times 2067 \times (273 - 263) + 0.1 \times 4154 \times (T - 273) \implies \tag{6.26.}$$

$$T = 325.6. \tag{6.27.}$$

根据常见的情况, 我们认为这是一个等压的环境.

$$\Delta S = 0.10 \times 2067 \times \ln \frac{273}{263} + \frac{333000 \times 0.1}{273} + 0.10 \times 4184 \times \ln \frac{325.6}{273} + 0.50 \times 4184 \times \ln \frac{325.6}{353} \tag{6.28.}$$

$$= 34.38. \tag{6.29.}$$

6.

先分别膨至整个容器, 该过程可看作等温可逆膨胀或者绝热真空膨胀, 二者末状态及熵变无区别:

$$V_{\mathrm{Ar},1} = 0.024942 \tag{6.30.}$$

$$V_{\mathrm{N_2},1} = 0.033256 \tag{6.31.}$$

$$V_2 = 0.058198 \tag{6.32.}$$

$$\Delta S_1 = 1 \times 8.314 \times \ln \frac{0.058198}{0.024942} + 2 \times 8.314 \times \ln \frac{0.058198}{0.033256} = 16.35 \tag{6.33.}$$

再进行温度交换, 设平衡温度为 T :

$$Q = C_{V,\mathrm{Ar}}(T - 300) = C_{V,\mathrm{N_2}}(400 - T) \Longrightarrow \tag{6.34.}$$

$$T = 376.9 \tag{6.35.}$$

$$\Delta S_2 = C_V \ln \frac{T_2}{T_1} = 0.37 \tag{6.36.}$$

$$\Delta S = 16.72. \tag{6.37.}$$

10.

这得看啥叫 “可逆”.
若为可实现时间反演变换者, 这就没法计算: 时间无限长的热传导就是准静态, 但是题里不知道.
若为等熵过程, 那不绝热的可逆就肯定不是等熵过程.

$$\Delta S = \int \frac{đQ}{T} = \frac{10}{3}. \tag{6.38.}$$

5.

(1)

$$V_{\mathrm{O_2}} = 0.024776 \tag{6.39.}$$

$$V_{\mathrm{N_2}} = 0.024776 \tag{6.40.}$$

$$V = 0.049551 \tag{6.41.}$$

$$p = 50000. \tag{6.42.}$$

(2)

$$\Delta U = 0,\ Q = 0,\ W = 0 \tag{6.43.}$$

$$\Delta S = nR \ln \frac{V_2}{V_1} = 5.763 \tag{6.44.}$$

$$\Delta G = -T\Delta S = -1717.3 \tag{6.45.}$$

(3)

$$Q = -T\Delta S = -1717.3 \tag{6.46.}$$

$$W = 1717.3. \tag{6.47.}$$

11.

先等压可逆升温:

$$\Delta S_1 = \int \frac{\mathrm{d}H}{T} = C_p \ln \frac{T_2}{T_1} = 2.810 \tag{6.48.}$$

然后可逆相变:

$$\Delta S_2 = \Delta H/T = -22.015 \tag{6.49.}$$

然后等压可逆降温:

$$\Delta S_3 = -1.407 \tag{6.50.}$$

整个过程:

$$\Delta S = -20.60 \tag{6.51.}$$

有温度差的传热, 则不等熵.

13.

$$T_1 = 298,\ p_1 = 100000,\ V_1 = 0.024776,\ \gamma = 7/5 \tag{6.52.}$$

$$p_2 = 600000,\ V_2 = 6.8898\mathrm{e}-3.\ T_2 = 497.2 \tag{6.53.}$$

$$Q = 0,\ \Delta S = \Delta S_{\mathrm{iso}} = 0. \tag{6.54.}$$

$$W = \int \frac{nR\,\mathrm{d}T}{\gamma - 1} = 4140.4,\ \Delta U = 4140.4,\ \Delta H = 5796.5,\ \Delta A = -36723.3,\ \Delta G = -35067.4. \tag{6.55.}$$

$$V_3 = 0.005,\ p_3 = 939909,\ T_3 = 565.3 \tag{6.56.}$$

$$Q = 0,\ \Delta S = 0. \tag{6.57.}$$

$$W = \int \frac{nR\,\mathrm{d}T}{\gamma - 1} = 5555.8,\ \Delta U = 5555.8,\ \Delta H = 7778.2. \tag{6.58.}$$

14.

$$T_1 = 100,\ V_1 = 0.0041,\ p_1 = 202780 \tag{6.59.}$$

$$T_2 = 600,\ V_2 = 0.0492,\ p_2 = 101390. \tag{6.60.}$$

系统熵变:

$$\mathrm{d}S = \frac{\mathrm{d}U}{T} + \frac{p}{T}\,\mathrm{d}V \Longrightarrow \tag{6.61.}$$

$$\Delta S_1 = \int \frac{C_V\,\mathrm{d}T}{T} + \int \frac{nR\,\mathrm{d}V}{V} = 37.12 + 20.66 = 57.78. \tag{6.62.}$$

环境熵变:

$$\mathrm{d}S = \frac{\mathrm{d}U}{T} + \frac{p}{T}\,\mathrm{d}V \Longrightarrow \tag{6.63.}$$

$$\Delta S_2 = \int -\frac{C_V\,\mathrm{d}T}{T} + \frac{p_{\mathrm{sur}}}{T_{\mathrm{sur}}}\Delta V_{\mathrm{sur}} = -17.29 - 7.616 = -24.91. \tag{6.64.}$$

宇宙熵变:

$$\Delta S = 32.87. \tag{6.65.}$$

16.

(1)

$$\Delta S = \frac{\Delta Q_{\mathrm{rev}}}{T} = 13.42. \tag{6.66.}$$

(2)

$$\Delta S_{\mathrm{sys}} = 13.42. \tag{6.67.}$$

$$\Delta S_{\mathrm{sur}} = \int \frac{1}{T}(\mathrm{d}U_{\mathrm{sur}} + p_{\mathrm{sur}}\,\mathrm{d}V_{\mathrm{sur}}) = \frac{1}{T}(-\Delta H_p) = \frac{-Q}{T} = 134.23. \tag{6.68.}$$

$$\Delta S = 147.65. \tag{6.69.}$$

隔离系统总熵变只能增加.

(3) 系统做的有用功需要去掉膨胀做的体积功:

$$\text{đ}W = \text{đ}W' - p_{\mathrm{e}}\,\mathrm{d}V = \mathrm{d}U - \text{đ}Q \geqslant \mathrm{d}U - T\,\mathrm{d}S \tag{6.70.}$$

$$\text{đ}W' \geqslant \mathrm{d}U - T\,\mathrm{d}S + p\,\mathrm{d}V = \mu\,\mathrm{d}N = \mathrm{d}G \tag{6.71.}$$

$$W' = \Delta G = \Delta H - T\Delta S = Q - Q_{\mathrm{rev}} = -44000. \tag{6.72.}$$

7. 第七周作业

8.

$$\Delta G = 237190 \quad \text{「7.1.」}$$

$$Q = UIt = UC = 424534 \quad \text{「7.2.」}$$

$$\Delta H = 285534 \quad \text{「7.3.」}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = 162.15 \quad \text{「7.4.」}$$

12.

$$(100000, 0.0248, 298) \mapsto (600000, 0.00413, 298) \quad \text{「7.5.」}$$

(1)

$$W = \int -p\,\mathrm{d}V = -nRT \ln \frac{V_2}{V_1} = 4439 \quad \text{「7.6.」}$$

$$Q = -4439,\ \Delta U = 0,\ \Delta H = 0 \quad \text{「7.7.」}$$

$$\Delta S = \int \frac{C_V\,\mathrm{d}T}{T} + \frac{nR\,\mathrm{d}V}{V} = -14.9 \quad \text{「7.8.」}$$

$$\Delta S_{\mathrm{sur}} = 14.9 \quad \text{「7.9.」}$$

$$\Delta A = \Delta U - T\Delta S = 4439 \quad \text{「7.10.」}$$

$$\Delta G = \Delta H - T\Delta S = 4439. \quad \text{「7.11.」}$$

(2)

$$W = -p_{\mathrm{e}}\Delta V = 12402 \quad \text{「7.12.」}$$

$$Q = -12402,\ \Delta U = 0,\ \Delta H = 0 \quad \text{「7.13.」}$$

$$\Delta S = -14.9 \quad \text{「7.14.」}$$

$$\Delta S_{\mathrm{sur}} = 41.6 \quad \text{「7.15.」}$$

$$\Delta A = 4439 \quad \text{「7.16.」}$$

$$\Delta G = 4439. \quad \text{「7.17.」}$$

15.

(1)

$$Q = \Delta H_p = 30770 \quad \text{「7.18.」}$$

$$W = -p\Delta V \sim -pV = -2935 \tag{7.19.}$$
$$\Delta U = 27835 \tag{7.20.}$$
$$\Delta H = 30770 \tag{7.21.}$$
$$\Delta S = \Delta H/T = 87.2 \tag{7.22.}$$
$$\Delta A = -2935 \tag{7.23.}$$
$$\Delta G = 0. \tag{7.24.}$$

(2)

$$W = 0 \tag{7.25.}$$
$$Q = \Delta U = 27835 \tag{7.26.}$$
$$\Delta S = \frac{\Delta U}{T} + \frac{p\Delta V}{T} = 87.2 \tag{7.27.}$$
$$\Delta G = 0. \tag{7.28.}$$
$$\Delta S_{\mathrm{sur}} = -\frac{\Delta U}{T} = -78.9 \tag{7.29.}$$

这不是准静态的, 不可能等熵.

18.

$$\Delta H = -46020 \tag{7.30.}$$
$$\Delta G = \int (S\,\mathrm{d}T + V\,\mathrm{d}p) = \int V\,\mathrm{d}p = \int \frac{nRT}{p}\,\mathrm{d}p + \int \frac{m}{\rho}\,\mathrm{d}p = -2150 \tag{7.31.}$$
$$\Delta S = \int \frac{\mathrm{d}H - V\,\mathrm{d}p}{T} = \frac{\Delta H - \Delta G}{T} = -117.6 \tag{7.32.}$$

26.

$$\mathrm{LHS} = \frac{-pV}{T} = -nR. \tag{7.33.}$$

32.

$$\Delta G = \int -S\,\mathrm{d}T + \int V\,\mathrm{d}p = \int \frac{nRT\,\mathrm{d}p}{p} = -64.27. \tag{7.34.}$$

8. 第八周作业

7.

$$(p+\frac{a}{V_{\mathrm{m}}^2})(V_{\mathrm{m}}-b)=RT \tag{8.1.}$$

$$\mathrm{d}S=\frac{\mathrm{d}U}{T}+\frac{p\,\mathrm{d}V}{T}=\frac{C_V\,\mathrm{d}T+\partial_V U_T\,\mathrm{d}V+p\,\mathrm{d}V}{T}=\frac{C_V\,\mathrm{d}T+T\partial_T p_V\,\mathrm{d}V}{T} \tag{8.2.}$$

$$C_V=g+hT,\ \partial_T p_V=\frac{R}{V_{\mathrm{m}}-b} \tag{8.3.}$$

$$\Delta S=\int_{T_1}^{T_2}(g+hT)\,\mathrm{d}T+\int_{V_1}^{V_2}\frac{R\,\mathrm{d}V}{V_{\mathrm{m}}-b}. \tag{8.4.}$$

9.

$$V_1=2.887\mathrm{e}-4,\ V_2=0.02689 \tag{8.5.}$$

$$W=p_1V_1-p_2V_2=198? \tag{8.6.}$$

$$\partial_V U_T=0 \tag{8.7.}$$

$$\mathrm{d}U=C_T\,\mathrm{d}T=0,\ \Delta U=0 \tag{8.8.}$$

$$W=-Q=202, \tag{8.9.}$$

$$\Delta H=\Delta U+\Delta(pV)=-198 \tag{8.10.}$$

$$\Delta S=\int\frac{\mathrm{d}U+p\,\mathrm{d}V}{T}=\int_{V_1}^{V_2}\frac{R}{V_{\mathrm{m}}-b}\,\mathrm{d}V=38.29. \tag{8.11.}$$

20.

(1)

$$\Delta_{\mathrm{trs}}H_{\mathrm{m}}^{\ominus}=395.40-393.51=1890 \tag{8.12.}$$

$$\Delta_{\mathrm{trs}}S_{\mathrm{m}}^{\ominus}=-3.363 \tag{8.13.}$$

$$\Delta_{\mathrm{trs}}G_{\mathrm{m}}^{\ominus}=2892.174 \tag{8.14.}$$

(2) 显然石墨更稳定.

(3) 考虑自由能变的微分:

$$\mathrm{d}\Delta G=\Delta V\,\mathrm{d}p \tag{8.15.}$$

$$\int_{2892}^{0}\mathrm{d}\Delta G=\int_{100000}^{p}\Delta V\,\mathrm{d}p,\ \Delta V=\frac{m}{\rho_2}-\frac{m}{\rho_1} \tag{8.16.}$$

$$p=148878994 \tag{8.17.}$$

24.

(1)

$$
\begin{aligned}
C_p - C_V &= \partial_T H_p - \partial_T U_V && 「8.18.」\\
&= T\partial_T S_p - T\partial_T S_V && 「8.19.」\\
&= T(\partial_T T_p \partial_T S_V + \partial_T V_p \partial_V S_T - \partial_T S_V) && 「8.20.」\\
&= T(\partial_T V_p \partial_T p_V) && 「8.21.」\\
&= T\frac{\partial(V,p)}{\partial(T,p)}\frac{\partial(V,p)}{\partial(T,p)}\frac{\partial(p,T)}{\partial(v,T)} && 「8.22.」\\
&= \frac{VT\alpha^2}{\beta}. && 「8.23.」
\end{aligned}
$$

(2)

$$
\begin{aligned}
\partial_p U_T = -\alpha TV + pV\beta \iff && 「8.24.」\\
T\partial_p S_T - p\partial_p V_T = -T\partial_T V_p - p\partial_p V_T \iff && 「8.25.」\\
-T\partial_T V_p - p\partial_p V_T = -T\partial_T V_p - p\partial_p V_T. && 「8.26.」
\end{aligned}
$$

28.

$$
\begin{aligned}
&\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p && 「8.27.」\\
&\mathrm{d}S = \frac{\mathrm{d}H}{T} = \frac{C_p\,\mathrm{d}T}{T} && 「8.28.」\\
&\Delta S = \int_{298}^{387} 54.68\,\mathrm{d}\ln T + \frac{15660}{387} + \int_{387}^{457} 79.59\,\mathrm{d}\ln T + \frac{25520}{457} = 123.83 && 「8.29.」\\
&S_{\mathrm{m}}^{\ominus} = 239.97. && 「8.30.」
\end{aligned}
$$

34.

$$
\begin{aligned}
&p_1 = 10^{9.93177 - \frac{1680.745}{1.53+273.15-45.41}} = 398.95 && 「8.31.」\\
&p_2 = 10^{9.93177 - \frac{1680.745}{25+273.15-45.41}} = 1912.82 && 「8.32.」
\end{aligned}
$$

$$
\begin{aligned}
\Delta S &= \frac{12657}{1.53+273.15} + \int_{1.53+273.15}^{25+273.15} \frac{C_p\,\mathrm{d}T}{T} - \int_{p_1}^{p_2} \partial_T V_p\,\mathrm{d}p + \frac{44769}{25+273.15} - \int_{p_2}^{100000} \frac{V\,\mathrm{d}p}{T} && 「8.33.」\\
&\sim 171.39 && 「8.34.」\\
S_{\mathrm{m}}^{\ominus} &= 238.54. && 「8.35.」
\end{aligned}
$$

3.

(1) 保持 $\omega_{C_2H_5OH} = 0.96$ 下对物质的量积分:

$$\begin{cases} \int_0^{10.0} \mathrm{d}V = Z_{H_2O} \int_0^{n_{H_2O}} \mathrm{d}n + Z_{C_2H_5OH} \int_0^{n_{C_2H_5OH}} \mathrm{d}n \\ \dfrac{n_{C_2H_5OH} \cdot 46.068}{n_{C_2H_5OH} \cdot 46.068 + n_{H_2O} \cdot 18.016} = 0.96 \end{cases} \Longrightarrow \tag{8.36.}$$

$$\begin{cases} n_{C_2H_5OH} = 167879 \\ n_{H_2O} = 17887 \end{cases} \tag{8.37.}$$

$$m_{C_2H_5OH} = 7734 \tag{8.38.}$$

$$m_{\mathrm{wine}} = 7734/0.96 = 8056 \tag{8.39.}$$

$$m'_{\mathrm{wine}} = 7734/0.56 = 13810 \tag{8.40.}$$

$$\Delta m_{H_2O} = 5754 \tag{8.41.}$$

$$\Delta V_{H_2O} = 5.759. \tag{8.42.}$$

(2) 保持 $\omega_{C_2H_5OH} = 0.56$ 下对物质的量积分:

$$n'_{H_2O} = 17887 + 5754000/18.016 = 337270 \tag{8.43.}$$

$$V = Z_{H_2O} \int_0^{337270} \mathrm{d}n + Z_{C_2H_5OH} \int_0^{167879} \mathrm{d}n = 15.27. \tag{8.44.}$$

4.

(1)

$$\begin{cases} \dfrac{n_{CH_3OH}}{n_{CH_3OH} + n_{H_2O}} = 0.30 \\ 10^3 = 17.765 n_{H_2O} + 38.632 n_{CH_3OH} \end{cases} \Longrightarrow \tag{8.45.}$$

$$\begin{cases} n_{CH_3OH} = 12.49 \\ n_{H_2O} = 29.14 \end{cases} \Longrightarrow \tag{8.46.}$$

$$V_{H_2O} = 5.265\mathrm{e}-4,\ V_{CH_3OH} = 5.086\mathrm{e}-4. \tag{8.47.}$$

(2)

$$\Delta V = (5.265\mathrm{e}-4) + (5.086\mathrm{e}-4) - (1\mathrm{e}-3) = 3.51\mathrm{e}-5. \tag{8.48.}$$

5.

$$n_{K_2SO_4}\, \mathrm{d}V_2 + n_{H_2O}\, \mathrm{d}V_1 = 0 \Longrightarrow \tag{8.49.}$$

$$m m_{H_2O}\, \mathrm{d}V_2 + \frac{m_{H_2O}}{18.016/1000}\, \mathrm{d}V_1 = 0 \Longrightarrow \tag{8.50.}$$

$$\mathrm{d}V_1 = -18.016/1000 \times m\,\mathrm{d}V_2 \Longrightarrow \tag{8.51.}$$

$$\int_{1.7963\mathrm{e}-5}^{V_2} \mathrm{d}V_2 = -18.016/1000 \times \int_0^m m\,\mathrm{d}((3.228\mathrm{e}-5) + (1.8216\mathrm{e}-5)\sqrt{m} + (2.22\mathrm{e}-8)m) \tag{8.52.}$$

$$V_2 - (1.7963\mathrm{e}-5) = -18.016/1000 \times \int_0^m m((0.9108\mathrm{e}-5)/\sqrt{m} + (2.22\mathrm{e}-8))\,\mathrm{d}m \tag{8.53.}$$

$$V_2 = -18.016/1000 \times ((6.072\mathrm{e}-6)m^{3/2} + (1.11\mathrm{e}-8)m^2) + 1.7963\mathrm{e}-5 \tag{8.54.}$$

$$V_2 = (1.7963\mathrm{e}-5) - (1.094\mathrm{e}-7)m^{3/2} - (2.000\mathrm{e}-10)m^2. \tag{8.55.}$$

9. 第九周作业

6.

(1) 转移小量, 不改变摩尔比.

$$\Delta G = n\Delta\mu \tag{9.1.}$$
$$= n(\mu^{\ominus} + RT\ln\frac{p_{\mathrm{B}}}{p^{\ominus}} - \mu^{\ominus} - RT\ln\frac{p_{\mathrm{A}}}{p^{\ominus}}) \tag{9.2.}$$
$$= nRT\ln\frac{p_{\mathrm{B}}}{p_{\mathrm{A}}} \tag{9.3.}$$
$$= -2642. \tag{9.4.}$$

(2)

$$\Delta G = n(\mu^{\ominus} + RT\ln\frac{p_{\mathrm{B}}}{p^{\ominus}} - \mu^{\ominus}) \tag{9.5.}$$
$$= nRT\ln\frac{p_{\mathrm{B}}}{p^{\ominus}} \tag{9.6.}$$
$$= -8100. \tag{9.7.}$$

8.

(1)

$$\begin{cases} 50660 = \frac{1}{3}p_{\mathrm{A}} + \frac{2}{3}p_{\mathrm{B}} \\ 70930 = \frac{2}{3}p_{\mathrm{A}} + \frac{1}{3}p_{\mathrm{B}} \end{cases} \Longrightarrow \tag{9.8.}$$
$$\begin{cases} p_{\mathrm{A}} = 91200 \\ p_{\mathrm{B}} = 30390. \end{cases} \tag{9.9.}$$

(2)

$$x_{\mathrm{A}} = \frac{\frac{1}{3}p_{\mathrm{A}}}{50660} = 0.6 \tag{9.10.}$$
$$x_{\mathrm{B}} = 0.4. \tag{9.11.}$$

9.

(1)

$$p_{\mathrm{A}} = p_{\mathrm{A}}^{*}x_{\mathrm{A}} = 49800 \tag{9.12.}$$
$$p_{\mathrm{B}} = p_{\mathrm{B}}^{*}x_{\mathrm{B}} = 14850. \tag{9.13.}$$

(2)

$$p = 64650. \tag{9.14.}$$

(3) 考虑等压等温判据:

$$T\,\mathrm{d}S \geqslant đQ \Longrightarrow \quad (9.15.)$$

$$đW \geqslant \mathrm{d}G \quad (9.16.)$$

考虑 Gibbs 自由能变:

$$\Delta G = (n-1)\mu_{\mathrm{A}} + 1\mu_{\mathrm{A}}^* - n\mu_{\mathrm{A}} = RT\ln\frac{p*}{p} = 1689. \quad (9.17.)$$

$$W_{\min} = 1689. \quad (9.18.)$$

(4)

$$\Delta G = 2\mu'_{\mathrm{A}} + 1\mu'_{\mathrm{B}} + 1\mu_{\mathrm{B}}^* - 2\mu_{\mathrm{A}} - 2\mu_{\mathrm{B}} \quad (9.19.)$$

$$= 2RT\ln\frac{p'_{\mathrm{A}}}{p_{\mathrm{A}}} + RT\ln\frac{p'_{\mathrm{B}}p_{\mathrm{B}}^*}{p_{\mathrm{B}}^2} \quad (9.20.)$$

$$= 2102. \quad (9.21.)$$

10.

$$p = \sum xp^* = 114970.3 \quad (9.22.)$$

初态:

$$x_{\mathrm{O_2}}^g = 0.21,\ x_{\mathrm{N_2}}^g = 0.79 \quad (9.23.)$$

$$p_i = x_i^g p = x_i^l p_i^* \Longrightarrow \quad (9.24.)$$

$$x_{\mathrm{N_2}}^l = 0.07525,\ x_{\mathrm{O_2}}^l = 0.92475. \quad (9.25.)$$

末态:

$$x_{\mathrm{O_2}}^l = 0.21,\ x_{\mathrm{N_2}}^l = 0.79 \quad (9.26.)$$

$$p_i = x_i^g p = x_i^l p_i^* \Longrightarrow \quad (9.27.)$$

$$x_{\mathrm{N_2}}^l = 0.99428,\ x_{\mathrm{O_2}}^l = 0.00572. \quad (9.28.)$$

12.

(1)

$$p_{\mathrm{C_6H_6}} = (1-0.0385)\times 10010 = 9624.615 \quad (9.29.)$$

$$p = p_{\mathrm{C_6H_6}}/x_{\mathrm{C_6H_6}}^g = 101311.7368 \quad (9.30.)$$

(2)

$$p_{\mathrm{HCl}} = 91687.12184 \quad (9.31.)$$

$$k_{x,\mathrm{B}} = \frac{p_{\mathrm{HCl}}}{x_{\mathrm{HCl}}} = 2381483. \quad (9.32.)$$

PPT 补充

$$\int_{\mu[T,p^\ominus]}^{\mu[T,p]} \mathrm{d}\mu = \int_{p^\ominus}^{p} V_\mathrm{m}\,\mathrm{d}p + f[T] \quad \text{「9.33.」}$$

$$\mu[T,p] - \mu[T,p^\ominus] = RT\ln\frac{p}{p^\ominus} + Bp + \frac{C}{2}p^2 + \cdots + f[T] - (Bp^\ominus + \frac{C}{2}p^{\ominus 2} + \cdots) \quad \text{「9.34.」}$$

$$p \to 0 \Longrightarrow \quad \text{「9.35.」}$$

$$\mu[T,p] - \mu[T,p^\ominus] = RT\ln\frac{p}{p^\ominus} + f[T] - (Bp^\ominus + \frac{C}{2}p^{\ominus 2} + \cdots) \Longrightarrow \quad \text{「9.36.」}$$

$$f[T] - (Bp^\ominus + \frac{C}{2}p^{\ominus 2} + \cdots) = 0 \quad \text{「9.37.」}$$

$$\mu[T,p] = \mu[T,p^\ominus] + RT\ln\frac{p}{p^\ominus} + Bp + \frac{C}{2}p^2 + \cdots \quad \text{「9.38.」}$$

$$\mu[T,p] \equiv \mu[T,p^\ominus] + RT\ln\frac{f}{p^\ominus} \quad \text{「9.39.」}$$

(1)

$$pV_\mathrm{m}(1-\beta p) = RT \quad \text{「9.40.」}$$

$$RT\ln\frac{f}{p} = \int_0^p \frac{RT}{p(1-\beta p)} - \frac{RT}{p}\,\mathrm{d}p = \beta RT\int_0^p \frac{\mathrm{d}p}{1-\beta p} = -RT\ln(1-\beta p) \quad \text{「9.41.」}$$

$$RT\ln f = RT\ln\frac{p}{1-\beta p}. \quad \text{「9.42.」}$$

(2)

$$(p + \frac{a}{V_\mathrm{m}^2})(V_\mathrm{m} - b) = RT \quad \text{「9.43.」}$$

$$\mathrm{Ans}: \ln f = \ln\frac{RT}{V_\mathrm{m}-b} + \frac{b}{V_\mathrm{m}-b} - \frac{2a}{RTV_\mathrm{m}}. \quad \text{「9.44.」}$$

考虑 f, p 的差异, 在 $p \to 0$ 时应有:

$$\mu[p] - \mu^\mathrm{i}[p] = RT\ln\frac{f}{p} = 0. \quad \text{「9.45.」}$$

其中角标 i 表示 ideal gas.

$$\Delta\mu[p] = \int \Delta V_\mathrm{m}\,\mathrm{d}p = \int_0^p V_\mathrm{m} - \frac{RT}{p}\,\mathrm{d}p = \int_0^p V_\mathrm{m}\,\mathrm{d}p - \int_0^p \frac{RT}{p}\,\mathrm{d}p \equiv I_1 - I_2. \quad \text{「9.46.」}$$

考虑此时的 V_m:

$$p = \frac{RT}{V_\mathrm{m}-b} - \frac{a}{V_\mathrm{m}^2} \to 0 \Longrightarrow \quad \text{「9.47.」}$$

$$p \sim \frac{RT}{V_\mathrm{m}}. \quad \text{「9.48.」}$$

$$I_1 = \int_0^p V_\mathrm{m} \,\mathrm{d}p \tag{9.49.}$$

$$= V_\mathrm{m} p\Big|_0^p - \int_{V_\mathrm{m}[0]}^{V_\mathrm{m}[p]} p \,\mathrm{d}V_\mathrm{m} \tag{9.50.}$$

$$= pV_\mathrm{m}[p] - RT - \int_{V_\mathrm{m}[0]}^{V_\mathrm{m}[p]} \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2} \,\mathrm{d}V_\mathrm{m} \tag{9.51.}$$

$$= pV_\mathrm{m}[p] - RT - (RT\ln(V_\mathrm{m} - b) + \frac{a}{V_\mathrm{m}})\Big|_{V_\mathrm{m}[0]}^{V_\mathrm{m}[p]} \tag{9.52.}$$

$$= pV_\mathrm{m}[p] - RT - \lim_{p_0\to 0} RT\ln\frac{V_\mathrm{m}[p] - b}{V_\mathrm{m}[p_0] - b} - \frac{a}{V_\mathrm{m}[p]}. \tag{9.53.}$$

$$I_2 = \int_0^p \frac{RT}{p} \,\mathrm{d}p \tag{9.54.}$$

$$= \lim_{p_0\to 0} RT\ln\frac{p}{p_0}. \tag{9.55.}$$

$$\Delta\mu[p] = I_1 - I_2 \tag{9.56.}$$

$$= pV_\mathrm{m}[p] - RT - \lim_{p_0\to 0} RT\ln\frac{V_\mathrm{m}[p] - b}{V_\mathrm{m}[p_0] - b} - \frac{a}{V_\mathrm{m}[p]} - \lim_{p_0\to 0} RT\ln\frac{p}{p_0} \tag{9.57.}$$

$$= pV_\mathrm{m}[p] - RT - \frac{a}{V_\mathrm{m}[p]} - RT\lim_{p_0\to 0}\ln\frac{p(V_\mathrm{m}[p] - b)}{p_0(V_\mathrm{m}[p_0] - b)} \tag{9.58.}$$

$$= pV_\mathrm{m}[p] - RT - \frac{a}{V_\mathrm{m}[p]} - RT\ln\frac{p(V_\mathrm{m}[p] - b)}{RT} \tag{9.59.}$$

$$= (\frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2})V_\mathrm{m} - RT - \frac{a}{V_\mathrm{m}} - RT\ln\frac{(\frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2})(V_\mathrm{m} - b)}{RT} \tag{9.60.}$$

$$= \frac{bRT}{V_\mathrm{m} - b} - \frac{2a}{V_\mathrm{m}} - RT\ln(1 - \frac{a(V_\mathrm{m} - b)}{RTV_\mathrm{m}^2}). \tag{9.61.}$$

然后你再把 $RT\ln p$ 加到两侧就完事了.

7.

(1)

$$\alpha \longrightarrow \beta \tag{9.62.}$$

$$\Delta_\mathrm{trs} G_\mathrm{m}^\ominus = -198000 + 200000 - 298(71.5 - 700) = 1553. \tag{9.63.}$$

(2)

$$K = \frac{m_\beta}{m_\alpha} \tag{9.64.}$$

$$\Delta G = -RT\ln K \Longrightarrow \tag{9.65.}$$

$$m_\beta = 18.72. \tag{9.66.}$$

11.

(1) 显然我们需要 298 K 时苯的饱和蒸汽压, 则只可认为相变焓不随温度改变:

$$\ln\frac{p_1}{p_2} = -\frac{\Delta H_{\mathrm{m}}}{R}(\frac{1}{T_1} - \frac{1}{T_2}) \tag{9.67.}$$

$$p_2 = 11997 \tag{9.68.}$$

$$k_{\mathrm{CH_4}} = 56976744 \tag{9.69.}$$

$$p = k_{\mathrm{CH_4}} x_{\mathrm{CH_4}} + p_2 x_{\mathrm{C_6H_6}} = 581644. \tag{9.70.}$$

(2)

$$p_{\mathrm{CH_4}} = 569767 \tag{9.71.}$$

$$p_{\mathrm{C_6H_6}} = 11887. \tag{9.72.}$$

14.

$$\int_1^{x_{\mathrm{A}}} \frac{\mathrm{d}x_{\mathrm{A}}}{x_{\mathrm{A}}} = \int_{T_{\mathrm{f}}^*}^{T_{\mathrm{f}}} \frac{\Delta H}{RT^2}\,\mathrm{d}T \tag{9.73.}$$

$$R\ln x_{\mathrm{A}} = \int_{T_{\mathrm{f}}^*}^{T_{\mathrm{f}}} \frac{a}{T^2} + \frac{b}{T} + c + dT\,\mathrm{d}T \tag{9.74.}$$

$$R\ln x_{\mathrm{A}} = -a(\frac{1}{T_{\mathrm{f}}^*} - \frac{1}{T_{\mathrm{f}}}) + b\ln\frac{T_{\mathrm{f}}}{T_{\mathrm{f}}^*} + c(T_{\mathrm{f}} - T_{\mathrm{f}}*) + \frac{d}{2}(T_{\mathrm{f}}^2 - T_{\mathrm{f}}^{*2}). \tag{9.75.}$$

15.

$$\Omega_2 = \frac{(\sum N)!}{\prod N!} = \frac{21A!}{8A!9A!4A!} \tag{9.76.}$$

$$\Omega_1 = \frac{12A!}{5A!7A!}\frac{9A!}{3A!2A!4A!} \tag{9.77.}$$

$$\Delta S = \Delta k\ln\Omega = k\ln\frac{\Omega_2}{\Omega_1} = 35.594. \tag{9.78.}$$

16.

只得认为萘不挥发, 此时

$$p = xp^* \tag{9.79.}$$

$$\ln 0.9 = -\frac{\Delta H_{\mathrm{fus}}}{R}(\frac{1}{T_{\mathrm{f}}} - \frac{1}{T_{\mathrm{f}}^*}) \tag{9.80.}$$

$$T_{\mathrm{f}} = 272.2, \tag{9.81.}$$

$$n_{\mathrm{C_6H_6}} = 0.745, \tag{9.82.}$$

$$\Delta n = 0.155. \tag{9.83.}$$

19.

(1)

$$m_{\mathrm{C_{10}H_8}} = 0.49936 \tag{9.84.}$$

$$k_\mathrm{b} = 2.343. \tag{9.85.}$$

(2)

$$k_\mathrm{b} = \frac{RT_\mathrm{b}^{*2}}{\Delta H} M_{\mathrm{CS_2}} = 2.411. \tag{9.86.}$$

(3)

$$\frac{\mathrm{d}p}{\mathrm{d}T} \sim \frac{p\Delta H}{RT^2} \tag{9.87.}$$

$$k_\mathrm{b} = \frac{\mathrm{d}T}{\mathrm{d}p} p M_{\mathrm{CS_2}} = 2.343. \tag{9.88.}$$

10. 第十周作业

21.

(1)

$$\Delta T = k_\mathrm{f} m_\mathrm{B} \quad \text{「10.1.」}$$

$$c = m_\mathrm{B}\rho \quad \text{「10.2.」}$$

$$\Pi = cRT = 693169. \quad \text{「10.3.」}$$

(2)

$$\Pi = m_\mathrm{B}\rho RT \quad \text{「10.4.」}$$

$$m_\mathrm{B} = 0.2827. \quad \text{「10.5.」}$$

22.

这与取出后浓度有关. 只得认为取出的是小量.

$$\Delta\mu = \mu^*_{\mathrm{H_2O}} - \mu_{\mathrm{H_2O}} = -RT\ln x_{\mathrm{H_2O}} \quad \text{「10.6.」}$$

$$\Pi = cRT \quad \text{「10.7.」}$$

$$c = 80.7242 \quad \text{「10.8.」}$$

$$\text{Let } V = 1\mathrm{m}^3 \implies \quad \text{「10.9.」}$$

$$m_{\mathrm{NaCl}} = 4.7175 \quad \text{「10.10.」}$$

$$m_{\mathrm{H_2O}} = 995.2825 \quad \text{「10.11.」}$$

$$n = 55244.365 \quad \text{「10.12.」}$$

$$x_{\mathrm{H_2O}} = 0.9985 \quad \text{「10.13.」}$$

$$\Delta\mu = 3.6176 \quad \text{「10.14.」}$$

23.

(1)

$$\Delta T_\mathrm{b} = \Delta T_\mathrm{f} \cdot \frac{k_\mathrm{b}}{k_\mathrm{f}} \quad \text{「10.15.」}$$

$$T_\mathrm{b} = 373.57. \quad \text{「10.16.」}$$

(2)

$$m_\mathrm{B} = \frac{\Delta T}{k} = 0.80645 \quad \text{「10.17.」}$$

$$x_\mathrm{B} = 0.014321 \quad \text{「10.18.」}$$

$$p = p^* x_{\mathrm{H_2O}} = 3132.49. \quad \text{「10.19.」}$$

(3)

$$\Pi = cRT = \rho mRT = 1999043. \quad 「10.20.」$$

27.

(1)

$$p_{\mathrm{A}} = 30396,\ p_{\mathrm{B}} = 20264 \quad 「10.21.」$$

$$a_x^{\mathrm{A}} = 0.81425,\ a_x^{\mathrm{B}} = 0.89426. \quad 「10.22.」$$

$$\gamma_x^{\mathrm{A}} = 1.6285,\ \gamma_X^{\mathrm{B}} = 1.7885. \quad 「10.23.」$$

(2)

$$\Delta G = \Delta(\mu n) = 2\sum RT \ln a_x = -1582.5527. \quad 「10.24.」$$

(3)

$$\Delta G = 2\sum RT \ln x = -6915.3908. \quad 「10.25.」$$

28.

(1)

$$\ln a = \frac{\Delta H}{R}\left(\frac{1}{T_{\mathrm{f}}^*} - \frac{1}{T}\right), \quad 「10.26.」$$

$$a = 0.89820, \quad 「10.27.」$$

$$x = 0.8937, \quad 「10.28.」$$

$$\gamma = 1.005. \quad 「10.29.」$$

(2)

$$\mathit{\Pi} V = -nRT \ln a, \quad 「10.30.」$$

$$\mathit{\Pi} = 1.478\mathrm{e}+7. \quad 「10.31.」$$

37.

$$a_{x,\mathrm{H_2O}} = 0.8067 \quad 「10.32.」$$

$$\gamma = 40.335. \quad 「10.33.」$$

1.

$$Q = \prod_i \left(\frac{p_i}{p^\ominus}\right)^{\nu_i} = \prod_i x_i^{\nu_i} \left(\frac{p}{p^\ominus}\right)^{\sum \nu_i} = 0.15625, \quad 「10.34.」$$

$$\Delta_{\mathrm{r}} G_{\mathrm{m}} = \Delta_{\mathrm{r}} G_{\mathrm{m}}^\ominus + RT \ln Q = 3856.74. \quad 「10.35.」$$

反应逆向进行.

2.

(1)

$$Q = 1.2501 > K_p^\ominus, \tag{10.36.}$$

故不能.

(2)

$$Q = 0.37502 < K_p^\ominus, \tag{10.37.}$$

此时可以反应.

3.

平衡时的分压给出平衡常数, 则以反应商比较即可.

(1) 此时有

$$p \in [1935, 2547], \tag{10.38.}$$
$$\eta \in [0.6110, 0.8042]. \tag{10.39.}$$

(2)

$$\eta \in [0, 0.6110]. \tag{10.40.}$$

(3)

$$\eta \in [0.8042, 1]. \tag{10.41.}$$

4.

(1)

$$\Delta C_p^\ominus = 0 \Longrightarrow \tag{10.42.}$$
$$\frac{\mathrm{d}\Delta_\mathrm{r} H_\mathrm{m}^\ominus}{\mathrm{d}T} = 0, \frac{\mathrm{d}\Delta_\mathrm{r} S_\mathrm{m}^\ominus}{\mathrm{d}T} = 0, \tag{10.43.}$$
$$\Delta_\mathrm{r} G_\mathrm{m}^\ominus[310\ \mathrm{K}] = 2000, \tag{10.44.}$$
$$Q = 2, \tag{10.45.}$$
$$\Delta_\mathrm{r} G_\mathrm{m} = \Delta_\mathrm{r} G_\mathrm{m}^\ominus + RT \ln Q = 3786.5 > 0, \tag{10.46.}$$

故逆向进行.

(2)

压力:

$$Q = 2(\frac{p}{p^\ominus})^{-1}, \tag{10.47.}$$

$$\Delta_{\mathrm{r}} G_{\mathrm{m}} < 0, \tag{10.48.}$$

$$p > 434550. \tag{10.49.}$$

温度:

$$\Delta_{\mathrm{r}} G_{\mathrm{m}} = \Delta_{\mathrm{r}} G_{\mathrm{m}}^\ominus[T] - RT\ln Q = \Delta_{\mathrm{r}} H_{\mathrm{m}} - T\Delta_{\mathrm{r}} S_{\mathrm{m}} + RT\ln Q < 0, \tag{10.50.}$$

$$T < 291.6. \tag{10.51.}$$

摩尔分数:

$$\Delta_{\mathrm{r}} G_{\mathrm{m}} = \Delta_{\mathrm{r}} G_{\mathrm{m}}^\ominus + RT\ln\frac{1-x_{\mathrm{A}}}{x_{\mathrm{A}}^2} < 0, \tag{10.52.}$$

$$x_{\mathrm{A}} > 0.745. \tag{10.53.}$$

6.

(1)

$$0 = \Delta_{\mathrm{r}} G_{\mathrm{m}} = -RT\ln K^\ominus + RT\ln Q, \tag{10.54.}$$

$$K^\ominus = Q, \tag{10.55.}$$

$$x_{\mathrm{H_2}} : x_{\mathrm{N_2}} = 3 : 1, \tag{10.56.}$$

$$x_{\mathrm{H_2}} = 0.721125,\ x_{\mathrm{N_2}} = 0.240375, \tag{10.57.}$$

$$Q = 1.6444\mathrm{e} - 4. \tag{10.58.}$$

(2)

$$x_{\mathrm{H_2}} = 0.7125,\ x_{\mathrm{N_2}} = 0.2375, \tag{10.59.}$$

$$Q = K^\ominus, \tag{10.60.}$$

$$p = 1330323. \tag{10.61.}$$

11. 第十一周作业

5.

(1)

$$\mathrm{MnO} + \mathrm{C} \longrightarrow \mathrm{Mn} + \mathrm{CO} \quad 「11.1.」$$

$$\Delta_r G_m^\ominus[T] = 2686 \times 10^2 - 158.37T \quad 「11.2.」$$

$$\Delta_r G_m^\ominus[T] = -RT \ln K^\ominus = -RT \times -13.528 \quad 「11.3.」$$

$$T = 991.7. \quad 「11.4.」$$

(2)

$$\Delta_r G_m^\ominus = 3754 \times 10^2 - 147723.6 = 227676. \quad 「11.5.」$$

$$\Delta_r G_m = \Delta_r G_m^\ominus + RT \ln Q = 116139 > 0. \quad 「11.6.」$$

故不能.

7.

$$\Delta_r G_m^\ominus = -457140, \quad 「11.7.」$$

$$K^\ominus = 1.3559\mathrm{e} + 80 \quad 「11.8.」$$

$$x_{\mathrm{H_2}} = \frac{0.995 - 2x}{1 - x}, \quad 「11.9.」$$

$$x_{\mathrm{O_2}} = \frac{0.005 - x}{1 - x}, \quad 「11.10.」$$

$$x_{\mathrm{H_2O}} = \frac{2x}{1 - x}, \quad 「11.11.」$$

$$K^\ominus = \prod \frac{p_i}{p^\ominus} = \prod \frac{p x_i}{p^\ominus} = \frac{(2x)^2}{(0.995 - 2x)^2 (0.005 - x)} \left(\frac{100000}{p^\ominus (1 - x)}\right)^{-1} \quad 「11.12.」$$

$$x = 0.005. \quad 「11.13.」$$

计算器寄了, 或者我们可以换一种非平衡的考虑:

$$\frac{x_{\mathrm{O_2}}}{x_{\mathrm{O_2}} + x_{\mathrm{H_2}}} = 10^{-6}, \quad 「11.14.」$$

$$x = 0.00499901, \quad 「11.15.」$$

$$Q = \frac{(2x)^2}{(0.995 - 2x)^2 (0.005 - x)} \left(\frac{100000}{p^\ominus (1 - x)}\right)^{-1} = 104.07 < K^\ominus. \quad 「11.16.」$$

故反应仍会正向进行, 故可除去.

9.

(1)

$$K_c = \prod c_i = \prod \frac{p_i}{RT} = K_p(RT)^{-\sum \nu_i}, \quad \text{「11.17.」}$$

$$K_p = K_c(RT)^{\sum \nu_i} = 29431.56, \quad \text{「11.18.」}$$

$$K_p^\ominus = \prod \frac{p_i}{p^\ominus} = K_p p^{\ominus -\sum \nu_i} = 0.29431, \quad \text{「11.19.」}$$

$$K_p = \prod x_i p = K_x p^{\sum \nu_i}, \quad \text{「11.20.」}$$

$$K_x = K_p p^{-\sum \nu_i} = 0.29431. \quad \text{「11.21.」}$$

(2) 各自开根号即可.

10.

(1) 标准平衡常数尽和温度有关, 故不变.

(2)

$$\mu[T] = \mu^\ominus + RT \ln \frac{p\gamma}{p^\ominus}, \quad \text{「11.22.」}$$

$$K_f^\ominus[T] = K_p^\ominus K_\gamma, \quad \text{「11.23.」}$$

$$K_\gamma > 1, \quad \text{「11.24.」}$$

故当向实际气体转变时, $K_p^\ominus$ 减小, 平衡左移.

15.

$$\mathrm{Hg_2Cl_2}(s) \longrightarrow \mathrm{Hg_2Cl_2}(aq), \quad \text{「11.25.」}$$

$$\Delta_\mathrm{r} G_\mathrm{m}^\ominus = -RT \ln K^\ominus = 35313.98. \quad \text{「11.26.」}$$

$$\mathrm{AgCl}(s) \longrightarrow \mathrm{AgCl}(aq), \quad \text{「11.27.」}$$

$$\Delta_\mathrm{r} G_\mathrm{m}^\ominus = -RT \ln K^\ominus = 27888.11. \quad \text{「11.28.」}$$

$$\Delta_\mathrm{r} G_\mathrm{m}^\ominus = 2(27888.11 - 109800) - 35313.98 + 210700 = 11562.24, \quad \text{「11.29.」}$$

$$K^\ominus = 9.425\mathrm{e} - 3. \quad \text{「11.30.」}$$

18.

(1)

$$K^\ominus = \prod \frac{p_i}{p^\ominus} = K_x \frac{p}{p^\ominus}, \quad \text{「11.31.」}$$

p 变小则 K_x 变大, 解离度增大.

(2) 反应的物料中 p 占比降低, 相当与总压减小, 解离度增大.

(3) 这未改变物料的总压, 故不变.

(4) 显然平衡将逆向移动, 故减小.

19.

(1)

$$\Delta_{\mathrm{r}} G_{\mathrm{m}}^{\ominus} = \Delta_{\mathrm{r}} H_{\mathrm{m}}^{\ominus} - T \Delta_{\mathrm{r}} S_{\mathrm{m}}^{\ominus} = 135610 - 298 \times 334.21 = 36015.42, \tag{11.32.}$$

$$K^{\ominus} = 4.8623\mathrm{e} - 7, \tag{11.33.}$$

$$K^{\ominus} = (\frac{p_i}{p^{\ominus}})^2, \tag{11.34.}$$

$$p = \sum p_i = 139.46. \tag{11.35.}$$

(2)

$$H[p, T], \tag{11.36.}$$

$$\mathrm{d}H = \partial_T H_p \, \mathrm{d}T = C_p \, \mathrm{d}T, \tag{11.37.}$$

$$\mathrm{d}H = T \, \mathrm{d}S + V \, \mathrm{d}p, \tag{11.38.}$$

$$\mathrm{d}S = \frac{\mathrm{d}H}{T} = \frac{C_p \, \mathrm{d}T}{T}, \tag{11.39.}$$

$$\Delta_{\mathrm{r}} H_{\mathrm{m}}^{\ominus}[T] = \Delta_{\mathrm{r}} H_{\mathrm{m}}^{\ominus}[298] + \int_{298}^{T} \Delta_{\mathrm{r}} C_{p,\mathrm{m}}^{\ominus} \, \mathrm{d}T = 133284.54 + 7.77T, \tag{11.40.}$$

$$\Delta_{\mathrm{r}} S_{\mathrm{m}}^{\ominus}[T] = \Delta_{\mathrm{r}} S_{\mathrm{m}}^{\ominus}[298] + \int_{298}^{T} \frac{\Delta_{\mathrm{r}} C_{p,\mathrm{m}}^{\ominus}}{T} \, \mathrm{d}T = 289.93 + 7.77 \ln T, \tag{11.41.}$$

$$\Delta_{\mathrm{r}} G_{\mathrm{m}}^{\ominus}[T] = -RT \ln K^{\ominus} = -RT \ln(\frac{100000/2}{p^{\ominus}})^2, \tag{11.42.}$$

$$T = 392. \tag{11.43.}$$

22.

(1)

$$(\frac{\partial(\Delta_{\mathrm{r}} G_{\mathrm{m}}^{\ominus}/T)}{\partial T})_p = -\frac{\Delta_{\mathrm{r}} H_{\mathrm{m}}^{\ominus}}{T^2}, \tag{11.44.}$$

$$\Delta_{\mathrm{r}} H_{\mathrm{m}}^{\ominus} = -T^2 (\frac{\mathrm{d}(-34585/T + 26.4 \ln T + 45.19)}{\mathrm{d}T}) = -34585 - 26.4T. \tag{11.45.}$$

(2)

$$\Delta_{\mathrm{r}} G_{\mathrm{m}}^{\ominus} = -RT \ln K^{\ominus}, \tag{11.46.}$$

$$K^{\ominus}[573] = 1.08\mathrm{e} - 8, \tag{11.47.}$$

$$\Delta_{\mathrm{r}} S_{\mathrm{m}}^{\ominus} = -\frac{\mathrm{d}\Delta_{\mathrm{r}} G_{\mathrm{m}}^{\ominus}}{\mathrm{d}T} = -239.25. \tag{11.48.}$$

25.

考试题.

$$\mathrm{d}H = C_p \,\mathrm{d}T, \tag{11.49.}$$

$$\Delta_{\mathrm{r}} H_{\mathrm{m}}^{\ominus}[T] = \Delta_{\mathrm{r}} H_{\mathrm{m}}^{\ominus}[368.5] + \int_{368.5}^{T} \Delta_{\mathrm{r}} C_{p,\mathrm{m}} \,\mathrm{d}T, \tag{11.50.}$$

$$(\frac{\partial(\Delta_{\mathrm{r}} G_{\mathrm{m}}^{\ominus}/T)}{\partial T})_p = -\frac{\Delta_{\mathrm{r}} H_{\mathrm{m}}^{\ominus}}{T^2} \tag{11.51.}$$

就行了.

27.

$$\Delta_{\mathrm{r}} G_{\mathrm{m}1}^{\ominus} = 29458.522, \tag{11.52.}$$

$$\Delta_{\mathrm{r}} G_{\mathrm{m}2}^{\ominus} = 29541.019, \tag{11.53.}$$

$$K_1^{\ominus} = \frac{p_i^1}{p^{\ominus}}, \tag{11.54.}$$

$$K_2^{\ominus} = \frac{p_i^2}{p^{\ominus}}, \tag{11.55.}$$

$$\frac{K_2^{\ominus}}{K_1^{\ominus}} = \frac{p_{\mathrm{NH}_3}}{p^{\ominus}}, \tag{11.56.}$$

$$p_{\mathrm{NH}_3} = 9.67\mathrm{e} + 4. \tag{11.57.}$$

12. 第十二周作业

2.

独立组分数 $C = 2$, 相数 $\Phi = 2$, $f = 2$;
$C = 2,\ \Phi = 2,\ f = 1$;
$C = 2,\ \Phi = 2,\ f = 1$;
$C = 2,\ \Phi = 3,\ f = 1$;
$C = 2,\ \Phi = 2,\ f = 2$(这是熔液).

4.

(1) 每增加一种水合盐, 相数 +1, 其余无变化, 故最大值为 $C + 1 = 3$. 故仅有 1 种盐.
(2) 独立组分数为 2, 故 2 种.
(3) 和固相共存, 故结晶水最少者.

7.

(1)

$$G = mg = 600, \tag{12.1.}$$

$$p = \frac{G}{2S} = 1.6\mathrm{e}+8. \tag{12.2.}$$

(2)

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}, \tag{12.3.}$$

$$\Delta\frac{m_{\mathrm{m}}}{\rho}\,\mathrm{d}p = \frac{\Delta H\,\mathrm{d}T}{T}, \tag{12.4.}$$

$$18.016\mathrm{e}-3(1/1000-1/920)\int_{10^5}^{1.6\mathrm{e}+8}\mathrm{d}p = 6.01\mathrm{e}+3\int_{273}^{T}\frac{\mathrm{d}T}{T}, \tag{12.5.}$$

$$-251 = 6.01\mathrm{e}+3\ln\frac{T}{273}, \tag{12.6.}$$

$$T = 262. \tag{12.7.}$$

10.

(1)

$$T = 333,\ p = 20959, \tag{12.8.}$$

$$V \sim 15\mathrm{e}-3, \tag{12.9.}$$

$$n = 0.1136, \tag{12.10.}$$

$$n^{\mathrm{l}} = 0.8864, \tag{12.11.}$$

$$m = 0.01597. \tag{12.12.}$$

(2)

$$p[T]V = nRT, \tag{12.13.}$$

$$T = 396.5. \tag{12.14.}$$

11.

$$p_{\mathrm{B}} = k_{\mathrm{B}}^{x} x_{\mathrm{B}} = 33180, \tag{12.15.}$$

$$\frac{\mathrm{d}p^*}{\mathrm{d}T} = \frac{40660p^*}{RT^2}, \tag{12.16.}$$

$$\ln \frac{p^*}{101325} = -\frac{40660}{R}(\frac{1}{360} - \frac{1}{373.15}), \tag{12.17.}$$

$$p^* = 62777, \tag{12.18.}$$

$$p_{\mathrm{A}} = 61459. \tag{12.19.}$$

13. 第十三周作业

8.

$$\Delta H_{\mathrm{m}} = 88T_{\mathrm{b}} = 30096, \tag{13.1.}$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{30096}{T\Delta V_{\mathrm{m}}}, \tag{13.2.}$$

$$(\frac{RT}{p} - \frac{86.172}{0.66\mathrm{e}+6})\,\mathrm{d}p = \frac{30096\,\mathrm{d}T}{T}, \tag{13.3.}$$

忽略小量:

$$\frac{R\,\mathrm{d}p}{p} = \frac{30098\,\mathrm{d}T}{T^2}, \tag{13.4.}$$

$$R\ln\frac{p}{101325} = -30098(\frac{1}{298} - \frac{1}{342}), \tag{13.5.}$$

$$p = 21240. \tag{13.6.}$$

对于存在空气的情况,

$$\mathrm{d}G^{\mathrm{l}} = \mathrm{d}G^{\mathrm{g}}, \tag{13.7.}$$

$$V^{\mathrm{l}}\,\mathrm{d}p_{\mathrm{sum}} = \frac{nRT}{p}\,\mathrm{d}p, \tag{13.8.}$$

$$\frac{86.172}{0.66\mathrm{e}+6}\,\mathrm{d}p = \frac{298R\,\mathrm{d}p}{p}, \tag{13.9.}$$

$$\frac{86.172}{0.66\mathrm{e}+6}(202200 - 21240) = 298R\ln\frac{p}{21240}, \tag{13.10.}$$

$$p = 21443. \tag{13.11.}$$

9.

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H}{T\Delta V}, \tag{13.12.}$$

$$\frac{\Delta H}{T\frac{RT}{p}} = \frac{\mathrm{d}p}{\mathrm{d}\ln p}\frac{\mathrm{d}\ln p}{\mathrm{d}T} = p(\frac{1921}{T^2} + \frac{1.75}{T} - 1.928\mathrm{e}-2), \tag{13.13.}$$

$$T = 169.5,\ p = 766.01, \tag{13.14.}$$

$$\Delta H = RT^2(\frac{1921}{T^2} + \frac{1.75}{T} - 1.928\mathrm{e}-2) = 13832. \tag{13.15.}$$

12.

(1) 略.

(2) 三相点.

(3) 石墨.

(4) 石墨.

(5) 没看懂整个坐标轴.

13.

$$n_{H_2O} = 5.5506, \tag{13.16.}$$
$$n_A = 0.32244, \tag{13.17.}$$
$$p_A = x_A p = 5561.56. \tag{13.18.}$$

同理, 有

$$n_A = 0.26535, \tag{13.19.}$$
$$p_A = 4024.15, \tag{13.20.}$$
$$\ln\frac{4024.15}{5561.56} = -\frac{\Delta H}{R}\left(\frac{1}{360.7} - \frac{1}{371.6}\right), \tag{13.21.}$$
$$\Delta H = 33080. \tag{13.22.}$$

15.

(1)

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_r H_m^\ominus}{RT^2} \implies \tag{13.23.}$$
$$p_2 = 15918.7. \tag{13.24.}$$

(2)

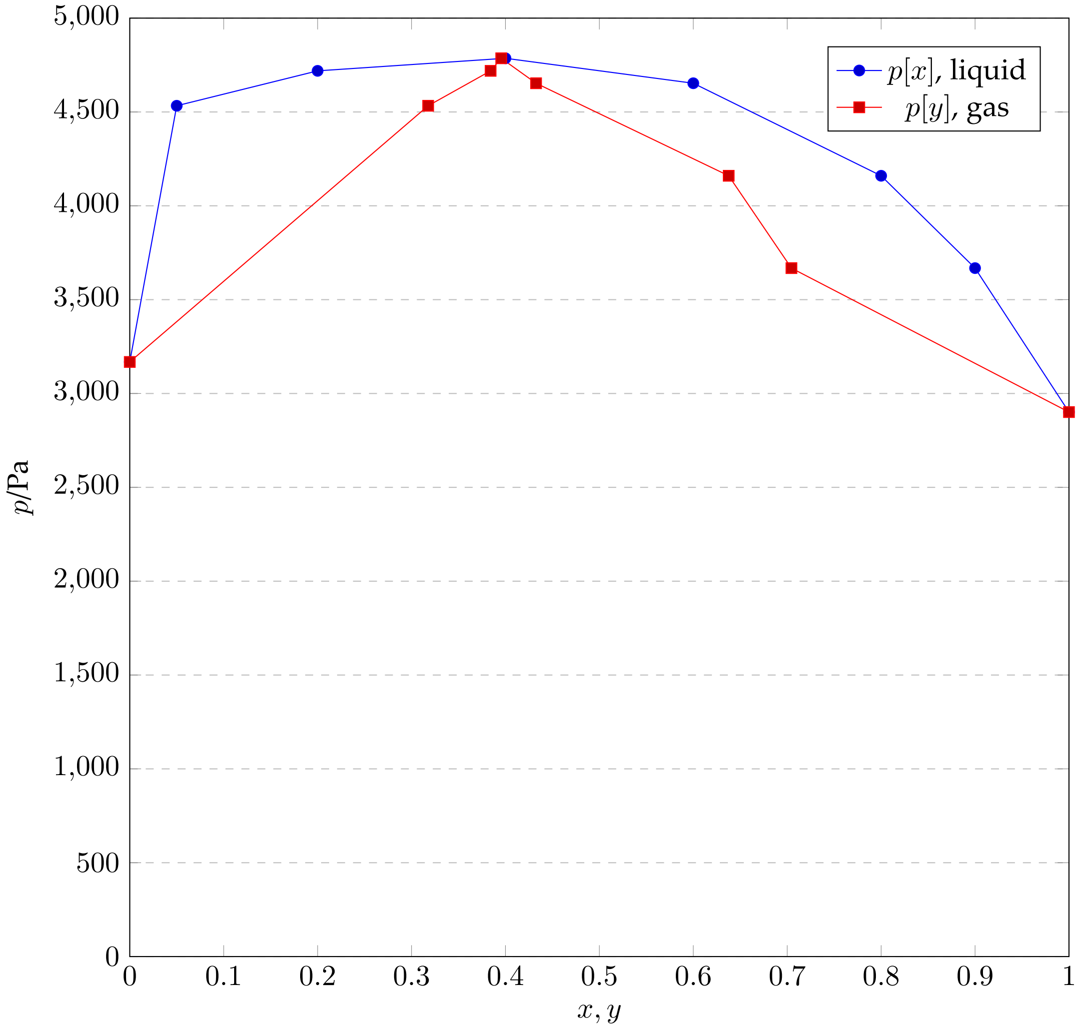
$$\Delta_r H_m^\ominus = \frac{R\ln(p_2/p_1)}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} = 44054.4. \tag{13.25.}$$

(3)

$$\Delta_r H_m^\ominus = 44054.4 - 34170 = 9884.4. \tag{13.26.}$$

16.

(1)



对于纯物质 A 或 B, 此时若存在气液平衡, 且温度已固定, 故自由度为 0;
蓝上方是纯液相, 具有组分和压强两个自由度;
红下方是纯气相, 具有组分和压强两个自由度;
对于压强的截线, 可存在红蓝皆有解, 此时解是固定的, 仅有一个自由度.
(2) 此时处在恒沸混合物右侧, 得到 $x_{\mathrm{B}} = 0.4$ 的恒沸混合物和纯丙醇.
(3)

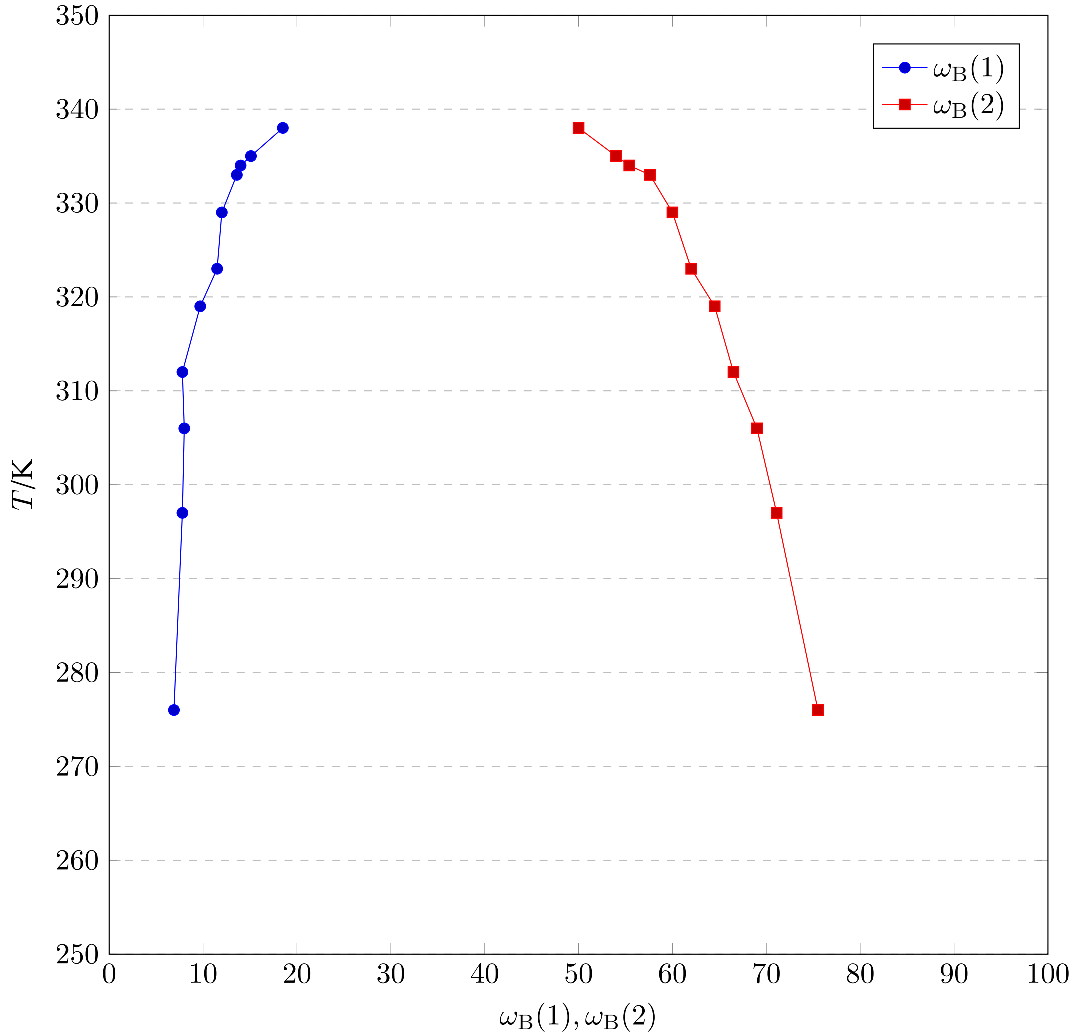
$$\mu^{\mathrm{l}} = \mu^{\mathrm{g}} = \mu^{\ominus} + RT\ln\frac{p}{p^{\ominus}}, \tag{13.27.}$$

$$a = \frac{p}{p^{\ominus}} = 0.6260, \tag{13.28.}$$

$$\gamma = \frac{a}{x} = 3.125. \tag{13.29.}$$

18.

(1)



(2) 温度 $T = 341.7$, 含量不知道.

(3) 将两点区间看成线性, 则有 300 K 时:

$$\omega_B(1) = 7.87, \tag{13.30}$$

$$\omega_B(2) = 70.4, \tag{13.31}$$

此时的广义坐标是两相各自的质量 q_1, q_2:

$$\begin{cases} q_1 + q_2 = 2, \\ 0.0787q_1 + 0.704q_2 = 1, \end{cases} \tag{13.32}$$

$$\begin{cases} q_1 = 0.6525, \\ q_2 = 1.3475. \end{cases} \tag{13.33}$$

(4) 此时:

$$\begin{cases} q_1 + q_2 = 3, \\ 0.0787q_1 + 0.704q_2 = 1, \end{cases} \tag{13.34}$$

$$\begin{cases} q_1 = 1.7783, \\ q_2 = 1.2217. \end{cases}$$ 「13.35.」

14. 第十四周作业

17.

(1) 略;
(2) 转折温度第二次消失代表生成稳定化合物, 又质量分数可知为 Sb_2Cd_3;
(3) 考虑物质的量:

$$n_{Cd} = 11.34,\ n_{Sb} = 5.954, \tag{14.1.}$$

这将得到 Sb_2Cd_3 与 Cd 的共熔物, 此时 $m = 1.729$.

19.

(1) 略;
(2) 略;
(3)

$$q_1 + q_2 = 85, \tag{14.2.}$$
$$q_1 + \omega_{Na} q_2 = 46, \tag{14.3.}$$
$$q_1 = 14.1,\ q_2 = 70.9. \tag{14.4.}$$

20.

(1) 略;
(2)

$$q_1 + q_2 = 1000, \tag{14.5.}$$
$$q_1 + 0.27 q_2 = 280, \tag{14.6.}$$
$$q_1 = 13.70,\ q_2 = 986.3; \tag{14.7.}$$

(3) 252 K;
(4) 考虑化学变化:

$$H_2O(s) \longrightarrow H_2O(aq), \tag{14.8.}$$

平衡时有:

$$\mu^{s}[T] = \mu^{aq}[T] = \mu^{\ominus}[T] + RT \ln a, \tag{14.9.}$$

其中 $\mu^{\ominus}[T]$ 给出该温度下假想纯液态水的化学势, 即:

$$H_2O(s) \longrightarrow H_2O(l), \quad 「14.10.」$$

$$\Delta G[T] = \mu^{\ominus}[T] - \mu^{s}[T], \quad 「14.11.」$$

$$\Delta H[T] = 6008, \quad 「14.12.」$$

$$\frac{\partial \frac{\Delta G}{T}}{\partial T} = -\frac{\Delta H}{T^2}, \quad 「14.13.」$$

$$\frac{\Delta G}{T}\Big|_{T=273}^{T=263} = \frac{\Delta H}{T}\Big|_{T=273}^{T=263}, \quad 「14.14.」$$

$$\frac{\Delta G[263]}{263} = 6008(\frac{1}{263} - \frac{1}{273}), \quad 「14.15.」$$

$$\Delta G[263] = 220, \quad 「14.16.」$$

$$RT \ln a = -220, \quad 「14.17.」$$

$$a = 0.9043. \quad 「14.18.」$$

22.

27.

(1) 略.

(2) 降低熔点, 节能.

(3)629 K, 因为要电解熔液.

(4) 先析出 KCl, 故大于 0.50.

15. 第十五周作业

23.

24.

33.

35.

1.

(1)

$$3; \qquad \text{「15.1.」}$$

$$\Omega = C[6,1] + P[6,2] + C[6,3] = 56, \qquad \text{「15.2.」}$$

$$P_1 = 6/56, P_2 = 30/56, P_3 = 20/56. \qquad \text{「15.3.」}$$

(2)

$$3; \qquad \text{「15.4.」}$$

$$\Omega = 10C[6,1] + 6P[6,2] + 1C[6,3] = 260, \qquad \text{「15.5.」}$$

$$P_1 = 60/260, P_2 = 180/260, P_3 = 20/260. \qquad \text{「15.6.」}$$

3.

$$\frac{N_1}{N_2} = \frac{g_1}{g_2}\exp[-\beta(\varepsilon_1 - \varepsilon_2)], \qquad \text{「15.7.」}$$

$$\frac{N_1}{N_2}[300] = 1.046, \qquad \text{「15.8.」}$$

$$\frac{N_1}{N_2}[3000] = 0.634. \qquad \text{「15.9.」}$$

4.

$$\varepsilon_1 = 18 \times 0.1 k_{\mathrm{B}} T \implies g_1 = 3, \qquad \text{「15.10.」}$$

$$g_2 = 27, \qquad \text{「15.11.」}$$

$$\frac{N_1}{N_2} = \frac{g_1 \exp[-\beta\varepsilon_1]}{g_2 \exp[-\beta\varepsilon_2]} = \frac{3}{4}\exp[0.9]. \qquad \text{「15.12.」}$$

16. 第十六周作业

6.

$$Z = g_i \exp[-\varepsilon_i \beta] = 3.935, \tag{16.1.}$$

$$N_2 = N_\mathrm{A} \frac{Z_2}{Z} = 2.785\mathrm{e}+23, \tag{16.2.}$$

$$1:3:5. \tag{16.3.}$$

7.

$$\ln \varOmega = N \ln N + N_i^* \ln g_i - N_i^* \ln N_i^* = \ln Z^N + U\beta, \tag{16.4.}$$

$$\varOmega = Z^N \exp[U\beta]. \tag{16.5.}$$

10.

13.

$$Z_\mathrm{t} = (\frac{2\pi mkT}{h^2})^{3/2} V = 2.016\mathrm{e}+30, \tag{16.6.}$$

$$Z = 8.645\mathrm{e}+30. \tag{16.7.}$$

$$S^\ominus = R(\ln \frac{Z_\mathrm{t}}{L} + \frac{5}{2}) + R \ln Z_\mathrm{e} = 157.8. \tag{16.8.}$$

17. 第十七周作业

14.

$$P_i = \frac{N_i}{N} = (2J+1)\frac{\sigma\Theta}{T}\exp[\frac{-J(J+1)\Theta}{T}], \tag{17.1.}$$

$$\left.\frac{\mathrm{d}P_i}{\mathrm{d}J}\right|_J = 0, \tag{17.2.}$$

$$J = \sqrt{\frac{T}{2\Theta}} - \frac{1}{2}, \tag{17.3.}$$

$$J = 6. \tag{17.4.}$$

20.

25.

26.