统计力学第五次作业

肖涵薄 31360164

2019 年 4 月 13 日

4.2

由于 μ 是强度量, 各组员 T, p 不变且比例不变时, 与 n 无关, 即对任意 λ, 有

$$\mu_{T,p}(\lambda n_i) = \mu_{T,p}(n_i)$$

根据 Euler 定理, 满足:

$$\sum n_i \frac{\partial \mu}{\partial n_i} = 0$$

上式对任意 T, p 均成立.

4.3

(a) 混合前: $G_1 = n_1 g_1 + n_2 g_2$. 混合后 $G_2 = n_1 \mu_1 + n_2 \mu_2$.

$$G_2 - G_1 = n_1 RT \ln x_1 + n_2 RT \ln x_2$$

(b) $pV = RT(n_1 + n_2)$, 等温等压下 $\Delta V = 0$.

(c) $\Delta S = -\Delta \left(\frac{\partial G}{\partial T}\right)_{p,n_i} = -n_1 R \ln x_1 - n_2 R \ln x_2$.

(d) $H(T, p)$ 是 T, p 的函数, 等温等压下 H 不变.

(e) $\Delta U = T\Delta S - P\Delta V = 0$.

4.6

化学势满足式

$$\mu = \sum RT[\varphi_i + \ln(x_i p)]$$

则水的化学势变化为:

$$\Delta\mu = RT[-\ln(p) + \ln((1-x)p)] = RT\ln(1-x)$$

又由于 $\Delta\mu = g_1(T,p) - g_1(T,p_0)$,

$$g_1(T,p_0) + RT\ln(1-x) = g_1(T,p)$$

4.8

(1)

$$p = \frac{n}{V} = \frac{n_1+n_2}{V_1+V_2}RT$$

(2)

由于

$$S = \sum n_i\left[\int \frac{c_{pi}}{T}\,\mathrm{d}T - R\ln(x_ip) + s_{i0}\right]$$

$$\Delta S = -n_1R\ln\frac{n_1}{n_1+n_2}p - n_2R\ln\frac{n_1}{n_1+n_2}p + n_1R\ln p_1 + n_2R\ln p_2$$

代入 (1) 中 p,

$$\Longrightarrow \Delta S = -n_1R\ln\frac{n_1RT}{V_1+V_2} - n_2R\ln\frac{n_1RT}{V_1+V_2} + n_1R\ln\frac{n_1RT}{V_1} + n_2R\ln\frac{n_2RT}{V_2}$$

$$\Delta S = n_1R\ln\frac{V_1+V_2}{V_1} + n_2R\ln\frac{V_1+V_2}{V_2}$$

(3)

利用式 $S = nC_{p,m}\ln T - nR\ln p + S_0$,

$$\Delta S = (n_1+n_2)C\ln T - (n_1+n_2)R\ln\frac{V_1+V_2}{n_1+n_2} - n_1C\ln T + n_1R\ln V_1/n_1 - n_2C\ln T + n_2R\ln V_2/n_2$$

$$= -(n_1+n_2)R\ln\frac{V_1+V_2}{n_1+n_2} + n_1R\ln V_1/n_1 + n_2R\ln V_2/n_2$$

4.9

$$K_1 = \frac{c_{NH_3}}{c_{N_2}^{1/2}c_{H_2}^{3/2}},\quad K_2 = \frac{c_{NH_3}^2}{c_{N_2}c_{H_2}^3} = K_1^2$$

$$\Longrightarrow K_2 = K_1^2 = \frac{27}{16}\times\frac{\varepsilon^4}{(1-\varepsilon^2)^2}p^2$$

4.11

表面张力系数为 $\sigma = \left(\frac{\partial G}{\partial A}\right)_{T,p}$. 热力学第三定律指出 $T \to 0$ 时, $\frac{\partial \Delta G}{\partial T} = -\left(\Delta S\right)_T = 0$. 则

$$\frac{\partial}{\partial A}\frac{\partial \Delta G}{\partial T} = 0 = \frac{\mathrm{d}}{\mathrm{d}T}\frac{\partial \Delta G}{\partial A} = \frac{\mathrm{d}}{\mathrm{d}T}\sigma$$

即 $\frac{\mathrm{d}\sigma}{\mathrm{d}T} = 0$.

4.13

设熵分别为

$$S = S_g\left(0\right) + \int_0^{T_0} \frac{c_g}{T} + L/T_0 \implies \Delta S = 51.80\mathrm{J/mol}$$

$$S = S_w\left(0\right) + \int_0^{T_0} \frac{c_w}{T} \implies \Delta S = 51.54\mathrm{J/mol}$$

二者误差范围内相等, 即 $S_g\left(0\right) = S_w\left(0\right)$.

6.2

$\mathrm{d}x\,\mathrm{d}p = \mathrm{d}x\,\mathrm{d}\sqrt{2m\varepsilon} = \frac{\sqrt{m}}{\sqrt{2\varepsilon}}\,\mathrm{d}x\,\mathrm{d}\varepsilon = h$. 则 $\mathrm{d}p = \frac{\sqrt{m}}{\sqrt{2\varepsilon}}\,\mathrm{d}\varepsilon$ 下, 量子态数为 $\frac{L\,\mathrm{d}p}{h} = \frac{L}{h}\sqrt{\frac{2\varepsilon}{m}}\,\mathrm{d}\varepsilon$

6.4

在 $\mathrm{d}p = \mathrm{d}\varepsilon/c$ 下, 量子态数为 $\frac{4\pi p^2 V\,\mathrm{d}p}{h^3}$. 代入 $\mathrm{d}p = \mathrm{d}\varepsilon/c,\ p = \varepsilon/c$.

$$D\,\mathrm{d}\varepsilon = \frac{4\pi\varepsilon^2 V\,\mathrm{d}\varepsilon}{c^3 h^3}$$

6.5

分布为玻耳兹曼分布. 则两个气体的微观状态数为:

$$\Omega = \frac{N!}{\prod a_l!}\prod \omega_l^{a_l}$$

$$\Omega' = \frac{N'!}{\prod a_l'!}\prod {\omega'}_l^{a_l'}$$

则总状态数为

$$\ln\Omega_0 = \ln\Omega\Omega' = N\ln N - \sum a_l \ln a_l + \sum a_l \ln\omega_l + N'\ln N' - \sum a_l' \ln a_l' + \sum a_l' \ln\omega_l'$$

Ω_0 为极大时, 变分为 0:

$$\delta\ln\Omega_0 = -\sum \ln\frac{a_l}{\omega_l}\delta a_l - \sum \ln\frac{a_l'}{\omega_l'}\delta a_l' = 0$$

又根据 $\sum a_l = 0, \sum a_l' = 0, \sum \varepsilon_l \delta a_l + \sum \varepsilon_l' \delta a_l' = 0$. 用拉氏乘子得

$$\delta\ln\Omega_0 - \alpha\delta N - \alpha'\delta N' - \beta\delta E = -\sum\left(\ln\frac{a_l}{\omega_l} + \alpha + \beta\varepsilon_l\right)\delta a_l - \sum\left(\ln\frac{a_l'}{\omega_l'} + \alpha' + \beta\varepsilon_l'\right)\delta a_l' = 0$$

各个变分项独立:

$$\ln\frac{a_l}{\omega_l} + \alpha + \beta\varepsilon_l = 0$$

$$\ln\frac{a_l'}{\omega_l'} + \alpha' + \beta\varepsilon_l'$$

即

$$a_l = \omega_l e^{-\alpha-\beta\varepsilon_l}$$

$$a_l' = \omega_l' e^{-\alpha'-\beta\varepsilon_l'}$$

6.6

约束条件不变. Ω 为玻色子, Ω' 为费米子, 微观状态数变为

$$\Omega = \prod \frac{(\omega_l + a_l - 1)!}{a_l!\,(\omega_l - 1)!}$$

$$\Omega' = \prod \frac{\omega_l'}{a_l'!\,(\omega_l' - a_l')!}$$

$$\ln\Omega_0 = \sum[(\omega_l + a_l)\ln(\omega_l + a_l) - a_l\ln a_l - \omega_l\ln\omega_l] + \sum[-(\omega_l' - a_l')\ln(\omega_l' - a_l') + a_l'\ln a_l' + \omega_l'\ln\omega_l']$$

$$\delta\ln\Omega_0 = \sum\frac{\ln(\omega_l + a_l)}{a_l}\delta a_l + \sum\ln\frac{\omega_l' - a_l'}{a_l'}\delta a_l' = 0$$

利用乘子法:

$$= \sum\left(\frac{\ln(\omega_l + a_l)}{a_l} - \alpha - \beta\varepsilon_l\right)\delta a_l + \sum\left(\ln\frac{\omega_l' - a_l'}{a_l'} - \alpha' - \beta\varepsilon_l'\right)\delta a_l' = 0$$

即

$$a_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} - 1}$$

$$a_l' = \frac{\omega_l'}{e^{\alpha'+\beta\varepsilon_l'} - 1}$$