统计力学第四次作业

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3.5

对 S 求微分, 平衡时: $\delta^2 S^\alpha = \sum \frac{\delta^2 U^\alpha - \delta T^\alpha \delta S^\alpha + p^\alpha \delta^2 V^\alpha + \delta p^\alpha \delta V^\alpha}{T} < 0$, 且 $\delta^2 U^1 + \delta^2 U^2 = \delta^2 V^1 + \delta^2 V^2 = 0,\ T_1 = T_2 = T,\ p_1 = p_2 = p.$

$$\implies \delta^2 S^\alpha = \sum \frac{-\delta T^\alpha \delta S^\alpha + \delta p^\alpha \delta V^\alpha}{T} < 0 \implies \delta T^\alpha \delta S^\alpha - \delta p^\alpha \delta V^\alpha > 0$$

□

将 $\delta S = \frac{\partial S}{\partial T}\delta T + \frac{\partial S}{\partial V}\delta V,\ \delta p = \frac{\partial p}{\partial T}\delta T + \frac{\partial p}{\partial V}\delta V$ 代入 $\delta T^\alpha \delta S^\alpha - \delta p^\alpha \delta V^\alpha > 0$, 可得

$$\frac{\partial S}{\partial T}(\delta T)^2 + \frac{\partial S}{\partial V}\delta V \delta T - \frac{\partial p}{\partial T}\delta T \delta V - \frac{\partial p}{\partial V}(\delta V)^2 > 0$$

又 Maxwell 关系式有 $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$, 因此

$$\frac{C_V}{T}(\delta T)^2 - \frac{\partial p}{\partial V}(\delta V)^2 > 0$$

即 $C_V^\alpha > 0,\ \left(\frac{\partial p}{\partial V^\alpha}\right)_T < 0 \implies \left(\frac{\partial V^\alpha}{\partial p}\right)_T < 0.$

□

同理, 将 $\delta S = \left(\frac{\partial S}{\partial T}\right)_p \delta T + \left(\frac{\partial S}{\partial p}\right)_T \delta p,\ \delta V = \left(\frac{\partial V}{\partial T}\right)_p \delta T + \left(\frac{\partial V}{\partial p}\right)_T \delta p$ 代入 $\delta T^\alpha \delta S^\alpha - \delta p^\alpha \delta V^\alpha > 0$, 可得

$$\left(\frac{\partial S}{\partial T}\right)_p (\delta T)^2 + \left(\frac{\partial S}{\partial p}\right)_T \delta p \delta T - \left(\frac{\partial V}{\partial T}\right)_p \delta p \delta T - \left(\frac{\partial V}{\partial p}\right)_T (\delta p)^2 > 0$$

又 Maxwell 关系式有 $-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$, 因此

$$\sum \frac{C_p}{T}(\delta T)^2 + 2\left(\frac{\partial S}{\partial p}\right)_T \delta p \delta T - \frac{\partial V}{\partial p}(\delta p)^2 > 0$$

即

$$\frac{C_p^1}{T}\left(\delta T\right)^2+\frac{C_p^2}{T}\left(\delta T\right)^2+2\left(\frac{\partial S_1}{\partial p}\right)_T\delta p\delta T+2\left(\frac{\partial S_2}{\partial p}\right)_T\delta p\delta T-\frac{\partial V_1}{\partial p}\left(\delta p\right)^2-\frac{\partial V_2}{\partial p}\left(\delta p\right)^2>0$$

孤立系统中 $2\left(\frac{\partial S_1}{\partial p}\right)_T\delta p\delta T+2\left(\frac{\partial S_2}{\partial p}\right)_T\delta p\delta T=0$.
即 $C_p^\alpha>0,\ \frac{\partial p}{\partial V^\alpha}<0$.

□

3.7

$$\mathrm{d}F=-S\mathrm{d}T-p\mathrm{d}V+\mu\mathrm{d}n$$

由微分变换关系可得:

$$\left(\frac{\partial S}{\partial n}\right)_{T,V}=-\left(\frac{\partial\mu}{\partial T}\right)_{V,n}$$

又由于 $U\left(S,V,n\right)=T\mathrm{d}S-p\mathrm{d}V+\mu\mathrm{d}n$, 则 $\left(\frac{\partial U}{\partial n}\right)_{T,V}=\frac{\partial U}{\partial S}\frac{\partial S}{\partial n}+\frac{\partial U}{\partial n}=-T\left(\frac{\partial\mu}{\partial T}\right)_{V,n}+\mu$.

3.8

$$\delta S^\alpha=\frac{\delta Q^\alpha}{T}=\frac{\delta U^\alpha+p\delta V^\alpha-\mu^\alpha\delta n}{T}$$

对 δS^α 求微分, 平衡时: $\delta^2S^\alpha=\sum\frac{\delta^2U^\alpha-\delta T^\alpha\delta S^\alpha+p^\alpha\delta V^\alpha-\delta\mu^\alpha\delta n^\alpha-\mu^\alpha\delta^2n^\alpha}{T}$, 且 $\delta^2U^1+\delta^2U^2=\delta^2V^1+\delta^2V^2=\delta^2n^1+\delta^2n^2=0,\ T_1=T_2=T,\ p_1=p_2=p,\ \mu_1=\mu_2=\mu$. 则

$$\delta^2S^\alpha=\sum\frac{-\delta T^\alpha\delta S^\alpha+\delta p^\alpha\delta V^\alpha-\delta\mu\delta n^\alpha}{T}<0$$

$$\Longrightarrow\ \sum-\delta T^\alpha\left(n^\alpha\delta S_m^\alpha+S_m^\alpha\delta n^\alpha\right)+\delta p^\alpha\left(n^\alpha\delta V_m^\alpha+V_m^\alpha\delta n^\alpha\right)-\left(-S_m\mathrm{d}T+V_m\mathrm{d}p\right)\delta n^\alpha<0$$

$$\Longrightarrow\ \delta T^\alpha\delta S^\alpha-\delta p^\alpha\delta V^\alpha>0$$

两个稳定平衡条件推导同 problem 3.5.

3.10

相变时 p,T 不变, $\Delta U_m=\Delta H_m-p\Delta V_m=L-p\Delta V$. 代入克拉珀龙方程 $\Delta V=\frac{L}{T}\frac{\mathrm{d}T}{\mathrm{d}p}$, $\Delta U_m=L-\frac{pL}{T}\frac{\mathrm{d}T}{\mathrm{d}p}$.

3.11

联立题中两式可得此时 $T=195.2\mathrm{K}$, $p=5934\mathrm{Pa}$.
由蒸气压计算式 $\ln p=-\frac{L}{RT}+A$.
对升华: $L_1/R=3754 \implies L_1=31210.8\mathrm{J}$.
对汽化: $L_2/R=3063 \implies L_2=25465.8\mathrm{J}$.
对熔解: $L_3=L_1-L_2=5745\mathrm{J}$.

3.15

$$\frac{1}{V_m}\frac{\mathrm{d}V_m}{\mathrm{d}T}=\frac{1}{V_m}\left(\frac{\partial V_m}{\partial p}\frac{\mathrm{d}p}{\mathrm{d}T}+\frac{\partial V_m}{\partial T}\right)$$

若为理想气体, 代入理想气体状态方程和克拉珀龙方程:

$$=\frac{1}{T}-\frac{1}{p}\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{1}{T}-\frac{L}{RT^2}$$

3.16

极值点即 $\left(\frac{\partial p}{\partial V_m}\right)_T=0$. 范氏气体满足 $\left(p+\frac{a}{V_m^2}\right)(V_m-b)=RT$,

$$\implies RTV_m^3=2a\left(V_m-b\right)^2$$

$$\implies p=\frac{2a}{V_m^3}\left(V_m-b\right)-\frac{a}{V_m^2} \implies pV_m^3=a\left(V_m-2b\right)$$

3.19

二级相变中, $\mathrm{d}s^{(1)}=\mathrm{d}s^{(2)}$, $\mathrm{d}v^{(1)}=\mathrm{d}v^{(2)}$.
且根据定义, $\mathrm{d}v=\alpha v\mathrm{d}T-\kappa v\mathrm{d}p$.

即 $\alpha v^{(1)}\mathrm{d}T-\kappa v^{(1)}\mathrm{d}p=\alpha v^{(2)}\mathrm{d}T-\kappa v^{(2)}\mathrm{d}p \implies \frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\alpha^{(2)}-\alpha^{(1)}}{\kappa_T^{(2)}-\kappa_T^{(1)}}$.

同理, $\mathrm{d}s=\frac{C_p}{T}\mathrm{d}T-\alpha v\mathrm{d}p$, $\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{C_p^{(2)}-C_p^{(1)}}{Tv\left(\alpha^{(2)}-\alpha^{(1)}\right)}$