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解 (a) 物体自发发生虚变动的条件为

$$dU < TdS - pdV$$

此处  $S, V$  不变, 故有

$$dU < 0$$

因此若物体达到了内能的极小值,  $dU > 0$ , 不可能自发变化, 亦即达到了平衡态。

(b)

$$dU < TdS - pdV$$

$$dH < TdS + Vdp$$

此处  $S, p$  不变, 故有

$$dH < 0$$

因此若物体达到了焓的极小值,  $dH > 0$ , 不可能自发变化, 亦即达到了平衡态。

(c)

$$dU < TdS - pdV$$

$$dH < TdS + Vdp$$

$$dS > \frac{dH}{T} - \frac{Vdp}{T}$$

此处  $H, p$  不变, 故有

$$dS > 0$$

因此若物体达到了熵的极大值,  $dS < 0$ , 不可能自发变化, 亦即达到了平衡态。

(d)

$$dU < TdS - pdV$$

$$dF < -SdT - pdV$$

$$-dF > SdT + pdV$$

$$dT < \frac{-dF}{S} - \frac{p}{S}dV$$



此处  $F, V$  不变, 故有

$$dT < 0$$

因此若物体达到了温度的极小值,  $dT > 0$ , 不可能自发变化, 亦即达到了平衡态。

(e)

$$dU < TdS - pdV$$

$$dG < -SdT + Vdp$$

$$-SdT > dG - Vdp$$

$$dT < \frac{V}{S}dp - \frac{dG}{S}$$

此处  $p, G$  不变, 故有

$$dT < 0$$

因此若物体达到了温度的极小值,  $dT > 0$ , 不可能自发变化, 亦即达到了平衡态。

(f)

$$dU < TdS - pdV$$

$$dV < \frac{T}{p}dS - \frac{dU}{p}$$

此处  $U, S$  不变, 故有

$$dV < 0$$

因此若物体达到了体积的极小值,  $dV > 0$ , 不可能自发变化, 亦即达到了平衡态。

(f)

$$dU < TdS - pdV$$

$$dF < -SdT - pdV$$

$$-dF > SdT + pdV$$

$$dV < -\frac{dF}{p} - \frac{S}{p}dT$$

此处  $F, T$  不变, 故有

$$dV < 0$$

因此若物体达到了体积的极小值,  $dV > 0$ , 不可能自发变化, 亦即达到了平衡态。



解

$$\begin{aligned}\delta S_1 &= \frac{\delta U_1}{T_1} + \frac{p_1 \delta V_1}{T_1} \\ \delta S_2 &= \frac{\delta U_2}{T_2} + \frac{p_2 \delta V_2}{T_2}\end{aligned}$$

故

$$\begin{aligned}\delta S &= \delta S_1 + \delta S_2 \\ &= \frac{\delta U_1}{T_1} + \frac{p_1 \delta V_1}{T_1} + \frac{\delta U_2}{T_2} + \frac{p_2 \delta V_2}{T_2}\end{aligned}$$

又因为

$$\delta U_1 + \delta U_2 = 0$$

$$\delta V_1 + \delta V_2 = 0$$

故得

$$T_1 = T_2$$

$$p_1 = p_2$$

$$\begin{aligned}\delta^2 S &= \delta^2 S_1 + \delta^2 S_2 \\ &= \sum_{\alpha=1}^2 \left[ -\frac{C_V^\alpha}{T^2} (\delta T)^2 + \frac{1}{T} \left( \frac{\partial p}{\partial V^\alpha} \right)_T (\delta V^\alpha)^2 \right] \\ &= \sum_{\alpha=1}^2 n^\alpha \left[ -\frac{C_{V,m}^\alpha}{T^2} (\delta T)^2 + \frac{1}{T} \left( \frac{\partial p}{\partial V_m^\alpha} \right)_T (\delta V_m^\alpha)^2 \right]\end{aligned}$$

故欲使

$$\delta^2 S < 0$$

又  $n^\alpha$  是广延量, 由于平衡只取决于强度量, 即无论  $n^\alpha$  取何值, 该式总成立, 故

$$-\frac{C_{V,m}^\alpha}{T^2} (\delta T)^2 + \frac{1}{T} \left( \frac{\partial p}{\partial V_m^\alpha} \right)_T (\delta V_m^\alpha)^2 < 0 (\alpha = 1, 2)$$



又  $\delta V_m^\alpha$  与  $\delta T$  独立, 故

$$C_{V,m}^\alpha > 0, \left(\frac{\partial p}{\partial V_m^\alpha}\right)_T < 0 (\alpha = 1, 2)$$

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解 (1)

$$dF = -SdT - pdV + \mu dn$$

故

$$\begin{aligned} \frac{\partial^2 F}{\partial n \partial T} &= \frac{\partial^2 F}{\partial T \partial n} \\ \left(\frac{\partial \mu}{\partial T}\right)_{V,n} &= -\left(\frac{\partial S}{\partial n}\right)_{V,T} \end{aligned}$$

(2)

$$dG = -SdT + Vdp + \mu dn$$

故

$$\begin{aligned} \frac{\partial^2 G}{\partial n \partial p} &= \frac{\partial^2 G}{\partial p \partial n} \\ \left(\frac{\partial \mu}{\partial p}\right)_{T,n} &= \left(\frac{\partial V}{\partial n}\right)_{p,T} \end{aligned}$$

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解

$$\begin{aligned} dU &= TdS - pdV + \mu dn \\ &= T\left(\frac{\partial S}{\partial n}\right)_{T,V}dn + T\left(\frac{\partial S}{\partial T}\right)_{n,V}dT + T\left(\frac{\partial S}{\partial V}\right)_{n,T}dV - pdV + \mu dn \end{aligned}$$

故

$$\begin{aligned} \left(\frac{\partial U}{\partial n}\right)_{T,V} &= T\left(\frac{\partial S}{\partial n}\right)_{T,V} + \mu \\ \left(\frac{\partial U}{\partial n}\right)_{T,V} - \mu &= T\left(\frac{\partial S}{\partial n}\right)_{T,V} \\ \left(\frac{\partial U}{\partial n}\right)_{T,V} - \mu &= -T\left(\frac{\partial \mu}{\partial T}\right)_{V,n} \end{aligned}$$

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解 平衡相变过程中  $T$ 、 $p$  不变, 故有

$$\Delta U_m = \Delta H_m - p\Delta V_m$$

$$\Delta H_m = L$$

又由克拉伯龙方程知

$$\frac{dp}{dT} = \frac{L}{T\Delta V_m}$$

故

$$\Delta V_m = \frac{LdT}{Tdp}$$

故

$$\begin{aligned}\Delta U_m &= L - p\frac{LdT}{Tdp} \\ &= L\left(1 - \frac{pdT}{Tdp}\right)\end{aligned}$$

对于理想气体至凝聚相的相变过程而言

$$\Delta V_m = \frac{RT}{p}$$

故

$$\begin{aligned}\frac{dp}{dT} &= \frac{L}{T\frac{RT}{p}} \\ &= \frac{Lp}{RT^2}\end{aligned}$$

故

$$\begin{aligned}\Delta U_m &= L\left(1 - \frac{pRT^2}{TLp}\right) \\ &= L\left(1 - \frac{RT}{L}\right)\end{aligned}$$

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解

$$L = H_m^\beta - H_m^\alpha$$

$$\frac{dL}{dT} = \left(\frac{\partial H_m^\beta}{\partial T}\right)_p + \left(\frac{\partial H_m^\beta}{\partial p}\right)_T \frac{dp}{dT} - \left(\frac{\partial H_m^\alpha}{\partial T}\right)_p - \left(\frac{\partial H_m^\alpha}{\partial p}\right)_T \frac{dp}{dT}$$



$$\begin{aligned}
 &= C_p^\beta - C_p^\alpha + \frac{L}{T(V_m^\beta - V_m^\alpha)} \left[ \left( \frac{\partial H_m^\beta}{\partial p} \right)_T - \left( \frac{\partial H_m^\alpha}{\partial p} \right)_T \right] \\
 &= C_p^\beta - C_p^\alpha + \frac{L}{T(V_m^\beta - V_m^\alpha)} \left[ V_m^\beta - T \left( \frac{\partial V_m^\beta}{\partial T} \right)_p - V_m^\alpha + T \left( \frac{\partial V_m^\alpha}{\partial T} \right)_p \right] \\
 &= C_p^\beta - C_p^\alpha + \frac{L}{T} - \frac{L}{V_m^\beta - V_m^\alpha} \left[ \left( \frac{\partial V_m^\beta}{\partial T} \right)_p - \left( \frac{\partial V_m^\alpha}{\partial T} \right)_p \right]
 \end{aligned}$$

若  $\beta$  相是气相  $\alpha$  相是凝聚相则可略去  $V_m^\alpha$  及  $T \left( \frac{\partial V_m^\alpha}{\partial T} \right)_p$  且  $pV_m^\beta = RT$ , 则

$$\left( \frac{\partial V_m^\beta}{\partial T} \right)_p = \frac{R}{p}$$

故

$$\begin{aligned}
 \frac{dL}{dT} &= C_p^\beta - C_p^\alpha + \frac{L}{T} - \frac{RL}{pV_m^\beta} \\
 &= C_p^\beta - C_p^\alpha + \frac{L}{T} - \frac{L}{T} \\
 &= C_p^\beta - C_p^\alpha
 \end{aligned}$$

7

解

$$\begin{aligned}
 p &= \frac{RT}{V_m - b} - \frac{a}{V_m^2} \\
 \left( \frac{\partial p}{\partial V_m} \right)_T &= \frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3}
 \end{aligned}$$

等温线极大值点和极小值点满足

$$\begin{aligned}
 \left( \frac{\partial p}{\partial V_m} \right)_T &= 0 \\
 \frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3} &= 0 \\
 \frac{RT}{(V_m - b)^2} &= \frac{2a}{V_m^3}
 \end{aligned}$$

联立此式与状态方程可得

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

故

$$pV_m^3 = a(V_m - 2b)$$



区域一、三满足  $(\frac{\partial p}{\partial V_m})_T < 0$ , 虽然化学势较高, 但是仍可作为亚稳态以单相存在。C 应处于气液不分的临界态, 区域二中各点除 C 外均不满足平衡稳定性的要求, 因此只能两相共存存在。

8

解

$$\begin{aligned} ds &= (\frac{\partial s}{\partial p})_T dp + (\frac{\partial s}{\partial T})_p dT \\ &= -\frac{\partial^2 \mu}{\partial T \partial p} dp + (\frac{\partial s}{\partial T})_p dT \\ &= -v \alpha dp + \frac{c_p}{T} dT \end{aligned}$$

相变点处

$$\begin{aligned} ds^{(1)} &= ds^{(2)} \\ -v^{(1)} \alpha^{(1)} dp + \frac{c_p^{(1)}}{T} dT &= -v^{(2)} \alpha^{(1)} dp + \frac{c_p^{(2)}}{T} dT \end{aligned}$$

又因为  $v^{(1)} = v^{(2)} = v$ , 故

$$\frac{dp}{dT} = \frac{c_p^{(2)} - c_p^{(1)}}{Tv(\alpha^{(2)} - \alpha^{(1)})}$$

$$\begin{aligned} dv &= (\frac{\partial v}{\partial p})_T dp + (\frac{\partial v}{\partial T})_p dT \\ &= -v \kappa_T dp + \alpha v dT \end{aligned}$$

相变点处

$$\begin{aligned} dv^{(1)} &= dv^{(2)} \\ -v^{(1)} \kappa_T^{(1)} dp + \alpha^{(1)} v^{(1)} dT &= -v^{(2)} \kappa_T^{(2)} dp + \alpha^{(2)} v^{(2)} dT \end{aligned}$$

又因为  $v^{(1)} = v^{(2)} = v$ , 故

$$\frac{dp}{dT} = \frac{\alpha^{(2)} - \alpha^{(1)}}{\kappa_T^{(2)} - \kappa_T^{(1)}}$$