1

解　(a) 物体自发发生虚变动的条件为

$$\mathrm{d}U < T\mathrm{d}S - p\mathrm{d}V$$

此处 S,V 不变,故有

$$\mathrm{d}U < 0$$

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

(b)

$$\mathrm{d}U < T\mathrm{d}S - p\mathrm{d}V$$

$$\mathrm{d}H < T\mathrm{d}S + V\mathrm{d}p$$

此处 S,p 不变,故有

$$\mathrm{d}H < 0$$

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

(c)

$$\mathrm{d}U < T\mathrm{d}S - p\mathrm{d}V$$

$$\mathrm{d}H < T\mathrm{d}S + V\mathrm{d}p$$

$$\mathrm{d}S > \frac{\mathrm{d}H}{T} - \frac{V\mathrm{d}p}{T}$$

此处 H,p 不变,故有

$$\mathrm{d}S > 0$$

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

(d)

$$\mathrm{d}U < T\mathrm{d}S - p\mathrm{d}V$$

$$\mathrm{d}F < -S\mathrm{d}T - p\mathrm{d}V$$

$$-\mathrm{d}F > S\mathrm{d}T + p\mathrm{d}V$$

$$\mathrm{d}T < \frac{-\mathrm{d}F}{S} - \frac{p}{S}\mathrm{d}V$$

此处 F,V 不变,故有

$$\mathrm{d}T < 0$$

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

(e)

$$\begin{aligned}
\mathrm{d}U &< T\mathrm{d}S - p\mathrm{d}V \\
\mathrm{d}G &< -S\mathrm{d}T + V\mathrm{d}p \\
-S\mathrm{d}T &> \mathrm{d}G - V\mathrm{d}p \\
\mathrm{d}T &< \frac{V}{S}\mathrm{d}p - \frac{\mathrm{d}G}{S}
\end{aligned}$$

此处 p,G 不变,故有

$$\mathrm{d}T < 0$$

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

(f)

$$\begin{aligned}
\mathrm{d}U &< T\mathrm{d}S - p\mathrm{d}V \\
\mathrm{d}V &< \frac{T}{p}\mathrm{d}S - \frac{\mathrm{d}U}{p}
\end{aligned}$$

此处 U,S 不变,故有

$$\mathrm{d}V < 0$$

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

(g)

$$\begin{aligned}
\mathrm{d}U &< T\mathrm{d}S - p\mathrm{d}V \\
\mathrm{d}F &< -S\mathrm{d}T - p\mathrm{d}V \\
-\mathrm{d}F &> S\mathrm{d}T + p\mathrm{d}V \\
\mathrm{d}V &< -\frac{\mathrm{d}F}{p} - \frac{S}{p}\mathrm{d}T
\end{aligned}$$

此处 F,T 不变,故有

$$\mathrm{d}V < 0$$

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

2

解

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

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

$$T_1 = T_2$$

$$p_1 = p_2$$

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

故欲使

$$\delta^2 S < 0$$

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

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

又 δV_m^α 与 δT 独立，故

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

3

解 (1)

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

故

$$\frac{\partial^2 F}{\partial n \partial T} = \frac{\partial^2 F}{\partial T \partial n}$$
$$(\frac{\partial \mu}{\partial T})_{V,n} = -(\frac{\partial S}{\partial n})_{V,T}$$

(2)

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

故

$$\frac{\partial^2 G}{\partial n \partial p} = \frac{\partial^2 G}{\partial p \partial n}$$
$$(\frac{\partial \mu}{\partial p})_{T,n} = (\frac{\partial V}{\partial n})_{p,T}$$

4

解

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

故

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

5

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

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T\Delta V_m}$$

故

$$\Delta V_m = \frac{L\mathrm{d}T}{T\mathrm{d}p}$$

故

$$\begin{aligned}\Delta U_m &= L - p\frac{L\mathrm{d}T}{T\mathrm{d}p}\\ &= L\left(1 - \frac{p\mathrm{d}T}{T\mathrm{d}p}\right)\end{aligned}$$

对于理想气体至凝聚相的相变过程而言

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

故

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

故

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

6

解

$$L = H_m^\beta - H_m^\alpha$$
$$\frac{\mathrm{d}L}{\mathrm{d}T} = (\frac{\partial H_m^\beta}{\partial T})_p + (\frac{\partial H_m^\beta}{\partial p})_T\frac{\mathrm{d}p}{\mathrm{d}T} - (\frac{\partial H_m^\alpha}{\partial T})_p - (\frac{\partial H_m^\alpha}{\partial p})_T\frac{\mathrm{d}p}{\mathrm{d}T}$$

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

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

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

故

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

7

解

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

等温线极大值点和极小值点满足

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

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

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

相变点处

$$\mathrm{d}s^{(1)} = \mathrm{d}s^{(2)}$$

$$-v^{(1)}\alpha^{(1)}\mathrm{d}p + \frac{c_p^{(1)}}{T}\mathrm{d}T = -v^{(2)}\alpha^{(1)}\mathrm{d}p + \frac{c_p^{(2)}}{T}\mathrm{d}T$$

又因为 $v^{(1)} = v^{(2)} = v$,故

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{c_p^{(2)} - c_p^{(1)}}{Tv(\alpha^{(2)} - \alpha^{(1)})}$$

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

相变点处

$$\mathrm{d}v^{(1)} = \mathrm{d}v^{(2)}$$

$$-v^{(1)}\kappa_T^{(1)}\mathrm{d}p + \alpha^{(1)}v^{(1)}\mathrm{d}T = -v^{(2)}\kappa_T^{(2)}\mathrm{d}p + \alpha^{(2)}v^{(2)}\mathrm{d}T$$

又因为 $v^{(1)} = v^{(2)} = v$,故

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\alpha^{(2)} - \alpha^{(1)}}{\kappa_T^{(2)} - \kappa_T^{(1)}}$$