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习题三，13，解

证明：已知一级相变中，$L = T(S^{\beta} - S^{\alpha})$，$S = S[T, p(T)]$

$$\begin{cases} \frac{dL}{dT} = S^{\beta} - S^{\alpha} + T\left(\Delta \frac{\partial S}{\partial T}\right) + T\left(\Delta \frac{\partial S}{\partial p} \frac{dp}{dT}\right) \\ \Delta \frac{\partial S}{\partial T} = \Delta\left(\frac{\partial S}{\partial T}\right) = \left(\frac{\partial S^{\beta}}{\partial T}\right)_p - \left(\frac{\partial S^{\alpha}}{\partial T}\right)_p \\ \Delta \frac{\partial S}{\partial T} \frac{dp}{dT} = \frac{dp}{dT} \cdot \left[\left(\frac{\partial S^{\beta}}{\partial T}\right)_p - \left(\frac{\partial S^{\alpha}}{\partial T}\right)_p\right] \end{cases}$$

由 $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$，$L = T(S^{\beta} - S^{\alpha})$，$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

解得：

$$\frac{dL}{dT} = C_p^{\beta} - C_p^{\alpha} + \frac{L}{T} - \left[\left(\frac{\partial V^{\beta}}{\partial T}\right)_p - \left(\frac{\partial V^{\alpha}}{\partial T}\right)_p\right] \frac{L}{V^{\beta} - V^{\alpha}}$$

当β为气相，α为凝聚相时有

$V^{\alpha} \sim 0$，$\left(\frac{\partial V^{\alpha}}{\partial T}\right)_p \sim 0$，$p_{\beta} V_{\beta} = R_{\beta} T_{\beta}$

解得：$\frac{dL}{dT} = C_p^{\beta} - C_p^{\alpha}$

证毕

3.18. 证明：由已知，$T^\alpha = T^\beta$，有相变潜热 $L = T(S_m^\beta - S_m^\alpha)$

令 $\mu^\alpha(T, p^\alpha) = \mu^\beta(T, p^\beta)$

$\mu = U_m - TS_m + pV_m$ 代入上式

解得：

$$U_m^\beta + p^\beta V_m^\beta - TS_m^\beta = U_m^\alpha + p^\alpha V_m^\alpha - TS_m^\alpha$$

整理得：

$$L = T(S_m^\beta - S_m^\alpha) = U_m^\beta + p^\beta V_m^\beta - (U_m^\alpha + p^\alpha V_m^\alpha)$$

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

证毕

3.19. 证明：由已知，$\begin{cases} \Delta dS = 0 \\ \Delta dV = 0 \end{cases} \Leftrightarrow \begin{cases} dS^{(2)} - dS^{(1)} = 0 \\ dV^{(2)} - dV^{(1)} = 0 \end{cases}$

$\because$ $dS^{(2)} = \left(\frac{\partial S^{(2)}}{\partial T}\right) dT + \left(\frac{\partial S^{(1)}}{\partial p}\right) dp$

$dS^{(1)} = \left(\frac{\partial S^{(1)}}{\partial T}\right) dT + \left(\frac{\partial S^{(1)}}{\partial p}\right) dp$

$\therefore$ $\Delta dS = 0 = -\left(\frac{\partial S^{(2)}}{\partial p} - \frac{\partial S^{(1)}}{\partial p}\right) dp = \left(\frac{\partial S^{(2)}}{\partial T} - \frac{\partial S^{(1)}}{\partial T}\right) dT$

变换得：

$$\frac{dp}{dT} = \frac{\frac{\partial S^{(2)}}{\partial T} - \frac{\partial S^{(1)}}{\partial T}}{\frac{\partial S^{(2)}}{\partial p} - \frac{\partial S^{(1)}}{\partial p}}$$，将 $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$ 代入，

由 $\frac{\partial S}{\partial p} = \frac{\partial^2 \mu}{\partial T \partial p} = -V\alpha$，代入解得：

$$\frac{dp}{dT} = \frac{C_p^{(2)} - C_p^{(1)}}{TV(\alpha^{(2)} - \alpha^{(1)})}$$ 证毕

同理由 $\Delta dV = 0 = dV^{(2)} - dV^{(1)}$ 证得

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

习题四.3.证明：$G=\sum_i n_i\mu_i = n_1\mu_1+n_2\mu_2$

将 $\mu_1 = g_1(T,p)+RT\ln x_1$，

$\mu_2 = g_2(T,p)+RT\ln x_2$，代入，

得 $G = n_1 g_1(T,p)+n_2 g_2(T,p)+n_1 RT\ln x_1 + n_2 RT\ln x_2$

$\Delta G = G_1 - G_0$

$\Delta G = G - [n_1 g_1(T,p)+n_2 g_2(T,p)]$

$\Delta G = n_1 RT\ln x_1 + n_2 RT\ln x_2$

$\Delta G = RT(n_1\ln x_1 + n_2 RT\ln x_2)$

(a) 得证

由 $V=\frac{\partial G}{\partial p}$，将 ΔG 代入，有 $\Delta V = \frac{\partial(\Delta G)}{\partial p}=0$

(b) 得证

同上，由 $S=-\frac{\partial G}{\partial T}$ 可证 $\Delta S = -R(n_1\ln x_1 + n_2\ln x_2)$

(c) 得证

$\Delta H = \Delta G + T\Delta S$，将 ΔG、ΔS 代入解得：

$\Delta H = 0$

(d) 得证

$\Delta U = \Delta H - p\Delta V = 0$

(e) 得证

习题六，1. ~~解~~

证明：
$$\begin{cases} p_x = \frac{2\pi\hbar}{L} n_x \\ p_y = \frac{2\pi\hbar}{L} n_y \\ p_z = \frac{2\pi\hbar}{L} n_z \end{cases}$$
由 $\varepsilon = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$，

有 $D(\varepsilon)d\varepsilon = \frac{V}{h^3}(dp_x\, dp_y\, dp_z)$

$V = L^3$ 由，有
$$\begin{cases} D(\varepsilon)d\varepsilon = \frac{4\pi V}{h^3} p^2 dp \\ \varepsilon = \frac{p^2}{2m} \Rightarrow p\,dp = m\,d\varepsilon \end{cases}$$
解得：
$$D(\varepsilon)d\varepsilon = \frac{2\pi V}{h^3}\sqrt{(2m)^3 \varepsilon}\, d\varepsilon$$
即 $D(\varepsilon)d\varepsilon = \frac{2\pi V}{h^3}(2m)^{\frac{3}{2}} \varepsilon^{\frac{1}{2}} d\varepsilon$

6.2.证明：$\begin{cases} D(\varepsilon)d\varepsilon\Big|_{p\sim p+dp} = \frac{L\,dp}{\hbar}\cdot 2 \\ \frac{p^2}{2m} = \varepsilon \end{cases}$

解得：$D(\varepsilon)d\varepsilon = \frac{2L}{\hbar}\sqrt{\frac{m}{2\varepsilon}}\,d\varepsilon$

即 $D(\varepsilon)d\varepsilon = \frac{2L}{\hbar}\left(\frac{m}{2\varepsilon}\right)^{\frac{1}{2}}d\varepsilon$

6.3.证明：与上问同理，有

$D(\varepsilon)\,d\varepsilon\big|_{\mu} = \frac{1}{\hbar^2}dx\,dy\,dp_x\,dp_y$

令 $\begin{cases} p_x = p\cos\theta \\ p_y = p\sin\theta \end{cases}$

有 $dx\,dy\,dp_x\,dp_y = p\,dp\,d\theta$

$\begin{cases} D(\varepsilon)d\varepsilon = \frac{L^2}{\hbar^2}p\,dp\,d\theta \\ \varepsilon = \frac{p^2}{2m} \end{cases}$

解得：$D(\varepsilon)d\varepsilon = \frac{2\pi L^2}{\hbar^2}m\,d\varepsilon$

6.4. 解：$\begin{cases} D(\varepsilon)d\varepsilon\Big|_{p\sim p+dp} = \dfrac{4\pi V}{h^3}p^2dp \\ 由已知，\varepsilon = cp \end{cases}$

解得：$D(\varepsilon)d\varepsilon = \dfrac{4\pi V}{(ch)^3}\varepsilon^2 d\varepsilon$

6.5. ~~解~~ 证明：设 $N = \sum_l a_l$，$N' = \sum_l a_l'$

有 $E = \sum_l \varepsilon_l a_l + \sum_l \varepsilon_l' a_l'$

当且仅当 $\{a_l\}$、$\{a_l'\}$ 满足以上条件时，

才可能实现

有 $\begin{cases} \Omega = \dfrac{N!}{\prod_l a_l!}\prod_l w_l^{a_l} \\ \Omega' = \dfrac{N'!}{\prod_l a_l'!}\prod_l w_l'^{a_l'} \end{cases}$

由 $\Omega^{(0)} = \Omega\Omega'$

解得：$\ln\Omega^{(0)} = N\ln N - \sum_l a_l \ln a_l + \sum_l a_l \ln w_l + N'\ln N' - \sum_l a_l'\ln a_l' + \sum_l a_l' \ln w_l'$

令 $\delta\ln\Omega^{(0)} = 0 = -\sum_l \ln\left(\dfrac{a_l}{w_l}\right)\delta a_l - \sum_l \ln\left(\dfrac{a_l'}{w_l'}\right)\delta a_l'$

有条件：$\begin{cases} \delta N = \delta N' = 0 \\ \delta E = 0 \end{cases}$

解得：$\delta\ln\Omega^{(0)} - \alpha\delta N - \alpha'\delta N' - \beta\delta E = 0$

令 $A\delta a_l$ 和 $B\delta a_l'$ 中 $A = B = 0$，即有

$\begin{cases} \ln\dfrac{a_l}{w_l} + \alpha + \beta\varepsilon_l = 0 \\ \ln\dfrac{a_l'}{w_l'} + \alpha' + \beta\varepsilon_l' = 0 \end{cases} \Leftrightarrow \begin{cases} a_l = w_l e^{-\alpha-\beta\varepsilon_l} \\ a_l' = w_l' e^{-\alpha'-\beta\varepsilon_l'} \end{cases}$