热力学习题答疑

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第一章 热力学的基本规律

物态方程

一般形式： $f(p, V, T) = 0$

体胀系数： $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ 压强系数： $\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$ 等温压缩系数： $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

链式关系： $\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_p = -1 \quad \alpha = \kappa_T \beta p$

热容

热力学第一定律： $dU = đQ + đW = TdS - pdV$

定压热容： $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$ 定容热容： $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$

以 T,V 为自变量： $dU = C_V dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] dV$

以 T,p 为自变量： $d(U + pV) = C_p dT - \left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] dp$

理想气体定压热容与定容热容之间的关系： $C_p - C_V = nR$

理想气体的多方过程

多方过程：$pV^n = C$

多方过程中的功：$W = -\int_{V_A}^{V_B} pdV = \frac{p_B V_B - p_A V_A}{n-1}$

多方过程中的热容：$C_{(n)} = \frac{n-\gamma}{n-1} C_V$

熵

可逆过程中系统的熵变：$dS = \frac{đQ}{T}$

卡诺效率：$\eta = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$

不可逆过程中系统的熵变：$dS > \frac{đQ}{T}$

热力学第二定律：$dS \geq \frac{đQ}{T}$

汪书 1.5

描述金属丝的几何参量是长度 L，力学参量是张力 $\mathscr{F}$，物态方程是 $f(\mathscr{F}, L, T) = 0$. 实验通常是在 $1p_n$ 下进行，其体积变化可以忽略. 线胀系数定义为 $\alpha = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_{\mathscr{F}}$. 等温弹性模量定义为 $E = \frac{L}{A}\left(\frac{\partial \mathscr{F}}{\partial L}\right)_T$，其中 A 是金属丝的截面积. 一般来说，$\alpha$ 和 E 是 T 的函数，对 $\mathscr{F}$ 仅有微弱的依赖关系. 如果温度的变化范围不大，可以看做常量. 假设金属丝两端固定. 试证明，当温度由 T_1 降至 T_2 时，其张力的增加为 $\Delta\mathscr{F} = -EA\alpha(T_2 - T_1)$.

$$\left(\frac{\partial \mathscr{F}}{\partial T}\right)_L = \frac{\partial(\mathscr{F},L)}{\partial(T,L)} = \frac{\partial(\mathscr{F},L)}{\partial(T,\mathscr{F})}\frac{\partial(T,\mathscr{F})}{\partial(T,L)} = -\left(\frac{\partial L}{\partial T}\right)_{\mathscr{F}}\left(\frac{\partial \mathscr{F}}{\partial L}\right)_T = -\alpha AE$$

$$\Delta\mathscr{F} = -EA\alpha(T_2 - T_1)$$

汪书 1.6

一理想弹性丝的物态方程为 $\mathscr{F} = bT\left(\frac{L}{L_0} - \frac{L_0^2}{L^2}\right)$，其中 L 是长度，L_0 是张力 $\mathscr{F}$ 为零时的 L 值，它只是温度 T 的函数，b 是常数. 试证明:

(a) 等温弹性模量为 $E = \frac{bT}{A}\left(\frac{L}{L_0} + \frac{2L_0^2}{L^2}\right)$. 在张力为零时，$E_0 = \frac{3bT}{A}$. 其中 A 是弹性线的截面面积。

(b) 线胀系数 $\alpha = \alpha_0 - \frac{1}{T}\frac{L^3/L_0^3 - 1}{L^3/L_0^3 + 2}$，其中 $\alpha_0 = \frac{1}{L_0}\frac{dL_0}{dT}$.

$$E = \frac{L}{A}\left(\frac{\partial \mathscr{F}}{\partial L}\right)_T = \frac{bT}{A}\left(\frac{L}{L_0} + \frac{2L_0^2}{L^2}\right)$$

$$\alpha = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_{\mathscr{F}} = -\frac{1}{L}\left(\frac{\partial \mathscr{F}}{\partial T}\right)_L\left(\frac{\partial L}{\partial \mathscr{F}}\right)_T = \frac{1}{L_0}\frac{dL_0}{dT} - \frac{1}{T}\frac{L^3/L_0^3 - 1}{L^3/L_0^3 + 2}$$

林书 1.8

抽成真空的小匣带有活门，打开活门让外面的空气冲入，当压强达到外界压强 p_0 时将活门关上.
(1) 证明小匣内的空气在没有与外界交换热量之前，他的内能 U 与原来在大气中的内能 U_0 之差为 $U - U_0 = p_0 V_0$，其中 V_0 是它原来在大气中的体积.
(2) 若气体是理想气体，求它的温度 T 与体积 V.

$$\Delta U = W = p_0 V_0$$

$$\Delta U = p_0 V_0 = C_V (T - T_0)$$

$$T - T_0 = \frac{C_p - C_V}{C_V} T_0 = (\gamma - 1) T_0$$

$$T = \gamma T_0 \quad V = \gamma V_0$$

林书 1.9

一理想气体 $\gamma = C_p/C_V$ 是温度的函数，求在准静态绝热过程 T，V 的关系和 T，p 的关系. 这些关系中用到一个函数 $F(T)$，它由下式决定：$\ln F(T) = \int \frac{\mathrm{d}T}{(\gamma-1)T}$

$$Tds = C_V dT + pdV = C_V dt + \frac{(C_p - C_V)T}{V} dV = 0$$

$$\frac{dT}{(\gamma-1)T} + \frac{dV}{V} = 0$$

$$\ln F(T) + \ln V = C$$

汪书 1.11

大气温度随高度变低的主要原因是在对流层中不同高度之间的空气不断发生对流．由于气压随高度变低，空气上升时膨胀，下降时收缩．空气的热导率很小，膨胀与收缩的过程可以认为是绝热过程．试计算大气温度随高度的变化率 $\frac{dT}{dz}$，并给出数值结果．

$$\frac{dp}{dz} = -\rho(z)gz = -\frac{Mg}{RT(z)}p(z)$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{\gamma-1}{\gamma}\frac{T}{p}$$

$$\frac{dT}{dz} = \left(\frac{\partial T}{\partial p}\right)_S \frac{dp}{dz} = \frac{\gamma-1}{\gamma}\frac{Mg}{R}$$

$$\gamma = 1.41 \quad M = 29\times 10^{-3}\ \mathrm{kg}\cdot\mathrm{mol}^{-1} \quad g = 9.8\ \mathrm{m}\cdot\mathrm{s}^{-2}$$

$$\frac{dT}{dz} = -10\ \mathrm{K}\cdot\mathrm{km}^{-1}$$

汪书 1.19

均匀杆的温度一端为 T_1，另一端为 T_2. 试计算达到均匀温度 $\frac{1}{2}(T_1+T_2)$ 后的熵增.

$$T(l) = T_2 + \frac{T_1 - T_2}{L} l$$

$$dS(l) = c_p dl \int_T^{\frac{T_1+T_2}{2}} \frac{dT}{T} = c_p dl \ln \frac{(T_1+T_2)/2}{T_2+(T_1-T_2)l/L}$$

$$\Delta S = c_p \int_0^l \left[\ln \frac{(T_1+T_2)/2}{T_2+(T_1-T_2)l/L} \right] dl = c_p L \left(\ln \frac{T_1+T_2}{2} - \frac{T_1 \ln T_1 - T_2 \ln T_2}{T_1 - T_2} + 1 \right)$$

汪书 1.22

有两个相同的物体，热容为常量，初始温度同为 T_1. 今令一制冷机在此两物体间工作，使其中一个物体的温度降低到 T_2 为止. 假设物体维持在定压下，并且不发生相变. 试根据熵增加原理证明，此过程所需的最小功为 $W_{\min} = C_p\left(\frac{T_1^2}{T_2} + T_2 - 2T_1\right)$

$$Q_1 = C_p(T_1 - T_i) \quad Q_2 = C_p(T_i - T_2)$$

$$W = Q_1 - Q_2 = C_p(T_1 + T_2 - 2T_i)$$

$$\Delta S = \Delta S_1 + \Delta S_2 = C_p \ln\frac{T_1}{T_i} + C_p \ln\frac{T_2}{T_i} \geq 0$$

$$T_1 T_2 \geq T_i^2$$

$$W_{\min} = C_p\left(\frac{T_i^2}{T_2} + T_2 - 2T_i\right)$$

热力学函数的全微分

$$dU = TdS - pdV \qquad dF = -SdT - pdV$$
$$dH = TdS + Vdp \qquad dG = -SdT + Vdp$$

麦克斯韦关系

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial p}{\partial S}\right)_V \qquad \left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 F}{\partial T \partial V} = \left(\frac{\partial p}{\partial T}\right)_V$$
$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{\partial^2 H}{\partial S \partial p} = \left(\frac{\partial V}{\partial S}\right)_p \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\frac{\partial^2 G}{\partial T \partial p} = -\left(\frac{\partial V}{\partial T}\right)_p$$

偏导数自变量的变换

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = T\frac{\partial(S,V)}{\partial(T,V)} = T\frac{\partial(S,V)/\partial(T,p)}{\partial(T,V)/\partial(T,p)} = T\frac{\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial V}{\partial p}\right)_T - \left(\frac{\partial S}{\partial p}\right)_T\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = C_p + T\left(\frac{\partial V}{\partial T}\right)_p^2\left(\frac{\partial p}{\partial V}\right)_T$$

汪书 2.6

水的体胀系数 α 在 $0°\mathrm{C} < t < 4°\mathrm{C}$ 时为负值. 试证明在这温度范围内，水在绝热压缩时变冷（其它液体和所有气体在绝热压缩时都升温）.

$$dU = TdS - pdV = C_V dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] dV$$

$$TdS = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV$$

$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_V \frac{1}{\alpha}\kappa_T = -1$$

$$dT = -\frac{T}{C_V}\frac{\alpha}{\kappa_T} dV$$

汪书 2.7

试证明在相同的压强降落下，气体在准静态绝热膨胀中的温度降落大于在节流过程中的温度涨落.

$$\left(\frac{\partial T}{\partial p}\right)_S = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p} = \frac{T\left(\frac{\partial V}{\partial T}\right)_p}{C_p}$$

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p}$$

汪书 2.12

求范式气体的特性函数 F_m，并导出其它的热力学函数。

$$dF_m = -S_m dT - p dV_m$$

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

$$\left(\frac{\partial F_m}{\partial V_m}\right)_T = -p = -\frac{RT}{V_m - b} + \frac{a}{V_m^2}$$

$$F_m(T, V_m) = -RT\ln(V_m - b) - \frac{a}{V_m} + f(T)$$

$$f(T) = \int C_{v,m} dT - T\int \frac{C_{V,m}}{T} dT + U_{m0} - TS_{m0}$$

汪书 2.14

X 射线衍射实验发现，橡皮带未被拉紧时具有无定型结构，当受张力而被拉伸时，具有晶形结构. 这一事实表明橡皮带具有大的分子链.

(a) 试讨论橡皮带在等温过程中被拉伸时它的熵是增加还是减少;

(b) 试证明它的膨胀系数 $\alpha = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_{\mathcal{F}}$ 是负的.

$$dF = -SdT + \mathcal{F}dL$$

$$\left(\frac{\partial \mathcal{F}}{\partial T}\right)_L = -\left(\frac{\partial S}{\partial L}\right)_T > 0$$

$$\left(\frac{\partial L}{\partial T}\right)_{\mathcal{F}} = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_L \left(\frac{\partial L}{\partial \mathcal{F}}\right)_T < 0$$

汪书 2.18

电介质的介电常量 $\epsilon(T)=\frac{D}{E}$ 与温度有关. 试求电路为闭路时电介质的热容与充电后再令电路断开后的热容之差.

$$dU = TdS + VEdD$$

$$C_E = T\left(\frac{\partial S}{\partial T}\right)_E = T\frac{\partial(S,E)/\partial(T,D)}{\partial(T,E)/\partial(T,D)} = T\frac{\left(\frac{\partial S}{\partial T}\right)_D\left(\frac{\partial E}{\partial D}\right)_T-\left(\frac{\partial S}{\partial D}\right)_T\left(\frac{\partial E}{\partial T}\right)_D}{\left(\frac{\partial E}{\partial D}\right)_T} = C_D - VT\left(\frac{\partial E}{\partial T}\right)_D\left(\frac{\partial D}{\partial T}\right)_E$$

$$\left(\frac{\partial E}{\partial T}\right)_D = -\frac{D}{\epsilon^2(T)}\frac{d\epsilon}{dt}$$

$$\left(\frac{\partial D}{\partial T}\right)_E = \frac{D}{\epsilon(T)}\frac{d\epsilon}{dt}$$

汪书 2.19

试证明磁介质 C_H 与 C_M 之差等于 $C_H - C_M = \mu_0 T \left(\frac{\partial H}{\partial T}\right)_M^2 \left(\frac{\partial M}{\partial H}\right)_T$.

$$dU = TdS + \mu_0 HdM$$

$$C_H = T\frac{\partial(S,H)/\partial(T,M)}{\partial(T,H)/\partial(T,M)} = T\frac{\left(\frac{\partial S}{\partial T}\right)_M\left(\frac{\partial H}{\partial M}\right)_T-\left(\frac{\partial S}{\partial M}\right)_T\left(\frac{\partial H}{\partial T}\right)_M}{\left(\frac{\partial H}{\partial M}\right)_T} = C_M + \mu_0 T \left(\frac{\partial H}{\partial T}\right)_M^2 \left(\frac{\partial M}{\partial H}\right)_T$$

汪书 2.21

已知超导体的磁感应强度 $B=\mu_0(H+M)=0$, 求证:
(a) C_M 与 M 无关，只是 T 的函数，其中 C_M 是在磁化强度 M 保持不变时的热容.
(b) $U=\int C_M\mathrm{d}T-\frac{\mu_0 M^2}{2}+U_0$
(c) $S=\int \frac{C_M}{T}\mathrm{d}T+S_0$

$$\left(\frac{\partial C_M}{\partial M}\right)_T=-\mu_0 T\left(\frac{\partial^2 H}{\partial T}\right)_M=0$$

$$dU= Tds+\mu_0 HdM$$

$$\left(\frac{\partial U}{\partial M}\right)_T=-\mu_0 T\left(\frac{\partial H}{\partial T}\right)_M+\mu_0 H=-\mu_0 M$$

$$dU=\left(\frac{\partial U}{\partial T}\right)_M dT+\left(\frac{\partial U}{\partial M}\right)_T dM$$

$$dS=\frac{C_M}{T}dT-\mu_0\left(\frac{\partial H}{\partial T}\right)_M dM$$

热动平衡判据

孤立系统熵判据: $\delta S = 0 \quad \delta^2 S < 0$
等温等容系统自由能判据: $\delta F = 0 \quad \delta^2 F > 0$
等温等压系统吉布斯函数判据: $\Delta G = 0 \quad \delta^2 G > 0$
等熵等容系统内能熵判据: $\delta U = 0 \quad \delta^2 U < 0$
其它约束条件下考察系统的虚变动是否满足热力学第二定律: $\delta U < T\delta S + \delta W$

单元复相系平衡

热平衡条件: $T^\alpha = T^\beta$
力学平衡条件: $p^\alpha = p^\beta$
相变平衡条件: $\mu^\alpha = \mu^\beta$
克拉珀龙方程: $\frac{dp}{dT} = \frac{L}{T(V_m^\beta - V_m^\alpha)} = \frac{S_m^\beta - S_m^\alpha}{V_m^\beta - V_m^\alpha}$

二级相变

朗道自由能： $F(T,M) = F_0(T) + \frac{1}{2}a_0\frac{T-T_c}{T_c}M^2 + \frac{1}{4}b(T)M^4$

无序态的序参量： $M = 0 \quad T > T_c$

有序态的序参量： $M^2 = -\frac{a_0(T-T_c)}{bT_c} \quad T < T_c$

无序态的熵： $S(T) = S_0(T) \quad T > T_c$

有序态的熵： $S(T) = S_0(T) + \frac{a_0^2(T-T_c)}{2bT_c^2} \quad T < T_c$

无序态的热容： $C_V(T) = C_{V,0}(T) \quad T > T_c$

有序态的热容： $C_V(T) = C_{V,0}(T) + \frac{a_0}{bT_c^2} \quad T < T_c$

汪书 3.2

试证明，以内能和体积为自变量，熵的二级微分为：

$$\delta^2 S = -\frac{1}{C_V T^2}(\delta U)^2 + \frac{2p}{C_V T}\left(\beta - \frac{1}{T}\right)\delta U \delta V + \left(\frac{2p^2\beta}{C_V T} - \frac{p^2}{C_V T^2} - \frac{p^2}{C_V}\beta^2 - \frac{1}{TVK_T}\right)(\delta V)^2$$

其中，$\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$ 是压强系数.

$$\delta^2 S = \frac{\partial^2 S}{\partial U^2}(\delta U)^2 + 2\frac{\partial^2 S}{\partial U \partial V}\delta U \delta V + \frac{\partial^2 S}{\partial V^2}(\delta V)^2$$

$$\frac{\partial^2 S}{\partial U^2} = \left(\frac{\partial}{\partial U}\frac{1}{T}\right)_V = -\frac{1}{C_V T^2}$$

$$\frac{\partial^2 S}{\partial U \partial V} = \left(\frac{\partial}{\partial V}\frac{1}{T}\right)_U = -\frac{1}{T^2}\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{T^2}\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V} = \frac{1}{C_V T^2}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] = \frac{p\beta}{C_V T} - \frac{p}{C_V T^2}$$

$$\frac{\partial^2 S}{\partial V^2} = \left(\frac{\partial}{\partial V}\frac{p}{T}\right)_U = \frac{T\left(\frac{\partial p}{\partial V}\right)_U - p\left(\frac{\partial T}{\partial V}\right)_U}{T^2} = -\frac{1}{T}\frac{\left(\frac{\partial U}{\partial V}\right)_p}{\left(\frac{\partial U}{\partial p}\right)_V} + \frac{p}{T^2}\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V} = \frac{2p^2\beta}{C_V T} - \frac{p^2}{C_V T^2} - \frac{p^2\beta^2}{C_V} - \frac{1}{TV\kappa_T}$$

汪书 3.5

孤立系统含两个子系统. 子系统间可以通过做功和传热的方式交换能量. 试根据熵判据, 从 $\delta^2 S < 0$ 导出不等式 $\delta T^\alpha \delta S^\alpha - \delta p^\alpha \delta V^\alpha > 0 (\alpha = 1, 2)$. 如果取 T, V 为自变量, 可得平衡稳定条件 $C_V^\alpha > 0$, $\left(\frac{\partial V^\alpha}{\partial p}\right)_T < 0 (\alpha = 1, 2)$; 如果取 T, p 为自变量, 可得平衡稳定条件 $C_p^\alpha > 0$, $\left(\frac{\partial V^\alpha}{\partial p}\right)_S < 0 (\alpha = 1, 2)$.

$$\delta S^\alpha = \frac{\delta U^\alpha + p^\alpha \delta V^\alpha}{T^\alpha}$$

$$\delta^2 S^\alpha = \frac{\delta^2 U^\alpha}{T^\alpha} - \frac{\delta U^\alpha \delta T^\alpha}{(T^\alpha)^2} + \frac{\delta p^\alpha \delta V^\alpha + p^\alpha \delta^2 U^\alpha}{T^\alpha} - \frac{p^\alpha \delta V^\alpha \delta T^\alpha}{(T^\alpha)^2} = \frac{\delta^2 U^\alpha + p^\alpha \delta^2 V^\alpha + \delta p^\alpha \delta V^\alpha - \delta T^\alpha \delta S^\alpha}{T^\alpha}$$

$$\delta^2 S = \sum_\alpha \delta S^\alpha = \sum_\alpha \frac{\delta p^\alpha \delta V^\alpha - \delta T^\alpha \delta S^\alpha}{T^\alpha}$$

汪书 3.13

试证明，相变潜热随温度的变化率为 $\frac{dL}{dT} = c_p^\beta - c_p^\alpha + \frac{L}{T} - \left[\left(\frac{\partial V_m^\beta}{\partial T}\right)_p - \left(\frac{\partial V_m^\alpha}{\partial T}\right)_p\right] \frac{L}{V_m^\beta - V_m^\alpha}$. 如果 β 相是气相，α 相是凝聚相，试证明上式可简化为 $\frac{dL}{dT} = c_p^\beta - c_p^\alpha$

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

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p \quad \left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$$

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

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

汪书 3.21

假设外磁场十分微弱，朗道自由能表达式 $\mu_0 H = \left(\frac{\partial F}{\partial M}\right)_T = aM + bM^3$ 仍近似适用，试导出无序相与有序相的 $C_H - C_M$.

$$C_H - C_M = \mu_0 T \left(\frac{\partial H}{\partial T}\right)_M^2 \left(\frac{\partial M}{\partial H}\right)_T$$

$$\left(\frac{\partial H}{\partial T}\right)_M = \frac{a_0}{\mu_0 T_C} M$$

$$\left(\frac{\partial M}{\partial H}\right)_T = \frac{\mu_0}{a_0(T/T_c - 1) + 3bM^2}$$

$$T > T_c \quad M = 0 \quad C_H - C_M = 0$$

$$T < T_c \quad M^2 = \frac{a_0(T_C - T)}{bT_c} \quad C_H - C_M = \frac{a_0^2 T}{2bT_c^2}$$

第四章 多元系的复相平衡和化学平衡

欧拉定理

m 齐次函数 $f(x_1,...x_k)$ 满足：$\sum_i x_i \frac{\partial f}{\partial x_i} = mf$

V，U，S 等广延量都是各组元物质的量的一次齐函数：$V = \sum_i n_i \frac{\partial f}{\partial n_i} = \sum_i n_i v_i$

吉布斯关系：$SdT - Vdp + \sum_i n_i d\mu_i = 0$

混合理想气体

各组元的化学势：$\mu_i = g_i(T) + RT\ln x_i$

吉布斯函数：$G = \sum_i n_i \mu_i$

体积：$V = \frac{\partial G}{\partial p} = \frac{\sum_i n_i RT}{p}$

热力学第三定律

$\lim_{T\to 0} S_0 = 0$

汪书 4.4

理想溶液中各组元的化学势为 $\mu_i = g_i(T,p) + RT\ln x_i$
(a) 假设溶质是非挥发性的．试证明，当溶液与溶剂的蒸气达到平衡时，相平衡条件为 $g_1' = g_1 + RT\ln(1-x)$，其中 g_1' 是蒸气的摩尔吉布斯函数，g_1 是纯溶剂的摩尔吉布斯函数，x 是溶质在溶液中的摩尔分数．
(b) 求证：在一定温度下，溶剂的饱和蒸气压随溶质浓度的变化率为 $\left(\frac{\partial p}{\partial x}\right)_T = -\frac{p}{1-x}$．
(c) 将上式积分，得 $p_x = p_0(1-x)$，其中 p_0 是该温度下纯溶剂的饱和蒸气压，p_x 是溶质浓度为 x 时的饱和蒸气压．

$$\mu_1(T,p,x) = \mu_1'$$

$$g_1(T,p) + RT\ln(1-x) = g_1'(T,p)$$

$$\left(\frac{\partial g_1}{\partial p}\right)_T dp + \frac{RT}{1-x}dx = \left(\frac{\partial g_1'}{\partial p}\right)_T dp$$

$$\left(\frac{\partial p}{\partial x}\right)_T = -\frac{RT}{(1-x)V_m'} = -\frac{p}{1-x}$$

汪书 4.6

开口玻璃管底端有半透膜将管中糖的水溶液与容器内的水隔开．半透膜只让水通过，不让糖通过．实验发现，糖水溶液的液面比容器内水的液面上升一个高度 h，表明糖水溶液的压强 p 与水的压强 p_0 之差为 $p-p_0=\rho gh$．这一压强差称为渗透压．试证明，糖水与水达到平衡时有 $g_1(T,p)+RT\ln(1-x)=g_1(T,p_0)$，其中 g_1 为纯水的摩尔吉布斯函数，x 是糖水中糖的摩尔分数，$x=\frac{n_2}{n_1+n_2}\approx\frac{n_2}{n_1}\ll 1$．试据此证明 $p-p_0=\frac{n_2RT}{V}$，其中 V 是糖水溶液的体积．

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

$$g_1(T,p)-g_1(T,p_0)=\left(\frac{\partial g_1}{\partial p}\right)_T(p-p_0)=V_m(p-p_0)$$

$$(p-p_0)=-\frac{RT}{V_m}\ln(1-x)=\frac{RT}{V_m}x=\frac{n_2RT}{V}$$

汪书 4.11

试根据热力学第三定律证明，在 $T \to 0$ 时，表面张力系数与温度无关，即 $\frac{d\sigma}{dT} \to 0$.

$$dF = -SdT + \sigma dA$$

$$\left(\frac{\partial \sigma}{\partial T}\right)_A = -\left(\frac{\partial S}{\partial A}\right)_T$$

$$\lim_{T\to 0} \frac{d\sigma}{dT} = -\lim_{T\to 0} \left(\frac{\partial S}{\partial A}\right)_T = 0$$

汪书 4.13

锡可以形成白锡（正方晶系）和灰锡（立方晶系）两种不同的结晶状态. 常压下相变温度 $T_0 = 292$ K. T_0 以上白锡是稳定的，T_0 以下灰锡是稳定的. 如果在 T_0 以上将白锡迅速冷却到 T_0 以下，样品将被冻结在亚稳态. 已知相变潜热 $L = 2242\ \mathrm{J{\cdot}mol^{-1}}$. 由热容的测量数据知，对于灰锡 $\int_0^{T_0} \frac{C_g(T)}{T} dT = 44.12\ \mathrm{J{\cdot}mol^{-1} \cdot K^{-1}}$, 对于白锡 $\int_0^{T_0} \frac{C_w(T)}{T} dT = 51.54\ \mathrm{J{\cdot}mol^{-1} \cdot K^{-1}}$. 试验证能氏定理对于亚稳态的白锡的适用性.

$$S_w(T_0) = S_w(0) + \int_0^{T_0} \frac{C_w(T)}{T} dT$$

$$S_w(T_0) = S_g(0) + \int_0^{T_0} \frac{C_g(T)}{T} dT + \frac{L}{T_0}$$

$$S_w(0) = S_g(0) + 0.25\ \mathrm{J{\cdot}mol^{-1} \cdot K^{-1}}$$

Fins