1.

$E(L_1,L_2) = 2(L_1\gamma_1 + L_2\gamma_2)$, $L_1L_2 = A$.

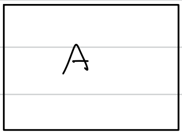
$E(L_2) = 2\left(\frac{A}{L_2}\gamma_1 + l_2\gamma_2\right)$

$\frac{d}{dL_2}E(L_2) = 2\left(-\frac{A}{L_2^2}\gamma_1+\gamma_2\right)=0 \Rightarrow \gamma_1\cdot\frac{A}{L_2^2}=\gamma_2 \quad \therefore \gamma_2/\gamma_1 = L_1/L_2$

$\frac{d^2}{dL_2^2}E(L_2) = 4A\gamma_1/L_2^3 > 0$ $\quad\therefore \gamma_2/\gamma_1 = L_1/L_2$ 일 때 $E(L_1,L_2)$는 최소이다.

$\Delta G_{sur} = 2(L_1\gamma_1+L_2\gamma_2)$ where $\gamma_2/\gamma_1 = L_1/L_2$

2.



$z = \sum \exp(-\varepsilon/kT)$ $\quad \varepsilon = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}\right)$

$\therefore z = \sum \exp(-n_x^2h^2/8ma^2kT)\cdot\sum\exp(-n_y^2h^2/8mb^2kT)$

$= \int_0^\infty \exp(-n_x^2h^2/8ma^2kT)dn_x \cdot \int_0^\infty \exp(-n_y^2h^2/8mb^2kT)dn_y$

$= \frac{a}{2}\cdot\sqrt{\frac{8\pi mkT}{h^2}}\cdot\frac{b}{2}\cdot\sqrt{\frac{8\pi mkT}{h^2}} = 2ab\pi mkT/h^2 = 2A\pi mkT/h^2$

$\therefore U = NkT^2\left(\frac{\partial \ln z}{\partial T}\right) = NkT^2\cdot\frac{1}{T} = NkT$

$P = Nk_BT\left(\frac{\partial z}{\partial A}\right)_T = \frac{nRT}{A}$ $\quad\therefore PA = nRT$

3.

$\bar{L} = \frac{1}{z}\cdot\{aN\cdot\exp(0/kT) + a(N-1)\cdot\exp(-\varepsilon/kT) + a(N-2)\cdot\exp(-2\varepsilon/kT)+\cdots+a\cdot\exp(-(N-1)\varepsilon/kT)\}$

$z = 1/\{1-\exp(-\varepsilon/kT)\}$

$\sum_{i=0}^{N-1}(N-i)\exp(-i\varepsilon/kT) = N\cdot\sum_{i=0}^{N-1}\exp(-i\varepsilon/kT) - \sum_{i=0}^{N-1} i\cdot\exp(-i\varepsilon/kT)$

$= N/\{1-\exp(-\varepsilon/kT)\} - \exp(-\varepsilon/kT)/\{1-\exp(-\varepsilon/kT)\}^2$

$\therefore \bar{L} = a\cdot\{1-\exp(-\varepsilon/kT)\}\cdot[N/\{1-\exp(-\varepsilon/kT)\} - \exp(-\varepsilon/kT)/\{1-\exp(-\varepsilon/kT)\}]$

$= a\cdot[N - \exp(-\varepsilon/kT)/\{1-\exp(-\varepsilon/kT)\}]$

$= a\cdot[N-\exp(-\varepsilon/kT)\cdot\{1+\exp(-\varepsilon/kT)\}]$

$= a[N - e^{-\frac{\varepsilon}{kT}} - e^{-\frac{2\varepsilon}{kT}}]$

4.

A	B
1mol	1mol

$\Delta S = \int \frac{1}{T} dq = \int \frac{nR}{V} dV$

$\therefore \Delta S_A = \int \frac{R}{V} dV = R\ln 2$, $\Delta S_B = \int \frac{R}{V} dV = R\ln 2$

$\therefore \Delta S_t = 2R\ln 2 = 11.5 J/K$

if) A : 2mol . $\Delta S_A = 2R\ln 2$ $\therefore \Delta S_t = 3R\ln 2 = 17.3 J/K$

if) $B \rightarrow A$, A: 1mol , 1mol $\Delta S = 0$

A : 1mol, 2mol $\Delta S_l = \int_{\frac{1}{2}}^{\frac{1}{3}} \frac{R}{V} dV = R\ln\frac{2}{3}$, $\Delta S_r = \int_{\frac{1}{2}}^{\frac{2}{3}} \frac{2R}{V} dV = 2R\ln\frac{4}{3}$

$\therefore \Delta S_t = R\ln\frac{32}{27} = 1.41 J/K$

5.

(1) $\Delta S_{600,s\to l} = \Delta H_{600,s\to l} / T = 8.02 J/K$

$\Delta S_{590,s\to l} = \Delta S_{600,s\to l} - \left(\int_{590}^{600} \frac{1}{T} C_{p,l} dT - \int_{590}^{600} \frac{1}{T} C_{p,s} dT \right)$

$= 8.02 - 0.514 + 0.0975 = 7.60 J/K$

$\therefore \Delta S_{590K,l\to s} = -7.60$

$\Delta S_{sur,590,l\to s} = \Delta H_{590,s\to l} / T$

$\Delta H_{600,s\to l} = \Delta H^\circ_{600,l} - \Delta H^\circ_{600,s}$

$\Delta H_{590,s\to l} = \Delta H^\circ_{590,l} - \Delta H^\circ_{590,s} = (\Delta H^\circ_{600,l} - \Delta H^\circ_{600,s}) - \left(\int_{590}^{600} C_{p,l} dT - \int_{590}^{600} C_{p,s} dT \right)$

$= 4810 - 306 + 58 = 4562$

$\therefore \Delta S_{sur,590,l\to s} = 4562/590 = 7.73$

$\Rightarrow \Delta S_t = \Delta S + \Delta S_{sur} = 0.13 > 0$ ∴ 자발적

(2) $\Delta G_{,590} = \Delta H_{590} - T\Delta S_{590} = -4562 + 590 \times 7.60 = -78 J < 0$ ∴ 자발적

단열용기 내 이므로 반응 전과 후의 $\Delta H = 0$ 이다, 1mol이라 가정하자.
이때 590K의 Pb(l)이 600K의 Pb(l)로 가는 과정의 $\Delta H_1 = 306 J$ 이고 600K의 Pb(l)이 600K의 Pb(s)로 가는 과정의 $\Delta H_2 = -4810 J$ 이다. 전체 $\Delta H = 0$ 이므로 매우 일부의 Pb(l)만 응고하고 나머지는 액체 상태로 존재한다. 1mol의 Pb(l)이 590K에서 600K으로 가면서 306J을 흡수했다면 x mol의 Pb(l)은 응고하며 306J을 방출한다 따라서 $x = 306/4810 = 0.0636$이다.
∴ 6.36%는 600K의 Pb(s)로 나머지 93.64는 600K의 Pb(l)로 존재한다.

6.

$$\Delta H_{P,d} = \Delta H_{1,d} + \int_1^P V_d (1-\alpha_d T) dp \qquad \Delta S_{P,d} = \Delta S_{1,d} - \int_1^P \alpha_d V_d dp$$

$$\Delta H_{P,g} = \Delta H_{1,g} + \int_1^P V_g (1-\alpha_g T) dp \qquad \Delta S_{P,g} = \Delta S_{1,g} - \int_1^P \alpha_g V_g dp$$

$$\Delta H_{P,g\to d} = \Delta H_{P,d} - \Delta H_{P,g} \qquad \Delta S_{P,g\to d} = \Delta S_{P,d} - \Delta S_{P,g}$$

$$\begin{aligned}\Delta G_{P,g\to d} &= \Delta H_{P,g\to d} - T\Delta S_{P,g\to d} \\ &= (\Delta H_{1,d} - \Delta H_{1,g}) - T(\Delta S_{1,d} - \Delta S_{1,g}) + \int_1^P V_d - V_g \, dp \\ &= \Delta H - T\Delta S + (V_d - V_g)(P-1)\end{aligned}$$

1mol 이라 가정하자

$\Delta H = 454 \text{ cal} = 1900 \text{ J}$ $\quad \Delta S = -3.31 \text{ J/K}$ $\quad \Rightarrow \Delta H - T\Delta S = 2886.38 \text{ J}$

$V_d = m_c/\rho_d = 3.42 \text{ cm}^3 = 3.42 \times 10^{-3} \text{ L}$

$V_g = m_c/\rho_g = 5.41 \text{ cm}^3 = 5.41 \times 10^{-3} \text{ L}$

$V_d - V_g = -1.99 \times 10^{-3} \text{ L}$

$\Delta G_{P,g\to d} \le 0$ $\quad \therefore 2886.38 - 1.99 \times 10^{-3} \times (P-1) \times 101.325 \le 0$

$\Rightarrow P \ge 14316 \text{ atm}$