8.044 Solutions Exam #3

1. a) $dP = \frac{\partial P}{\partial T}\Big|_V dT + \frac{\partial P}{\partial V}\Big|_T dV$

$\frac{\partial P}{\partial V}\Big|_T = -2cV^{-3}$ FROM GIVEN

$\frac{\partial P}{\partial T}\Big|_V = \frac{\partial S}{\partial V}\Big|_T = \frac{5}{2}aT^{3/2}$ FROM MAXWELL RELATION + GIVEN

$dP = \frac{5}{2}aT^{3/2}dT - 2cV^{-3}dV$

$P = aT^{5/2} + f(V), \quad \frac{\partial P}{\partial V}\Big|_T = f'(V) = -2cV^{-3}$

$\Rightarrow f(V) = cV^{-2} + (0)$ ↙ FROM LIMITING BEHAVIOR

$\underline{P = aT^{5/2} + cV^{-2}}$

b) $dE = TdS - PdV = T\frac{\partial S}{\partial T}\Big|_V dT + \left(T\frac{\partial S}{\partial V}\Big|_T - P\right)dV$

$= \frac{15}{4}aT^{3/2}V\,dT + \left(\frac{3}{2}aT^{5/2} - cV^{-2}\right)dV$

$E = \frac{3}{2}aT^{5/2}V + g(V), \quad \frac{\partial E}{\partial V}\Big|_T = \frac{3}{2}aT^{5/2} + g'(V)$

$g'(V) = -cV^{-2} \Rightarrow g(V) = cV^{-1} + E_0$

$\underline{E = \frac{3}{2}aT^{5/2}V + cV^{-1}} + E_0$

c) MODEL OBEYS 3RD LAW BECAUSE $\underline{\lim_{T\to 0} S(T,V) = 0}$

2. FOR A SPONTANEOUS PROCESS $\Delta S \geq 0$. THE EQUALITY ONLY APPLIES TO REVERSIBLE, QUASI-STATIC PROCESSES. THIS CASE IS NEITHER. IV IS THE ONLY POSSIBLE RESULT.

3. a) $\mathcal{H}$ IS SEPERABLE: THE 6 VARIABLES ARE S.I.

$$p(\theta_1,\theta_2,\theta_3,L_1,L_2,L_3) = \left(\frac{1}{2\pi}\right)\left(\frac{1}{2\pi}\right)\left(\frac{1}{2\pi}\right)\frac{1}{\sqrt{2\pi I_1 kT}}e^{-\frac{L_1^2}{2I_1kT}}\frac{1}{\sqrt{2\pi I_2 kT}}e^{-\frac{L_2^2}{2I_2kT}} \times \frac{1}{\sqrt{2\pi I_3 kT}}e^{-\frac{L_3^2}{2I_3kT}}$$

b) $\langle L_1^2\rangle = \langle L_2^2\rangle = I_1kT \gg \langle L_3^2\rangle = I_3kT$

$\Rightarrow \vec{L}$ IS ALMOST $\perp$ TO AXIS 3, THE LONG AXIS

c) $Z_R = (Z_{1,R})^N = \left[(2\pi)^{9/2}\sqrt{I_1I_2I_3}\,(kT)^{3/2}\right]^N$

$F_R = -NkT\ln Z_{1,R}$

$S_R = -\left.\frac{\partial F_R}{\partial T}\right|_N = Nk\ln Z_{1,R} + NkT\frac{1}{Z_{1,R}}\frac{3}{2}\frac{1}{T}Z_{1,R}$

$S_R = Nk\ln Z_{1,R} + \frac{3}{2}Nk$

d) 3RD LAW IS VIOLATED: $\lim_{T\to 0} S_R = Nk\ln(0) = -\infty$

e) THERE IS NO ENERGY GAP BEHAVIOR BECAUSE THERE IS NO GAP IN THE CLASSICALLY ALLOWED ROTATIONAL ENERGIES.

4 a) $Z_1 = \sum_{\text{STATES}} e^{-\epsilon_{\text{STATE}}/kT} = \underline{0.01M + 0.14M e^{-\Delta/kT} + 0.85M e^{-1.5\Delta/kT}}$

$\underline{Z = (Z_1)^N / N!}$

b) $\dfrac{n_{\text{FACE}}}{n_{\text{CORNER}}} = \dfrac{p_{\text{FACE}}}{p_{\text{CORNER}}} = \dfrac{0.85M e^{-1.5\Delta/kT}}{0.01M} = \underline{85 e^{-1.5\Delta/kT}}$

c) CONSIDER ONLY 2 LOWEST ENERGY LEVELS

$$E = N\langle \epsilon_{\text{ONE}} \rangle = N\left[(0)\frac{0.01M}{0.01M + 0.14M e^{-\Delta/kT}} + (\Delta)\frac{0.14M e^{-\Delta/kT}}{0.01M + 0.14M e^{-\Delta/kT}}\right]$$

$$\approx 14 N \Delta e^{-\Delta/kT}$$

$$C = \left.\frac{\partial E}{\partial T}\right|_{\text{AREA}} = 14 N \Delta \left(\frac{\Delta}{kT^2}\right) e^{-\Delta/kT} = \underline{14 N k \left(\frac{\Delta}{kT}\right)^2 e^{-\Delta/kT}}$$

d) ALL STATES EQUALLY LIKELY $\Rightarrow$ $\underline{p_{\text{FACE}} = 0.85}$

e) M POSSIBLE SITES FOR EACH ATOM $\Rightarrow$ $\underline{\lim_{T\to\infty} S = Nk \ln M}$

f) <u>ONE EXPECTS ENERGY GAP BEHAVIOR</u> BECAUSE THERE IS AN ENERGY GAP FOR THE EXCITATION OF A SINGLE ATOM.