

8.044 Solutions Exam #3

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

$$\left. \frac{\partial P}{\partial V} \right|_T = -2cV^{-3} \quad \text{FROM GIVEN}$$

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

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

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

FROM LIMITING BEHAVIOR

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

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

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

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

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

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

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

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

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) χ IS SEPERABLE: THE 6 VARIABLES ARE S-I.

$$p(\theta_1, \theta_2, \theta_3, l_1, l_2, l_3) = \left(\frac{1}{2\pi}\right)\left(\frac{1}{2\pi}\right)\left(\frac{1}{2\pi}\right) \frac{1}{\sqrt{2\pi I_1 kT}} e^{-\frac{l_1^2}{2I_1 kT}} \frac{1}{\sqrt{2\pi I_2 kT}} e^{-\frac{l_2^2}{2I_2 kT}} \times \frac{1}{\sqrt{2\pi I_3 kT}} e^{-\frac{l_3^2}{2I_3 kT}}$$

b) $\langle L_1^2 \rangle = \langle L_2^2 \rangle = I_1 kT \gg \langle L_3^2 \rangle = I_3 kT$

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

c) $Z_R = (Z_{1,R})^N = \left[(2\pi)^{3/2} \sqrt{I_1 I_2 I_3} (kT)^{3/2} \right]^N$

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

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

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

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

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

$$4) a) Z_1 = \sum_{STATES} e^{-E_{STATES}/kT} = 0.01M + 0.14Me^{-\Delta/RT} + 0.85Me^{-1.5\Delta/RT}$$

$$Z = (Z_1)^N / N!$$

$$b) \frac{\eta_{FACE}}{\eta_{CORNER}} = \frac{p_{FACE}}{p_{CORNER}} = \frac{0.85Me^{-1.5\Delta/RT}}{0.01M} = 85e^{-1.5\Delta/RT}$$

c) CONSIDER ONLY 2 LOWEST ENERGY LEVELS

$$E = N \langle E_{ONE} \rangle = N \left[(0) \frac{0.01M}{0.01M + 0.14Me^{-\Delta/RT}} + (\Delta) \frac{0.14Me^{-\Delta/RT}}{0.01M + 0.14Me^{-\Delta/RT}} \right]$$

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

$$C = \frac{\partial E}{\partial T} \Big|_{AREA} = 14N\Delta \left(\frac{\Delta}{RT^2} \right) e^{-\Delta/RT} = 14Nk \left(\frac{\Delta}{RT} \right)^2 e^{-\Delta/RT}$$

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

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

f) ONE EXPECTS ENERGY GAP BEHAVIOR BECAUSE

THERE IS AN ENERGY GAP FOR THE EXCITATION OF A SINGLE ATOM.

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