

1. $Z = 1 + e^{\frac{mB}{\tau}} + e^{-\frac{mB}{\tau}} \approx 1 + 1 + \frac{mB}{\tau} + \frac{1}{2} \left(\frac{mB}{\tau}\right)^2 + 1 - \frac{mB}{\tau} + \frac{1}{2} \left(\frac{mB}{\tau}\right)^2 = 3\left(1 + \frac{1}{3} \left(\frac{mB}{\tau}\right)^2\right)$
 $F = -\tau \ln Z = -\tau \left[\ln 3 + \ln\left(1 + \frac{1}{3} \left(\frac{mB}{\tau}\right)^2\right) \right] \approx -\tau \left[\ln 3 + \frac{1}{3} \left(\frac{mB}{\tau}\right)^2 \right]$ $\sigma = -\frac{\partial F}{\partial \tau V} = \ln 3 - \frac{1}{3} \left(\frac{mB}{\tau}\right)^2$. The decrease in entropy is $\frac{1}{3} \left(\frac{mB}{\tau}\right)^2$ and $A = \frac{1}{3} (mB)^2$
2. Count the states in a box of size L . After some steps one reaches at (eq 7 page 185 KK) $\tau_F = (3\pi^2 n)^{2/3} \frac{\hbar^2}{2m}$ this gives $T_F = k_B \tau_F = 5.0\text{K}$ which much less than $T = 0.5\text{K}$ so the approximation of the Fermi-Dirac distribution function as a step function will be fairly good. Calculate U (along lines according to eq 27 page 189 KK) after some steps $C_v = \frac{1}{2} \pi^2 N k_B T / T_F$ is reached. Evaluating the fermi contribution gives $C_v = 0.49 N k_B = 4.10 \text{ J/mole/K}$ at $T = 0.5\text{K}$.
3. a) $\frac{1}{\tau} = \frac{\partial \sigma}{\partial E} = \frac{8\pi G M}{\hbar c^3}$
 b) $U = \frac{3}{2} \tau = 1 \text{ eV}$ will give ratio $\frac{18e^{13.6/3^2\tau}}{8e^{13.6/2^2\tau}} = \frac{18}{8} e^{20.4(1/9-1/4)/\tau} = \frac{18}{8} e^{-2.833/\tau} = 0.13$
4. The partition function is $Z_{\text{rot}} = \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1) \frac{\hbar^2}{2I\tau}} \approx 1 + 3e^{-\frac{\hbar^2}{I\tau}} = 1 + 3e^{-x}$ where $x = \frac{\hbar^2}{I\tau} \gg 1$. For N identical molecules $Z_{\text{rot}}^{(N)} = \frac{1}{N!} Z_{\text{rot}}^N$ And hence $F_{\text{rot}} = -N\tau \ln Z_{\text{rot}} + \tau \ln N! = -N\tau \ln(1 + 3e^{-x}) + \tau \ln N! \approx -3N\tau e^{-x} + \tau \ln N!$ $\sigma_{\text{rot}} = -\frac{\partial F}{\partial \tau V} \approx 3N(1+x)e^{-x} + \ln N!$ and $(C_v)_{\text{rot}} = \tau \frac{\partial \sigma}{\partial \tau V} \approx 3Nx^2 e^{-x} = 3N \left(\frac{\hbar^2}{I\tau}\right)^2 e^{-\frac{\hbar^2}{I\tau}}$
5. The total number of atoms is conserved use this to introduce a parameter α controlling the degree of dissociation. $N_A = N_B = \alpha N_0$ and $N_{AB} = (1-\alpha)N_0$ where N_0 is the number of molecules AB if nothing is dissociated. The total number of particles is hence $(1+\alpha)N_0$. Initially there are equal number of the A, B and AB and therefore $\alpha = 0.5$ The partial pressures are $1/3 \text{ atm}$. Ideal gas law $pV = n\tau$ gives constant in law of mass action $K_p = \left(\frac{1}{3}\right)^1 \cdot \left(\frac{1}{3}\right)^1 \cdot \left(\frac{1}{3}\right)^{-1} = \frac{1}{3} \text{ atm}$ We also know $p_0 = 1.5N_0\tau/V = 1 \text{ atm}$. Now double V . The new pressure will be $p_1 = (1+\alpha)N_0\tau/2V = (1+\alpha)p_0/3$ We also have $K_p = \frac{1}{3} = \frac{p_A p_B}{p_{AB}} = \frac{(p_1 \alpha / (1+\alpha))^2}{p_1 (1-\alpha) / (1+\alpha)} = \frac{\alpha^2}{3(1-\alpha)}$ This is an equation for α : $\alpha^2 + \alpha - 1 = 0$ with solution $\alpha = \frac{\sqrt{5}-1}{2} \approx 0.618$ (only solutions in interval (0,1)). This gives $p_1 = (\sqrt{5}+1)/6 \approx 0.54\text{atm}$. and $p_A = p_B = (\sqrt{5}-1)/6 \approx 0.21\text{atm}$. $p_{AB} = (3-\sqrt{5})/6 \approx 0.13\text{atm}$.