Instructions: You have fifty minutes to complete this exam. Please place your name on all pages of this exam. Exams submitted without a name will not be graded. Show all work when calculating answers. You are allowed to use a calculator for the exam.

1. (15 points) One mole of an ideal gas is compressed reversibly and isothermally at a temperature of 300 K from a volume of 10 L to a volume of 1 L. Determine ΔU, q, and w for the process.

for isothermal process $\Delta U = 0$

$w = -q$

$w = -nRT \ln \frac{V_2}{V_1}$

$= -(1 \, mol)(8.3145 \, J/k \, mol)(300 \, k) \ln \frac{1 \, L}{10 \, L}$

$= 5743 \, J$ (+) work is being done on the gas

$q = -5743 \, J$

2. (8 points) In the derivation of the translational molecular partition function the following expression had to be evaluated.

$$q_{trans} = \left(\sum_{n=1}^{\infty} e^{-\frac{\beta h^2 n^2}{8ma}} \right)^3$$

There is no analytical solution for the summation written above. Instead the summation was approximated as an integral over the respective quantum states. Why was the approximation justified?

The approximation was justified since the energy difference between adjacent translational energy levels was much smaller than $k_B T$.

3. (10 points, True/False) Determine whether each of the following statements is true or false. Write the __entire word__ TRUE or FALSE or else no credit will be give

  a. The internal energy, U, is a state function   TRUE

  b. The work performed by the expansion of an ideal gas against and external pressure is a state function. FALSE

  c. The temperature change of a gas undergoing an adiabatic expansion (no heat exchange between system and surroundings) is zero. FALSE

  d. For an ideal gas $\left(\frac{\partial U}{\partial V}\right)_T = \frac{3}{2}RT$ FALSE

  e. If work is performed on a system and no heat is transferred between system and surroundings then the internal energy increases. TRUE

4. (7 points) Argon was discovered by Lord Rayleigh and Sir William Ramsay based on the masses of various gas samples. A sample was prepared from air by removing O_2, CO_2, and water. The result was a sample that contained both N_2 and Ar with a total mass of 2.3102 g. The value of PV/RT = 0.0821 mol, the molar masses are N_2 = 28 g/mol and Ar = 40 g/mol, and all gases can be treated as ideal. What is the mole fraction of Ar in the sample? (*Hint*: start with the equation $n_{N_2} + n_{Ar} = \frac{PV}{RT} = 0.0821\ mol$)

$$n_{N_2} + n_{Ar} = \frac{PV}{RT} = 0.0821\ mol$$

$$\frac{g_{N_2}}{MW_{N_2}} + \frac{g_{Ar}}{MW_{Ar}} = 0.0821\ mol$$

$$\frac{MW_{Ar}\ g_{N_2} + MW_{N_2}\ g_{Ar}}{MW_{N_2}\ MW_{Ar}} = 0.0821\ mol$$

$$MW_{Ar}\ g_{N_2} + MW_{N_2}\ g_{Ar} = (0.0821\ mol)(MW_{N_2}\ MW_{Ar})$$

$$MW_{Ar}\ g_{N_2} + MW_{N_2}(2.3102\ g - g_{N_2}) = (0.0821\ mol)(MW_{N_2}\ MW_{Ar})$$

$$g_{N_2}(MW_{Ar} - MW_{N_2}) = (0.0821\ mol)(MW_{N_2}\ MW_{Ar}) - MW_{N_2}(2.3102\ g)$$

$$g_{N_2} = \frac{(0.0821\ mol)(28\ g/mol)(40\ g/mol) - (28\ g/mol)(2.3102\ g)}{(40\ g/mol - 28\ g/mol)}$$
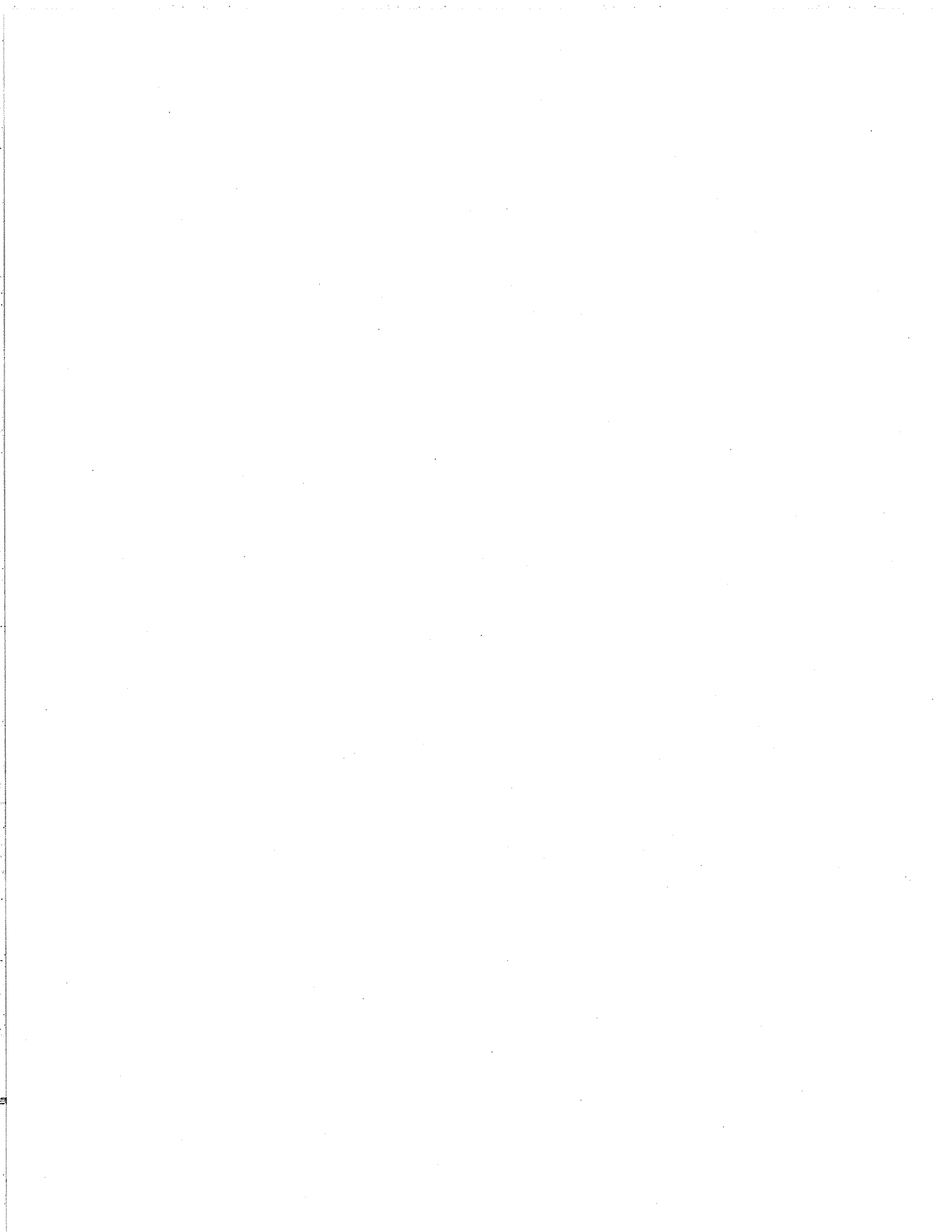
$g_{N_2} = 2.2722\ g$ $n_{N_2} = 0.08115\ mol$ $X_{Ar} = 0.0116$
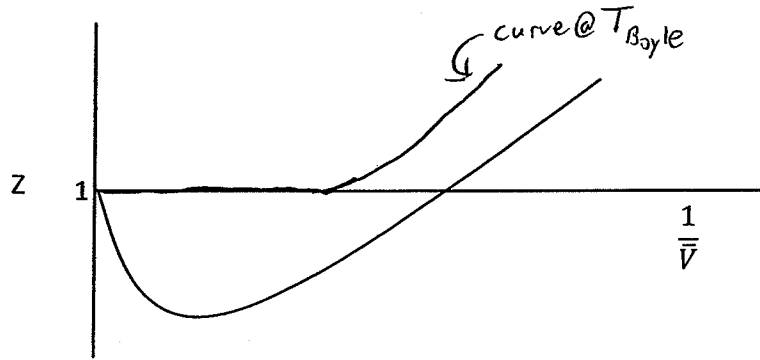
$g_{Ar} = 0.038\ g$ $n_{Ar} = 9.5 \cdot 10^{-4}\ mol$

6. (25 points) The compressibility, Z, of CH_4 is shown below for a temperature below the Boyle temperature. Answer the following 5 questions.

a. What would the value of the compressibility be if CH_4 behaved ideally?

   $|$

b. What is the reason for the negative deviations at low inverse molar volumes?

   attractive forces

c. What is the reason for the positive deviations at high inverse molar volumes?

   finite volume of gas molecules

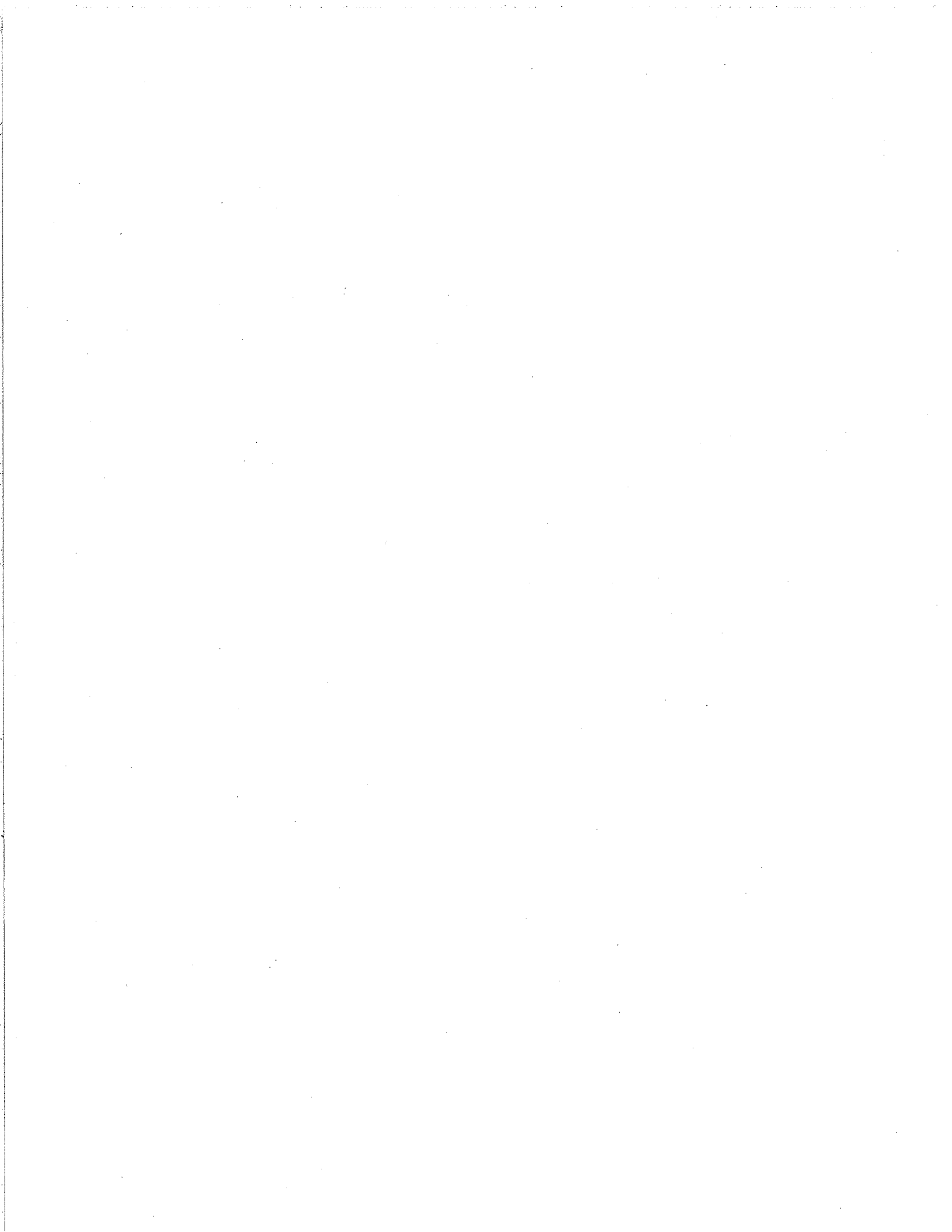d. Assuming that CH_4 can be represented as a van der Waals gas an expression for the second virial coefficient is:

$$B_{2V} = b - \frac{a}{RT}$$

For CH_4, a = 2.283 L^2 bar/mol^2 and b = 0.04278 L/mol. What is the Boyle temperature?

$$B_{2v} = 0 = b - \frac{a}{RT_{Boyle}}$$

$$T_{Boyle} = \frac{a}{Rb}$$

$$= \frac{2.283 \frac{L^2 bar}{mol^2}}{\left(0.083 \frac{Lbar}{kmol}\right)\left(0.04278 \frac{L}{mol}\right)}$$

$$= 643 \, K$$

e. Schematically plot Z versus pressure for CH_4 at the Boyle temperature on the graph above.

5. (15 points) ONCl is a non-linear, polyatomic molecule with three rotational constants (B_A, B_B, B_C), one for each axis of rotation and 3 distinct vibrations label $\tilde{v}_1$, $\tilde{v}_2$, $\tilde{v}_3$. The total partition function is given below:

$$Q = \frac{\left\{ \overbrace{[g_1 e^{\beta D_e}]}^{q_{elec}} \overbrace{[(\frac{2\pi m}{\beta h^2})^{\frac{3}{2}} * V]}^{q_{trans}} \overbrace{\frac{\sqrt{\pi}}{2}\left(\frac{1}{\beta hcB_A}\right)^{\frac{1}{2}}\left(\frac{1}{\beta hcB_B}\right)^{\frac{1}{2}}\left(\frac{1}{\beta hcB_C}\right)^{\frac{1}{2}}}^{q_{rot}} \overbrace{\left(\frac{e^{-\frac{\beta hc\tilde{v}_1}{2}}}{1-e^{-\beta hc\tilde{v}_1}}\right)\left(\frac{e^{-\frac{\beta hc\tilde{v}_2}{2}}}{1-e^{-\beta hc\tilde{v}_2}}\right)\left(\frac{e^{-\frac{\beta hc\tilde{v}_3}{2}}}{1-e^{-\beta hc\tilde{v}_3}}\right)}^{q_{vib}} \right\}^N}{N!}$$

Derive an expression for the average pressure of the gas.

$$<P> = k_B T \left(\frac{d \ln Q}{dV}\right)$$

only q_{trans} depends on Volume.

$$\ln Q = N\ln q_{elec} + N\ln q_{trans} + N\ln q_{rot} + N\ln q_{vib} - \ln N!$$

$$\left(\frac{d \ln Q}{dV}\right) = \frac{d}{dV}\left\{ N\ln q_{elec} + N\ln q_{trans} + N\ln q_{rot} + N\ln q_{vib} - \ln N! \right\}$$
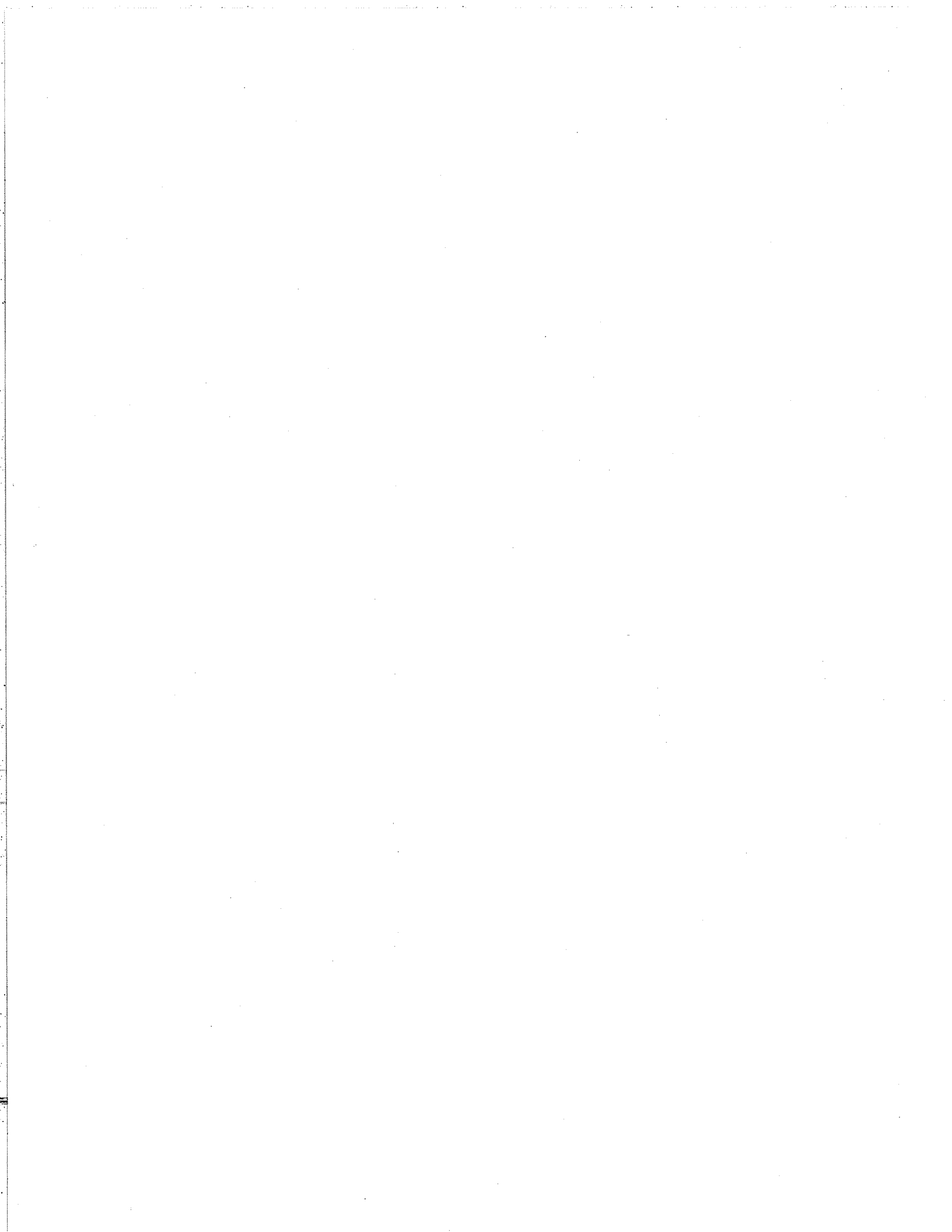
$$= \frac{d}{dV}\left\{ N\ln q_{trans} \right\}$$

$$= \frac{d}{dV}\left\{ N\ln\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} + N\ln V \right\}$$

$$= \frac{d}{dV}\left\{ N\ln V \right\}$$

$$= \frac{N}{V}$$

$$<P> = \frac{k_B T N}{V}$$

7. (20 points) Deuterium, ^2H can be used in NMR spectroscopy. The nuclear spin, I, of ^2H is 1. The nuclear spin states of ^2H can be described in the form of (I, m_I). Even though there are more than two nuclear spin states for ^2H each individual state is still an eigenstate of the nuclear spin angular momentum operator I_z where

$$\hat{I}_z(I, m_I) = m_I \hbar (I, m_I)$$

   a. Construct an energy level diagram for ^2H in an externally applied magnetic field of strength B_0 directed along the z-axis. Label each state with its wavefunction in the form of (I, m_I) and give its energy in terms of the constants g_N, β_N, and B_0. You may ignore the shielding constant and use the following nuclear Zeeman Hamiltonian
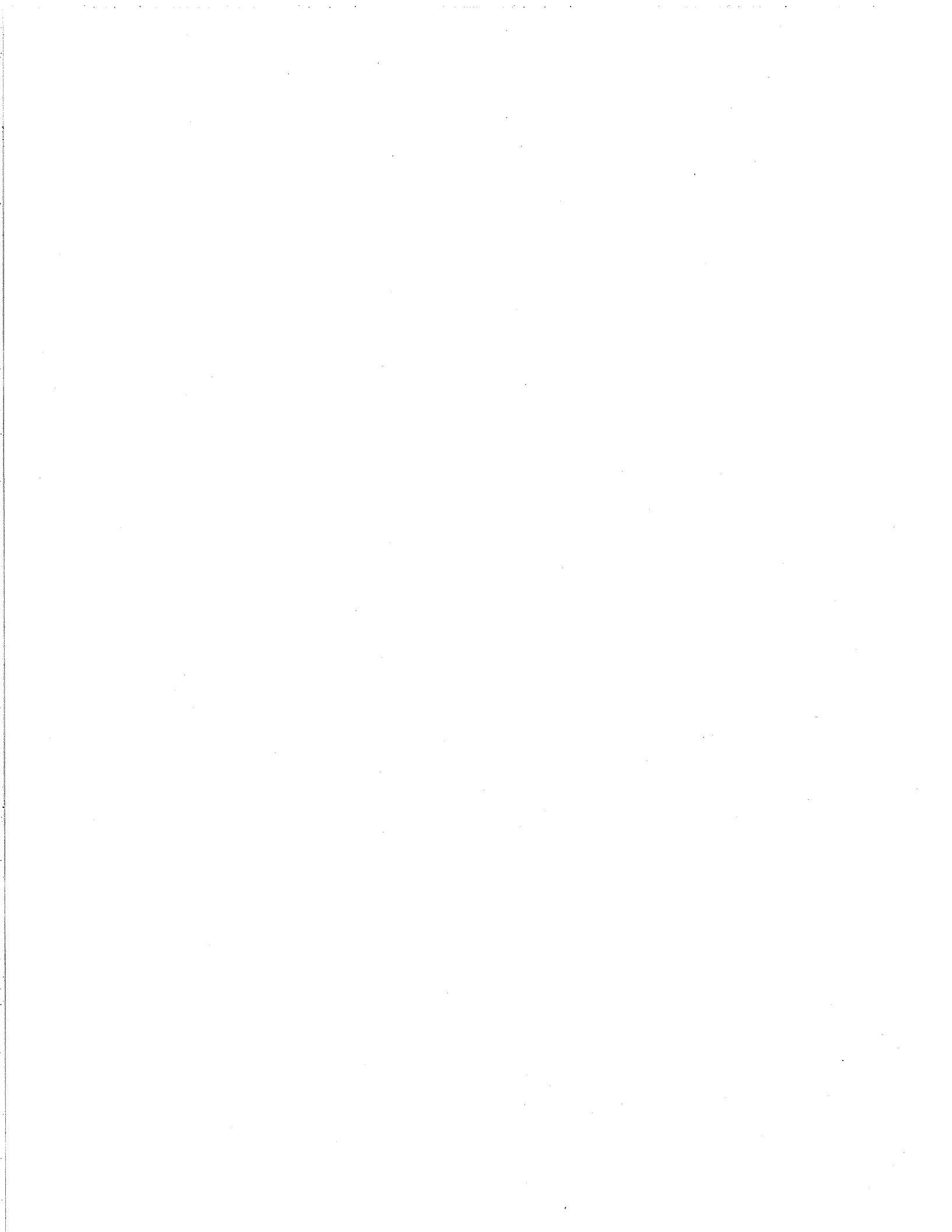
E

$g_N \beta_N B_0$ ———————— $(1, -1)$ $\hat{H}_{NZ} = \dfrac{-g_N \beta_N B_0}{\hbar} \hat{I}_z$

0 ———————— $(1, 0)$

$-g_N \beta_N B_0$ ———————— $(1, 1)$

   b. Write out the partition function for $\overset{a\ single\ particle}{\cancel{using}}$ the energy level diagram constructed in part (a).

$$Q = \sum_i^3 e^{-\beta E_i} = e^{-\beta g_N \beta_N B_0} + e^{0} + e^{\beta g_N \beta_N B_0} = 1 + e^{-\beta g_N \beta_N B_0} + e^{\beta g_N \beta_N B_0}$$

   c. Derive an expression for the energy of the system

$$\langle E \rangle = -\left(\frac{d \ln Q}{d\beta}\right) \qquad \ln Q = \ln\left(1 + e^{-\beta g_N \beta_N B_0} + e^{\beta g_N \beta_N B_0}\right)$$

$$= -\left(\frac{1}{1 + e^{-\beta g_N \beta_N B_0} + e^{\beta g_N \beta_N B_0}}\right)\left(-g_N \beta_N B_0\, e^{-\beta g_N \beta_N B_0} + g_N \beta_N B_0\, e^{\beta g_N \beta_N B_0}\right)$$

$$= -g_N \beta_N B_0 \left(\frac{e^{\beta g_N \beta_N B_0} - e^{-\beta g_N \beta_N B_0}}{1 + e^{-\beta g_N \beta_N B_0} + e^{\beta g_N \beta_N B_0}}\right)$$

8. (extra credit, 7 points) Shown below are the energy and constant volume heat capacity for the deuterium NRM system as a function of temperature. The heat capacity rapidly goes to zero at high temperatures. Why?
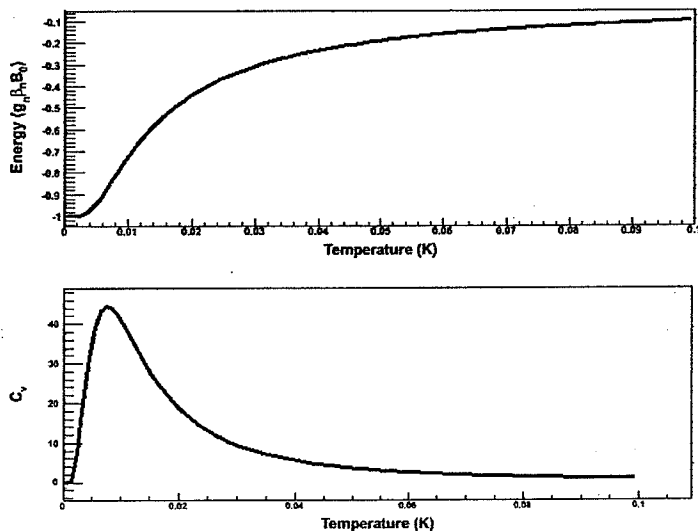
At high temperatures all levels are equally occupied ($<E>$ goes to 0) so there is no place to put the extra energy.

9. (extra credit, 7 points) In some cases it can be simpler to determine the value of a partition function by directly summing over the energy levels available by brute force rather than attempting to derive an analytical expression. Consider a system of 10 particles confined to the lowest 10 translational levels of the 3D particle-in-a-box. Shown in the graph below is a plot of ln Q as a function of temperature. Determine the average energy of the system at 150 K. (Hint: the answer is not 53.88).
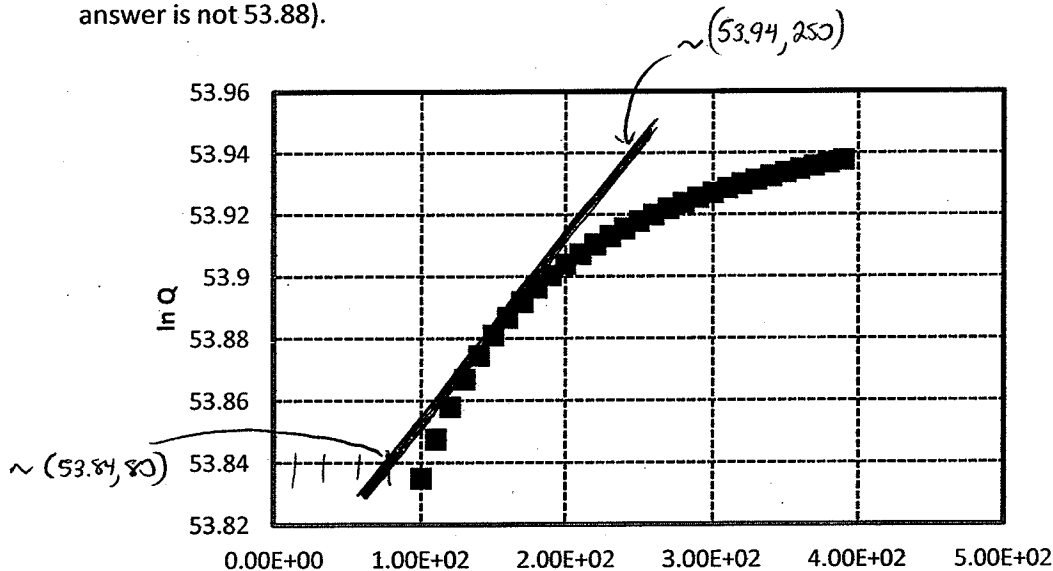
$\text{slope of tangent} = \dfrac{0.1}{170} = 5.88 \cdot 10^{-4} \, k^{-1}$

$<E> = k_B T^2 \left(\dfrac{d \ln Q}{dT} \right) = k_B T^2 (5.88 \cdot 10^{-4})$

$= (1.38 \cdot 10^{-23} \, \text{J}/k)(150 \, k)^2 (5.88 \cdot 10^{-4} \, k^{-1}) = 1.83 \cdot 10^{-22} \, \text{J}$