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① (a) $Z_R = \sum_{l=0}^{\infty} (2l+1)e^{-\epsilon l(l+1)/kT} = \sum_{l=0}^{\infty} (2l+1)e^{-\epsilon l(l+1)/kT}$

where the factor of $2l+1$ accounts for the degeneracy of the l^{th} energy level.

(b) For $kT \gg \epsilon$, it is a good approximation to convert the sum into an integral:

$$Z_R \approx \int_0^{\infty} (2l+1)e^{-\epsilon l(l+1)/kT} dl$$

Let $x = \epsilon l(l+1)/kT$. Then $dx = \epsilon(2l+1)dl/kT$ and we obtain:

$$Z_R \approx \frac{kT}{\epsilon} \int_0^{\infty} e^{-x} dx = \frac{kT}{\epsilon}$$

(c) For $kT \ll \epsilon$, we approximate Z_R by the sum of the first two terms:

$$Z_R \approx 1 + 3e^{-2\epsilon/kT}$$

(d) First consider the low-temperature limit ($kT \ll \epsilon$)

$$\langle E \rangle = kT^2 \frac{\partial}{\partial T} \ln Z_R = \frac{kT^2 \partial Z_R}{Z_R \partial T}$$

Inserting $Z_R \approx 1 + 3e^{-2\epsilon/kT}$

②

$$\langle E \rangle = \frac{6\epsilon e^{-2\epsilon/kT}}{1 + 3e^{-2\epsilon/kT}}$$

Since $kT \ll \epsilon$, we have $e^{-2\epsilon/kT} \ll 1$ and we can neglect the $3e^{-2\epsilon/kT}$ in the denominator above. Hence,

$$\langle E \rangle \approx 6\epsilon e^{-2\epsilon/kT}$$

Then,

$$C_V = \frac{\partial \langle E \rangle}{\partial T} \approx \frac{12\epsilon^2}{kT^2} e^{-2\epsilon/kT}$$

Second, in the high temperature limit ($kT \gg \epsilon$),

$$Z_R = \frac{kT}{\epsilon}$$

$$\langle E \rangle = kT^2 \frac{\partial}{\partial T} \ln Z_R = kT$$

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = k$$

In class, I showed that the equipartition theorem implies that the internal degrees of freedom contribute

$$C_V = \frac{1}{2}(n_r + 2n_v)k$$

for n_r rotational degrees of freedom and n_v vibrational degrees of freedom. A rigid rotor (such as a diatomic molecule) consists of $n_r = 2$ degrees of freedom, since we can neglect rotation about the axis that connects the two atoms. That is, we expect a contribution of $C_V = k$ per molecule, in agreement with our calculation above.

(a) Applying the Euler-Maclaurin summation formula to

$$Z_E = \sum_{p=0}^{\infty} (2p+1) e^{-\epsilon(2p+1)/kT}$$

$$= \int_0^{\infty} (2x+1) e^{-\epsilon(2x+1)/kT} dx + \frac{1}{2} + \sum_{p=1}^{\infty} \frac{B_{2p}}{(2p)!} [f^{(2p-1)}(\infty) - f^{(2p-1)}(0)]$$

where $f(x) = \frac{dx^{2p}}{dx^{2p}}$ and $f(x) = (2x+1)e^{-\epsilon(2x+1)/kT}$

Let $x = \epsilon(2p+1)/kT$ Then $dx = \frac{\epsilon(2p+1)/kT}{kT}$, and

$$Z_E = \frac{kT}{\epsilon} \int_0^{\infty} e^{-x} dx + \frac{1}{2} + \sum_{p=1}^{\infty} \frac{B_{2p}}{(2p)!} [f^{(2p-1)}(\infty) - f^{(2p-1)}(0)]$$

We wish to include all terms up to $O(\frac{\epsilon}{kT})$

$$\frac{dT}{d\epsilon} = 2e^{-\epsilon(2p+1)/kT} - \frac{\epsilon}{kT} (2p+1)^2 e^{-\epsilon(2p+1)/kT}$$

$$\frac{d^2T}{d\epsilon^2} = -2(2p+1) \frac{\epsilon}{kT} e^{-\epsilon(2p+1)/kT} - 2 \frac{\epsilon}{kT} (2p+1) e^{-\epsilon(2p+1)/kT} + O(\frac{\epsilon^2}{kT^2})$$

$$= -6(2p+1) \frac{\epsilon}{kT} e^{-\epsilon(2p+1)/kT} + O(\frac{\epsilon^2}{kT^2})$$

$$\frac{d^3T}{d\epsilon^3} = -12 \frac{\epsilon}{kT} e^{-\epsilon(2p+1)/kT} + O(\frac{\epsilon^2}{kT^2})$$

All higher derivatives will be of order ϵ^2 or higher, so we can stop here. Thus

$$Z_E = \frac{kT}{\epsilon} + \frac{1}{2} - \frac{1}{6} B_2 \left(2 - \frac{\epsilon}{kT}\right) + \frac{1}{24} B_4 \frac{12 \epsilon}{kT}$$

Putting $B_2 = \frac{1}{6}$ and $B_4 = -\frac{1}{30}$,

$$Z_E = \frac{kT}{\epsilon} + \frac{1}{2} - \frac{1}{6} + \frac{\epsilon}{kT} \left(\frac{1}{12} - \frac{1}{60}\right)$$

$$= \frac{kT}{\epsilon} + \frac{1}{3} + \frac{1}{15} \frac{\epsilon}{kT}$$

(b) $\langle E \rangle = kT^2 \frac{\partial \ln Z_E}{\partial T} = \frac{kT^2}{Z_E} \frac{\partial Z_E}{\partial T}$

$$= \frac{kT^2}{Z_E} \left(\frac{1}{\epsilon} - \frac{1}{15} \frac{\epsilon}{kT^2} \right)$$

$$= (kT)^2 \left(\frac{1}{\epsilon} - \frac{1}{15} \frac{\epsilon}{kT^2} \right)$$

$$\frac{kT}{\epsilon} + \frac{1}{3} + \frac{1}{15} \frac{\epsilon}{kT}$$

Multiply numerator and denominator by $\frac{\epsilon}{kT}$ to obtain

$$\langle E \rangle = kT \left(1 - \frac{1}{15} \frac{\epsilon^2}{kT^2} \right)$$

$$1 + \frac{1}{3} \frac{\epsilon}{kT} + \frac{1}{15} \frac{\epsilon^2}{kT^2}$$

Next, expand out the denominator, using

$$\frac{1}{1+x} = \sum_{n=0}^{\infty} (-1)^n x^n \approx 1 - x + x^2$$

We see that [putting $x = \frac{1}{3} \frac{\epsilon}{kT} + \frac{1}{15} \frac{\epsilon^2}{(kT)^2}$]:

$$\begin{aligned} \frac{1}{\frac{1 + \frac{1}{3} \frac{\epsilon}{kT} + \frac{1}{15} \frac{\epsilon^2}{(kT)^2}}{3kT + \frac{1}{15} \frac{\epsilon^2}{(kT)^2}}} &\approx \frac{1}{3kT} \left(1 - \frac{1}{3} \frac{\epsilon}{kT} - \frac{1}{15} \frac{\epsilon^2}{(kT)^2} + \frac{1}{9} \frac{\epsilon^2}{(kT)^2} + \frac{0}{(kT)^3} \right) \\ &\approx \frac{1}{3kT} + \frac{2}{45} \frac{\epsilon^2}{(kT)^2} \end{aligned}$$

Thus,

$$\begin{aligned} \langle E \rangle &\approx kT \left(1 - \frac{1}{15} \frac{\epsilon^2}{(kT)^2} \right) \left(1 - \frac{1}{3} \frac{\epsilon}{kT} + \frac{2}{45} \frac{\epsilon^2}{(kT)^2} \right) \\ &\approx kT \left(1 - \frac{1}{3} \frac{\epsilon}{kT} + \frac{2}{45} \frac{\epsilon^2}{(kT)^2} - \frac{1}{15} \frac{\epsilon^2}{(kT)^2} \right) \\ &\approx kT \left(1 - \frac{1}{3} \frac{\epsilon}{kT} - \frac{1}{45} \frac{\epsilon^2}{(kT)^2} \right) \end{aligned}$$

Finally,

$$C_V = \frac{\partial \langle E \rangle}{\partial T} \approx k \left(1 + \frac{1}{45} \frac{\epsilon^2}{(kT)^2} \right)$$

Note that as $T \rightarrow \infty$, $C_V \rightarrow 1$ from above.

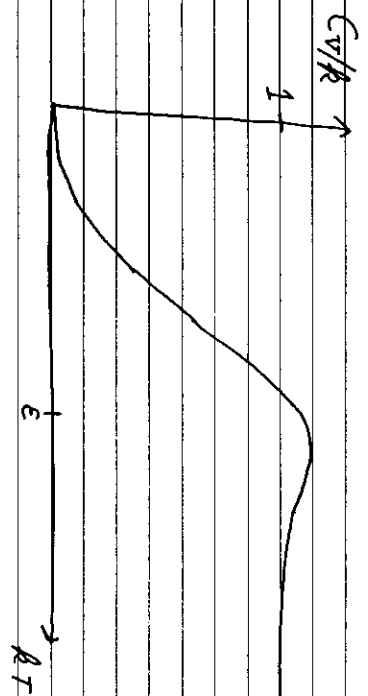
(c) As $T \rightarrow 0$, we use the result of part (b) of problem 1:

$$C_V \approx \frac{12k^2}{RT^2} e^{-2\epsilon/kT}$$

As $T \rightarrow 0$, we use the result of part (b) of this problem:

$$C_V \approx k \left(1 + \frac{1}{45} \frac{\epsilon^2}{(kT)^2} \right)$$

Hence, the graph of C_V vs. T just look something like:



Note that the slope of the curve is zero as $T \rightarrow 0$ since the derivative of C_V vanishes there. We also note that the function $\frac{12k^2}{RT^2} e^{-2\epsilon/kT}$ has a maximum at $kT = \epsilon$ since (for $T \equiv kT$):

$$0 = \frac{d}{dT} \left(\frac{1}{T^2} e^{-2\epsilon/T} \right) = \frac{-2}{T^3} e^{-2\epsilon/T} + \frac{2\epsilon}{T^4} e^{-2\epsilon/T}$$

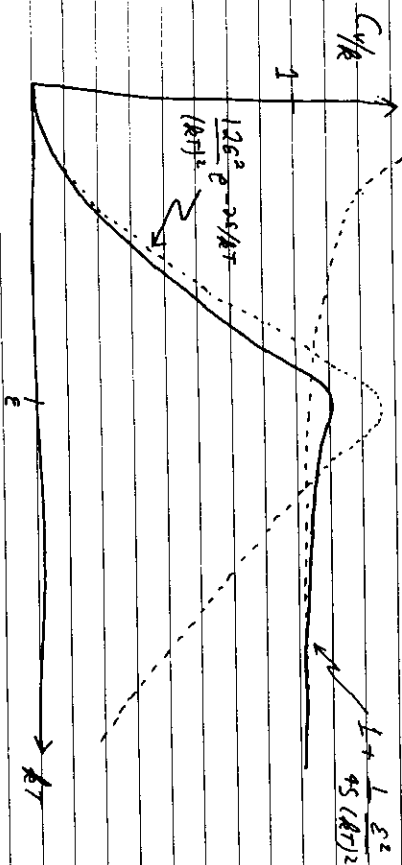
implies that $\epsilon = T$.

At $\epsilon = kT$, the function $\frac{12\epsilon^2}{(kT)^2} e^{-2\epsilon/kT}$ reaches its maximum value δ :

$$\frac{12\epsilon^2}{(kT)^2} e^{-2\epsilon/kT} = 12e^{-2} = 1.634$$

Of course, since $C_V \approx \frac{12\epsilon^2}{(kT)^2} e^{-2\epsilon/kT}$ is valid only for $kT \ll \epsilon$,

we don't expect this to be good approximation for C_V at $kT = \epsilon$. Nevertheless, it is not too far from 1, so we conclude that the maximum of C_V/k is in the vicinity of $kT \approx \epsilon$ although it probably occur at a value slightly below $kT = \epsilon$. That is, the true picture must look something like this:



where the solid curve is the exact value of C_V/k .

③ RB Chapter 13, problem 9

Table 11.2 on p.253 of RB gives the following data:

	B_V (K)	B_R (K)
H ₂	6,320	87.5
CO	3,120	2.78
I ₂	309	0.054

For $T \gg B_V$, the vibrational modes are excited while for $T \gg B_R$, the rotational modes are excited.

For a diatomic molecule, there are two rotational modes and one vibrational mode. Thus, assuming that we can approximate a gas of such molecules by a classical ideal gas,

$$C_P = C_V + NR$$

where

$$C_V = \begin{cases} \frac{3}{2} NR & T \ll B_V, B_R \\ \frac{5}{2} NR & \theta_r \ll T \ll B_V \\ \frac{7}{2} NR & T \gg B_V, \theta_r \end{cases}$$

(a) CO at $T = 300$ K. Here, $B_r \ll T \ll B_V$.

Thus $C_V = \frac{5}{2} NR$, $C_P = \frac{7}{2} NR$ and $\gamma = \frac{C_P}{C_V} = \frac{7}{5}$.

(b) I₂ at $T = 500$ K. Here $T \gg B_V, B_r$ so

$$C_V = \frac{7}{2} NR, C_P = \frac{9}{2} NR \text{ and } \gamma = \frac{9}{7}$$

(c) H₂ at $T = 10$ K. Here $T \ll B_r, B_V$ so

$$C_V = \frac{3}{2} NR, C_P = \frac{5}{2} NR \text{ and } \gamma = \frac{5}{3}$$

④ RB Chapter 7, problem 1

(a) Given the column of atmosphere with cross-sectional area A , consider a small interval of the column from z to $z+\Delta z$. The forces acting on this column consist of

(i) downward force due to pressure on the top of the small interval:

$$P(z+\Delta z)A$$

(ii) downward force due to weight of the small interval

$$m(z)A\Delta z g$$

where m is the mass of one molecule, $n(z)$ is the number of molecules per unit volume at height z and $A\Delta z$ is the volume of the small interval. The acceleration is due to gravity g since the mass gives the weight.

(iii) upward force due to pressure on the bottom of the small interval

$$P(z)A$$

In mechanical equilibrium, the forces must balance. Thus,

$$P(z)A = P(z+\Delta z)A + m n(z)A\Delta z g$$

The common factor of A cancels and we end up with

$$P(z) = P(z+\Delta z) + m n(z)g \Delta z.$$

(b) Rewrite the above equation as

$$\frac{P(z+\Delta z) - P(z)}{\Delta z} = -m n(z)g$$

In the limit of $\Delta z \rightarrow 0$, we end up with

$$\frac{dP}{dz} = -m n(z)g$$

Use the ideal gas law ($PV = NkT$) to obtain

$$n(z) = \frac{P(z)}{kT} \quad n \equiv \frac{N}{V}$$

Thus,

$$\frac{dP}{dz} = -\frac{mg}{kT} P$$

This is easily solved:

$$\frac{dP}{P} = -\frac{mg}{kT} dz$$

$$\ln \frac{P(z)}{P(0)} = -\frac{mgz}{kT}$$

Exponentiating yields (assuming T is a constant):

$$P(z) = P(0)e^{-mgz/kT}$$

(c) The ideal gas law implies that $n(z) = \frac{P(z)}{kT}$. Thus,

$$n(z) = n(0)e^{-mgz/kT}$$

Let us take $T = 300K$. According to Appendix A on page 20 of RB, the mass of diatomic nitrogen is $m_{N_2} = 4.653 \times 10^{-26} \text{ kg}$.

Thus,

$$\frac{N(z)}{N(0)} = \exp \left[- \frac{(9.653 \times 10^{-24} \text{ kg})(9.8 \text{ ms}^{-2})z}{(1.381 \times 10^{-23} \text{ J/K})(300 \text{ K})} \right]$$

$$= \exp \left[- \frac{z}{9.1 \text{ km}} \right]$$

Putting $\frac{N(z)}{N(0)} = \frac{1}{2}$

$$z = (9.1 \text{ km}) \ln 2$$

$$= 6.3 \text{ km}$$

⑤ RB Chapter 7, problem 7

(a) Method 1

We can use the technique of the previous problem. Consider an infinitesimal volume of gas at a distance r from the axis of rotation, with cross-sectional area A and length Δr

(i) There is an inward force due to pressure on the outside of the infinitesimal volume

$$= P(r+\Delta r)A$$

(ii) There is an outward force due to pressure on the inside of the infinitesimal volume

$$= P(r)A$$

Thus, the net radially inward force is

$$[P(r+\Delta r) - P(r)]A$$

This must provide the centripetal force necessary to keep the infinitesimal volume rotating at angular speed ω .

The centripetal force is given by

$$m\omega^2 r A \Delta r$$

where $N(r)$ is the number of molecules per unit volume at a distance r from the rotation axis, m is the mass of one molecule, $A \Delta r$ is the infinitesimal volume and the centripetal acceleration is

$$a = \frac{v^2}{r} = \omega^2 r$$

Thus,

$$\frac{P(r+\Delta r) - P(r)}{\Delta r} = m n(r) A r \omega^2$$

Taking $\Delta r \rightarrow 0$ gives

$$A \frac{dP}{dr} = m n(r) A r \omega^2$$

Along the ideal gas law, $n(r) = \frac{P(r)}{RT}$. Then,

$$\frac{dn}{dr} = -\frac{m n r \omega^2}{RT}$$

Solving the differential equation,

$$\frac{dn}{n} = -\frac{m \omega^2}{RT} r dr$$

$$\ln \frac{n(r)}{n(0)} = -\frac{m \omega^2 r^2}{2RT}$$

Hence,
$$n(r) = n(0) \exp \frac{m \omega^2 r^2}{2RT}$$

Method 2

Consider a gas molecule located a distance r from the axis of rotation. Go to the reference frame rotating with angular velocity ω . The molecule feels an outward centrifugal force

$$F = m \omega^2 r$$

The force is related to the potential energy according to

$$F = -\nabla V$$

Since the force is purely radial, ϕ is V

$$\frac{\partial V}{\partial r} = -m \omega^2 r$$

$$V(r) = -\frac{1}{2} m \omega^2 r^2$$

Following the logic on pp 153-154 of RB, we enforce the condition of diffusive equilibrium by requiring the total chemical potential to be constant.

$$\mu(r) = -\frac{1}{2} m \omega^2 r^2 + RT \ln [n(r) \lambda_{th}^3]$$

In particular, set

$$\mu(r) = \mu(0)$$

$$RT \ln [n(r) \lambda_{th}^3] = -\frac{1}{2} m \omega^2 r^2 + RT \ln [n(0) \lambda_{th}^3]$$

Hence,

$$RT \ln \frac{n(r)}{n(0)} = \frac{1}{2} m \omega^2 r^2$$

That is,

$$n(r) = n(0) \exp \frac{m \omega^2 r^2}{2RT}$$

which is the same result obtained by Method 1.

(b) The radial wave function is spherically symmetric, so the probability mass m is larger. Using the results of part (a),

$$\frac{n(r)_{338}}{n(r)_{335}} = \frac{n(r)_{338}}{n(r)_{335}} \exp\left[\frac{(m_{338} - m_{335}) \frac{1}{2} r^2}{kT}\right]$$

The gas near the periphery contains more ^{338}U , while the gas near the center contains more ^{335}U . In this way, the two isotopes can be separated.

(c) Suppose the cylinder has length L and radius R . Then, the total volume of the cylinder is $\pi R^2 L$. If N_0 is the number of molecules per unit volume in the cylinder (when $\omega = 0$), then the total number of molecules in the cylinder is $\pi R^2 L N_0$. When the cylinder spins, the total number of molecules does not change, so

$$\int_0^R n(r) 2\pi r dr L = \pi R^2 L N_0$$

is equal to the total number of molecules. Inserting

$$n(r) = N_0 \exp\left[\frac{m \omega^2 r^2}{2kT}\right]$$

into the integral above,

$$N_0 \int_0^R r \exp\left[\frac{m \omega^2 r^2}{2kT}\right] dr = \frac{R^2 N_0}{2}$$

Let $x = \frac{m \omega^2 r^2}{2kT}$. Then $dx = \frac{m \omega^2}{kT} r dr$ and we get

$$N_0 \int_0^{\frac{m \omega^2 R^2}{2kT}} \frac{dx}{2} = \frac{R^2 N_0}{2}$$

$$N_0 \int_0^{\frac{m \omega^2 R^2}{2kT}} \left[\exp\left(\frac{m \omega^2 r^2}{2kT}\right) - 1 \right] = \frac{R^2 N_0}{2}$$

Thus,

$$N_0 = N_0 \left(\frac{\exp\left(\frac{m \omega^2 R^2}{2kT}\right) - 1}{\frac{m \omega^2 R^2}{2kT}} \right)$$

The problem asks us to find a value of r such that $n(r) = N_0$. But, we can write

$$n(r) = N_0 \exp\left(\frac{m \omega^2 r^2}{2kT}\right) = N_0 \frac{\exp\left(\frac{m \omega^2 R^2}{2kT}\right) - \exp\left(\frac{m \omega^2 r^2}{2kT}\right)}{\exp\left(\frac{m \omega^2 R^2}{2kT}\right) - 1}$$

Thus, if $n(r) = N_0$, we must have

$$\frac{\exp\left(\frac{m \omega^2 R^2}{2kT}\right) - \exp\left(\frac{m \omega^2 r^2}{2kT}\right)}{\exp\left(\frac{m \omega^2 R^2}{2kT}\right) - 1} = 1$$

which can be solved for r .

Suppose the rotation is very slow. Specifically,

$$\frac{m \omega^2 R^2}{2kT} \ll 1$$

Then we can simplify the previous equation by expanding the square root.

$$\frac{m v^2 R^2}{2kT} \left[1 + \frac{m v^2 r^2}{2kT} \right] \approx \frac{m v^2 R^2}{2kT} + \frac{1}{2} \left(\frac{m v^2 R^2}{2kT} \right)^2$$

Note that the right hand side must be expanded out to second order in order to obtain a non-trivial result. We then find:

$$\frac{m v^2 R^2}{2kT} \approx \frac{1}{2} \left(\frac{m v^2 R^2}{2kT} \right)$$

$$r \approx \frac{1}{\sqrt{2}} R$$

If the relation is not particularly clear, someone must solve the problem exactly. The result is:

$$r^2 = \frac{2kT}{m v^2} \ln \left[\frac{2kT}{m v^2 R^2} \left(\exp \left(\frac{m v^2 R^2}{2kT} \right) - 1 \right) \right]$$

which is pretty ugly but can be easily evaluated.

16 RB Chapter 10, problem 5

(a) Since E is a function of S, V and N, we proceed in analogy with the Helmholtz free energy. In that case, we defined

$$F(T, V, N) = E - T \left(\frac{\partial E}{\partial S} \right)_{V, N}$$

Here, we wish to define the enthalpy which is a function of S, P, and N. Thus, instead of eliminating S in favor of T we will eliminate T in favor of P. Thus

$$H(S, P, N) = E - T \left(\frac{\partial E}{\partial V} \right)_{S, N}$$

The partial derivative is easily evaluated. Using

$$dE = T dS + P dV + \mu dN$$

we see that at constant S and N,

$$\left(\frac{\partial E}{\partial V} \right)_{S, N} = -P$$

Thus,

$$H(S, P, N) = E + PV$$

(b) Now we compute

$$dH = dE + P dV + V dP = T dS + V dP + \mu dN$$

It immediately follows that

$$T = \left(\frac{\partial H}{\partial S} \right)_{P,N}$$

$$V = \left(\frac{\partial H}{\partial P} \right)_{S,N}$$

$$\mu = \left(\frac{\partial H}{\partial N} \right)_{S,P}$$

by successively considering the remaining cases in which two of the three variables S , P and N are held fixed.

③ RB Chapter 10, problem 8

We are given

$$G = -kTN \ln \left(\frac{aT^{5/2}}{P} \right)$$

(a) From

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P,N} \quad \left[\text{eg (10.29) or (2.31) of RB} \right]$$

we obtain

$$S = kN \left[\ln \left(\frac{aT^{5/2}}{P} \right) + \frac{5}{2} \right]$$

(b) Using eg (1.13) or p12 of RB

$$C_p = \frac{\Delta E + P \Delta V}{\Delta T} \quad \text{at fixed pressure}$$

Since $\Delta E = T \Delta S - P \Delta V$ (assuming N is constant), we can write the above result as

$$C_p = \frac{T \Delta S}{\Delta T} \quad \text{at fixed pressure and } N.$$

or

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_{P,N}$$

Using the result of part (a)

$$C_p = \frac{5}{2} kN$$

(c) To obtain the equation of state, we

$$V = \left(\frac{\partial G}{\partial P} \right)_{T,N} = \frac{kTN}{P}$$

Thus, $PV = NkT$

which is the ideal gas law!

(d) The Gibbs free energy is defined by [eg (10.25) or p231 of RB]

$$G = E - TS + PV$$

Thus,

$$E = G + TS - PV$$

$$= -kTN \ln \left(\frac{qT^{5/2}}{P} \right) + kTN \left[\ln \left(\frac{qT^{5/2}}{P} \right) + \frac{5}{2} \right] - NkT$$

or

$$E = \frac{5}{2} NkT$$

where we have used the results of parts (a) and (c).

Since $E \approx \langle E \rangle$ for a state in thermal equilibrium, we conclude that

$$\langle E \rangle = \frac{5}{2} NkT.$$