

CHM 6461, Spring 2008 HW#5 solutions

1. Evaluate the isothermal-isobaric partition function of a monatomic ideal gas by converting the summation over V in the following equation to an integral:

$$\Delta(N, T, p) = \sum_{\epsilon, V} \Omega(N, V, \epsilon) e^{-\epsilon/kT} e^{-pV/kT}$$

Solution: rewrite in terms of Q .

$$\Delta(N, T, p) = \sum_V Q(N, V, T) e^{-pV/kT}$$

$$\text{where } Q(N, V, T) = \frac{q^N}{N!} = \frac{1}{N!} \left(\frac{V}{\Lambda^3} \right)^N$$

$$\Delta(N, T, p) = \frac{1}{N! \Lambda^{3N}} \sum_V (V)^N e^{-pV/kT}$$

Convert to an integral :

$$\Delta(N, T, p) = \frac{1}{N! \Lambda^{3N}} \int_0^\infty (V)^N e^{-pV/kT} dV$$

$$\int_0^\infty (V)^N e^{-pV/kT} dV = \frac{N!}{\left(\frac{p}{kT}\right)^{N+1}} = N! \left(\frac{kT}{p}\right)^{N+1} \approx N! \left(\frac{kT}{p}\right)^N$$

$$\text{Thus, } \Delta(N, T, p) = \frac{1}{N! \Lambda^{3N}} N! \left(\frac{kT}{p}\right)^N = \left(\frac{kT}{p\Lambda^3}\right)^N$$

2. Given that D_0 for H_2 is 103.2 kcal/mole and that $\Theta_v = 6214 K$, calculate D_0 for both D_2 and T_2 .

In the Harmonic oscillator approximation, the energy is

$$\epsilon = -D_e + \hbar \omega_v \left(v + \frac{1}{2} \right)$$

The bond dissociation energy is D_0

$$\text{Recall } D_e - D_0 = \frac{\hbar \omega_v}{2}$$

$$\text{Thus, } D_e = \frac{\hbar \omega_v}{2} + D_0$$

From the given information, $\Theta_v = \hbar \omega_v / k$, so $\omega_v = k \Theta_v / \hbar$

where $\omega_v = \sqrt{\frac{k}{\mu}}$. For a homonuclear diatomic $\mu = \frac{1}{2} m$,

where m is the molecular mass.

$$D_e = \frac{\hbar \omega_v}{2} + D_0 = \frac{\hbar}{2} \frac{k \Theta_v}{\hbar} + D_0 = \frac{k \Theta_v}{2} + D_0$$

Thus, for one mole,

$$D_e (H_2) =$$

$$d_e = \frac{r \Theta_v}{2} + d_0 / . \{r \rightarrow 8.314 \frac{j}{K} \frac{cal}{4.184 j}, d_0 \rightarrow 103.2 kcal \frac{1000 cal}{kcal}, \Theta_v \rightarrow 6214 K\}$$

$$109374. cal$$

Assuming D_e is the same for all three species, we solve for D_0 for each :

$$D_0 = D_e - \frac{\hbar \omega_v}{2}$$

$$\frac{\Theta_v (H_2)}{\Theta_v (D_2)} = \frac{\omega_v (H_2)}{\omega_v (D_2)} = \sqrt{\frac{\mu (D_2)}{\mu (H_2)}} = \sqrt{\frac{m (D)}{m (H)}} = \sqrt{2}$$

$$\Theta_v (D_2) = \frac{1}{\sqrt{2}} \Theta_v (H_2)$$

$$\Theta_v (T_2) = \frac{1}{\sqrt{3}} \Theta_v (H_2)$$

Thus, for D_2

$$D_0 (D_2) = 103200. cal - \frac{r}{2} \frac{1}{\sqrt{2}} \Theta_v (H_2) =$$

$$D_0 = d_e - \frac{r}{2} \frac{1}{\sqrt{2}} \Theta_v / . \{r \rightarrow 8.314 \frac{j}{K} \frac{cal}{4.184 j}, \Theta_v \rightarrow 6214 K\}$$

$$105008. cal$$

For T_2

$$D_0 = d_e - \frac{r}{2} \frac{1}{\sqrt{3}} \Theta_v / . \{r \rightarrow 8.314 \frac{j}{K} \frac{cal}{4.184 j}, \Theta_v \rightarrow 6214 K\}$$

$$105809. cal$$

3. Use the Euler-MacLaurin summation formula to simplify the rotational partition function. The result is

$$q_{rot} (T) = \frac{T}{\Theta_r} \left(1 + \frac{1}{3} \left(\frac{\Theta_r}{T} \right) + \frac{1}{15} \left(\frac{\Theta_r}{T} \right)^2 + \frac{4}{315} \left(\frac{\Theta_r}{T} \right)^3 + \dots \right)$$

The rotational partition function is $q_r =$

$$\sum_{j=-\infty}^{\infty} (2j+1) e^{-\Theta_r j(j+1)/T} = \sum_{j=-\infty}^{\infty} (2j+1) e^{-\Theta_r (j^2+j)/T}$$

Let

$$F[j_] = (2j+1) e^{-\Theta_r (j^2+j)/T}$$

$$e^{-\frac{(j+j^2)\Theta_r}{T}} (1+2j)$$

```
fb = Limit[F[b], b -> infinity, Assumptions -> Re[theta_r / T] > 0]
```

```
0
```

```
fa = F[0]
```

```
1
```

To prevent the condition output, use the Assumptions option :

```
f0 = Integrate[F[j], {j, 0, infinity}, Assumptions -> Re[theta_r / T] > 0]
```

$$\frac{T}{\Theta_r}$$

We define the $2j - 1$ derivative evaluated at a :

```
dfj[j_, a_] = Derivative[2 j - 1][F][a]
```

```
F(-1+2 j)[a]
```

Euler-MacLauren formula for a summation (using Mathematica's definition of the Bernoulli numbers (different from McQuarrie) is:

$$q_r = f_0 + \frac{1}{2} (f_a + f_b) + \sum_{j=1}^5 \frac{1}{(2j)!} \text{BernoulliB}[2j] (dfj[j, b] - dfj[j, 0]);$$

```
q[T_] = Limit[q_r, b -> infinity, Assumptions -> Re[theta_r / T] > 0]
```

$$\frac{1}{3} + \frac{T}{\Theta_r} + \frac{\Theta_r}{15 T} + \frac{4 \Theta_r^2}{315 T^2} + \frac{\Theta_r^3}{315 T^3} + \frac{4 \Theta_r^4}{3465 T^4} + \frac{61 \Theta_r^5}{66528 T^5} - \frac{19 \Theta_r^6}{39600 T^6} + \frac{689 \Theta_r^7}{13305600 T^7} - \frac{\Theta_r^8}{532224 T^8} + \frac{\Theta_r^9}{47900160 T^9}$$

The expressions agrees with McQuarrie's.

4. Using the Euler-MacLaurin expansion, derive the 2nd and 3rd order corrections to the first order high-temperature limit of E_r and C_{vr} . Express your result in terms of a power series.

$$q_r = f_0 + \frac{1}{2} (f_a + f_b) + \sum_{j=1}^2 \frac{1}{(2j)!} \text{BernoulliB}[2j] (dfj[j, b] - dfj[j, 0]);$$

```
q[T_] = Limit[q_r, b -> infinity, Assumptions -> Re[theta_r / T] > 0]
```

$$\frac{1}{3} + \frac{T}{\Theta_r} + \frac{\Theta_r}{15 T} + \frac{\Theta_r^2}{60 T^2} - \frac{\Theta_r^3}{720 T^3}$$

Energy is calculated from $-\frac{k T^2}{q} \frac{dq}{dT}$

$$\epsilon = \text{Factor}\left[k T^2 \frac{1}{q[T]} D[q[T], T]\right]$$

$$\frac{3 k T (240 T^4 - 16 T^2 \Theta_r^2 - 8 T \Theta_r^3 + \Theta_r^4)}{720 T^4 + 240 T^3 \Theta_r + 48 T^2 \Theta_r^2 + 12 T \Theta_r^3 - \Theta_r^4}$$

$$cv = \text{Factor}[D[\epsilon, T]]$$

$$(3 k (172800 T^8 + 115200 T^7 \Theta_r + 46080 T^6 \Theta_r^2 + 23040 T^5 \Theta_r^3 - 2208 T^4 \Theta_r^4 - 864 T^3 \Theta_r^5 - 96 T^2 \Theta_r^6 + 16 T \Theta_r^7 - \Theta_r^8)) / (720 T^4 + 240 T^3 \Theta_r + 48 T^2 \Theta_r^2 + 12 T \Theta_r^3 - \Theta_r^4)^2$$

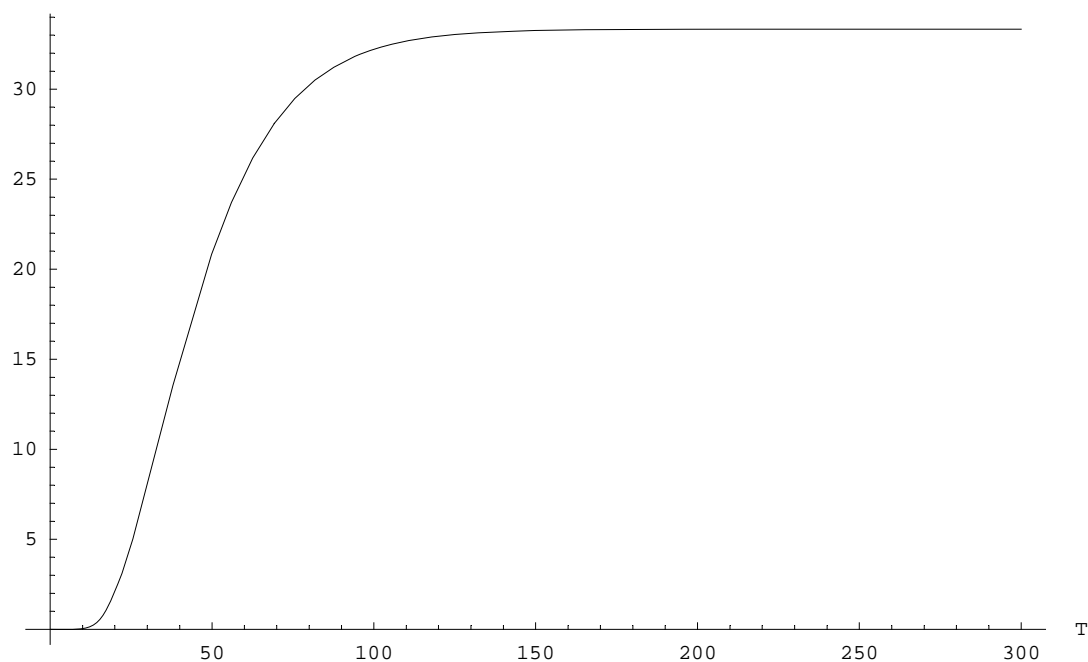
5. Calculate and plot the percent of para-D2 as a function of temperature (assuming thermal equilibrium).

The rotational temperature of D2 is 42.7 K. $f = \frac{n_{ortho}}{n_{para}}$. Taking terms up to $j=100$ is sufficient for temperatures up to at least 300K.

$$f[T_] := \frac{6 \text{Sum}[(2 j + 1) e^{-(42.7 j (j+1)/T)}, \{j, 0, 100, 2\}]}{3 \text{Sum}[(2 j + 1) e^{-(42.7 j (j+1)/T)}, \{j, 1, 100, 2\}]}$$

```
Plot[100  $\frac{1}{1 + f[T]}$ , {T, .1, 300}, AxesLabel → {"T", "% para D2"}]
```

```
% para D2
```



```
- Graphics -
```

b. Plot the temperature dependence of the constant volume heat capacity of an equilibrium mixture, ortho/para-D2.

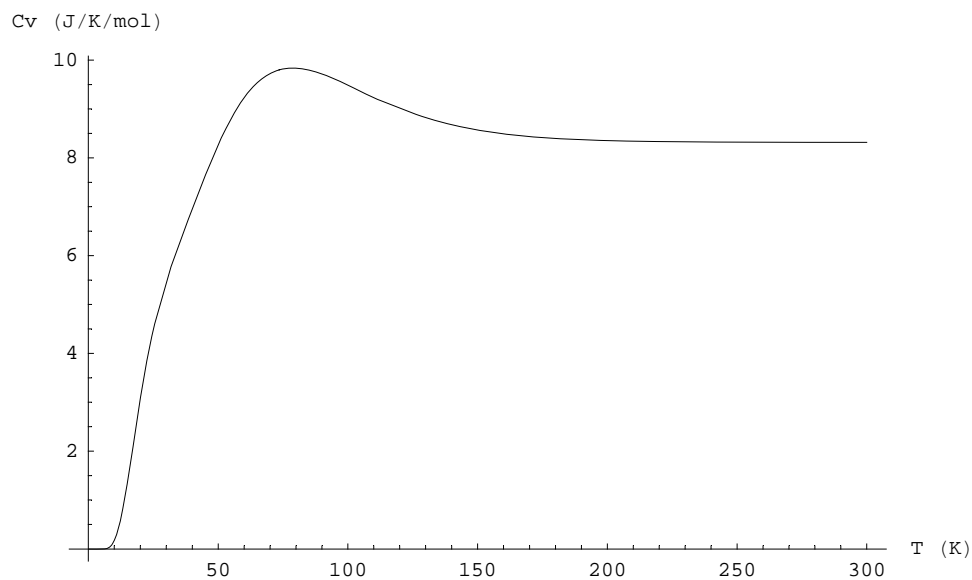
Form the partition function for D2 :

$$q[T_] = 6 \text{Sum}[(2j+1) e^{-(42.7j(j+1)/T)}, \{j, 0, 100, 2\}] + 3 \text{Sum}[(2j+1) e^{-(42.7j(j+1)/T)}, \{j, 1, 100, 2\}];$$

$$\epsilon[T_] = nkT^2 (1/q[T]) D[q[T], T] /. \{k \rightarrow 1.38 \cdot 10^{-23}, n \rightarrow 6.022 \cdot 10^{23}\};$$

$$Cv[T_] = D[\epsilon[T], T];$$

```
Plot[Cv[T], {T, .1, 300}, PlotRange -> All, AxesLabel -> {"T (K)", "Cv (J/K/mol)"}]
```

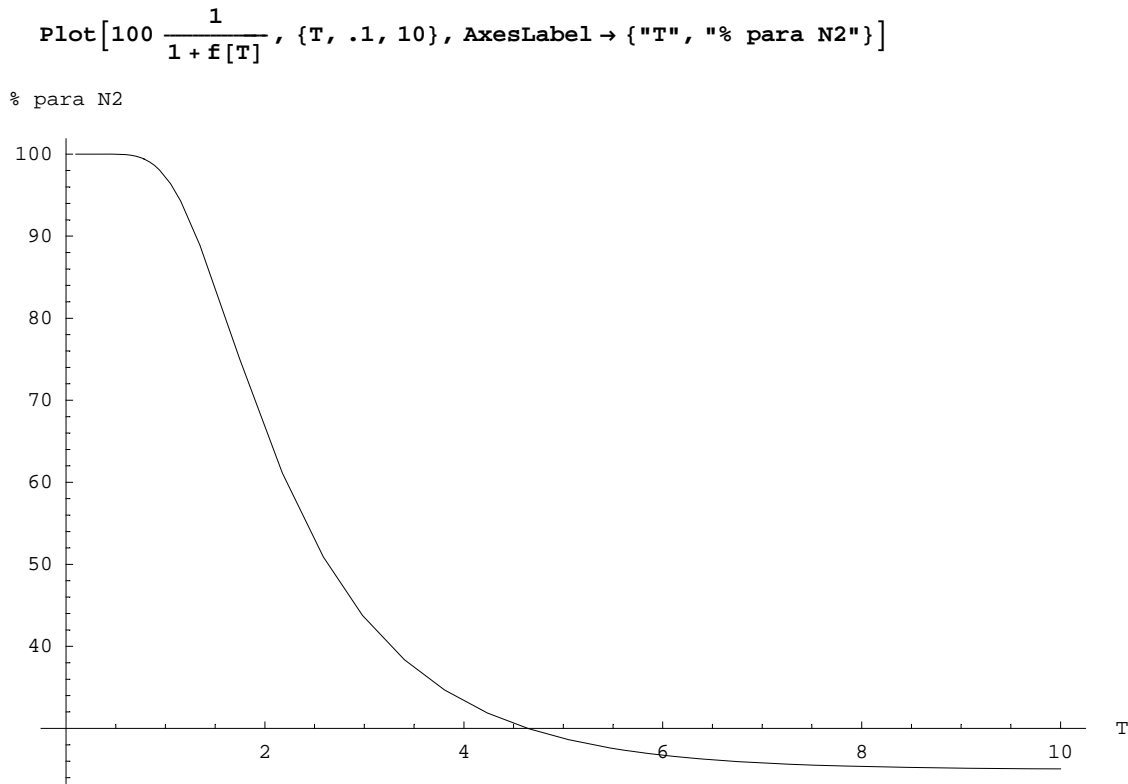


c. Repeat part (a) for ortho/para $^{15}\text{N}_2$. To what temperature must one go to get >50% para- $^{15}\text{N}_2$?

For N_2 , the characteristic rotational temperature is 2.88 K. The fraction para is

$$\% \text{ para} = 100 \frac{n_{\text{para}}}{n_{\text{para}} + n_{\text{ortho}}} =$$

$$f[T_] := \frac{3 \text{Sum}[(2j+1) e^{-2.88(j(j+1)/T)}, \{j, 1, 100, 2\}]}{1 \text{Sum}[(2j+1) e^{-(2.88j(j+1)/T)}, \{j, 0, 100, 2\}]}$$



- Graphics -

Need to go down below $3K$ for $> 50\%$ para - N_2 (nitrogen - 15, spin - $1/2$).

6. Derive the symmetric and anti - symmetric nuclear spin states of D_2 .

Using *Mathematica*'s built - in function,
 ClebschGordan[{ j_1, m_1 }, { j_2, m_2 }, { j, m }]

Let the direct products be specified as $s[m_1, m_2]$. For D_2 there are 9 DP states : $s[1, 1]$,
 $s[1, 0]$, $s[1, -1]$,

$s[0, 1]$... The Clebsch - Gordon series gives the possible total spin I :

$I = 2, 1, 0$, with degeneracies 5, 3, 1,

respectively. These are the eigenstates of the rotational Hamiltonian,

i.e. eigenstates of I^2 . These states will be specified as $t[I, m]$

$$t[I_, m_] := \sum_{m_1=-1}^1 \sum_{m_2=-1}^1 \text{If}[m_1 + m_2 == m, \text{ClebschGordan}[\{1, m_1\}, \{1, m_2\}, \{I, m\}] s[m_1, m_2], 0]$$

Note the use of the `:=`

operator to delay evaluation. We use the conditional since the $C - G$ vanishes unless $m_1 + m_2 == m$.

Thus we can quickly generate all 9 states :

For $I = 2$:

t[2, 2]

t[2, 1]

t[2, 0]

t[2, -1]

t[2, -2]

s[1, 1]

$$\frac{s[0, 1]}{\sqrt{2}} + \frac{s[1, 0]}{\sqrt{2}}$$

$$\frac{s[-1, 1]}{\sqrt{6}} + \sqrt{\frac{2}{3}} s[0, 0] + \frac{s[1, -1]}{\sqrt{6}}$$

$$\frac{s[-1, 0]}{\sqrt{2}} + \frac{s[0, -1]}{\sqrt{2}}$$

s[-1, -1]

For I = 1 :

t[1, 1]

t[1, 0]

t[1, -1]

$$-\frac{s[0, 1]}{\sqrt{2}} + \frac{s[1, 0]}{\sqrt{2}}$$

$$-\frac{s[-1, 1]}{\sqrt{2}} + \frac{s[1, -1]}{\sqrt{2}}$$

$$-\frac{s[-1, 0]}{\sqrt{2}} + \frac{s[0, -1]}{\sqrt{2}}$$

For I = 0 :

$\mathbf{t}[0, 0]$

$$\frac{s[-1, 1]}{\sqrt{3}} - \frac{s[0, 0]}{\sqrt{3}} + \frac{s[1, -1]}{\sqrt{3}}$$

7. A more accurate expression for the vibrational energy of a diatomic molecule is

$$\varepsilon_n = \left(n + \frac{1}{2}\right) h\nu - \chi_e \left(n + \frac{1}{2}\right) h\nu$$

where χ_e is the anharmonicity. Calculate some thermodynamic functions

Constructing the partition function :

$$\begin{aligned} q &= \sum_{n=0}^{\infty} e^{-\varepsilon_n/kT} = \sum_{n=0}^{\infty} e^{-\varepsilon_n/kT} = \sum_{n=0}^{\infty} e^{-((n+\frac{1}{2}) h\nu - \chi_e (n+\frac{1}{2}) h\nu) / kT} \\ &= \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2}) h\nu (1+\chi_e) / kT} = e^{-\frac{1}{2} h\nu (1+\chi_e) / kT} \sum_{n=0}^{\infty} e^{-nh\nu (1+\chi_e) / kT} \end{aligned}$$

Use the series expansion for the exponential, $\sum_n e^{-a n} = \frac{1}{1 - e^{-a}}$

$$q = \frac{e^{-\frac{1}{2} h\nu (1+\chi_e) / kT}}{1 - e^{-h\nu (1+\chi_e) / kT}}, \quad Q = q^N$$

For example, the Helmholtz energy is thus calculated :

$$\begin{aligned} A &= -kT \ln Q = -NkT \ln \left(\frac{e^{-\frac{1}{2} h\nu (1+\chi_e) / kT}}{1 - e^{-h\nu (1+\chi_e) / kT}} \right) \\ &= -NkT \ln \left(e^{-\frac{1}{2} h\nu (1+\chi_e) / kT} \right) + NkT \ln \left(1 - e^{-h\nu (1+\chi_e) / kT} \right) \\ &= \frac{1}{2} N h\nu (1 + \chi_e) + NkT \ln \left(1 - e^{-h\nu (1+\chi_e) / kT} \right) \end{aligned}$$

In most cases, $h\nu \gg kT$, so

$$A = \frac{1}{2} N h\nu (1 + \chi_e)$$