Solutions for P.S. 3

Note Title 27/03/2008

1. (a) + (b)

There are various ways to solve this problem using a computer. One can use symbolic math program such as Mathematica or Maple, or even Matlab. However, you can even use a humble spreadsheet to solve this problem, since the summation requires only a few terms.

The partition fn. for parahydrogen is

$$Z = \sum_{j=0}^{\infty} (2j+1)\, e^{-j(j+1)\epsilon/kT} \quad \text{for even } j$$

Following the problem 6.28, we will keep only terms up to 6 ($j = 0, 2, 4, 6$)

For orthohydrogen, we will keep also 4 terms ($j = 1, 3, 5, 7$).

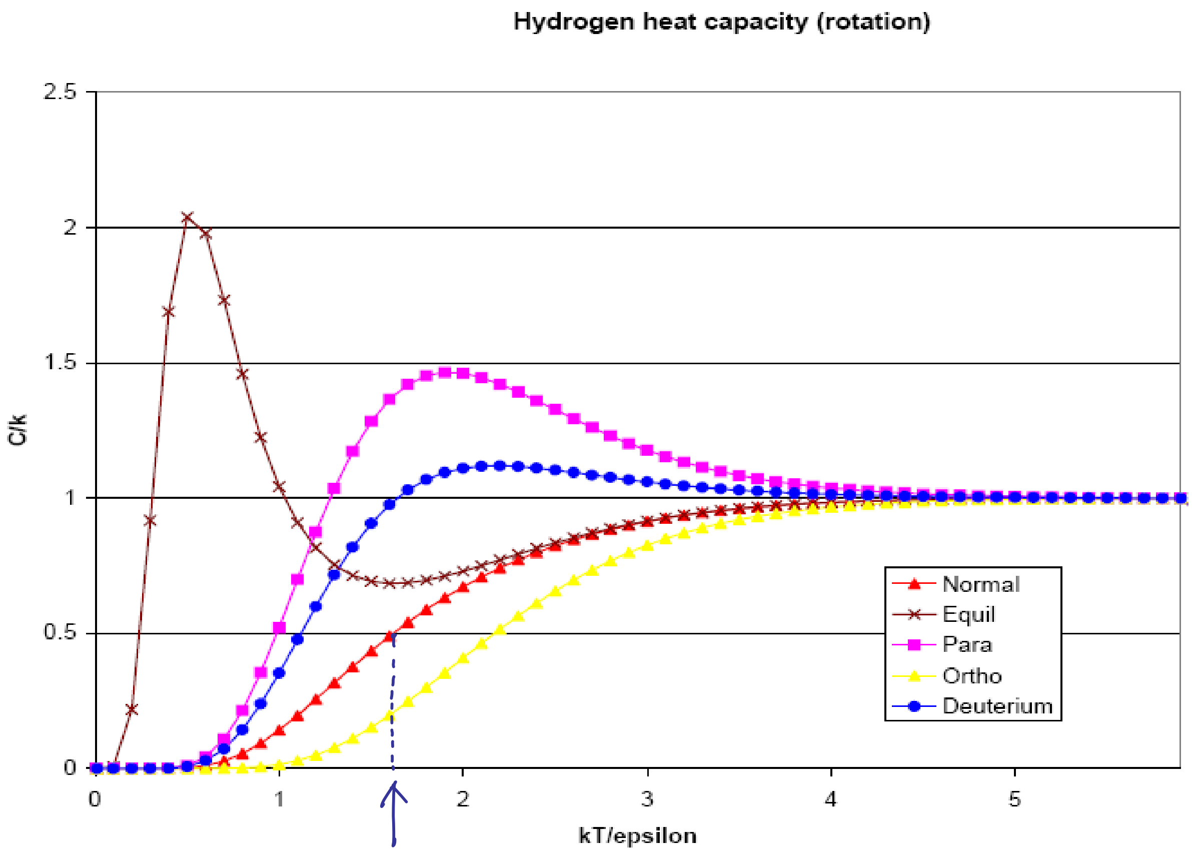
Average energy U is obtained by Boltzmann average:

$$U = \sum_{j=0}^{6} \left[j(j+1)\epsilon \right] \left[\frac{(2j+1)\, e^{-j(j+1)\epsilon/kT}}{Z} \right]$$

C_v is obtained by simple numerical derivative

$$C_v = \frac{\Delta U}{\Delta T}$$

The graph is plotted here for ortho and para hydrogen. The Excel spreadsheet is attached at the end of this solution.
(Z_odd, E_odd, C_odd for ortho
Z_even, E_even, C_even for para)



(c) For this "normal" hydrogen, we can just add the separate heat capacity, weighted by corresponding fractions. See the plot above. Note the arrow in the plot showing the temp. for $\frac{C_V}{Nk} = 0.5$. This is about $\frac{kT}{\varepsilon} \approx 1.67$

kT/epsilon	Z_even	Z_odd	Z_equil	E_even	E_odd	E_equil	C_even	C_odd	C_norm	C_equil	C_deut
0.01	1.0000	0.0000	1.0000	0.0000	2.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	1.0000	0.0000	1.0000	0.0000	2.0000	0.0000	0.0000	0.0000	0.0000	0.0082	0.0000
0.2	1.0000	0.0001	1.0004	0.0000	2.0000	0.0008	0.0000	0.0000	0.0000	0.2183	0.0000
0.3	1.0000	0.0038	1.0115	0.0000	2.0000	0.0226	0.0001	0.0000	0.0000	0.9171	0.0001
0.4	1.0000	0.0202	1.0606	0.0000	2.0000	0.1144	0.0018	0.0000	0.0004	1.6882	0.0012
0.5	1.0000	0.0549	1.1649	0.0002	2.0000	0.2832	0.0118	0.0000	0.0030	2.0384	0.0079
0.6	1.0002	0.1070	1.3213	0.0014	2.0000	0.4870	0.0432	0.0001	0.0109	1.9782	0.0288
0.7	1.0009	0.1723	1.5178	0.0057	2.0000	0.6848	0.1087	0.0007	0.0277	1.7314	0.0727
0.8	1.0028	0.2463	1.7415	0.0165	2.0001	0.8580	0.2139	0.0026	0.0554	1.4581	0.1435
0.9	1.0064	0.3251	1.9817	0.0379	2.0003	1.0038	0.3551	0.0071	0.0941	1.2237	0.2391
1	1.0124	0.4060	2.2305	0.0735	2.0011	1.1262	0.5217	0.0157	0.1422	1.0425	0.3530
1.1	1.0214	0.4871	2.4827	0.1256	2.0026	1.2304	0.6994	0.0298	0.1972	0.9097	0.4762
1.2	1.0337	0.5669	2.7345	0.1956	2.0056	1.3214	0.8742	0.0503	0.2563	0.8162	0.5996
1.3	1.0495	0.6448	2.9840	0.2830	2.0106	1.4030	1.0345	0.0777	0.3169	0.7532	0.7156
1.4	1.0688	0.7203	3.2297	0.3864	2.0184	1.4783	1.1720	0.1120	0.3770	0.7138	0.8187
1.5	1.0916	0.7931	3.4710	0.5036	2.0296	1.5497	1.2825	0.1524	0.4349	0.6923	0.9058
1.6	1.1176	0.8634	3.7078	0.6319	2.0448	1.6189	1.3648	0.1980	0.4897	0.6844	0.9759
1.7	1.1467	0.9311	3.9400	0.7684	2.0646	1.6874	1.4204	0.2477	0.5409	0.6866	1.0295
1.8	1.1785	0.9965	4.1680	0.9104	2.0894	1.7560	1.4523	0.3002	0.5882	0.6963	1.0683
1.9	1.2128	1.0597	4.3919	1.0556	2.1194	1.8257	1.4643	0.3543	0.6318	0.7111	1.0943
2	1.2493	1.1210	4.6123	1.2021	2.1549	1.8968	1.4606	0.4088	0.6717	0.7294	1.1100
2.1	1.2878	1.1806	4.8295	1.3481	2.1957	1.9697	1.4451	0.4626	0.7082	0.7498	1.1176
2.2	1.3280	1.2386	5.0439	1.4926	2.2420	2.0447	1.4212	0.5148	0.7414	0.7712	1.1190
2.3	1.3697	1.2954	5.2558	1.6347	2.2935	2.1218	1.3919	0.5648	0.7716	0.7927	1.1162
2.4	1.4126	1.3510	5.4656	1.7739	2.3500	2.2011	1.3595	0.6121	0.7990	0.8139	1.1104
2.5	1.4566	1.4057	5.6736	1.9099	2.4112	2.2825	1.3260	0.6562	0.8237	0.8341	1.1027
2.6	1.5016	1.4595	5.8801	2.0425	2.4768	2.3659	1.2927	0.6970	0.8459	0.8532	1.0941
2.7	1.5473	1.5127	6.0853	2.1717	2.5465	2.4512	1.2605	0.7343	0.8658	0.8709	1.0851
2.8	1.5937	1.5652	6.2894	2.2978	2.6199	2.5383	1.2301	0.7681	0.8836	0.8871	1.0761
2.9	1.6407	1.6173	6.4926	2.4208	2.6967	2.6270	1.2020	0.7985	0.8994	0.9018	1.0675
3	1.6881	1.6690	6.6950	2.5410	2.7766	2.7172	1.1763	0.8257	0.9134	0.9150	1.0594
3.1	1.7360	1.7203	6.8969	2.6586	2.8592	2.8087	1.1531	0.8498	0.9257	0.9268	1.0520
3.2	1.7842	1.7713	7.0982	2.7740	2.9441	2.9014	1.1324	0.8711	0.9364	0.9372	1.0453
3.3	1.8326	1.8222	7.2991	2.8872	3.0312	2.9951	1.1140	0.8898	0.9458	0.9463	1.0392
3.4	1.8813	1.8728	7.4997	2.9986	3.1202	3.0897	1.0978	0.9061	0.9540	0.9544	1.0339
3.5	1.9302	1.9233	7.7000	3.1084	3.2108	3.1851	1.0836	0.9202	0.9611	0.9613	1.0292
3.6	1.9793	1.9736	7.9002	3.2167	3.3029	3.2813	1.0713	0.9325	0.9672	0.9673	1.0250
3.7	2.0285	2.0239	8.1001	3.3239	3.3961	3.3780	1.0607	0.9430	0.9724	0.9725	1.0214
3.8	2.0778	2.0740	8.2999	3.4299	3.4904	3.4753	1.0515	0.9521	0.9769	0.9770	1.0183
3.9	2.1272	2.1241	8.4996	3.5351	3.5856	3.5730	1.0436	0.9598	0.9807	0.9808	1.0157
4	2.1767	2.1742	8.6992	3.6394	3.6816	3.6710	1.0368	0.9664	0.9840	0.9840	1.0134
4.1	2.2262	2.2242	8.8988	3.7431	3.7782	3.7694	1.0311	0.9720	0.9867	0.9868	1.0114
4.2	2.2758	2.2742	9.0983	3.8462	3.8754	3.8681	1.0262	0.9767	0.9891	0.9891	1.0097
4.3	2.3254	2.3241	9.2978	3.9488	3.9731	3.9670	1.0220	0.9807	0.9910	0.9910	1.0082
4.4	2.3751	2.3741	9.4973	4.0510	4.0712	4.0661	1.0185	0.9841	0.9927	0.9927	1.0070
4.5	2.4248	2.4240	9.6968	4.1529	4.1696	4.1654	1.0155	0.9869	0.9940	0.9940	1.0059
4.6	2.4746	2.4739	9.8962	4.2544	4.2683	4.2648	1.0129	0.9892	0.9952	0.9952	1.0050
4.7	2.5243	2.5238	10.0957	4.3557	4.3672	4.3643	1.0108	0.9912	0.9961	0.9961	1.0042
4.8	2.5741	2.5737	10.2952	4.4568	4.4663	4.4639	1.0089	0.9929	0.9969	0.9969	1.0036
4.9	2.6239	2.6236	10.4946	4.5577	4.5656	4.5636	1.0073	0.9942	0.9975	0.9975	1.0030

(d) For this one needs to calculate new partition function; Z_equil, by adding up all terms, while counting odd-j terms three times. From this one can calculate E_equil, and C_equil. Plot is shown in the previous page.
Note the huge peak at fairly low temp.

(e) Normal deuterium case is similar to normal hydrogen case (part c), except for different weighting factors.
Note that "para" $\longleftrightarrow$ odd
"ortho" $\longleftrightarrow$ even
in deuterium case. (opposite of hydrogen)

2. (6.48) (a)

From eq. (6.84)-(6.85)

$$Z_1 = \frac{V}{v_Q} Z_{int} = \frac{V}{v_Q} Z_{rot} Z_e$$

$$\therefore \quad Z = \frac{(Z_1)^N}{N!} = \left(\frac{V Z_e Z_{rot}}{v_Q}\right)^N \frac{1}{N!}$$

$$F = -kT \ln Z = -NkT\left[\ln\left(\frac{V Z_e Z_{rot}}{v_Q}\right) - \ln N + 1\right]$$

$$= \underbrace{-NkT\left[\ln\left(\frac{V}{v_Q}\right) - \ln N + 1\right]}_{(6.90)} \underbrace{- NkT \ln\left(Z_e Z_{rot}\right)}_{F_{int}}$$

Note that F is the sum of $F_{trans} + F_{int}$, where F_{trans} is given by (6.90).
Therefore the entropy due to F_{int} is

$$S_{int} = -\frac{\partial F_{int}}{\partial T} = +Nk\ln(Z_e Z_{rot}) + NkT\frac{\partial}{\partial T}\ln(Z_e Z_{rot})$$

At room temperature, Z_{rot} is in the high temperature limit (eq. 6.31 or 6.33), but Z_e is a constant
(Why? Remember that electron levels in hydrogen are given by $-13.6\,eV$, $-3.4\,eV$, $\cdots$ and this becomes even larger in nitrogen or oxygen. That is, electronic energy scale is much larger than the kT of room temp.)

Then $$\frac{\partial}{\partial T}\left[\ln Z_e + \ln\left(\frac{kT}{\epsilon}\right)\right] = \frac{\cancel{\epsilon}}{\cancel{k}T}\cdot\frac{\cancel{k}}{\cancel{\epsilon}} = \frac{1}{T}$$

Therefore,

$$S_{int} = +Nk\ln(Z_e Z_{rot}) + Nk\cancel{T}\frac{1}{\cancel{T}}$$

$$S_{total} = Nk\left[\ln\left(\frac{V}{Nv_Q}\right) + \frac{5}{2}\right] + Nk\ln(Z_e Z_{rot}) + Nk$$

$$= Nk\left[\ln\left(\frac{VZ_eZ_{rot}}{Nv_Q}\right) + \frac{7}{2}\right]$$

For oxygen, $Z_e = 3$,

$$Z_{rot} = \frac{kT}{2\epsilon} = \frac{(8.67\times10^{-5}\,eV/\cancel{k})\cdot(300\,\cancel{k})}{2\cdot(0.00018\,eV)} \approx 70$$

(from prob 6.24)

The quantum volume is:

$$v_Q = \left(\frac{h}{\sqrt{2\pi m kT}}\right)^3 = \left(\frac{6.6\times 10^{-34}\ J\cdot s}{\sqrt{2\pi\cdot 32\cdot(1.66\times10^{-27})(1.38\times10^{-23})\cdot 300}}\right)^3$$

$$\approx \underline{5.73\times 10^{-33}\ m^3}$$

The average volume per particle

$$\frac{V}{N} = \frac{kT}{P} = \frac{(1.38\times10^{-23}\ J/K)(300\,K)}{10^5\ N/m^2} = \underline{4\times10^{-26}\ m^3}$$

atmospheric pressure

Now,

$$\ln\left(\frac{V}{N}\cdot\frac{Z_e Z_{rot}}{v_Q}\right) = \ln\left(\frac{4\times10^{-26}\cdot 3.70}{5.73\times10^{-33}}\right) \simeq 21.14$$

Thus

$$S = Nk\left[21.14 + 3.5\right] = 24.6\ nR$$

Therefore the entropy of a mole of oxygen at room temperature is $\boxed{24.6R \text{ or } 205\ J/K}$

This is exactly the measured value (on p. 405)

3. (6.17)

(a) The average is 3eV, so the deviations are $-3\,eV$, $-3\,eV$, $1\,eV$, $1\,eV$, and $4\,eV$.

(b) $$\overline{(\Delta E_i)^2} = \frac{9+9+1+1+16}{5} = 7.2\ (eV)^2$$

$$\therefore\ \sigma_E = \sqrt{7.2} \approx \underline{2.7\ eV}$$

(c) $$\sigma_E^2 = \overline{(\Delta E_i)^2} = \frac{1}{N}\sum_i (\Delta E_i)^2 = \frac{1}{N}\sum_i (\overline{E} - E_i)^2$$

$$= \frac{1}{N}\sum_i \left(\overline{E}^2 - 2E_i\overline{E} + E_i^2\right)$$

$$= \overline{E}^2 \frac{1}{\cancel{N}} \underbrace{\sum_i 1}_{\cancel{N}} - 2\overline{E}\underbrace{\frac{1}{N}\sum_i E_i}_{\overline{E}} + \underbrace{\frac{1}{N}\sum_i E_i^2}_{\overline{E^2}}$$

$$= \overline{E}^2 - 2\overline{E}^2 + \overline{E^2} = \overline{E^2} - (\overline{E})^2$$

(d) $$\sigma_E^2 = \overline{E^2} - (\overline{E})^2 = 16.2 - 9 = 7.2\ (eV)^2$$

$$\overline{E^2} = \frac{0+0+16+16+49}{5} = 16.2\ eV^2$$

$$(\overline{E})^2 = (3\ eV)^2$$

4. (a) For antiferromagnetic Ising model, the energy is just $-\epsilon$ if the dipoles are antiparallel and $+\epsilon$ if they are parallel. Then,

$\uparrow\uparrow$ or $\downarrow\downarrow$ states : $e^{-\epsilon/kT}$

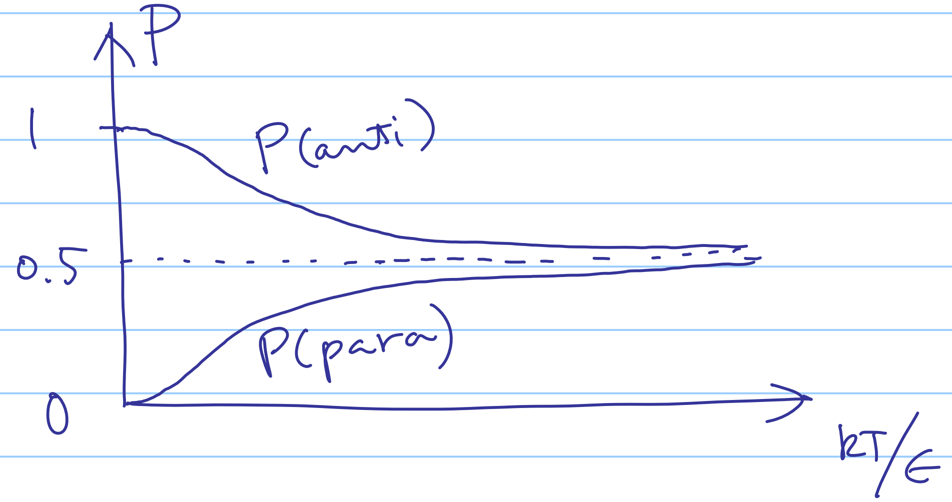
$\uparrow\downarrow$ or $\downarrow\uparrow$ " ; $e^{-\epsilon/kT}$

(b) The partition fn is therefore

$$Z = 2e^{\epsilon/kT} + 2e^{-\epsilon/kT} = 4\cosh\left(\frac{\epsilon}{kT}\right)$$

(c)
$$P(\text{para}) = \frac{2e^{-\epsilon/kT}}{2e^{-\epsilon/kT}+2e^{\epsilon/kT}} = \frac{1}{1+e^{2\epsilon/kT}}$$

$$P(\text{anti}) = \frac{2e^{\epsilon/kT}}{2e^{-\epsilon/kT}+2e^{\epsilon/kT}} = \frac{1}{1+e^{-2\epsilon/kT}}$$



(d) antiparallel config. is always preferred. However, the tendency becomes stronger at low temperature