Phys. 807 — Statistical Mechanics

HW5 Solution.

Problem:

The partition function for the rotational degrees of freedom of N diatomic molecules is given by

$$\mathcal{Z} = \mathcal{Z}_m^N$$

$$\mathcal{Z}_m = \sum_l (2l+1)(2s+1)e^{-Kl(l+1)}$$

with

$$K = \beta \frac{\hbar^2}{2I}$$

where I is the moment of inertia, $(2s+1)$ is the degeneracy factor corresponding to the total nuclear spin s and l is summed over all allowed states of the molecular system. Calculate in the limits (a) and (b) (see below) the contribution of the rotational degrees of freedom to the specific heat c_v for one mole of one mole of para-H_2 and one mole of orto-H_2.

$a)$ Low-temperature limit (K large). Keep only terms $l \leq 2$ in the partition function.

$b)$ High-temperature limit. Evaluate c_V to the lowest finite power in $1/T$ occurring in this limit using the Euler-MacLaurin formula

$$\sum_{m=0}^{\infty} f(m) = \int_0^{\infty} f(x)dx + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) + \dots$$

Solution

(a)

For a mole of orthohydrogen at a low temperature

$$E = -N_A \frac{\partial}{\partial \beta} \ln\left(1 + 5e^{-6K}\right) \simeq -N_A \frac{\partial}{\partial \beta}\left(30e^{-6K}\right) = \frac{30\hbar^2}{2I}N_A e^{-6K}$$

so

$$c_V = \frac{30\hbar^2}{2I} N_A \frac{\partial}{\partial T} e^{-\frac{6\hbar^2}{2Ik_BT}} = 180RK^2e^{-6K}$$

For a mole of parahydrogen

$$E = -N_A \frac{\partial}{\partial \beta} \ln 9e^{-2K} = 2N_A \frac{\partial}{\partial \beta} \frac{\hbar^2}{2I}\beta = \frac{\hbar^2}{I}N_A \Rightarrow c_V = \frac{\partial}{\partial T}\frac{\hbar^2}{I}N_A = 0$$

(b)

For a molecule of orthohydrogen at a high temperature ($K \ll 1$)

$$\mathcal{Z}_m = \sum_{l=2n} (4n+1)e^{-2Kn(2n+1)} \simeq \int_0^\infty dn \ (4n+1)e^{-2Kn(2n+1)} + \frac{1}{2} + \frac{K-2}{6} - \frac{K^3 - 12K^2 + 12K}{90}$$

$$\simeq \frac{1}{2K} + \frac{1}{6} + \frac{K}{30}$$

where I used $f'(0) = 4 - 2K$, $f'''(0) = -96K + 96K^2 - 8K^3$ for $f(x) = (4x+1)e^{-2x(2x+1)K}$.

The energy of 1 mole of orthohydrogen is

$$E = -N_A\frac{\partial}{\partial \beta} \ln \frac{1}{2K}(1 + \frac{K}{3} + \frac{K^2}{15}) \simeq N_A\frac{\partial}{\partial \beta}(\ln K - \frac{K}{3} - \frac{K^2}{90})$$

$$= \frac{N_A}{\beta} - \frac{N_A\hbar^2}{2I} - \frac{N_A\beta}{45}(\frac{\hbar^2}{2I})^2$$

and therefore

$$c_V = R\Big[1 + \frac{1}{45k_B^2T^2}(\frac{\hbar^2}{2I})^2\Big] = R\Big[1 + \frac{T_*^2}{45T^2}\Big]$$

For a molecule of parahydrogen at a high temperature

$$\mathcal{Z}_m = 3\sum_{l=2n+1} (4n+2)e^{-2K(n+1)(2n+1)} \simeq 3\int_0^\infty dn \ (4n+3)e^{-2K(n+1)(2n+1)}$$

$$+ 3e^{-2K}\Big[\frac{1}{2} - \frac{1}{3} + \frac{3}{2}K - \frac{4K - 36K^2 + 27K^3}{30}\Big] \simeq 3(\frac{1}{2K} + \frac{1}{6} + \frac{9}{10}K)$$

where I used $f'(0) = 2e^{-2K}(2 - 9K)$, $f'''(0) = 24e^{-2K}(-4K + 36K^2 - 27K^3)$ for $f(x) = (4x+3)e^{-2(x+1)(2x+1)K}$.

2

The energy of 1 mole of parahydrogen is

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\begin{aligned}
E &= -N_A \frac{\partial}{\partial \beta} \ln \frac{3}{2K}\left(1 + \frac{K}{3} + \frac{9K^2}{5}\right) \simeq N_A \frac{\partial}{\partial \beta}\left(\ln K - \frac{K}{3} - \frac{157K^2}{90}\right) \\
&= \frac{N_A}{\beta} - \frac{N_A \hbar^2}{2I} - 157 \frac{N_A \beta}{45}\left(\frac{\hbar^2}{2I}\right)^2
\end{aligned}
$$

and therefore

$$
c_V = R\left[1 + \frac{157}{45 k_B^2 T^2}\left(\frac{\hbar^2}{2I}\right)^2\right] = R\left[1 + 157\frac{T_*^2}{45T^2}\right]
$$