Spring 2000 #6

· Diatomic molecule with moment of inertia I.

a) Using classical statistics, caculate C_v

$E = 2(\frac{1}{2}KT)$ [$\frac{1}{2}KT$ per degree of rotational freedom]

$C_v = \left(\frac{\partial E}{\partial T}\right)_V \Rightarrow C_v = K$

b) In quantum mechanics

Find Z & $\langle E \rangle$

$$E_j = \frac{\hbar^2}{2I} j(j+1) \quad j = 0, 1, 2 \ldots$$

The degeneracy is $(2j+1)$

$$Z = \sum e^{-\beta E}$$

$$Z = \sum_{j=0}^{\infty} \left[(2j+1) \, e^{\left(-\frac{\hbar^2}{2IKT} j(j+1)\right)}\right]$$

$$\langle E \rangle = \frac{\sum_j \frac{\hbar^2}{2I} j(j+1)(2j+1) \, e^{\left(-\frac{\hbar^2}{2IKT} j(j+1)\right)}}{\sum_j (2j+1) \, e^{\left(-\frac{\hbar^2}{2IKT} j(j+1)\right)}}$$

c) Find low temperature limit of heat capacity

$\Rightarrow$ only first two states are occupied. $(j = 0, 1)$

$$\langle E \rangle = \frac{\frac{\hbar^2}{2I}\, 1(1+1)(2+1)\, e^{\left(\frac{-\hbar^2}{2IKT}\, 2\right)}}{e^{\left(\frac{-\hbar^2}{2IKT}\cdot 0\right)} + 3e^{\left(\frac{-\hbar^2}{2IKT}\, 2\right)}}$$

$$= \frac{3\hbar^2}{I}\, e^{\left(\frac{-\beta\hbar^2}{I}\right)} \cdot \frac{1}{\left(1 + 3e^{\frac{-\beta\hbar^2}{I}}\right)}$$

$$C_v = \left(\frac{d\langle E\rangle}{dT}\right)_v = \frac{\partial\langle E\rangle}{\partial\beta}\frac{\partial\beta}{\partial T}$$

$$= \frac{3\hbar^2}{I}\left[\frac{-\hbar^2}{I}\, e^{\left(\frac{-\hbar^2\beta}{I}\right)}\left(1+3e^{-\beta\hbar^2 \cdots}\right)^{-1} \cdots \left[e^{-\frac{\beta\hbar^2}{I}}(-1)\left(1+3e^{\left(\frac{-\beta\hbar^2}{I}\right)}\right)^{-2}\left(\frac{-\hbar^2}{I}\right)\right]\right]$$

$$\beta = \frac{1}{KT} \Rightarrow \frac{\partial\beta}{\partial T} = \frac{-1}{KT^2}$$

$$C_v = \frac{3\hbar^4}{I^2KT^2}\, \frac{e^{\left(\frac{-\hbar^2}{IKT}\right)}}{\left(1+3e^{\left(-\hbar^2/IKT\right)}\right)^3}$$

This is valid for $e^{\left(\frac{-\hbar^2}{2IKT}\, 2(2+1)\right)} \approx 0$

since only $j = 0,1$ survive

$$\Rightarrow \frac{3\hbar^2}{IKT} \gg 1 \Rightarrow T \ll \frac{3\hbar^2}{IK}$$

$$\Rightarrow KT \ll \frac{\hbar^2}{I}$$

d) Derive a high temperature expression for specific heat.

$\Rightarrow \sum \to \int$

$$\langle E \rangle = \frac{\int_0^\infty \frac{\hbar^2}{2I}\, j(j+1)(2j+1)\, e^{\left(\frac{-\hbar^2}{2IKT}\, j(j+1)\right)}\, dj}{\int_0^\infty (2j+1)\, e^{\left(\frac{-\hbar^2\, j(j+1)}{2KTI}\right)}\, dj}$$

$$= \frac{-\partial}{\partial\beta}\ln\left[\int_0^\infty (2j+1)\, e^{\left(\frac{-\hbar^2\, j(j+1)}{2KTI}\right)}\, dj\right]$$

$U = j(j+1) \quad dU = (2j+1)dj$

$$\langle E \rangle = \frac{-\partial}{\partial\beta} \ln\left[\int_0^\infty e^{\frac{-\hbar^2 U}{2IKT}}\, dU \right] = \frac{-\partial}{\partial\beta} \ln\left[\frac{2IKT}{-\hbar^2} e^{\frac{-\hbar^2 U}{2IKT}} \Big|_0^\infty \right] = \frac{-\partial}{\partial\beta} \ln\left(\frac{2IKT}{\hbar^2}\right)$$

$$= \frac{-\partial}{\partial\beta} \ln\left(\frac{2I}{\hbar^2\beta}\right) = \frac{-1}{\frac{2I}{\hbar^2\beta}} \frac{\partial}{\partial\beta}\left(\frac{2I}{\hbar^2\beta}\right) = \frac{+1}{\frac{2I}{\hbar^2\beta}} \cdot \frac{2I}{\hbar^2\beta^2}$$

$$= \frac{\hbar^2\beta}{\hbar^2\beta^2} = \frac{1}{\beta} = KT \qquad \Rightarrow C_v = K$$

For high temperatures

$$e^{\left(\frac{-\hbar^2}{2IKT} j(j+1)\right)} \approx \text{large} \quad \Rightarrow \frac{\hbar^2}{2IKT} << 1$$

$$\Rightarrow KT >> \frac{\hbar^2}{I}$$