① $E = E_A + E_B + E_C + \dots$

then

$$Z = \sum_{ABC} e^{-\beta(E_A+E_B+E_C)} = \left(\sum_A e^{-\beta E_A}\right)\left(\sum_B e^{-\beta E_B}\right)\left(\sum_C e^{-\beta E_C}\right) =$$

$$= Z_A Z_B Z_C$$

$$\langle E\rangle = \frac{\partial \ln Z}{\partial(-\beta)} = \frac{\partial \ln Z_A}{\partial(-\beta)} + \frac{\partial \ln Z_B}{\partial(-\beta)} + \dots$$

$$C_V = -\beta^2 \frac{\partial \langle E\rangle}{\partial \beta} = \beta^2 \left[\frac{\partial^2 \ln Z_A}{\partial \beta^2} + \frac{\partial^2 \ln Z_B}{\partial \beta^2} + \dots\right] = C_V^{(A)} + C_V^{(B)} + C_V^{(C)} + \dots$$

Now let $E = E_A + E_0$, E_0 = zero-point energy

Then
$$Z = \sum_A e^{-\beta(E_A+E_0)} = e^{-\beta E_0} \sum_A e^{-\beta E_A}$$

$$\langle E\rangle = \frac{\partial \ln Z}{\partial(-\beta)} = \frac{\partial}{\partial(-\beta)}\left[-\beta E_0 + \ln \sum_A e^{-\beta E_A}\right] =$$

$$= E_0 + \sum_A E_A \frac{e^{-\beta E_A}}{Z}$$

$$\Downarrow$$

$$C_V = -\beta^2 \frac{\partial \langle E\rangle}{\partial \beta} = -\beta^2 \frac{\partial}{\partial \beta}\left(\sum_A \frac{E_A e^{-\beta E_A}}{Z}\right)$$ is

independent of E_0

② $Z_{elec} = g_0 + g_1 e^{-\beta \varepsilon_1} + g_2 e^{-\beta \varepsilon_2}$

where energies ε_1 and ε_2 are relative to ε_0, our choice of zero energy

$$C_V^{(elec)} = T^2 \frac{\partial^2}{\partial \beta^2} \ln Z_{elec} =$$

$$= T^2 \left[\frac{1}{Z_{elec}}\left[g_1 \varepsilon_1^2 e^{-\beta \varepsilon_1} + g_2 \varepsilon_2^2 e^{-\beta \varepsilon_2}\right] - \right.$$

$$\left. - \frac{1}{Z_{elec}^2}\left[g_1 \varepsilon_1 e^{-\beta \varepsilon_1} + g_2 \varepsilon_2 e^{-\beta \varepsilon_2}\right]\right]$$

③ $Z = Z_{trans} Z_{elec} Z_{nuc} Z_{rot} Z_{vib} \cdot \frac{1}{\sigma_{AB}}$ so

$$C_v = C_v^{trans} + C_v^{elec} + C_v^{nuc} + C_v^{rot} + C_v^{vib}$$

Now

$$C_v^{elec} = \beta^2 \left[\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 \right] \leftarrow \text{see section ②}$$

$$\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = \frac{g_1 \varepsilon_1^2 e^{-\beta \varepsilon_1} + \dots}{g_0 + \dots} - \left(\frac{g_1 \varepsilon_1 e^{-\beta \varepsilon_1} + \dots}{g_0 + \dots} \right)^2$$

$$\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 \lesssim e^{-50000/300} < e^{-100}$$

$$\therefore \; C_v^{(elec)} < \beta^2 e^{-100}$$ - a negligible number at room temperature.

Because of the high energies of the excited electronic states, the contribution to C_v of those states is negligible. Also, the above calculation shows that the ground state degeneracy does not enter into the heat capacity.