

TOPIC

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Thermodynamic functions due to
Rotational Partition Function
of
AB-type Molecule

$$q_{rot} = \left(\frac{T}{\theta_r}\right) \left\{ 1 + \frac{1}{3} \left(\frac{\theta_r}{T}\right) + \frac{1}{15} \left(\frac{\theta_r}{T}\right)^2 + \dots \right\}$$
$$= \left(T/\theta_r\right) F(T)$$

$$\Rightarrow E_{rot} = Nk_B T^2 \left(\frac{\partial \ln(q_{rot})}{\partial T} \right)$$

$$= Nk_B T^2 \left(\frac{\partial}{\partial T} \right) \left\{ \ln \left(\frac{T}{\theta_r} \right) + \ln \left(1 + \frac{1}{3} \left(\frac{\theta_r}{T}\right) + \frac{1}{15} \left(\frac{\theta_r}{T}\right)^2 + \dots \right) \right\}$$

$$\Rightarrow E_{rot} = Nk_B T^2 \left\{ \frac{1}{T} + \left(\frac{(\partial F/\partial T)}{F} \right) \right\}$$

$$= Nk_B T^2 \left\{ \left(\frac{1}{T}\right) + \left(0 - \frac{1}{3} \frac{\theta_r}{T^2} + \dots \right) F^{-1} \right\}$$

"F" can be approximated to unity for the expanded terms

$$\Rightarrow E_{rot} = Nk_B T \left\{ 1 - \frac{1}{3} \left(\frac{\theta_r}{T}\right) + \dots \right\}$$

$$\Rightarrow C_{v,rot} = \left(\frac{\partial E_{rot}}{\partial T} \right)_V = Nk_B + \dots +$$

Fraction of molecules in the Jth rotational state

$$f = \left(\frac{N_J}{N} \right) = \frac{(2J+1) e^{-J(J+1)(\theta_r/T)}}{q_{rot}}$$

$$\Rightarrow \left(\frac{\partial f}{\partial J} \right) = 0 \quad (\text{To find maximum population})$$

$$\Rightarrow \left[\begin{array}{l} 2 e^{-J(J+1)(\theta_r/T)} \\ + (2J+1) e^{-J(J+1)(\theta_r/T)} \left(- (2J+1) \left(\frac{\theta_r}{T} \right) \right) \end{array} \right] = 0$$

$J = J_{max}$

$$\Rightarrow - (2J_{max}+1)^2 \left(\frac{\theta_r}{T} \right) + 2 = 0$$

$$\Rightarrow (2J_{max}+1)^2 \left(\frac{\theta_r}{T} \right) = 2$$

$$\Rightarrow (2J_{max}+1) = \left(\frac{2T}{\theta_r} \right)^{1/2}$$

$$\Rightarrow J_{max} = \frac{1}{2} \left(\frac{2T}{\theta_r} \right)^{1/2} - \frac{1}{2}$$

$$\Rightarrow J_{max} = \left(\frac{T}{2\theta_r} \right)^{1/2} - \frac{1}{2}$$

- J_{max} increases with T
- J_{max} can hardly be ground state, i.e., $J_{max} \neq 0$
- J_{max} increases with moment of inertia of molecule.