Specific heat due to vibrational degrees of freedom of diatomic molecules

Note: In case of any assistance, I can be reached at the email id: daminisood@icloud.com

Internal energy of diatomic molecules due to vibrations can be written as:

$$E = NK\theta_v\left[\frac{1}{2} + \frac{1}{e^{\theta_v/T}-1}\right]$$

Now specific heat, C_V is defined as: $C_V = \left(\frac{\partial E}{\partial T}\right)_V$

$$\Rightarrow C_V = \frac{\partial}{\partial T}\left[\frac{NK\theta_v}{2} + \frac{NK\theta_v}{e^{\theta_v/T}-1}\right]$$

$$C_V = \frac{\partial}{\partial T}\left(\frac{NK\theta_v}{2}\right) + \frac{\partial}{\partial T}\left(\frac{NK\theta_v}{e^{\theta_v/T}-1}\right)$$

$$C_V = 0 - \frac{NK\theta_v e^{\theta_v/T}}{(e^{\theta_v/T}-1)^2}\left(-\frac{\theta_v}{T^2}\right)$$

$$\boxed{C_V = NK\left(\frac{\theta_v}{T}\right)^2\frac{e^{\theta_v/T}}{(e^{\theta_v/T}-1)^2}}$$

C_V at high temperature limit

$$\lim_{T\to\infty}(C_V) = NK\lim_{T\to\infty}\left(\left(\frac{\theta_v}{T}\right)^2\frac{e^{\theta_v/T}}{(e^{\theta_v/T}-1)^2}\right)$$

Let $\frac{\theta_v}{T} = x$

$$\Rightarrow C_V = NK\lim_{\substack{T\to\infty \\ \Rightarrow x\to 0}}\left(\frac{x^2e^x}{(e^x-1)^2}\right) = NK$$

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Method - I Rearranging the limits of functions.

$$\lim_{x\to 0}\left(\frac{x}{e^x-1}\right)^2 e^x$$

Since $\lim_{x\to 0}\left(\frac{e^x-1}{x}\right)=1$

$\Rightarrow 1^2 . e^0 = 1$

Thus, $C_0 =$ NK

Method :- II Applying L'Hopital Rule

$$\left(\lim_{x\to 0}\frac{x^2}{e^x-1}\right)\left(\lim_{x\to 0}e^x\right) = \lim_{x\to 0}\left(\frac{2x}{2(e^x-1)e^x}\right)\cdot 1$$

$$= \lim_{x\to 0}\left(\frac{x}{e^x-1}\right)\cdot\lim_{x\to 0}\left(\frac{1}{e^x}\right)$$

$$= \lim_{x\to 0}\left(\frac{1}{e^x}\right)\cdot 1 = \frac{1}{1} = 1$$ (Applying L'Hopital's Rule.

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