TOPIC
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April 14, 2020

SPECIFIC HEAT DUE TO VIBRATIONAL DEGREES OF FREEDOM OF DIATOMIC MOLECULES

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

$$E_V = Nk_B\left(\left(\frac{\theta_V}{2}\right) + \left(\frac{\theta_V}{e^{\theta_V/T}-1}\right)\right)$$

Specific heat, C_V can be defined as:

$$C_V = \left(\frac{\partial E_V}{\partial T}\right)_{\text{volume}}$$

$$\Rightarrow C_V = \frac{\partial}{\partial T}\left(Nk_B\left\{\left(\frac{\theta_V}{2}\right) + \left(\frac{\theta_V}{e^{\theta_V/T}-1}\right)\right\}\right)_{\text{Volume}}$$

$$\Rightarrow C_V = Nk_B\,\theta_V\,\frac{\partial}{\partial T}\left[\left(e^{\theta_V/T}-1\right)^{-1}\right]_{\text{vol.}}$$

$$= \left(Nk_B\,\theta_V\right)\left[-\left(e^{\theta_V/T}-1\right)^{-2}\right]\left(e^{\theta_V/T}\right)\left(-\frac{\theta_V}{T^2}\right)$$

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$$\Rightarrow \boxed{C_V = Nk_B \left(\frac{\theta_V}{T}\right)^2 \frac{e^{\theta_V/T}}{\left(e^{\theta_V/T}-1\right)^2}}$$

Specific heat at high temperature limit

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

$\left(\because \text{Letting } x = (\theta_V/T)\right)$

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

Method-1 : Rearranging the limit of functions

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

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

From (10+2)-standard limit Theorems

Method-2 : Applying L'Hospital's rule

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

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

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

Applying $\left(\frac{0}{0}\right)$ form of L'Hospital's Rule