

The curve in Figure 16.11 of the text shows how the vibrational heat capacity depends on temperature. Note that even when the temperature is only slightly above the vibrational temperature, the heat capacity is close to its equipartition value.

The total heat capacity of a molecular substance is the sum of each contribution (Figure 16.12 of the text). When equipartition is valid (when the temperature is well above the characteristic temperature of the mode $T \gg \theta_M$) we can estimate the heat capacity by counting the numbers of modes that are active. In gases, all three translational modes are always active and contribute $\frac{3}{2}R$ to the molar heat capacity. If we denote the number of active rotational modes by ν_R^\ddagger (so for most molecules at normal temperatures $\nu_R^\ddagger = 2$ for linear molecules, and 3 for non-linear molecules), then

the total heat capacity is given by $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$, where ν_V is the number of active vibrational modes. In the equipartition limit $\nu_V = 6$ for linear molecules and $\nu_V = 9$ for non-linear molecules. The total heat capacity is then

$$C_{V,m} = \left(\frac{3}{2} + \frac{\nu_R^\ddagger}{2} + \frac{\nu_V}{2}\right)R$$

The equipartition value of $C_{V,m}$ for a linear molecule is $\frac{3}{2}R + \frac{2}{2}R + \frac{6}{2}R = \frac{11}{2}R$ and for a non-linear molecule is $\frac{3}{2}R + \frac{3}{2}R + \frac{9}{2}R = \frac{15}{2}R$. However, if the temperature is just above $T = \theta_V$, the vibrational modes are not yet fully active, so that the heat capacity is less than the equipartition value. For $T = \theta_V$, the equipartition value is $\frac{11}{2}R$ for linear molecules and $\frac{15}{2}R$ for non-linear molecules. The heat capacity is then $C_{V,m} = \frac{11}{2}R$ for linear molecules and $C_{V,m} = \frac{15}{2}R$ for non-linear molecules. The heat capacity is then $C_{V,m} = \frac{11}{2}R$ for linear molecules and $C_{V,m} = \frac{15}{2}R$ for non-linear molecules.

Solutions to exercises

The thermal energy is given by $U = \frac{1}{2}k_B T$ per degree of freedom. When equipartition is valid, the total energy is then $U = \frac{1}{2}k_B T$ per degree of freedom.

$$U = \frac{1}{2}k_B T \left(\frac{3}{2} + \frac{\nu_R^\ddagger}{2} + \frac{\nu_V}{2} \right)$$

For a linear molecule, $\nu_R^\ddagger = 2$ and $\nu_V = 6$. For a non-linear molecule, $\nu_R^\ddagger = 3$ and $\nu_V = 9$.

$$U = \frac{1}{2}k_B T \left(\frac{3}{2} + \frac{\nu_R^\ddagger}{2} + \frac{\nu_V}{2} \right) = \frac{1}{2}k_B T \left(\frac{3}{2} + \frac{2}{2} + \frac{6}{2} \right) = \frac{11}{2}k_B T$$

For a non-linear molecule,

$$U = \frac{1}{2}k_B T \left(\frac{3}{2} + \frac{\nu_R^\ddagger}{2} + \frac{\nu_V}{2} \right) = \frac{1}{2}k_B T \left(\frac{3}{2} + \frac{3}{2} + \frac{9}{2} \right) = \frac{15}{2}k_B T$$

$$C_{V,m} = \left(\frac{3}{2} + \frac{\nu_R^\ddagger}{2} + \frac{\nu_V}{2} \right)R$$

For a linear molecule, $\nu_R^\ddagger = 2$ and $\nu_V = 6$.

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Xiaolong Qi



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