

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 $\nu_R^\ddagger$ (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 $\nu_V = 3N - \nu_R^\ddagger - 3$, so that $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{3N - \nu_R^\ddagger - 3}{2}R = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{3N}{2}R - \frac{\nu_R^\ddagger}{2}R - \frac{3}{2}R = \frac{3N}{2}R$.

For a diatomic molecule, $\nu_R^\ddagger = 2$ and $\nu_V = 3N - \nu_R^\ddagger - 3 = 3(2) - 2 - 3 = 1$, so that

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{5}{2}R$$

The equipartition value of $C_{V,m}$ for a diatomic molecule is $\frac{5}{2}R$, which is approximately 29.1 J K⁻¹ mol⁻¹. However, if we use the value of $C_{V,m}$ for a diatomic molecule at room temperature, we find that it is about 25 J K⁻¹ mol⁻¹. This is because the vibrational modes are not fully active at room temperature. The vibrational temperature for a diatomic molecule is $\theta_V = \frac{h\nu}{k}$, where ν is the vibrational frequency. For a diatomic molecule, θ_V is typically in the range of 1000 to 3000 K. At room temperature, $T \approx 300$ K, so $T < \theta_V$ and the vibrational modes are not fully active. The vibrational heat capacity is given by $C_{V,m}^{\text{vib}} = \frac{R}{\theta_V/T} \left(\frac{\theta_V/T}{e^{\theta_V/T} - 1} + \frac{1}{2} \right)$. For a diatomic molecule, θ_V/T is typically in the range of 3 to 10, so $C_{V,m}^{\text{vib}}$ is typically in the range of 0.5 to 1.5 R.

Solutions to exercises

The thermal energy is given by $U = \frac{1}{2} \sum_{i=1}^N \langle \epsilon_i \rangle$, where ϵ_i is the energy of the i th molecule. When equipartition is valid, the thermal energy is given by $U = \frac{1}{2} N \langle \epsilon \rangle$, where $\langle \epsilon \rangle$ is the average energy per molecule.

$$U = \frac{1}{2} N \langle \epsilon \rangle = \frac{1}{2} N \left(\frac{3}{2} R + \frac{\nu_R^\ddagger}{2} R + \frac{\nu_V}{2} R \right)$$

For a diatomic molecule, $\nu_R^\ddagger = 2$ and $\nu_V = 3N - \nu_R^\ddagger - 3 = 3(2) - 2 - 3 = 1$, so that

$$U = \frac{1}{2} N \left(\frac{3}{2} R + \frac{2}{2} R + \frac{1}{2} R \right) = \frac{1}{2} N \left(\frac{5}{2} R \right) = \frac{5}{4} N R$$

For a diatomic molecule,

$$U = \frac{1}{2} N \left(\frac{3}{2} R + \frac{2}{2} R + \frac{1}{2} R \right) = \frac{1}{2} N \left(\frac{5}{2} R \right) = \frac{5}{4} N R$$

$$C_{V,m} = \frac{1}{N} \left(\frac{dU}{dT} \right) = \frac{1}{N} \left(\frac{5}{4} N R \right) = \frac{5}{4} R$$

For a diatomic molecule, $C_{V,m} = \frac{5}{4} R$.

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Xiang Xie



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