

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

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

16.10 The equipartition theorem states that the average energy of a degree of freedom is $\frac{1}{2}kT$. The molar heat capacity is the derivative of the average energy with respect to temperature. For a diatomic molecule, the translational degrees of freedom are always active and contribute $\frac{3}{2}R$ to the heat capacity. The rotational degrees of freedom are active when $T \gg \theta_R$. The vibrational degrees of freedom are active when $T \gg \theta_V$. The average energy of a diatomic molecule is $\frac{3}{2}kT + \frac{\nu_R^\ddagger}{2}kT + \frac{\nu_V^\ddagger}{2}kT$. The molar heat capacity is $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V^\ddagger}{2}R$.

Solutions to exercises

16.11 The vibrational energy of a diatomic molecule is $\epsilon = \frac{1}{2}h\nu + h\nu \left(\frac{1}{2} + n \right)$. The vibrational energy levels are $\epsilon_n = \frac{1}{2}h\nu + h\nu \left(\frac{1}{2} + n \right)$. The vibrational energy levels are $\epsilon_n = \frac{1}{2}h\nu + h\nu \left(\frac{1}{2} + n \right)$.

$$Z_V = \sum_{n=0}^{\infty} e^{-\beta \epsilon_n} = e^{-\beta \frac{1}{2}h\nu} \sum_{n=0}^{\infty} e^{-\beta h\nu \left(\frac{1}{2} + n \right)}$$

where $\beta = 1/kT$. The vibrational energy is $\epsilon = \frac{1}{2}h\nu + h\nu \left(\frac{1}{2} + n \right)$.

$$\langle \epsilon \rangle = \frac{1}{Z_V} \sum_{n=0}^{\infty} \epsilon_n e^{-\beta \epsilon_n} = \frac{1}{Z_V} \left(\frac{1}{2}h\nu + h\nu \right) \sum_{n=0}^{\infty} e^{-\beta h\nu \left(\frac{1}{2} + n \right)}$$

16.12 The vibrational energy is $\epsilon = \frac{1}{2}h\nu + h\nu \left(\frac{1}{2} + n \right)$.

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16.13 The vibrational energy is $\epsilon = \frac{1}{2}h\nu + h\nu \left(\frac{1}{2} + n \right)$.

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