

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 per degree of freedom is $\frac{1}{2}kT$. For a diatomic molecule, there are three translational degrees of freedom, two rotational degrees of freedom, and one vibrational degree of freedom. The vibrational energy is $\frac{1}{2}kT$ for the kinetic energy and $\frac{1}{2}kT$ for the potential energy, for a total of kT . The total energy is $\frac{3}{2}kT + 2 \times \frac{1}{2}kT + kT = \frac{7}{2}kT$. The heat capacity is $\frac{7}{2}R$.

Solutions to exercises

16.11 The vibrational energy is given by $\epsilon = \frac{1}{2}h\nu$. The vibrational energy is $\frac{1}{2}h\nu$ for the ground state and $\frac{3}{2}h\nu$ for the first excited state.

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R \left(\frac{e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}} \right)$$

$$= \frac{3}{2}R + R + \frac{1}{2}R \left(\frac{e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}} \right)$$

16.12 The vibrational energy is $\epsilon = \frac{1}{2}h\nu$. The vibrational energy is $\frac{1}{2}h\nu$ for the ground state and $\frac{3}{2}h\nu$ for the first excited state.

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R \left(\frac{e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}} \right)$$

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Terry C. Jones



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