

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 heat capacity is given by $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + C_{V,m}^{\text{vib}}$. For a diatomic molecule, $\nu_R^\ddagger = 2$ and $C_{V,m}^{\text{vib}} = 0$ at low temperatures, so $C_{V,m} = \frac{5}{2}R$. At high temperatures, $C_{V,m}^{\text{vib}} = R$ and $C_{V,m} = \frac{7}{2}R$.

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

The equipartition theorem states that each degree of freedom contributes $\frac{1}{2}kT$ to the internal energy of a molecule. For a diatomic molecule, there are three translational degrees of freedom, two rotational degrees of freedom, and one vibrational degree of freedom. At high temperatures, all degrees of freedom are active and contribute $\frac{1}{2}kT$ to the internal energy. At low temperatures, only the translational and rotational degrees of freedom are active and contribute $\frac{5}{2}kT$ to the internal energy. The vibrational degree of freedom is not active at low temperatures and contributes nothing to the internal energy. The equipartition theorem states that $C_{V,m} = \frac{5}{2}R$ at low temperatures and $C_{V,m} = \frac{7}{2}R$ at high temperatures.

Solutions to exercises

The thermal energy is given by $\epsilon = \frac{1}{2}kT$. When $\epsilon \gg \epsilon_{\text{vib}}$, the vibrational energy is given by $\epsilon_{\text{vib}} = \frac{1}{2}kT$.

$$\epsilon_{\text{vib}} = \frac{1}{2}kT = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})$$

At 298 K, the vibrational energy is $\epsilon_{\text{vib}} = 2.07 \times 10^{-21} \text{ J}$.

$$\epsilon_{\text{vib}} = \frac{1}{2}kT = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K}) = 2.07 \times 10^{-21} \text{ J}$$

At 298 K, the vibrational energy is

$$\epsilon_{\text{vib}} = \frac{1}{2}kT = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K}) = 2.07 \times 10^{-21} \text{ J}$$

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

At 298 K, the vibrational energy is

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