

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

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

16B.1 The equipartition theorem states that the average energy of a degree of freedom is $\frac{1}{2}kT$ per molecule. For a diatomic molecule, the translational degrees of freedom are always active and contribute $\frac{3}{2}kT$ to the average energy. The rotational degrees of freedom are active when $T \gg \theta_R$ and contribute kT to the average energy. The vibrational degrees of freedom are active when $T \gg \theta_V$ and contribute kT to the average energy. The total average energy per molecule is $\frac{3}{2}kT + kT + kT = \frac{5}{2}kT$. The molar average energy is $\frac{5}{2}RT$.

Solutions to exercises

16B.2 The vibrational energy of a diatomic molecule is $\epsilon = \frac{1}{2}h\nu$. The vibrational energy of a diatomic molecule is $\epsilon = \frac{1}{2}h\nu$. The vibrational energy of a diatomic molecule is $\epsilon = \frac{1}{2}h\nu$.

$$\epsilon = \frac{1}{2}h\nu = \frac{1}{2}h \frac{c}{\lambda} = \frac{1}{2}hc \frac{1}{\lambda}$$

where λ is the wavelength of the radiation. The vibrational energy of a diatomic molecule is $\epsilon = \frac{1}{2}h\nu$.

$$\lambda = \frac{1}{2} \frac{hc}{\epsilon} = \frac{1}{2} \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{(0.025 \text{ eV})(1.602 \times 10^{-19} \text{ J eV}^{-1})} = 1.59 \times 10^{-7} \text{ m}$$

16B.3 The vibrational energy of a diatomic molecule is $\epsilon = \frac{1}{2}h\nu$.

$$\epsilon = \frac{1}{2}h\nu = \frac{1}{2}h \frac{c}{\lambda} = \frac{1}{2}hc \frac{1}{\lambda}$$

16B.4 The vibrational energy of a diatomic molecule is $\epsilon = \frac{1}{2}h\nu$.

The vibrational energy of a diatomic molecule is $\epsilon = \frac{1}{2}h\nu$.

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R Bogdan



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