

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 $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + C_{V,m}^{\text{vib}}$. When equipartition is valid for the vibrational modes, $C_{V,m}^{\text{vib}} = \frac{1}{2}R$ per vibrational degree of freedom. For a diatomic molecule, $\nu_R^\ddagger = 2$ and $C_{V,m}^{\text{vib}} = \frac{1}{2}R$, so $C_{V,m} = \frac{7}{2}R$. For a triatomic molecule, $\nu_R^\ddagger = 3$ and $C_{V,m}^{\text{vib}} = \frac{1}{2}R$, so $C_{V,m} = \frac{7}{2}R$.

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{1}{2}R$$

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. The total internal energy of a diatomic molecule is $U = \frac{7}{2}kT$. The molar internal energy is $U_m = \frac{7}{2}RT$. The molar heat capacity is $C_{V,m} = \frac{dU_m}{dT} = \frac{7}{2}R$. For a triatomic molecule, there are three translational degrees of freedom, three rotational degrees of freedom, and one vibrational degree of freedom. The total internal energy of a triatomic molecule is $U = \frac{7}{2}kT$. The molar internal energy is $U_m = \frac{7}{2}RT$. The molar heat capacity is $C_{V,m} = \frac{dU_m}{dT} = \frac{7}{2}R$.

Solutions to exercises

The thermal energy is given by $\epsilon = \frac{1}{2}kT$. The thermal energy is $\epsilon = \frac{1}{2}kT$. The thermal energy is $\epsilon = \frac{1}{2}kT$. The thermal energy is $\epsilon = \frac{1}{2}kT$.

$$\epsilon = \frac{1}{2}kT = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})$$

so $\epsilon = 2.07 \times 10^{-21} \text{ J}$. The thermal energy is $\epsilon = 2.07 \times 10^{-21} \text{ J}$.

$$\epsilon = \frac{1}{2}kT = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K}) = 2.07 \times 10^{-21} \text{ J}$$

so $\epsilon = 2.07 \times 10^{-21} \text{ J}$.

$$\epsilon = \frac{1}{2}kT = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K}) = 2.07 \times 10^{-21} \text{ J}$$

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{1}{2}R$$

so $C_{V,m} = \frac{7}{2}R$.

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