

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

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V^\ddagger}{2}R \quad (16.1)$$

16.10 The equipartition theorem states that the average energy per degree of freedom is $\frac{1}{2}kT$. The molar heat capacity at constant volume is the derivative of the internal energy with respect to temperature. For a diatomic molecule, the internal energy is the sum of the translational, rotational, and vibrational energies. The translational energy is $\frac{3}{2}RT$, the rotational energy is $\frac{\nu_R^\ddagger}{2}RT$, and the vibrational energy is $\frac{\nu_V^\ddagger}{2}RT$. The total internal energy is $U = \frac{3}{2}RT + \frac{\nu_R^\ddagger}{2}RT + \frac{\nu_V^\ddagger}{2}RT$. The molar heat capacity at constant volume is $C_{V,m} = \frac{dU}{dT} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V^\ddagger}{2}R$.

Solutions to exercises

16.11 The molar heat capacity at constant volume is $C_{V,m} = \frac{dU}{dT}$. The internal energy is the sum of the translational, rotational, and vibrational energies. The translational energy is $\frac{3}{2}RT$, the rotational energy is $\frac{\nu_R^\ddagger}{2}RT$, and the vibrational energy is $\frac{\nu_V^\ddagger}{2}RT$. The total internal energy is $U = \frac{3}{2}RT + \frac{\nu_R^\ddagger}{2}RT + \frac{\nu_V^\ddagger}{2}RT$. The molar heat capacity at constant volume is $C_{V,m} = \frac{dU}{dT} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V^\ddagger}{2}R$.

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

For a diatomic molecule, $\nu_R^\ddagger = 2$ and $\nu_V^\ddagger = 1$. The molar heat capacity at constant volume is

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{7}{2}R = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

16.12 The molar heat capacity at constant volume is

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

16.13 $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V^\ddagger}{2}R$

For a diatomic molecule, $\nu_R^\ddagger = 2$ and $\nu_V^\ddagger = 1$.

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Kathleen Armour



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