

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, so the total heat capacity is  $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{1}{2}R$ . For a linear molecule,  $\nu_R^\ddagger = 2$ , so the total heat capacity is  $C_{V,m} = \frac{7}{2}R$ .

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

The equipartition theorem is valid for the translational and rotational degrees of freedom at  $T = 298 \text{ K}$ , but not for the vibrational degrees of freedom. The vibrational degrees of freedom are not active at  $T = 298 \text{ K}$  because the characteristic temperature of the vibrational modes is  $\theta_{\text{vib}} = 3300 \text{ K}$ . The vibrational heat capacity is given by  $C_{V,m}^{\text{vib}} = \frac{1}{2}R$  per vibrational degree of freedom. The total heat capacity is  $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + C_{V,m}^{\text{vib}} = \frac{7}{2}R$ . For a linear molecule,  $\nu_R^\ddagger = 2$ , so the total heat capacity is  $C_{V,m} = \frac{7}{2}R$ . For a non-linear molecule,  $\nu_R^\ddagger = 3$ , so the total heat capacity is  $C_{V,m} = \frac{9}{2}R$ .

### Solutions to exercises

The thermal energy is given by  $U = \frac{1}{2}k_B T$  per degree of freedom. When equipartition is valid, the total thermal energy is  $U = \frac{1}{2}k_B T$  per degree of freedom.

$$U = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})$$

so the total thermal energy is  $U = \frac{1}{2}k_B T$  per degree of freedom.

$$U = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K}) = 2.05 \times 10^{-21} \text{ J}$$

so the total thermal energy is

$$U = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K}) = 2.05 \times 10^{-21} \text{ J}$$

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

so the total thermal energy is

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**RJ Shavelson**



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