

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

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

The equipartition value  $C_{V,m} = 1.5R$  is reached when all the degrees of freedom are active. In the middle of the 20th century, it was discovered that some degrees of freedom are not active at all temperatures. For example, the vibrational degrees of freedom are not active at room temperature. The vibrational temperature  $\theta_{vib}$  is the temperature at which the vibrational energy is equal to  $kT$ . For a diatomic molecule, the vibrational energy is  $\frac{1}{2}h\nu$  and the vibrational temperature is  $\theta_{vib} = \frac{h\nu}{k}$ . For a diatomic molecule, the vibrational energy is  $\frac{1}{2}h\nu$  and the vibrational temperature is  $\theta_{vib} = \frac{h\nu}{k}$ .

### Solutions to exercises

The vibrational energy is given by  $\epsilon = \frac{1}{2}h\nu$  and the vibrational temperature is  $\theta_{vib} = \frac{h\nu}{k}$ . The vibrational energy is  $\epsilon = \frac{1}{2}h\nu$  and the vibrational temperature is  $\theta_{vib} = \frac{h\nu}{k}$ .

$$\theta_{vib} = \frac{h\nu}{k} = \frac{6.626 \times 10^{-34} \text{ J s} \times 1.0 \times 10^{14} \text{ s}^{-1}}{1.38 \times 10^{-23} \text{ J K}^{-1}} = 4.77 \text{ K}$$

At room temperature,  $T = 298 \text{ K}$ , the vibrational energy is  $\epsilon = \frac{1}{2}h\nu = 2.38 \text{ K}$ .

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{2.38 \text{ K}}{298 \text{ K}} R = 2.5R + 0.016R = 2.516R = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

At room temperature,

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{2.38 \text{ K}}{298 \text{ K}} R = 2.5R + 0.016R = 2.516R = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

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At room temperature,  $T = 298 \text{ K}$ ,

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**Katrin Zwirgmaier**



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