

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  $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R$  is reached when the temperature is high enough so that  $T \gg \theta_M$  for all the modes. However, if the temperature is lower, then the modes with higher characteristic temperatures are not active, and the heat capacity is lower than the equipartition value. The number of active modes is  $\nu_R^\ddagger$  for all temperatures in the range  $\theta_1 < T < \theta_2$ , and  $\nu_R^\ddagger + 1$  for all temperatures in the range  $\theta_2 < T < \theta_3$ , and so on. The number of active modes is  $\nu_R^\ddagger + 2$  for all temperatures in the range  $\theta_3 < T < \theta_4$ , and so on. The number of active modes is  $\nu_R^\ddagger + 3$  for all temperatures in the range  $\theta_4 < T < \theta_5$ , and so on. The number of active modes is  $\nu_R^\ddagger + 4$  for all temperatures in the range  $\theta_5 < T < \theta_6$ , and so on.

### Solutions to exercises

The number of vibrational degrees of freedom is  $\nu_{\text{vib}} = 3N - 5$  for linear molecules and  $\nu_{\text{vib}} = 3N - 6$  for non-linear molecules. The number of vibrational degrees of freedom is  $\nu_{\text{vib}} = 3N - 5$  for linear molecules and  $\nu_{\text{vib}} = 3N - 6$  for non-linear molecules.

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

At 298 K, all the vibrational modes are inactive, so  $\nu_{\text{vib}} = 0$ .

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{0}{2}R = \frac{5}{2}R = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

At 1000 K, all the vibrational modes are active, so  $\nu_{\text{vib}} = 3N - 5$ .

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{3N - 5}{2}R = \frac{3N + 1}{2}R = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

At 1000 K, all the vibrational modes are active, so  $\nu_{\text{vib}} = 3N - 6$ .

$$C_{V,m} = \frac{3}{2}R + \frac{3}{2}R + \frac{3N - 6}{2}R = \frac{3N + 3}{2}R = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

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