

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

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

The equipartition value $C_{V,m} = \frac{3}{2}R + \nu_R^\ddagger R$ is reached when the temperature is high enough so that $T \gg \theta_M$ for all the modes. However, if the temperature is lower, some of the modes are not yet fully excited and their contribution to the heat capacity is less than the equipartition value. The total heat capacity is then given by $C_{V,m} = \frac{3}{2}R + \nu_R^\ddagger R + \dots$, where the ellipsis represents the contribution of the vibrational modes. The equipartition value $C_{V,m} = \frac{3}{2}R + \nu_R^\ddagger R$ is reached when $T \gg \theta_M$ for all the modes.

Solutions to exercises

16.1 The vibrational energy is given by $\epsilon = \frac{h\nu}{2} + \frac{h\nu}{2} + \dots$. The vibrational energy is $\epsilon = \frac{h\nu}{2} + \frac{h\nu}{2} + \dots$.

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

16.2 The vibrational energy is given by $\epsilon = \frac{h\nu}{2} + \frac{h\nu}{2} + \dots$.

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The vibrational energy is $\epsilon = \frac{h\nu}{2} + \frac{h\nu}{2} + \dots$.

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Padhraic Smyth



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