

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

the total heat capacity is given by $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$, where ν_V is the number of active vibrational modes. In the equipartition limit $\nu_V = 3N - \nu_R^\ddagger - 3$, so that the total heat capacity is

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

The equipartition limit is only valid when the temperature is high enough for all the degrees of freedom to be active. If the temperature is not high enough, then the heat capacity will be less than the equipartition value. For example, for a diatomic molecule, if the temperature is not high enough for the vibrational modes to be active, then the heat capacity will be less than the equipartition value. For a polyatomic molecule, if the temperature is not high enough for all the vibrational modes to be active, then the heat capacity will be less than the equipartition value. The equipartition limit is only valid when the temperature is high enough for all the degrees of freedom to be active.

Solutions to exercises

The thermal energy is given by $\epsilon = \frac{1}{2}k_B T$, where k_B is the Boltzmann constant. When the temperature is high, the thermal energy is much greater than the spacing between the energy levels.

$$\epsilon = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})$$

so that $\epsilon \gg \Delta E$, and the equipartition theorem is valid.

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R = \frac{3}{2}R + \frac{2}{2}R + \frac{3N - 2 - 3}{2}R = \frac{3}{2}R + R + \frac{3N - 5}{2}R$$

so that $C_{V,m} = \frac{3}{2}R + R + \frac{3N - 5}{2}R$

$$C_{V,m} = \frac{3}{2}R + R + \frac{3N - 5}{2}R = \frac{3}{2}R + R + \frac{3(3) - 5}{2}R = \frac{3}{2}R + R + \frac{4}{2}R = \frac{3}{2}R + R + 2R = \frac{7}{2}R$$

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

so that $C_{V,m} = \frac{3}{2}R + R + \frac{3N - 5}{2}R$

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Peter Atkins



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