

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

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

16B.1 The equipartition theorem states that the average energy of a mode is $\frac{1}{2}kT$ per molecule. For a diatomic molecule, there are three translational degrees of freedom, two rotational degrees of freedom, and one vibrational degree of freedom. The vibrational energy is kT per molecule because it has two degrees of freedom (kinetic and potential energy). The total energy per molecule is $\frac{7}{2}kT$. The molar heat capacity is $C_{V,m} = \frac{7}{2}R$.

Solutions to exercises

16B.2 The vibrational energy is given by $\epsilon = \frac{h\nu}{2} \left(2 + 2e^{-\beta h\nu} + 2e^{-2\beta h\nu} + \dots \right)$. When $\beta h\nu \gg 1$, the series can be approximated by $\epsilon \approx \frac{h\nu}{2} \left(2 + 2e^{-\beta h\nu} \right)$.

$$\epsilon \approx \frac{h\nu}{2} \left(2 + 2e^{-\beta h\nu} \right)$$

and the vibrational energy per mole is $U_{vib} = N_A \epsilon$.

$$U_{vib} \approx \frac{h\nu N_A}{2} \left(2 + 2e^{-\beta h\nu} \right) = h\nu N_A \left(1 + e^{-\beta h\nu} \right)$$

16B.3 The vibrational energy is

$$U_{vib} = \frac{h\nu N_A}{2} \left(2 + 2e^{-\beta h\nu} + 2e^{-2\beta h\nu} + \dots \right)$$

16B.4 $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V^\ddagger}{2}R$

where $\nu_V^\ddagger = 3N - 5$ for linear molecules

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