

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 $\nu_V = 6$ for linear molecules and $\nu_V = 9$ for non-linear molecules. The total heat capacity is then

$$C_{V,m} = \left(\frac{3}{2} + \frac{\nu_R^\ddagger}{2} + 3\right)R$$

The equipartition value of $C_{V,m}$ for a diatomic molecule is $\frac{7}{2}R$ (the value of ν_R^\ddagger is 2). However, if the temperature is just above θ_V , the vibrational modes are not yet fully active, so that some vibrational energy is missing. In this case, $\nu_V < 6$, corresponding to all degrees of freedom in the molecule being active. When $\theta_V \ll T < \theta_R$, the equipartition is in the upper limit. The average vibrational temperature θ_V for diatomic molecules is approximately 3300 K in the equipartition limit. The average θ_V for polyatomic molecules is approximately 1000 K . The number of vibrational degrees of freedom of the molecule is the number of atoms minus 1.

Solutions to exercises

The thermal energy is given by $\epsilon = \frac{1}{2}k_B T$, where k_B is the Boltzmann constant. When equipartition is valid, the thermal energy is the same as the average vibrational energy.

$$\epsilon = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})$$

so that $\epsilon = 2.05 \times 10^{-21} \text{ J}$, which is the average vibrational energy.

$$\epsilon = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K}) = 2.05 \times 10^{-21} \text{ J}$$

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