

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

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 $\nu_V = 3N - 5$ for linear molecules and $\nu_V = 3N - 6$ for non-linear molecules, where N is the number of atoms in the molecule.

For a diatomic molecule, $\nu_V = 1$ and $\nu_R^\ddagger = 2$, so

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{5}{2}R$$

The equipartition value of $C_{V,m}$ for a diatomic molecule is $\frac{5}{2}R$, which is approximately $20.8 \text{ J K}^{-1} \text{ mol}^{-1}$. However, if we calculate $C_{V,m}$ using the vibrational partition function and other quantities we will see that this value is reached only at very high temperatures. For $T = 298 \text{ K}$, the vibrational partition function is $q_v = 1.0000000000000000$, so the vibrational contribution to the heat capacity is zero. The rotational partition function is $q_r = 1.0000000000000000$, so the rotational contribution to the heat capacity is zero. The translational partition function is $q_t = 1.0000000000000000$, so the translational contribution to the heat capacity is $\frac{3}{2}R$. The total heat capacity is $C_{V,m} = \frac{3}{2}R = 12.47 \text{ J K}^{-1} \text{ mol}^{-1}$, which is much less than the equipartition value of $\frac{5}{2}R$.

Solutions to exercises

The vibrational partition function is given by $q_v = \frac{1}{1 - e^{-\theta_v/T}}$, where $\theta_v = \frac{h\nu}{k}$ is the characteristic vibrational temperature. When $T \gg \theta_v$, the partition function is given by $q_v \approx \frac{T}{\theta_v}$.

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

For a diatomic molecule, $\nu_R^\ddagger = 2$ and $\nu_V = 1$, so

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{5}{2}R$$

For a triatomic molecule,

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

$$C_{V,m} = \frac{3}{2}R + \frac{3}{2}R + \frac{1}{2}R = \frac{7}{2}R$$

For a linear molecule, $\nu_R^\ddagger = 2$ and $\nu_V = 3N - 5$.

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Didier Musso



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