

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

For CO_2 , $\nu_R^\ddagger = 2$ and $\nu_V = 4$, so that

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{4}{2}R = 3R$$

The equipartition value of $C_{V,m}$ for CO_2 is $3R$. The experimental value is $2.5R$ at 298 K . The difference is due to the fact that not all vibrational modes are active at 298 K . The characteristic temperatures for the vibrational modes of CO_2 are 1330 K , 2200 K , and 3300 K . The characteristic temperatures for the rotational modes are 2.07 K and 0.35 K . The characteristic temperatures for the translational modes are 0.000145 K , 0.000145 K , and 0.000145 K . The characteristic temperatures for the vibrational modes are 1330 K , 2200 K , and 3300 K . The characteristic temperatures for the rotational modes are 2.07 K and 0.35 K . The characteristic temperatures for the translational modes are 0.000145 K , 0.000145 K , and 0.000145 K .

Solutions to exercises

The thermal energy is given by $U = \frac{1}{2} \sum_{i=1}^N \hbar \omega_i$. When equipartition is valid, $U = \frac{1}{2} N k_B T$, so that $\frac{1}{2} \sum_{i=1}^N \hbar \omega_i = \frac{1}{2} N k_B T$.

$$\sum_{i=1}^N \hbar \omega_i = N k_B T$$

For CO_2 , $\nu_R^\ddagger = 2$ and $\nu_V = 4$, so that $N = 6$.

$$\sum_{i=1}^6 \hbar \omega_i = 6 k_B T = 6 \times (1.38 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K}) = 2.47 \times 10^{-21} \text{ J}$$

For CO_2 , $\nu_R^\ddagger = 2$ and $\nu_V = 4$, so that $N = 6$.

$$\sum_{i=1}^6 \hbar \omega_i = 6 k_B T = 6 \times (1.38 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K}) = 2.47 \times 10^{-21} \text{ J}$$

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{4}{2}R = 3R$$

For CO_2 , $\nu_R^\ddagger = 2$ and $\nu_V = 4$, so that $N = 6$.

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