

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 $\nu_V = 3N - \nu_R^\ddagger - 3$, where N is the number of atoms in the molecule. For example, for a diatomic molecule $\nu_V = 3(2) - 2 - 3 = 1$, and the total heat capacity is $C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{7}{2}R$.

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

The equipartition value of $C_{V,m}$ is $\frac{7}{2}R$ for a diatomic molecule. The degrees of freedom are $\frac{7}{2}R$ for a diatomic molecule. However, if the temperature is lower than the characteristic temperatures of the vibrational modes, the heat capacity will be lower than the equipartition value. For example, for a diatomic molecule at a temperature T such that $T \gg \theta_R$ but $T \ll \theta_V$, the heat capacity will be $C_{V,m} = \frac{5}{2}R$. This is because the vibrational modes are not active. The heat capacity will be $C_{V,m} = \frac{7}{2}R$ if the temperature is high enough that all the vibrational modes are active. The heat capacity will be $C_{V,m} = \frac{5}{2}R$ if the temperature is low enough that only the translational and rotational modes are active.

Solutions to exercises

The thermal energy is given by $U = \frac{1}{2}k_B T$ per degree of freedom. When equipartition is valid, the total thermal energy is $U = \frac{7}{2}k_B T$ for a diatomic molecule.

$$U = \frac{1}{2}k_B T \left(\frac{7}{2} \right) = \frac{7}{4}k_B T$$

At 298 K, the thermal energy is $U = \frac{7}{4}k_B T = 1.05 \times 10^{-20}$ J.

$$U = \frac{1}{2}k_B T \left(\frac{7}{2} \right) = \frac{7}{4}k_B T = 1.05 \times 10^{-20} \text{ J}$$

For a diatomic molecule,

$$U = \frac{1}{2}k_B T \left(\frac{7}{2} \right) = \frac{7}{4}k_B T = 1.05 \times 10^{-20} \text{ J}$$

$$C_{V,m} = \frac{7}{2}R = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

At 298 K, the thermal energy is $U = 1.05 \times 10^{-20}$ J.

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Rose Arny



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