

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.

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

The equipartition value of $C_{V,m}$ is the value that the heat capacity approaches as $T \rightarrow \infty$. The value of $C_{V,m}$ at a given temperature is given by the sum of the equipartition value and the vibrational contribution. The vibrational contribution is given by $\frac{\nu_V}{2}R$, where ν_V is the number of active vibrational modes. The number of active vibrational modes is given by $\nu_V = 3N - 5$ for linear molecules and $\nu_V = 3N - 6$ for non-linear molecules. The number of active vibrational modes is given by $\nu_V = 3N - 5$ for linear molecules and $\nu_V = 3N - 6$ for non-linear molecules.

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 thermal energy is given by $U = \frac{1}{2}k_B T$ per degree of freedom.

$$U = \frac{1}{2}k_B T$$

At 298 K, the thermal energy is given by $U = \frac{1}{2}k_B T$.

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

At 1000 K, the thermal energy is given by $U = \frac{1}{2}k_B T$.

$$U = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K}) = 6.90 \times 10^{-21} \text{ J}$$

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

At 298 K, the thermal energy is given by $U = \frac{1}{2}k_B T$.

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Rose Arny



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