

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 the total heat capacity is

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

The equipartition limit is only valid when the temperature is high compared to the characteristic temperatures of the modes. If the temperature is lower than the characteristic temperature of a mode, then the energy of the mode is not enough to excite it, and $\nu_V = 0$ corresponding to all degrees of freedom in the mode being inactive. When $T < \theta_V$, the vibrational contribution to the heat capacity is zero. The average vibrational temperature θ_V for all diatomic molecules is approximately 3300 K (in the equipartition limit the vibrational heat capacity is R), so a good approximation is that $\nu_V = 0$ for diatomic molecules at room temperature. For polyatomic molecules, the number of vibrational degrees of freedom is larger, and the characteristic temperatures are lower.

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 energy is distributed to the degrees of freedom

$$\epsilon = \frac{1}{2}k_B T = \frac{1}{2} \left(\frac{1}{2} m \overline{v^2} + \frac{1}{2} I \overline{\omega^2} + \frac{1}{2} k \overline{x^2} \right)$$

so that $\overline{v^2}$, $\overline{\omega^2}$, and $\overline{x^2}$ are independent of T , and are

$$\overline{v^2} = \frac{k_B T}{m}, \quad \overline{\omega^2} = \frac{k_B T}{I}, \quad \overline{x^2} = \frac{k_B T}{k} = \frac{1}{k} \left(\frac{1}{2} m \overline{v^2} + \frac{1}{2} I \overline{\omega^2} + \frac{1}{2} k \overline{x^2} \right)$$

so that we have

$$\overline{v^2} = \frac{1}{2} \overline{\omega^2} = \frac{1}{2} \overline{x^2} = \frac{k_B T}{m + I + k} = \frac{k_B T}{m + I + \frac{1}{\frac{1}{m} + \frac{1}{I} + \frac{1}{k}}}$$

so that we have $\overline{v^2} = \frac{k_B T}{m + I + \frac{1}{\frac{1}{m} + \frac{1}{I} + \frac{1}{k}}}$

which is independent of T , and

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