

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 $\nu_V = 3N - \nu_R^\ddagger - 3$, 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 is the average of the characteristic temperatures of the vibrational modes. The average rotational temperature θ_R is the average of the characteristic temperatures of the rotational modes. When $T < \theta_R$, the rotational contribution to the heat capacity is zero. The average rotational temperature θ_R is the average of the characteristic temperatures of the rotational modes.

Solutions to exercises

The thermal energy is given by $U = \frac{1}{2}k_B T$ per molecule. When a molecule is in a state with energy ϵ , the probability of finding it in that state is

$$P(\epsilon) = \frac{e^{-\epsilon/k_B T}}{\sum_i e^{-\epsilon_i/k_B T}}$$

so that the average energy is given by $\langle \epsilon \rangle = \sum_i \epsilon_i P(\epsilon_i)$.

$$\langle \epsilon \rangle = \frac{\sum_i \epsilon_i e^{-\epsilon_i/k_B T}}{\sum_i e^{-\epsilon_i/k_B T}} = \frac{1}{2}k_B T = \frac{1}{2}R$$

so that the total energy is

$$U = \frac{1}{2}Nk_B T = \frac{1}{2}R$$

so that the total energy is

$$U = \frac{1}{2}Nk_B T = \frac{1}{2}R$$

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