

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 value $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{3N - \nu_R^\ddagger - 3}{2}R$ is the value of the heat capacity in the limit of high temperature. In the equipartition limit, the heat capacity is independent of temperature. In the limit of low temperature, the heat capacity is zero. In the intermediate temperature region, the heat capacity is a function of temperature. The heat capacity is a function of temperature in the intermediate temperature region. The heat capacity is a function of temperature in the intermediate temperature region. The heat capacity is a function of temperature in the intermediate temperature region.

Solutions to exercises

The thermal energy is given by $U = \frac{1}{2} \sum_{i=1}^N \epsilon_i$, where ϵ_i is the energy of the i th molecule. When equipartition is valid, the thermal energy is given by $U = \frac{1}{2} \sum_{i=1}^N \epsilon_i$.

$$U = \frac{1}{2} \sum_{i=1}^N \epsilon_i = \frac{1}{2} \sum_{i=1}^N \left(\frac{1}{2} m \langle v^2 \rangle \right)$$

where $\langle v^2 \rangle$ is the mean square velocity. In the equipartition limit, $\langle v^2 \rangle = \frac{3}{2} \frac{k_B T}{m}$.

$$U = \frac{1}{2} \sum_{i=1}^N \left(\frac{1}{2} m \left(\frac{3}{2} \frac{k_B T}{m} \right) \right) = \frac{3}{4} N k_B T = \frac{3}{2} N \left(\frac{1}{2} k_B T \right)$$

which is the equipartition value.

$$U = \frac{1}{2} \sum_{i=1}^N \epsilon_i = \frac{1}{2} \sum_{i=1}^N \left(\frac{1}{2} m \langle v^2 \rangle \right) = \frac{1}{4} m \sum_{i=1}^N \langle v^2 \rangle$$

which is the equipartition value.

which is the equipartition value.

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Harry Linn Fisher



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