

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 enough for all the degrees of freedom to be active. If the temperature is not high enough, then the heat capacity will be less than the equipartition value. For example, if the temperature is only slightly above the vibrational temperature, then the vibrational modes will not be active and the heat capacity will be less than the equipartition value. In the equipartition limit, the heat capacity is given by $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{3N - \nu_R^\ddagger - 3}{2}R$. In the equipartition limit, the heat capacity is given by $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{3N - \nu_R^\ddagger - 3}{2}R$.

Solutions to exercises

The thermal energy is given by $\epsilon = \frac{1}{2}k_B T$. When the thermal energy is much greater than the spacing between energy levels, then the equipartition theorem is valid and the 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_R^\ddagger is the number of active rotational modes, and ν_V is the number of active vibrational modes.

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

For diatomic molecules,

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{3N - 2 - 3}{2}R = \frac{3}{2}R + \frac{2}{2}R + \frac{3N - 5}{2}R$$

For triatomic molecules,

$$C_{V,m} = \frac{3}{2}R + \frac{3}{2}R + \frac{3N - 3 - 3}{2}R = \frac{3}{2}R + \frac{3}{2}R + \frac{3N - 6}{2}R$$

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