

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

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

The equipartition value of $C_{V,m}$ for a diatomic molecule is $\frac{7}{2}R$ (the number of degrees of freedom is 5) and for a triatomic molecule is $\frac{9}{2}R$ (the number of degrees of freedom is 6). The vibrational temperature of a diatomic molecule is $\theta_{vib} = \frac{h\nu}{k}$, where ν is the vibrational frequency. For a diatomic molecule, $\theta_{vib} = \frac{h\nu}{k} = \frac{h}{k} \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$, where μ is the reduced mass. For a triatomic molecule, $\theta_{vib} = \frac{h\nu}{k} = \frac{h}{k} \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$, where μ is the reduced mass. The vibrational temperature of a diatomic molecule is $\theta_{vib} = \frac{h\nu}{k} = \frac{h}{k} \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$, where μ is the reduced mass. The vibrational temperature of a triatomic molecule is $\theta_{vib} = \frac{h\nu}{k} = \frac{h}{k} \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$, where μ is the reduced mass.

Solutions to exercises

The vibrational energy is given by $\epsilon_{vib} = \frac{1}{2}h\nu + h\nu \left(\frac{1}{2} + n \right)$, where $n = 0, 1, 2, \dots$ is the vibrational quantum number. The vibrational energy levels are $\epsilon_{vib} = \frac{1}{2}h\nu, \frac{3}{2}h\nu, \frac{5}{2}h\nu, \dots$

$$Z_{vib} = \sum_{n=0}^{\infty} e^{-\beta \epsilon_{vib}} = e^{-\beta \frac{1}{2}h\nu} \sum_{n=0}^{\infty} e^{-\beta n h\nu}$$

where $\beta = \frac{1}{kT}$ and ν is the vibrational frequency.

$$Z_{vib} = e^{-\beta \frac{1}{2}h\nu} \frac{1}{1 - e^{-\beta h\nu}} = \frac{e^{-\beta \frac{1}{2}h\nu}}{1 - e^{-\beta h\nu}}$$

Therefore, the vibrational energy is

$$U_{vib} = \frac{1}{Z_{vib}} \sum_{n=0}^{\infty} \epsilon_{vib} e^{-\beta \epsilon_{vib}} = \frac{1}{Z_{vib}} \sum_{n=0}^{\infty} \left(\frac{1}{2}h\nu + h\nu n \right) e^{-\beta \left(\frac{1}{2}h\nu + h\nu n \right)}$$

The vibrational energy is $U_{vib} = \frac{1}{2}h\nu + \frac{h\nu}{e^{\beta h\nu} - 1}$

where $\beta = \frac{1}{kT}$.

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