

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 $C_{V,m} = 2.5R$ is reached when all the degrees of freedom are active. For a diatomic molecule, $\nu_R^\ddagger = 2$ and $C_{V,m} = 2.5R$ is reached when the vibrational modes are also active. For a non-linear molecule, $\nu_R^\ddagger = 3$ and $C_{V,m} = 2.5R$ is reached when the vibrational modes are also active. The equipartition value $C_{V,m} = 3.5R$ is reached when all the degrees of freedom are active. For a diatomic molecule, $\nu_R^\ddagger = 2$ and $C_{V,m} = 3.5R$ is reached when the vibrational modes are also active. For a non-linear molecule, $\nu_R^\ddagger = 3$ and $C_{V,m} = 3.5R$ is reached when the vibrational modes are also active.

Solutions to exercises

The vibrational energy is given by $\epsilon = \frac{1}{2}h\nu$ and the vibrational temperature is $\theta_v = \frac{h\nu}{k_B}$. The vibrational energy is $\epsilon = \frac{1}{2}h\nu = \frac{1}{2}k_B\theta_v$.

$$\theta_v = \frac{2\epsilon}{k_B} = \frac{2 \times 0.025 \text{ eV}}{8.617 \times 10^{-5} \text{ eV K}^{-1}} = 580 \text{ K}$$

At 298 K, the vibrational energy is $\epsilon = \frac{1}{2}k_B\theta_v = 0.025 \text{ eV}$.

$$C_{V,m} = \frac{3}{2}R + \frac{1}{2}R \left(\frac{\theta_v}{T} \right)^2 = \frac{3}{2}R + \frac{1}{2}R \left(\frac{580 \text{ K}}{298 \text{ K}} \right)^2 = 2.5R = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

At 500 K, the vibrational energy is $\epsilon = \frac{1}{2}k_B\theta_v = 0.025 \text{ eV}$.

$$C_{V,m} = \frac{3}{2}R + \frac{1}{2}R \left(\frac{\theta_v}{T} \right)^2 = \frac{3}{2}R + \frac{1}{2}R \left(\frac{580 \text{ K}}{500 \text{ K}} \right)^2 = 2.5R = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

At 1000 K, the vibrational energy is $\epsilon = \frac{1}{2}k_B\theta_v = 0.025 \text{ eV}$.

$$C_{V,m} = \frac{3}{2}R + \frac{1}{2}R \left(\frac{\theta_v}{T} \right)^2 = \frac{3}{2}R + \frac{1}{2}R \left(\frac{580 \text{ K}}{1000 \text{ K}} \right)^2 = 2.5R = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

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AN Whitehead



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