

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  $\nu_V$  is the number of active vibrational modes. In the equipartition limit  $\nu_V = 6$  for linear molecules and  $\nu_V = 9$  for non-linear molecules. The total heat capacity is

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

The equipartition limit is valid only when the temperature is high enough for all the degrees of freedom to be active. If the temperature is low, then some degrees of freedom are not active and the heat capacity is lower. For example, for a diatomic molecule at low temperatures, only the translational degrees of freedom are active and  $C_{V,m} = \frac{3}{2}R$ . As the temperature increases, the heat capacity increases in steps. When  $T \approx \theta_R$ , the rotational degrees of freedom become active and the heat capacity increases to  $C_{V,m} = \frac{5}{2}R$ . When  $T \approx \theta_V$ , the vibrational degrees of freedom become active and the heat capacity increases to  $C_{V,m} = \frac{7}{2}R$ . The equipartition limit is reached when  $T \gg \theta_M$  for all the degrees of freedom.

### Solutions to exercises

The thermal energy is given by  $U = \frac{1}{2}k_B T$  per degree of freedom. When equipartition is valid, the total thermal energy is

$$U = \frac{1}{2}k_B T \left( \frac{3}{2} + \frac{\nu_R^\ddagger}{2} + \frac{\nu_V}{2} \right)$$

For a diatomic molecule,  $\nu_R^\ddagger = 2$  and  $\nu_V = 6$ . The total thermal energy is

$$U = \frac{1}{2}k_B T \left( \frac{3}{2} + \frac{2}{2} + \frac{6}{2} \right) = \frac{7}{2}k_B T$$

For a triatomic molecule,

$$U = \frac{1}{2}k_B T \left( \frac{3}{2} + \frac{3}{2} + \frac{9}{2} \right) = \frac{15}{2}k_B T$$

For a linear molecule,  $\nu_R^\ddagger = 2$  and  $\nu_V = 6$ .

For a non-linear molecule,  $\nu_R^\ddagger = 3$  and  $\nu_V = 9$ .

# Physical Chemistry 9th Edition Instructors Solution Guide

**Angela M. O'Donnell**



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