

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,  $\nu_V = 3N - 5$  for linear molecules and  $\nu_V = 3N - 6$  for non-linear molecules, where  $N$  is the number of atoms in the molecule.

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

The equipartition limit is only valid when the temperature is high compared to the characteristic temperatures of the modes. If the temperature is lower than the characteristic temperature of a mode, then the energy of the mode is not enough to excite it, and  $\nu_V = 0$  or  $\nu_R^\ddagger = 0$  depending on the degrees of freedom that are frozen out. For example, for a diatomic molecule at low temperatures,  $\nu_V = 0$  and  $\nu_R^\ddagger = 2$  (only rotational degrees of freedom are active). The equipartition limit is only valid when the temperature is high compared to the characteristic temperatures of the modes. In the equipartition limit, the total heat capacity is given by  $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$ .

### Solutions to exercises

The thermal energy is given by  $\epsilon = \frac{1}{2}k_B T$ , where  $k_B$  is the Boltzmann constant. When the thermal energy is much smaller than the energy of the mode, the probability of excitation is small.

$$P = \frac{\epsilon}{\epsilon + \theta_M} = \frac{\frac{1}{2}k_B T}{\frac{1}{2}k_B T + \theta_M}$$

At high temperatures, the probability of excitation is close to 1.

$$P = \frac{\epsilon}{\epsilon + \theta_M} = \frac{\frac{1}{2}k_B T}{\frac{1}{2}k_B T + \theta_M} \approx 1 - \frac{\theta_M}{\frac{1}{2}k_B T} = 1 - \frac{2\theta_M}{k_B T}$$

At low temperatures, the probability of excitation is small.

$$P = \frac{\epsilon}{\epsilon + \theta_M} = \frac{\frac{1}{2}k_B T}{\frac{1}{2}k_B T + \theta_M} \approx \frac{\frac{1}{2}k_B T}{\theta_M} = \frac{k_B T}{2\theta_M}$$

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

At high temperatures,  $\nu_V = 3N - 5$ .

# Physical Chemistry 9th Edition Instructors Solution Guide

**Rachel Sandford**



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    - Chapter 3: Physical Chemistry 9th Edition Instructors Solution Guide in Everyday Life
    - Chapter 4: Physical Chemistry 9th Edition Instructors Solution Guide in Specific Contexts
    - Chapter 5: Conclusion
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