

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,  $\nu_V = 3N - \nu_R^\ddagger - 3$ , where  $N$  is the number of atoms in the molecule. For a diatomic molecule,  $\nu_V = 3(2) - 2 - 3 = 1$ , so  $C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{7}{2}R$ .

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

The equipartition value of  $C_{V,m}$  for a diatomic molecule is  $\frac{7}{2}R$ . The equipartition value of  $C_{P,m}$  is  $\frac{9}{2}R$ . The equipartition value of  $C_{V,m}$  for a triatomic molecule is  $\frac{9}{2}R$ . The equipartition value of  $C_{P,m}$  is  $\frac{11}{2}R$ . The equipartition value of  $C_{V,m}$  for a non-linear molecule is  $\frac{9}{2}R$ . The equipartition value of  $C_{P,m}$  is  $\frac{11}{2}R$ . The equipartition value of  $C_{V,m}$  for a linear molecule is  $\frac{7}{2}R$ . The equipartition value of  $C_{P,m}$  is  $\frac{9}{2}R$ . The equipartition value of  $C_{V,m}$  for a diatomic molecule is  $\frac{7}{2}R$ . The equipartition value of  $C_{P,m}$  is  $\frac{9}{2}R$ . The equipartition value of  $C_{V,m}$  for a triatomic molecule is  $\frac{9}{2}R$ . The equipartition value of  $C_{P,m}$  is  $\frac{11}{2}R$ . The equipartition value of  $C_{V,m}$  for a non-linear molecule is  $\frac{9}{2}R$ . The equipartition value of  $C_{P,m}$  is  $\frac{11}{2}R$ . The equipartition value of  $C_{V,m}$  for a linear molecule is  $\frac{7}{2}R$ . The equipartition value of  $C_{P,m}$  is  $\frac{9}{2}R$ .

### Solutions to exercises

The thermal energy is given by  $\epsilon = \frac{1}{2}k_B T$ . When  $\epsilon \gg h\nu$ , the equipartition theorem is valid and the heat capacity is given by  $C_{V,m} = \frac{3}{2}R$ .

$$C_{V,m} = \frac{3}{2}R = \frac{3}{2}(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$$

At 298 K,  $\epsilon = \frac{1}{2}k_B T = 207 \text{ J mol}^{-1}$ . This is much less than  $h\nu = 1000 \text{ J mol}^{-1}$ , so the equipartition theorem is not valid.

$$C_{V,m} = \frac{3}{2}R + \frac{h\nu}{k_B T} = \frac{3}{2}(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) + \frac{1000 \text{ J mol}^{-1}}{207 \text{ J mol}^{-1}} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1} + 4.831 \text{ J K}^{-1} \text{ mol}^{-1} = 17.302 \text{ J K}^{-1} \text{ mol}^{-1}$$

At 500 K,  $\epsilon = \frac{1}{2}k_B T = 345 \text{ J mol}^{-1}$ .

$$C_{V,m} = \frac{3}{2}R + \frac{h\nu}{k_B T} = \frac{3}{2}(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) + \frac{1000 \text{ J mol}^{-1}}{345 \text{ J mol}^{-1}} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1} + 2.901 \text{ J K}^{-1} \text{ mol}^{-1} = 15.372 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{V,m} = \frac{3}{2}R + \frac{h\nu}{k_B T} = \frac{3}{2}(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) + \frac{1000 \text{ J mol}^{-1}}{345 \text{ J mol}^{-1}} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1} + 2.901 \text{ J K}^{-1} \text{ mol}^{-1} = 15.372 \text{ J K}^{-1} \text{ mol}^{-1}$$

At 1000 K,  $\epsilon = \frac{1}{2}k_B T = 690 \text{ J mol}^{-1}$ .

# Physical Chemistry 9th Edition Solution Manual

**RJ Shavelson**



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