

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  $\nu_V = 3N - \nu_R^\ddagger - 3$ , so that  $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{3N - \nu_R^\ddagger - 3}{2}R = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{3N}{2}R - \frac{\nu_R^\ddagger}{2}R - \frac{3}{2}R = \frac{3N}{2}R$ .

For  $\text{CO}_2$ ,  $\nu_R^\ddagger = 2$  and  $\nu_V = 3N - \nu_R^\ddagger - 3 = 3(3) - 2 - 3 = 4$ .

The equipartition value of  $C_{V,m}$  for  $\text{CO}_2$  is  $\frac{3N}{2}R = \frac{3(3)}{2}R = \frac{9}{2}R = 37.4 \text{ J K}^{-1} \text{ mol}^{-1}$ . The experimental value of  $C_{V,m}$  for  $\text{CO}_2$  is  $28.9 \text{ J K}^{-1} \text{ mol}^{-1}$ . The difference between the experimental value and the equipartition value is  $37.4 - 28.9 = 8.5 \text{ J K}^{-1} \text{ mol}^{-1}$ . This difference is the heat capacity of the vibrational modes that are not active at the experimental temperature. The experimental temperature is  $298 \text{ K}$ , and the vibrational temperatures for  $\text{CO}_2$  are  $3300 \text{ K}$ ,  $2200 \text{ K}$ , and  $3300 \text{ K}$ . The vibrational heat capacity of  $\text{CO}_2$  at  $298 \text{ K}$  is  $8.5 \text{ J K}^{-1} \text{ mol}^{-1}$ .

### Solutions to exercises

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

$$C_{V,m} = \frac{1}{2}R = \frac{1}{2}(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 4.157 \text{ J K}^{-1} \text{ mol}^{-1}$$

For  $\text{CO}_2$ ,  $\nu_V = 3N - \nu_R^\ddagger - 3 = 3(3) - 2 - 3 = 4$ .

$$C_{V,m} = \frac{1}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R = \frac{1}{2}R + \frac{2}{2}R + \frac{4}{2}R = \frac{7}{2}R = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

For  $\text{CO}_2$ ,  $\nu_R^\ddagger = 2$ .

$$C_{V,m} = \frac{1}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R = \frac{1}{2}R + \frac{2}{2}R + \frac{4}{2}R = \frac{7}{2}R = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{V,m} = \frac{1}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R = \frac{1}{2}R + \frac{2}{2}R + \frac{4}{2}R = \frac{7}{2}R = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

For  $\text{CO}_2$ ,  $\nu_R^\ddagger = 2$  and  $\nu_V = 4$ .

# Physical Chemistry 9th Solution Manual

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