

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

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

The equipartition value  $C_{V,m} = 2.5R$  is reached when all the vibrational modes are active. At  $T = 298 \text{ K}$ , the vibrational temperatures of most molecules are well above  $T$ , so the vibrational modes are not active. However, for some molecules (like  $\text{H}_2$ ) the vibrational temperature is close to  $T$ , and the vibrational modes are partially active. The vibrational heat capacity of  $\text{H}_2$  at  $T = 298 \text{ K}$  is  $0.94R$ , so the total heat capacity is  $C_{V,m} = 2.5R + 0.94R = 3.44R$ .

### Solutions to exercises

The vibrational heat capacity is given by  $C_{V,m} = \frac{R}{2} \left( \frac{\theta_V}{T} \right)^2 \frac{e^{-\theta_V/T}}{1 + e^{-\theta_V/T}}$ . When  $\theta_V \gg T$ ,  $e^{-\theta_V/T} \approx 0$ , and  $C_{V,m} \approx 0$ .

$$C_{V,m} = \frac{R}{2} \left( \frac{\theta_V}{T} \right)^2 \frac{e^{-\theta_V/T}}{1 + e^{-\theta_V/T}}$$

When  $\theta_V \ll T$ ,  $e^{-\theta_V/T} \approx 1$ , and  $C_{V,m} \approx \frac{R}{2}$ .

$$C_{V,m} = \frac{R}{2} \left( \frac{\theta_V}{T} \right)^2 \frac{e^{-\theta_V/T}}{1 + e^{-\theta_V/T}} \approx \frac{R}{2} \left( \frac{\theta_V}{T} \right)^2 \frac{1}{2} = \frac{R}{4} \left( \frac{\theta_V}{T} \right)^2$$

Therefore,  $C_{V,m} \approx \frac{R}{4} \left( \frac{\theta_V}{T} \right)^2$ .

$$C_{V,m} = \frac{R}{4} \left( \frac{\theta_V}{T} \right)^2 = \frac{R}{4} \left( \frac{1000 \text{ K}}{298 \text{ K}} \right)^2 = 0.94R$$

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + 0.94R = 3.44R$$

Therefore,  $C_{V,m} = 3.44R$ .

# Physical Chemistry 9th Solution Manual

**C. A. Trapp, M. P. Cady, Carmen Giunta**



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