

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

$$C_{V,m} = \frac{1}{2}R(3 + \nu_R^\ddagger + \nu_V^\ddagger)$$

The equipartition value of  $C_{V,m}$  is  $\frac{1}{2}R(3 + \nu_R^\ddagger + \nu_V^\ddagger)$  and is the value that would be obtained if all the modes were active. However, if the temperature is not high enough to excite all the modes, the heat capacity will be less than the equipartition value. The heat capacity is a function of temperature and is not constant. The heat capacity is a function of temperature and is not constant. The heat capacity is a function of temperature and is not constant.

### Solutions to exercises

The heat capacity is given by  $C_{V,m} = \frac{1}{2}R(3 + \nu_R^\ddagger + \nu_V^\ddagger)$ . The equipartition value is  $\frac{1}{2}R(3 + \nu_R^\ddagger + \nu_V^\ddagger)$ .

$$C_{V,m} = \frac{1}{2}R(3 + 2 + 0) = \frac{5}{2}R$$

The heat capacity is given by  $C_{V,m} = \frac{1}{2}R(3 + \nu_R^\ddagger + \nu_V^\ddagger)$ .

$$C_{V,m} = \frac{1}{2}R(3 + 3 + 0) = \frac{6}{2}R = 3R$$

The heat capacity is given by  $C_{V,m} = \frac{1}{2}R(3 + \nu_R^\ddagger + \nu_V^\ddagger)$ .

$$C_{V,m} = \frac{1}{2}R(3 + 3 + 0) = \frac{6}{2}R = 3R$$

The heat capacity is given by  $C_{V,m} = \frac{1}{2}R(3 + \nu_R^\ddagger + \nu_V^\ddagger)$ .

The heat capacity is given by  $C_{V,m} = \frac{1}{2}R(3 + \nu_R^\ddagger + \nu_V^\ddagger)$ .

# Physical Chemistry Atkins 9th Solutions Manual

**Lei Shi**



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