

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 ν_V is the number of active vibrational modes. In the equipartition limit $\nu_V = 3N - \nu_R^\ddagger - 3$, so that the total heat capacity is

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

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 being shared with the rest of the system, and the equipartition limit is not valid. In this case, the heat capacity is lower than the equipartition value. The equipartition limit is only valid when the temperature is high compared to the characteristic temperatures of the modes. In the equipartition limit, the heat capacity is given by $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$, where $\nu_V = 3N - \nu_R^\ddagger - 3$. The equipartition limit is only valid when the temperature is high compared to the characteristic temperatures of the modes.

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 temperature is high compared to the characteristic temperature of the mode, the equipartition limit is valid.

$$\epsilon = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})$$

which is $\epsilon = 2.07 \times 10^{-21} \text{ J}$. The characteristic temperature of the mode is

$$\theta_M = \frac{h\nu}{k_B} = \frac{(6.626 \times 10^{-34} \text{ J s})(1.0 \times 10^{14} \text{ s}^{-1})}{1.38 \times 10^{-23} \text{ J K}^{-1}} = 4.8 \times 10^{-2} \text{ K}$$

which is $\theta_M = 0.048 \text{ K}$.

$$\epsilon = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K}) = 2.07 \times 10^{-21} \text{ J}$$

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

which is $C_{V,m} = 2.5R$.

Physical Chemistry 9th Ed Solution Manual

JR Anderson



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