

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 ν_R^\ddagger (so for most molecules at normal temperatures $\nu_R^\ddagger = 2$ for linear molecules, and 3 for non-linear molecules), then

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

The equipartition value of $C_{V,m}$ for a diatomic molecule is $\frac{7}{2}R$ (the number of degrees of freedom is 5) and for a triatomic molecule is $\frac{9}{2}R$ (the number of degrees of freedom is 6). The vibrational contribution to the heat capacity is $\frac{1}{2}R$ for each vibrational mode that is active. The vibrational temperature of a diatomic molecule is $\theta_{vib} = \frac{h\nu}{k}$ and for a triatomic molecule is $\theta_{vib} = \frac{h\nu}{k}$. The vibrational temperature of a diatomic molecule is $\theta_{vib} = \frac{h\nu}{k}$ and for a triatomic molecule is $\theta_{vib} = \frac{h\nu}{k}$.

Solutions to exercises

The vibrational temperature is given by $\theta_{vib} = \frac{h\nu}{k}$. The vibrational temperature of a diatomic molecule is $\theta_{vib} = \frac{h\nu}{k}$ and for a triatomic molecule is $\theta_{vib} = \frac{h\nu}{k}$.

$$\theta_{vib} = \frac{h\nu}{k} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3.0 \times 10^{14} \text{ s}^{-1}}{1.38 \times 10^{-23} \text{ J K}^{-1}} = 143.8 \text{ K}$$

At 298 K, $T < \theta_{vib}$, so the vibrational modes are not active.

$$C_{V,m} = \frac{3}{2}R + \nu_R^\ddagger R = \frac{3}{2}R + 2R = \frac{7}{2}R = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

At 1000 K, $T > \theta_{vib}$, so the vibrational modes are active.

$$C_{V,m} = \frac{3}{2}R + \nu_R^\ddagger R + \frac{1}{2}R = \frac{3}{2}R + 2R + \frac{1}{2}R = \frac{7}{2}R + \frac{1}{2}R = 30.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

At 2000 K, $T > \theta_{vib}$, so the vibrational modes are active.

$$C_{V,m} = \frac{3}{2}R + \nu_R^\ddagger R + R = \frac{3}{2}R + 2R + R = \frac{9}{2}R = 36.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

Physical Chemistry 9th Solution Manual

Katrin Zwirgmaier



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