

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

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

The equipartition value $C_{V,m} = 2.5R$ is reached when all the vibrational modes are active. At $T = 298 \text{ K}$, the vibrational temperature of the lowest energy vibrational mode is $\theta_{\text{vib}} = 2140 \text{ K}$ for CO_2 and $\theta_{\text{vib}} = 3370 \text{ K}$ for H_2O . At $T = 298 \text{ K}$, the vibrational modes are not active and the heat capacity is $C_{V,m} = 2.5R$. At $T = 1000 \text{ K}$, the vibrational modes are active and the heat capacity is $C_{V,m} = 2.5R + \frac{1}{2}R = 3R$. At $T = 2000 \text{ K}$, the vibrational modes are active and the heat capacity is $C_{V,m} = 2.5R + R = 3.5R$. At $T = 3000 \text{ K}$, the vibrational modes are active and the heat capacity is $C_{V,m} = 2.5R + 1.5R = 4R$. At $T = 4000 \text{ K}$, the vibrational modes are active and the heat capacity is $C_{V,m} = 2.5R + 2R = 4.5R$. At $T = 5000 \text{ K}$, the vibrational modes are active and the heat capacity is $C_{V,m} = 2.5R + 2.5R = 5R$.

Solutions to exercises

The vibrational energy is given by $\epsilon_{\text{vib}} = \frac{1}{2}h\nu_{\text{vib}}$ and the vibrational temperature is $\theta_{\text{vib}} = \frac{h\nu_{\text{vib}}}{k_B}$. The vibrational energy is $\epsilon_{\text{vib}} = \frac{1}{2}h\nu_{\text{vib}} = \frac{1}{2}k_B\theta_{\text{vib}}$.

$$\theta_{\text{vib}} = \frac{2\epsilon_{\text{vib}}}{k_B} = \frac{2 \times 0.025 \text{ eV}}{8.617 \times 10^{-5} \text{ eV K}^{-1}} = 580 \text{ K}$$

At $T = 298 \text{ K}$, the vibrational energy is $\epsilon_{\text{vib}} = \frac{1}{2}k_B\theta_{\text{vib}} = 0.025 \text{ eV}$.

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{1}{2}R = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = 2.5R = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

At $T = 1000 \text{ K}$,

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{1}{2}R = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = 2.5R = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

At $T = 2000 \text{ K}$,

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{1}{2}R = 3R = 24.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

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Scott C. Dulebohn



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 - The Rise of Digital Reading Physical Chemistry 9th Edition Instructors Solution Guide
 - Advantages of eBooks Over Traditional Books
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 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
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 - Features to Look for in an Physical Chemistry 9th Edition Instructors Solution Guide
 - User-Friendly Interface
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 - Participating in Virtual Book Clubs
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 - Benefits of a Digital Library
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 - Minimizing Distractions
 - Managing Screen Time
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 - Carving Out Dedicated Reading Time
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