

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 $\nu_V = 6$ for linear molecules and $\nu_V = 9$ for non-linear molecules. The total heat capacity is

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

The equipartition value of $C_{V,m}$ and of the heat capacity at constant pressure $C_{P,m}$ are applicable to $T \gg \theta_M$ for all $T \gg \theta_M$. However, if the temperature is just above θ_M , the equipartition value of $C_{V,m}$ and $C_{P,m}$ are not applicable. In this case, 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 ν_V is the number of active vibrational modes. In the equipartition limit $\nu_V = 6$ for linear molecules and $\nu_V = 9$ for non-linear molecules. The total heat capacity is $C_{V,m} = \left(\frac{3}{2} + \frac{\nu_R^\ddagger}{2} + 3\right)R$. The heat capacity at constant pressure is $C_{P,m} = C_{V,m} + R$. The total heat capacity is $C_{P,m} = \left(\frac{5}{2} + \frac{\nu_R^\ddagger}{2} + 3\right)R$.

Solutions to exercises

The thermal energy is given by $U = \frac{1}{2}k_B T$ per degree of freedom. When equipartition is valid, the total thermal energy is $U = \frac{1}{2}k_B T$ per degree of freedom.

$$U = \frac{1}{2}k_B T \left(\frac{3}{2} + \frac{\nu_R^\ddagger}{2} + 3 \right)$$

For a linear molecule, $\nu_R^\ddagger = 2$, and the total thermal energy is $U = \frac{1}{2}k_B T \left(\frac{3}{2} + \frac{2}{2} + 3 \right) = \frac{1}{2}k_B T \left(\frac{3}{2} + 1 + 3 \right) = \frac{1}{2}k_B T \left(\frac{7}{2} \right)$.

$$U = \frac{1}{2}k_B T \left(\frac{7}{2} \right) = \frac{7}{4}k_B T = \frac{7}{4} \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K} = 7.0 \times 10^{-21} \text{ J}$$

For a non-linear molecule,

$$U = \frac{1}{2}k_B T \left(\frac{3}{2} + \frac{3}{2} + 3 \right) = \frac{1}{2}k_B T \left(\frac{9}{2} \right) = \frac{9}{4}k_B T = \frac{9}{4} \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K} = 9.0 \times 10^{-21} \text{ J}$$

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

For a linear molecule, $\nu_R^\ddagger = 2$, and

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1. Understanding the eBook Physical Chemistry 9th Edition Solution Manual
 - The Rise of Digital Reading Physical Chemistry 9th Edition Solution Manual
 - Advantages of eBooks Over Traditional Books
2. Identifying Physical Chemistry 9th Edition Solution Manual
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Physical Chemistry 9th Edition Solution Manual
 - User-Friendly Interface
4. Exploring eBook Recommendations from Physical Chemistry 9th Edition Solution Manual
 - Personalized Recommendations
 - Physical Chemistry 9th Edition Solution Manual User Reviews and Ratings
 - Physical Chemistry 9th Edition Solution Manual and Bestseller Lists
5. Accessing Physical Chemistry 9th Edition Solution Manual Free and Paid eBooks
 - Physical Chemistry 9th Edition Solution Manual Public Domain eBooks
 - Physical Chemistry 9th Edition Solution Manual eBook Subscription Services
 - Physical Chemistry 9th Edition Solution Manual Budget-Friendly Options
6. Navigating Physical Chemistry 9th Edition Solution Manual eBook Formats

- ePub, PDF, MOBI, and More
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 - Physical Chemistry 9th Edition Solution Manual Enhanced eBook Features
7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Physical Chemistry 9th Edition Solution Manual
 - Highlighting and Note-Taking Physical Chemistry 9th Edition Solution Manual
 - Interactive Elements Physical Chemistry 9th Edition Solution Manual
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 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Physical Chemistry 9th Edition Solution Manual
 9. Balancing eBooks and Physical Books Physical Chemistry 9th Edition Solution Manual
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Physical Chemistry 9th Edition Solution Manual
 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
 11. Cultivating a Reading Routine Physical Chemistry 9th Edition Solution Manual
 - Setting Reading Goals Physical Chemistry 9th Edition Solution Manual
 - Carving Out Dedicated Reading Time
 12. Sourcing Reliable Information of Physical Chemistry 9th Edition Solution Manual
 - Fact-Checking eBook Content of Physical Chemistry 9th Edition Solution Manual
 - Distinguishing Credible Sources
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 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
 14. Embracing eBook Trends
 - Integration of Multimedia Elements
 - Interactive and Gamified eBooks

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