

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 $\theta_{\text{vib}} = 2140 \text{ K}$. The vibrational heat capacity is given by $C_{V,m} = \frac{1}{2}R \left(\frac{\theta_{\text{vib}}}{T} \right)^{-2} \left(1 - \frac{\theta_{\text{vib}}}{T} \right)^{-1}$. The vibrational heat capacity is $C_{V,m} = \frac{1}{2}R \left(\frac{2140}{298} \right)^{-2} \left(1 - \frac{2140}{298} \right)^{-1} = 0.0001 \text{ J K}^{-1} \text{ mol}^{-1}$. The vibrational heat capacity is $C_{V,m} = 0.0001 \text{ J K}^{-1} \text{ mol}^{-1}$.

Solutions to exercises

The vibrational heat capacity is given by $C_{V,m} = \frac{1}{2}R \left(\frac{\theta_{\text{vib}}}{T} \right)^{-2} \left(1 - \frac{\theta_{\text{vib}}}{T} \right)^{-1}$. The vibrational heat capacity is $C_{V,m} = \frac{1}{2}R \left(\frac{2140}{298} \right)^{-2} \left(1 - \frac{2140}{298} \right)^{-1} = 0.0001 \text{ J K}^{-1} \text{ mol}^{-1}$.

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The vibrational heat capacity is $C_{V,m} = 0.0001 \text{ J K}^{-1} \text{ mol}^{-1}$.

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Table of Contents Physical Chemistry Atkins 9th Edition Solutions Manual

1. Understanding the eBook Physical Chemistry Atkins 9th Edition Solutions Manual
 - The Rise of Digital Reading Physical Chemistry Atkins 9th Edition Solutions Manual
 - Advantages of eBooks Over Traditional Books
2. Identifying Physical Chemistry Atkins 9th Edition Solutions 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 Atkins 9th Edition Solutions Manual
 - User-Friendly Interface
4. Exploring eBook Recommendations from Physical Chemistry Atkins 9th Edition Solutions Manual
 - Personalized Recommendations
 - Physical Chemistry Atkins 9th Edition Solutions Manual User Reviews and Ratings
 - Physical Chemistry Atkins 9th Edition Solutions Manual and Bestseller Lists
5. Accessing Physical Chemistry Atkins 9th Edition Solutions Manual Free and Paid eBooks

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 - Physical Chemistry Atkins 9th Edition Solutions Manual Enhanced eBook Features
 7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Physical Chemistry Atkins 9th Edition Solutions Manual
 - Highlighting and Note-Taking Physical Chemistry Atkins 9th Edition Solutions Manual
 - Interactive Elements Physical Chemistry Atkins 9th Edition Solutions Manual
 8. Staying Engaged with Physical Chemistry Atkins 9th Edition Solutions Manual
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Physical Chemistry Atkins 9th Edition Solutions Manual
 9. Balancing eBooks and Physical Books Physical Chemistry Atkins 9th Edition Solutions Manual
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Physical Chemistry Atkins 9th Edition Solutions Manual
 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
 11. Cultivating a Reading Routine Physical Chemistry Atkins 9th Edition Solutions Manual
 - Setting Reading Goals Physical Chemistry Atkins 9th Edition Solutions Manual
 - Carving Out Dedicated Reading Time
 12. Sourcing Reliable Information of Physical Chemistry Atkins 9th Edition Solutions Manual
 - Fact-Checking eBook Content of Physical Chemistry Atkins 9th Edition Solutions Manual
 - Distinguishing Credible Sources
 13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development

- Exploring Educational eBooks

14. Embracing eBook Trends

- Integration of Multimedia Elements
- Interactive and Gamified eBooks

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