

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 $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R$ is reached when the temperature is high enough so that $T \gg \theta_M$ for all the modes. However, if the temperature is lower, some of the modes are not fully active and the heat capacity is lower than the equipartition value. 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.

Solutions to exercises

The vibrational heat capacity is given by $C_{V,m} = \frac{R}{\theta_M} \sum_{j=1}^{\infty} j e^{-j\theta_M/T}$. When $\theta_M \gg T$, the exponential term is small and the series can be approximated by $\sum_{j=1}^{\infty} j e^{-j\theta_M/T} \approx \sum_{j=1}^{\infty} j e^{-j\theta_M/T} \approx \frac{e^{-\theta_M/T}}{1 - e^{-\theta_M/T}}$.

$$C_{V,m} \approx \frac{R}{\theta_M} \frac{e^{-\theta_M/T}}{1 - e^{-\theta_M/T}}$$

When $\theta_M \ll T$, the exponential term is close to 1 and the series can be approximated by $\sum_{j=1}^{\infty} j e^{-j\theta_M/T} \approx \sum_{j=1}^{\infty} j = \frac{1}{2}$.

$$C_{V,m} \approx \frac{R}{\theta_M} \frac{1}{2} = \frac{R}{2\theta_M} = \frac{1}{2}R$$

Therefore, when $\theta_M \ll T$,

$$C_{V,m} \approx \frac{3}{2}R + \frac{1}{2}R = 2R$$

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

Therefore, when $\theta_M \ll T$,

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1. Understanding the eBook Physical Chemistry 9th Solution Manual
 - The Rise of Digital Reading Physical Chemistry 9th Solution Manual
 - Advantages of eBooks Over Traditional Books
2. Identifying Physical Chemistry 9th 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 Solution Manual
 - User-Friendly Interface
4. Exploring eBook Recommendations from Physical Chemistry 9th Solution Manual
 - Personalized Recommendations
 - Physical Chemistry 9th Solution Manual User Reviews and Ratings

- Physical Chemistry 9th Solution Manual and Bestseller Lists
- 5. Accessing Physical Chemistry 9th Solution Manual Free and Paid eBooks
 - Physical Chemistry 9th Solution Manual Public Domain eBooks
 - Physical Chemistry 9th Solution Manual eBook Subscription Services
 - Physical Chemistry 9th Solution Manual Budget-Friendly Options
- 6. Navigating Physical Chemistry 9th Solution Manual eBook Formats
 - ePub, PDF, MOBI, and More
 - Physical Chemistry 9th Solution Manual Compatibility with Devices
 - Physical Chemistry 9th Solution Manual Enhanced eBook Features
- 7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Physical Chemistry 9th Solution Manual
 - Highlighting and Note-Taking Physical Chemistry 9th Solution Manual
 - Interactive Elements Physical Chemistry 9th Solution Manual
- 8. Staying Engaged with Physical Chemistry 9th Solution Manual
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 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Physical Chemistry 9th Solution Manual
- 9. Balancing eBooks and Physical Books Physical Chemistry 9th Solution Manual
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Physical Chemistry 9th Solution Manual
- 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
- 11. Cultivating a Reading Routine Physical Chemistry 9th Solution Manual
 - Setting Reading Goals Physical Chemistry 9th Solution Manual
 - Carving Out Dedicated Reading Time
- 12. Sourcing Reliable Information of Physical Chemistry 9th Solution Manual
 - Fact-Checking eBook Content of Physical Chemistry 9th Solution 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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