

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

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

16.10 The equipartition theorem states that the average energy per degree of freedom is $\frac{1}{2}kT$. For a diatomic molecule, there are three translational degrees of freedom, two rotational degrees of freedom, and one vibrational degree of freedom. The vibrational energy is $\frac{1}{2}kT$ for the kinetic energy and $\frac{1}{2}kT$ for the potential energy, for a total of kT . The total energy is $\frac{3}{2}kT + 2 \times \frac{1}{2}kT + kT = 3kT$. The heat capacity is $C_V = \frac{dU}{dT} = 3k$.

Solutions to exercises

16.11 The vibrational energy is given by $\epsilon = \frac{1}{2}h\nu$. The vibrational energy is $\frac{1}{2}h\nu$ for the ground state and $\frac{3}{2}h\nu$ for the first excited state.

$$C_{V,m} = \frac{dU}{dT} = \frac{d}{dT} \left(\frac{1}{2}R\theta_V \frac{e^{-\theta_V/2T}}{1 + e^{-\theta_V/2T}} + R\theta_V \frac{e^{-\theta_V/2T}}{1 + e^{-\theta_V/2T}} \right)$$

$$= \frac{1}{2}R \frac{\theta_V^2}{4T^2} \frac{e^{-\theta_V/2T}}{1 + e^{-\theta_V/2T}} + R \frac{\theta_V^2}{2T^2} \frac{e^{-\theta_V/2T}}{1 + e^{-\theta_V/2T}}$$

16.12 The vibrational energy is

$$U = \frac{1}{2}R\theta_V \frac{e^{-\theta_V/2T}}{1 + e^{-\theta_V/2T}} + R\theta_V \frac{e^{-\theta_V/2T}}{1 + e^{-\theta_V/2T}}$$

16.13 $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V^\ddagger}{2}R$

For a diatomic molecule, $\nu_R^\ddagger = 2$ and $\nu_V^\ddagger = 1$.

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Judd E. Hollander



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1. Understanding the eBook Physical Chemistry 9th Edition Instructors Solution Guide
 - The Rise of Digital Reading Physical Chemistry 9th Edition Instructors Solution Guide
 - Advantages of eBooks Over Traditional Books
2. Identifying Physical Chemistry 9th Edition Instructors Solution Guide
 - 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 Instructors Solution Guide
 - User-Friendly Interface
4. Exploring eBook Recommendations from Physical Chemistry 9th Edition Instructors Solution Guide
 - Personalized Recommendations
 - Physical Chemistry 9th Edition Instructors Solution Guide User Reviews and Ratings
 - Physical Chemistry 9th Edition Instructors Solution Guide and Bestseller Lists
5. Accessing Physical Chemistry 9th Edition Instructors Solution Guide Free and Paid eBooks
 - Physical Chemistry 9th Edition Instructors Solution Guide Public Domain eBooks
 - Physical Chemistry 9th Edition Instructors Solution Guide eBook Subscription Services
 - Physical Chemistry 9th Edition Instructors Solution Guide Budget-Friendly Options
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 - Physical Chemistry 9th Edition Instructors Solution Guide Enhanced eBook Features
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 - Highlighting and Note-Taking Physical Chemistry 9th Edition Instructors Solution Guide
 - Interactive Elements Physical Chemistry 9th Edition Instructors Solution Guide
 8. Staying Engaged with Physical Chemistry 9th Edition Instructors Solution Guide
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Physical Chemistry 9th Edition Instructors Solution Guide
 9. Balancing eBooks and Physical Books Physical Chemistry 9th Edition Instructors Solution Guide
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Physical Chemistry 9th Edition Instructors Solution Guide
 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
 11. Cultivating a Reading Routine Physical Chemistry 9th Edition Instructors Solution Guide
 - Setting Reading Goals Physical Chemistry 9th Edition Instructors Solution Guide
 - Carving Out Dedicated Reading Time
 12. Sourcing Reliable Information of Physical Chemistry 9th Edition Instructors Solution Guide
 - Fact-Checking eBook Content of Physical Chemistry 9th Edition Instructors Solution Guide
 - Distinguishing Credible Sources
 13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
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 14. Embracing eBook Trends
 - Integration of Multimedia Elements
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