

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

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 then

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

The equipartition value of $C_{V,m}$ is 12.47 J K⁻¹ mol⁻¹ for linear molecules and 15.71 J K⁻¹ mol⁻¹ for non-linear molecules. If the temperature is only slightly above the vibrational temperature, the heat capacity is close to the equipartition value. If the temperature is only slightly below the vibrational temperature, the heat capacity is close to the equipartition value. If the temperature is only slightly above the vibrational temperature, the heat capacity is close to the equipartition value. If the temperature is only slightly below the vibrational temperature, the heat capacity is close to the equipartition value.

Solutions to exercises

The thermal energy is given by $U = \frac{1}{2} \sum_{i=1}^N \epsilon_i$, where ϵ_i is the energy of the i th molecule. When equipartition is valid, the thermal energy is given by $U = \frac{1}{2} N k_B T$.

$$U = \frac{1}{2} N k_B T = \frac{1}{2} (6.022 \times 10^{23}) (1.38 \times 10^{-23}) T$$

so that $U = 4.184 \times 10^4 T$ J, where T is in K. The thermal energy is then

$$U = \frac{1}{2} N k_B T = \frac{1}{2} (6.022 \times 10^{23}) (1.38 \times 10^{-23}) T = 4.184 \times 10^4 T \text{ J}$$

The thermal energy is then

$$U = \frac{1}{2} N k_B T = \frac{1}{2} (6.022 \times 10^{23}) (1.38 \times 10^{-23}) T = 4.184 \times 10^4 T \text{ J}$$

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

with $\nu_R^\ddagger = 2$ for linear molecules

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John R. Holum



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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
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
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 - 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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 - 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
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 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
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 - Carving Out Dedicated Reading Time
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 - 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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