

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, $\nu_V = 3N - \nu_R^\ddagger - 3$, where N is the number of atoms in the molecule. For example, for a diatomic molecule, $\nu_V = 3(2) - 2 - 3 = 1$, and the total heat capacity is $C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{7}{2}R$.

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

The equipartition value of $C_{V,m}$ for a diatomic molecule is $\frac{7}{2}R$. The equipartition value of $C_{V,m}$ for a triatomic molecule is $\frac{9}{2}R$. The equipartition value of $C_{V,m}$ for a non-linear molecule is $\frac{6}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$. The equipartition value of $C_{V,m}$ for a linear molecule is $\frac{5}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$. The equipartition value of $C_{V,m}$ for a non-linear molecule is $\frac{6}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$. The equipartition value of $C_{V,m}$ for a linear molecule is $\frac{5}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$. The equipartition value of $C_{V,m}$ for a non-linear molecule is $\frac{6}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$.

Solutions to exercises

The thermal energy is given by $\epsilon = \frac{1}{2}k_B T$. When $\epsilon \gg h\nu$, the thermal energy is much greater than the energy of the vibrational mode.

$$\epsilon = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K}) = 2.07 \times 10^{-21} \text{ J}$$

When $\epsilon \gg h\nu$, the thermal energy is much greater than the energy of the vibrational mode.

$$\epsilon = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K}) = 2.07 \times 10^{-21} \text{ J}$$

The thermal energy is given by

$$\epsilon = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K}) = 2.07 \times 10^{-21} \text{ J}$$

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

When $\epsilon \gg h\nu$, the thermal energy is much greater than the energy of the vibrational mode.

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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

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 - Highlighting and Note-Taking Physical Chemistry 9th Edition Instructors Solution Guide
 - Interactive Elements Physical Chemistry 9th Edition Instructors Solution Guide
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 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Physical Chemistry 9th Edition Instructors Solution Guide
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 - 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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 - Setting Reading Goals Physical Chemistry 9th Edition Instructors Solution Guide
 - Carving Out Dedicated Reading Time
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 - Fact-Checking eBook Content of Physical Chemistry 9th Edition Instructors Solution Guide
 - 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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