

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  $\nu_R^\ddagger$  (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 equipartition value is reached when the temperature is high enough so that  $T \gg \theta_M$  for all the modes. The equipartition value is reached when the temperature is high enough so that  $T \gg \theta_M$  for all the modes. The equipartition value is reached when the temperature is high enough so that  $T \gg \theta_M$  for all the modes.

### Solutions to exercises

The vibrational energy is given by  $\epsilon = \frac{1}{2}h\nu$  and the vibrational temperature is  $\theta_M = \frac{h\nu}{k_B}$ . The vibrational energy is  $\epsilon = \frac{1}{2}h\nu$  and the vibrational temperature is  $\theta_M = \frac{h\nu}{k_B}$ .

$$\theta_M = \frac{h\nu}{k_B} = \frac{6.626 \times 10^{-34} \text{ J s} \times 1.0 \times 10^{14} \text{ s}^{-1}}{1.38 \times 10^{-23} \text{ J K}^{-1}} = 4.8 \text{ K}$$

At 298 K,  $T \gg \theta_M$  and the vibrational energy is given by  $\epsilon = \frac{1}{2}h\nu$ .

$$\epsilon = \frac{1}{2}h\nu = \frac{1}{2} \times 6.626 \times 10^{-34} \text{ J s} \times 1.0 \times 10^{14} \text{ s}^{-1} = 3.3 \times 10^{-20} \text{ J}$$

The vibrational energy is  $\epsilon = \frac{1}{2}h\nu$ .

$$\epsilon = \frac{1}{2}h\nu = \frac{1}{2} \times 6.626 \times 10^{-34} \text{ J s} \times 1.0 \times 10^{14} \text{ s}^{-1} = 3.3 \times 10^{-20} \text{ J}$$

The vibrational energy is  $\epsilon = \frac{1}{2}h\nu$ .

The vibrational energy is  $\epsilon = \frac{1}{2}h\nu$ .

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**ML Morrison**



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## **Table of Contents Physical Chemistry 9th Edition Instructors Solution Guide**

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
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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

- Exploring Educational eBooks
14. Embracing eBook Trends
- Integration of Multimedia Elements
  - Interactive and Gamified eBooks

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