

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, then the modes with higher characteristic temperatures are not active, and the heat capacity is lower than the equipartition value. The number of active modes is  $\nu_R^\ddagger$  for all temperatures in the range  $\theta_M < T < \theta_{M+1}$ , where  $\theta_{M+1}$  is the next higher characteristic temperature. The number of active modes is  $\nu_R^\ddagger + 1$  for a range of temperatures above  $\theta_M$  and below  $\theta_{M+1}$ .

### Solutions to exercises

**16.1** The molar heat capacity is given by  $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \dots$ . The equipartition value is  $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R$ .

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

At 298 K, only the translational and rotational modes are active.

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R = \frac{5}{2}R = 20.79 \text{ J K}^{-1} \text{ mol}^{-1}$$

**16.2** At 298 K, only the translational and rotational modes are active.

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R = \frac{5}{2}R = 20.79 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

At 298 K, only the translational and rotational modes are active.

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**KJ Lindholm-Leary**



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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
- 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
- 6. Navigating Physical Chemistry 9th Edition Instructors Solution Guide eBook Formats
  - ePub, PDF, MOBI, and More
  - Physical Chemistry 9th Edition Instructors Solution Guide Compatibility with Devices
  - Physical Chemistry 9th Edition Instructors Solution Guide Enhanced eBook Features
- 7. Enhancing Your Reading Experience
  - Adjustable Fonts and Text Sizes of Physical Chemistry 9th Edition Instructors Solution Guide
  - 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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