

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 vibrational heat capacity is the sum of the contributions of the vibrational modes. The vibrational heat capacity is given by  $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \sum_{i=1}^{\nu_{\text{vib}}} \frac{R}{\theta_{v,i}} \left( \frac{T}{\theta_{v,i}} \right)^2 \frac{e^{-T/\theta_{v,i}}}{1 - e^{-T/\theta_{v,i}}} \left( 1 + \frac{T}{\theta_{v,i}} \right)$ . The vibrational heat capacity is the sum of the contributions of the vibrational modes.

### Solutions to exercises

**16.1** The vibrational heat capacity is given by  $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \sum_{i=1}^{\nu_{\text{vib}}} \frac{R}{\theta_{v,i}} \left( \frac{T}{\theta_{v,i}} \right)^2 \frac{e^{-T/\theta_{v,i}}}{1 - e^{-T/\theta_{v,i}}} \left( 1 + \frac{T}{\theta_{v,i}} \right)$ . The vibrational heat capacity is the sum of the contributions of the vibrational modes.

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \sum_{i=1}^{\nu_{\text{vib}}} \frac{R}{\theta_{v,i}} \left( \frac{T}{\theta_{v,i}} \right)^2 \frac{e^{-T/\theta_{v,i}}}{1 - e^{-T/\theta_{v,i}}} \left( 1 + \frac{T}{\theta_{v,i}} \right)$$

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

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

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

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

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

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

# Physical Chemistry Atkins 9th Edition Solutions Manual

**TD Snyder**



**Physical Chemistry Atkins 9th Edition Solutions Manual:**

## **Physical Chemistry Atkins 9th Edition Solutions Manual** Book Review: Unveiling the Magic of Language

In an electronic era where connections and knowledge reign supreme, the enchanting power of language has become much more apparent than ever. Its ability to stir emotions, provoke thought, and instigate transformation is really remarkable. This extraordinary book, aptly titled "**Physical Chemistry Atkins 9th Edition Solutions Manual**," written by a very acclaimed author, immerses readers in a captivating exploration of the significance of language and its profound effect on our existence. Throughout this critique, we shall delve into the book's central themes, evaluate its unique writing style, and assess its overall influence on its readership.

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### **Table of Contents Physical Chemistry Atkins 9th Edition Solutions Manual**

1. Understanding the eBook Physical Chemistry Atkins 9th Edition Solutions Manual
  - The Rise of Digital Reading Physical Chemistry Atkins 9th Edition Solutions Manual
  - Advantages of eBooks Over Traditional Books
2. Identifying Physical Chemistry Atkins 9th Edition Solutions Manual
  - 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 a Physical Chemistry Atkins 9th Edition Solutions Manual
  - User-Friendly Interface
4. Exploring eBook Recommendations from Physical Chemistry Atkins 9th Edition Solutions Manual
  - Personalized Recommendations
  - Physical Chemistry Atkins 9th Edition Solutions Manual User Reviews and Ratings
  - Physical Chemistry Atkins 9th Edition Solutions Manual and Bestseller Lists

5. Accessing Physical Chemistry Atkins 9th Edition Solutions Manual Free and Paid eBooks
  - Physical Chemistry Atkins 9th Edition Solutions Manual Public Domain eBooks
  - Physical Chemistry Atkins 9th Edition Solutions Manual eBook Subscription Services
  - Physical Chemistry Atkins 9th Edition Solutions Manual Budget-Friendly Options
6. Navigating Physical Chemistry Atkins 9th Edition Solutions Manual eBook Formats
  - ePub, PDF, MOBI, and More
  - Physical Chemistry Atkins 9th Edition Solutions Manual Compatibility with Devices
  - Physical Chemistry Atkins 9th Edition Solutions Manual Enhanced eBook Features
7. Enhancing Your Reading Experience
  - Adjustable Fonts and Text Sizes of Physical Chemistry Atkins 9th Edition Solutions Manual
  - Highlighting and Note-Taking Physical Chemistry Atkins 9th Edition Solutions Manual
  - Interactive Elements Physical Chemistry Atkins 9th Edition Solutions Manual
8. Staying Engaged with Physical Chemistry Atkins 9th Edition Solutions Manual
  - Joining Online Reading Communities
  - Participating in Virtual Book Clubs
  - Following Authors and Publishers Physical Chemistry Atkins 9th Edition Solutions Manual
9. Balancing eBooks and Physical Books Physical Chemistry Atkins 9th Edition Solutions Manual
  - Benefits of a Digital Library
  - Creating a Diverse Reading Collection Physical Chemistry Atkins 9th Edition Solutions Manual
10. Overcoming Reading Challenges
  - Dealing with Digital Eye Strain
  - Minimizing Distractions
  - Managing Screen Time
11. Cultivating a Reading Routine Physical Chemistry Atkins 9th Edition Solutions Manual
  - Setting Reading Goals Physical Chemistry Atkins 9th Edition Solutions Manual
  - Carving Out Dedicated Reading Time
12. Sourcing Reliable Information of Physical Chemistry Atkins 9th Edition Solutions Manual
  - Fact-Checking eBook Content of Physical Chemistry Atkins 9th Edition Solutions Manual
  - 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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