

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

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 $\nu_V = 3N - 5$ for linear molecules and $\nu_V = 3N - 6$ for non-linear molecules, where N is the number of atoms in the molecule.

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

The equipartition value of $C_{V,m}$ is the value that would be obtained if all degrees of freedom were active. For a linear molecule, $C_{V,m}^{\text{eq}} = \frac{3}{2}R + \frac{2}{2}R + \frac{3N-5}{2}R = \frac{3N+1}{2}R$. For a non-linear molecule, $C_{V,m}^{\text{eq}} = \frac{3}{2}R + \frac{3}{2}R + \frac{3N-6}{2}R = \frac{3N+3}{2}R$. The difference between the actual heat capacity and the equipartition value is the difference between the actual number of active degrees of freedom and the equipartition value. For a linear molecule, $C_{V,m} - C_{V,m}^{\text{eq}} = \frac{\nu_V - (3N-5)}{2}R$. For a non-linear molecule, $C_{V,m} - C_{V,m}^{\text{eq}} = \frac{\nu_V - (3N-6)}{2}R$.

Solutions to exercises

The thermal energy is given by $U = \frac{1}{2}k_B T$ per degree of freedom. When equipartition is valid, the thermal energy is given by $U = \frac{1}{2}k_B T$ per degree of freedom.

$$U = \frac{1}{2}k_B T \times \frac{3N+1}{2} = \frac{3N+1}{4}k_B T$$

For a non-linear molecule, $U = \frac{1}{2}k_B T \times \frac{3N+3}{2} = \frac{3N+3}{4}k_B T$.

$$U = \frac{1}{2}k_B T \times \frac{3N+1}{2} = \frac{3N+1}{4}k_B T$$

For a linear molecule,

$$U = \frac{1}{2}k_B T \times \frac{3N+1}{2} = \frac{3N+1}{4}k_B T$$

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

where $\nu_V = 3N - 5$ for linear molecules.

Physical Chemistry 9th Solution Manual

**Hans Kuhn, David H. Waldeck, Horst-
Dieter Försterling**



Physical Chemistry 9th Solution Manual:

Instructor's Solutions Manual to Accompany Atkins' Physical Chemistry, Ninth Edition C. A. Trapp, M. P. Cady, Carmen Giunta, 2010 The Instructor's solutions manual to accompany Atkins Physical Chemistry provides detailed solutions to the exercises and the even numbered discussion questions and problems that feature in the ninth edition of Atkins Physical Chemistry The manual is intended for instructors and consists of material that is not available to undergraduates The manual is free to all adopters of the main text Solutions Manual to Accompany Elements of Physical Chemistry David Smith, 2013-05-30 The Solutions Manual to accompany Elements of Physical Chemistry 6th edition contains full worked solutions to all end of chapter discussion questions and exercises featured in the book The manual provides helpful comments and friendly advice to aid understanding It is also a valuable resource for any lecturer who wishes to use the extensive selection of exercises featured in the text to support either formative or summative assessment and wants labour saving ready access to the full solutions to these questions *Solutions Manual for Principles of Physical Chemistry, 3rd Edition, Solutions Manual* Hans Kuhn, David H. Waldeck, Horst-Dieter Försterling, 2024-10-25 This is a Solutions Manual to Accompany with solutions to the exercises in the main volume of Principles of Physical Chemistry Third Edition This book provides a unique approach to introduce undergraduate students to the concepts and methods of physical chemistry which are the foundational principles of Chemistry The book introduces the student to the principles underlying the essential sub fields of quantum mechanics atomic and molecular structure atomic and molecular spectroscopy statistical thermodynamics classical thermodynamics solutions and equilibria electrochemistry kinetics and reaction dynamics macromolecules and organized molecular assemblies Importantly the book develops and applies these principles to supramolecular assemblies and supramolecular machines with many examples from biology and nanoscience In this way the book helps the student to see the frontier of modern physical chemistry developments The book begins with a discussion of wave particle duality and proceeds systematically to more complex chemical systems in order to relate the story of physical chemistry in an intellectually coherent manner The topics are organized to correspond with those typically given in each of a two course semester sequence The first 13 chapters present quantum mechanics and spectroscopy to describe and predict the structure of matter atoms molecules and solids Chapters 14 to 29 present statistical thermodynamics and kinetics and applies their principles to understanding equilibria chemical transformations macromolecular properties and supramolecular machines Each chapter of the book begins with a simplified view of a topic and evolves to more rigorous description in order to provide the student and instructor flexibility to choose the level of rigor and detail that suits them best The textbook treats important new directions in physical chemistry research including chapters on macromolecules principles of interfaces and films for organizing matter and supramolecular machines as well as including discussions of modern nanoscience spectroscopy and reaction dynamics throughout the text *Solutions Manual for Principles of Physical Chemistry, 3rd Edition* Hans

Kuhn, David H. Waldeck, Horst-Dieter Försterling, 2024-10-29 This is a Solutions Manual to Accompany with solutions to the exercises in the main volume of Principles of Physical Chemistry Third Edition This book provides a unique approach to introduce undergraduate students to the concepts and methods of physical chemistry which are the foundational principles of Chemistry The book introduces the student to the principles underlying the essential sub fields of quantum mechanics atomic and molecular structure atomic and molecular spectroscopy statistical thermodynamics classical thermodynamics solutions and equilibria electrochemistry kinetics and reaction dynamics macromolecules and organized molecular assemblies Importantly the book develops and applies these principles to supramolecular assemblies and supramolecular machines with many examples from biology and nanoscience In this way the book helps the student to see the frontier of modern physical chemistry developments The book begins with a discussion of wave particle duality and proceeds systematically to more complex chemical systems in order to relate the story of physical chemistry in an intellectually coherent manner The topics are organized to correspond with those typically given in each of a two course semester sequence The first 13 chapters present quantum mechanics and spectroscopy to describe and predict the structure of matter atoms molecules and solids Chapters 14 to 29 present statistical thermodynamics and kinetics and applies their principles to understanding equilibria chemical transformations macromolecular properties and supramolecular machines Each chapter of the book begins with a simplified view of a topic and evolves to more rigorous description in order to provide the student and instructor flexibility to choose the level of rigor and detail that suits them best The textbook treats important new directions in physical chemistry research including chapters on macromolecules principles of interfaces and films for organizing matter and supramolecular machines as well as including discussions of modern nanoscience spectroscopy and reaction dynamics throughout the text

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

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