

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  $\nu_V$  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 a diatomic molecule,  $\nu_V = 3(2) - 2 - 3 = 1$ , so  $C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{7}{2}R$ .

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

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 polyatomic molecule is  $\frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$ . 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 polyatomic molecule is  $\frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$ . 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 polyatomic molecule is  $\frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$ .

### Solutions to exercises

The thermal energy is given by  $U = \frac{1}{2}k_B T$ . When a molecule is in a state of thermal equilibrium with a reservoir at temperature  $T$ , the probability of finding it in a state of energy  $\epsilon$  is given by  $P(\epsilon) = \frac{e^{-\epsilon/k_B T}}{Z}$ , where  $Z$  is the partition function.

$$P(\epsilon) = \frac{e^{-\epsilon/k_B T}}{Z}$$

For a diatomic molecule, the energy levels are given by  $\epsilon = \frac{1}{2}k_B T$ .

$$P(\epsilon) = \frac{e^{-\epsilon/k_B T}}{Z} = \frac{e^{-\frac{1}{2}k_B T/k_B T}}{Z} = \frac{e^{-1/2}}{Z}$$

For a diatomic molecule,

$$P(\epsilon) = \frac{e^{-\epsilon/k_B T}}{Z} = \frac{e^{-\frac{1}{2}k_B T/k_B T}}{Z} = \frac{e^{-1/2}}{Z}$$

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

For a diatomic molecule,  $\nu_V = 1$ .

# Physical Chemistry 9th Ed Solution Manual

**C. A. Trapp, M. P. Cady, Carmen Giunta**



## **Physical Chemistry 9th Ed 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 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 **Student Solutions Manual to Accompany Atkins' Physical Chemistry 11th Edition** Peter Bolgar, Vladimiras Oleinikovas, Aimee North, Haydn Lloyd, James Keeler, Stephanie Smith, 2018 The Student Solutions Manual to accompany Atkins Physical Chemistry 11th Edition provides full worked solutions to the exercises and the odd numbered discussion questions and problems presented in the parent book The manual is intended for students and provides helpful comments and friendly advice to aid understanding [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

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