

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 $\nu_V = 3N - \nu_R^\ddagger - 3$, so that the total heat capacity is

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

The equipartition limit is only valid when the temperature is high compared to the characteristic temperatures of the modes. If the temperature is lower than the characteristic temperature of a mode, then the energy of the mode is not enough to excite it, and $\nu_V = 0$ corresponding to all degrees of freedom in the mode being inactive. When $T < \theta_V$, the total heat capacity is in the equipartition limit. The average temperature is $T = 298$ K, and all three translational degrees of freedom are active in the equipartition limit. The average temperature is $T = 298$ K, and all three translational degrees of freedom are active in the equipartition limit. The average temperature is $T = 298$ K, and all three translational degrees of freedom are active in the equipartition limit.

Solutions to exercises

The thermal energy is given by $\epsilon = \frac{1}{2}k_B T$, where k_B is the Boltzmann constant. When the temperature is high, the thermal energy is much greater than the spacing of the levels.

$$\epsilon = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})$$

which is much greater than the spacing of the levels, so that

$$\epsilon \gg \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K}) = 2.07 \times 10^{-21} \text{ J}$$

which is much greater than

$$\epsilon = \frac{1}{2}k_B T = \frac{1}{2}(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K}) = 2.07 \times 10^{-21} \text{ J}$$

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

with $\nu_V = 3N - \nu_R^\ddagger - 3$

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**Thirumalaisamy P.
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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 a 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
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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
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 - Integration of Multimedia Elements
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