

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 ν_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 $C_{V,m} = 2.5R$ is reached when all the vibrational modes are active. At $T = 298 \text{ K}$, the vibrational temperatures of the modes of CO_2 are 3300 K , 2200 K , 1330 K , 690 K , 470 K , and 430 K . The vibrational temperatures of the modes of H_2O are 5400 K , 3650 K , 2280 K , 1590 K , 940 K , and 870 K . The vibrational temperatures of the modes of CH_4 are 4300 K , 2900 K , 1900 K , 1300 K , 960 K , and 850 K . The vibrational temperatures of the modes of NH_3 are 4700 K , 3100 K , 2000 K , 1400 K , 980 K , and 890 K .

Solutions to exercises

The vibrational energy is given by $\epsilon = \frac{h\nu}{2} + \frac{h\nu}{2} + \dots$. The vibrational energy is $\epsilon = \frac{h\nu}{2} + \frac{h\nu}{2} + \dots$.

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Peter William Atkins



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 - 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 an 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

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 - Highlighting and Note-Taking Physical Chemistry 9th Solution Manual
 - Interactive Elements Physical Chemistry 9th Solution Manual
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 - 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
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- Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
14. Embracing eBook Trends
- Integration of Multimedia Elements
 - Interactive and Gamified eBooks

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