

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

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

16B.1 The equipartition theorem states that the average energy of a degree of freedom is $\frac{1}{2}kT$. The molar heat capacity is the derivative of the internal energy with respect to temperature. If the temperature is well above the characteristic temperature of the mode, then the energy of the mode is $\frac{1}{2}kT$ and the contribution to the heat capacity is $\frac{1}{2}R$. The average energy of a mode is $\frac{1}{2}kT$ and the contribution to the heat capacity is $\frac{1}{2}R$. The average energy of a mode is $\frac{1}{2}kT$ and the contribution to the heat capacity is $\frac{1}{2}R$.

Solutions to exercises

16B.2 The internal energy of a gas is $U = \frac{3}{2}nRT + \frac{\nu_R^\ddagger}{2}nRT + \frac{\nu_V^\ddagger}{2}nRT$. The molar heat capacity is $C_{V,m} = \frac{1}{n} \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V^\ddagger}{2}R$.

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

For a diatomic gas, $\nu_R^\ddagger = 2$ and $\nu_V^\ddagger = 5$. The molar heat capacity is $C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{5}{2}R = \frac{10}{2}R = 5R$.

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{5}{2}R = \frac{10}{2}R = 5R$$

16B.3 For a diatomic gas, $\nu_R^\ddagger = 2$ and $\nu_V^\ddagger = 5$.

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{5}{2}R = \frac{10}{2}R = 5R$$

16B.4 $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V^\ddagger}{2}R$

For a diatomic gas, $\nu_R^\ddagger = 2$ and $\nu_V^\ddagger = 5$.

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The Lancet, 1927 The Chemical News : and Journal of Physical Science, 1908

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 - The Rise of Digital Reading Physical Chemistry 9th Edition Solutions
 - Advantages of eBooks Over Traditional Books
2. Identifying Physical Chemistry 9th Edition Solutions
 - 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 Edition Solutions
 - User-Friendly Interface
4. Exploring eBook Recommendations from Physical Chemistry 9th Edition Solutions
 - Personalized Recommendations
 - Physical Chemistry 9th Edition Solutions User Reviews and Ratings
 - Physical Chemistry 9th Edition Solutions and Bestseller Lists
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 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Physical Chemistry 9th Edition Solutions
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 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Physical Chemistry 9th Edition Solutions
10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
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 - Setting Reading Goals Physical Chemistry 9th Edition Solutions
 - Carving Out Dedicated Reading Time
12. Sourcing Reliable Information of Physical Chemistry 9th Edition Solutions
 - Fact-Checking eBook Content of Physical Chemistry 9th Edition Solutions
 - 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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