

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

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 $\nu_V = 6$ for linear molecules and $\nu_V = 9$ for non-linear molecules. The total heat capacity is then

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

The equipartition value of $C_{V,m}$ is the value of the heat capacity when all degrees of freedom are active. For a linear molecule $\nu_R^\ddagger = 2$ and $\nu_V = 6$, so the equipartition value of $C_{V,m}$ is $\frac{3}{2}R + \frac{2}{2}R + \frac{6}{2}R = \frac{11}{2}R$. For a non-linear molecule $\nu_R^\ddagger = 3$ and $\nu_V = 9$, so the equipartition value of $C_{V,m}$ is $\frac{3}{2}R + \frac{3}{2}R + \frac{9}{2}R = \frac{15}{2}R$. The total heat capacity of a molecule is the sum of the equipartition value and the difference between the actual value and the equipartition value. The difference between the actual value and the equipartition value is the difference between the actual value and the equipartition value.

Solutions to exercises

The total heat capacity is given by $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$. When equipartition is valid, $\nu_R^\ddagger = 2$ for linear molecules and $\nu_R^\ddagger = 3$ for non-linear molecules. The total heat capacity is then

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

For a linear molecule $\nu_R^\ddagger = 2$ and $\nu_V = 6$, so the equipartition value of $C_{V,m}$ is $\frac{11}{2}R$.

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{6}{2}R = \frac{11}{2}R = 45.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

For a non-linear molecule $\nu_R^\ddagger = 3$ and $\nu_V = 9$, so the equipartition value of $C_{V,m}$ is $\frac{15}{2}R$.

$$C_{V,m} = \frac{3}{2}R + \frac{3}{2}R + \frac{9}{2}R = \frac{15}{2}R = 60.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

The total heat capacity is given by $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$.

For a linear molecule $\nu_R^\ddagger = 2$ and $\nu_V = 6$, so the equipartition value of $C_{V,m}$ is $\frac{11}{2}R$.

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 - The Rise of Digital Reading Physical Chemistry 9th Edition Instructors Solution Guide
 - Advantages of eBooks Over Traditional Books
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 - 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 Instructors Solution Guide
 - User-Friendly Interface
4. Exploring eBook Recommendations from Physical Chemistry 9th Edition Instructors Solution Guide
 - Personalized Recommendations
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 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
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 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Physical Chemistry 9th Edition Instructors Solution Guide
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 - Minimizing Distractions
 - Managing Screen Time
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 - Carving Out Dedicated Reading Time
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 - Fact-Checking eBook Content of Physical Chemistry 9th Edition Instructors Solution Guide
 - 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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