

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 $\nu_V = 3N - \nu_R^\ddagger - 3$, 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 enough for all the degrees of freedom to be active. If the temperature is not high enough, then the heat capacity will be less than the equipartition value. For example, for a diatomic molecule, if the temperature is not high enough for the vibrational modes to be active, then the heat capacity will be less than the equipartition value. For a polyatomic molecule, if the temperature is not high enough for all the vibrational modes to be active, then the heat capacity will be less than the equipartition value. The equipartition limit is only valid when the temperature is high enough for all the degrees of freedom to be active.

Solutions to exercises

The thermal energy is given by $U = \frac{1}{2}k_B T$ per degree of freedom. When equipartition is valid, the total thermal energy is

$$U = \frac{1}{2}k_B T \left(\frac{3}{2} + \frac{\nu_R^\ddagger}{2} + \frac{\nu_V}{2} \right)$$

and the heat capacity is the derivative of U with respect to T , so that

$$C_{V,m} = \frac{1}{2}k_B \left(\frac{3}{2} + \frac{\nu_R^\ddagger}{2} + \frac{\nu_V}{2} \right) = \frac{1}{2}k_B \left(\frac{3}{2} + \frac{\nu_R^\ddagger}{2} + \frac{3N - \nu_R^\ddagger - 3}{2} \right) = \frac{3}{2}k_B N$$

For a diatomic molecule,

$$C_{V,m} = \frac{1}{2}k_B \left(\frac{3}{2} + \frac{2}{2} + \frac{3N - 2 - 3}{2} \right) = \frac{1}{2}k_B \left(\frac{3}{2} + 1 + \frac{3N - 5}{2} \right) = \frac{1}{2}k_B \left(\frac{3}{2} + 1 + \frac{3N - 5}{2} \right)$$

For a polyatomic molecule,

$$C_{V,m} = \frac{1}{2}k_B \left(\frac{3}{2} + \frac{\nu_R^\ddagger}{2} + \frac{3N - \nu_R^\ddagger - 3}{2} \right)$$

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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
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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
 - Physical Chemistry 9th Edition Instructors Solution Guide User Reviews and Ratings
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 - 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
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 - Utilizing eBooks for Skill Development
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14. Embracing eBook Trends
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