

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

For a diatomic molecule, $\nu_R^\ddagger = 2$ and $\nu_V = 1$, so that

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{5}{2}R$$

The equipartition value of $C_{V,m}$ for a diatomic molecule is $\frac{5}{2}R$. The equipartition value of $C_{V,m}$ for a monatomic gas is $\frac{3}{2}R$. The equipartition value of $C_{V,m}$ for a polyatomic gas is $\frac{3N}{2}R$, where N is the number of atoms in the molecule. For a diatomic molecule, $N = 2$, so that $C_{V,m} = \frac{3 \times 2}{2}R = 3R$. The equipartition value of $C_{V,m}$ for a diatomic molecule is $\frac{5}{2}R$, which is less than the equipartition value of $C_{V,m}$ for a polyatomic gas. The equipartition value of $C_{V,m}$ for a diatomic molecule is $\frac{5}{2}R$, which is less than the equipartition value of $C_{V,m}$ for a polyatomic gas. The equipartition value of $C_{V,m}$ for a diatomic molecule is $\frac{5}{2}R$, which is less than the equipartition value of $C_{V,m}$ for a polyatomic gas.

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 thermal energy is $U = \frac{1}{2}k_B T$ per degree of freedom. The thermal energy is $U = \frac{1}{2}k_B T$ per degree of freedom.

$$U = \frac{1}{2}k_B T = \frac{1}{2} \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K} = 2.05 \times 10^{-21} \text{ J}$$

For a diatomic molecule, $\nu_R^\ddagger = 2$ and $\nu_V = 1$, so that

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{5}{2}R = 2.5 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

For a diatomic molecule,

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{5}{2}R = 2.5 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{5}{2}R$$

For a diatomic molecule, $\nu_R^\ddagger = 2$ and $\nu_V = 1$, so that

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RJ Shavelson



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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
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 - Personalized Recommendations
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 - Physical Chemistry 9th Edition Instructors Solution Guide and Bestseller Lists

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 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Physical Chemistry 9th Edition Instructors Solution Guide
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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
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
- Exploring Educational eBooks

14. Embracing eBook Trends

- Integration of Multimedia Elements
- Interactive and Gamified eBooks

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