

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 $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R$ is reached when the temperature is high enough so that $T \gg \theta_M$ for all the modes. However, if the temperature is lower, then the modes with higher characteristic temperatures are not active, and the heat capacity is lower than the equipartition value. The number of active modes is ν_R^\ddagger for all temperatures in the range $\theta_1 < T < \theta_2$, and all temperatures in the range $\theta_2 < T < \theta_3$, and so on. The average heat capacity is $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R$ for all temperatures in the range $\theta_1 < T < \theta_2$, and so on. The number of active modes is ν_R^\ddagger for all temperatures in the range $\theta_1 < T < \theta_2$, and so on.

Solutions to exercises

The number of vibrational modes is given by $\nu_{\text{vib}} = \frac{3N - 5}{2}$ for linear molecules and $\nu_{\text{vib}} = \frac{3N - 6}{2}$ for non-linear molecules. For a diatomic molecule, $\nu_{\text{vib}} = 1$.

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

At 298 K, $\theta_{\text{vib}} = 3000$ K, so $\nu_{\text{vib}} = 0$.

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{0}{2}R = \frac{5}{2}R = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

At 1000 K, $\theta_{\text{vib}} = 3000$ K, so $\nu_{\text{vib}} = 0$.

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{0}{2}R = \frac{5}{2}R = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

At 3000 K, $\theta_{\text{vib}} = 3000$ K, so $\nu_{\text{vib}} = 1$.

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{6}{2}R = 25.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

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Wilder Dwight Bancroft



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The production of textile materials comprises a very large and complex global industry that utilises a diverse range of fibre types and creates a variety of textile products As the great majority of such products are coloured predominantly using aqueous dyeing processes the coloration of textiles is a large scale global business in which complex procedures are used to apply different types of dye to the various types of textile material The development of such dyeing processes is the result of substantial research activity undertaken over many decades into the physico chemical aspects of dye adsorption and the establishment of dyeing theory which seeks to describe the mechanism by which dyes interact with textile fibres Physico Chemical Aspects of Textile Coloration provides a comprehensive treatment of the physical chemistry involved in the dyeing of the major types of natural man made and synthetic fibres with the principal types of dye The book covers fundamental aspects of the physical and chemical structure of both fibres and dyes together with the structure and properties of water in relation to dyeing dyeing as an area of study as well as the terminology employed in dyeing technology and science

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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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 - Creating a Diverse Reading Collection Physical Chemistry 9th Edition Solutions
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 - 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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