

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 CO_2 , $\nu_R^\ddagger = 2$ and $\nu_V = 4$, so that

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{4}{2}R = 3R$$

The equipartition value of $C_{V,m}$ for CO_2 is $3R$. The experimental value is $2.5R$ at 298 K . The difference of $0.5R$ is due to the fact that not all vibrational modes are active at 298 K . The vibrational temperatures of CO_2 are 3300 K , 2200 K , and 1300 K . The vibrational modes with the highest frequencies are the most difficult to excite, and the vibrational modes with the lowest frequencies are the easiest to excite. The vibrational modes with the lowest frequencies are the most difficult to excite, and the vibrational modes with the highest frequencies are the easiest to excite. The vibrational modes with the lowest frequencies are the most difficult to excite, and the vibrational modes with the highest frequencies are the easiest to excite.

Solutions to exercises

The thermal energy is given by $U = \frac{1}{2} \sum_{i=1}^N \hbar \omega_i$. When equipartition is valid, the thermal energy is given by $U = \frac{1}{2} N k_B T$.

$$U = \frac{1}{2} N k_B T = \frac{1}{2} (1.00 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K})$$

so that $U = 1.23 \text{ kJ}$ at 298 K . The experimental value is 1.23 kJ .

$$U = \frac{1}{2} N k_B T = \frac{1}{2} (1.00 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K}) = 1.23 \text{ kJ}$$

For CO_2 , $\nu_R^\ddagger = 2$ and $\nu_V = 4$, so that

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{4}{2}R = 3R$$

$$C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{4}{2}R = 3R$$

so that $C_{V,m} = 3R$ at 298 K .

Physical Chemistry 9th Solution Manual

Harry Linn Fisher



Physical Chemistry 9th Solution Manual:

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Cady, Carmen Giunta, 2010 The Instructor's solutions manual to accompany Atkins Physical Chemistry provides detailed solutions to the odd exercises and the even numbered discussion questions and problems that feature in the ninth edition of Atkins Physical Chemistry. The manual is intended for instructors and consists of material that is not available to undergraduates. The manual is free to all adopters of the main text. [Solutions Manual to Accompany Elements of Physical Chemistry](#) David Smith, 2013-05-30 The Solutions Manual to accompany Elements of Physical Chemistry 6th edition contains full worked solutions to all end of chapter discussion questions and exercises featured in the book. The manual provides helpful comments and friendly advice to aid understanding. It is also a valuable resource for any lecturer who wishes to use the extensive selection of exercises featured in the text to support either formative or summative assessment and wants labour saving ready access to the full solutions to these questions. **Solutions Manual for Principles of Physical**

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series and then drag the fill handle across or down the cells next analyze data

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