

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, $\nu_V = 3N - \nu_R^\ddagger - 3$, where N is the number of atoms in the molecule. For a diatomic molecule, $\nu_V = 3(2) - 2 - 3 = 1$, so $C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{1}{2}R = \frac{7}{2}R$.

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

The equipartition value of $C_{V,m}$ for a diatomic molecule is $\frac{7}{2}R$. The equipartition value of $C_{V,m}$ for a triatomic molecule is $\frac{9}{2}R$. The equipartition value of $C_{V,m}$ for a polyatomic molecule is $\frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$. The equipartition value of $C_{V,m}$ for a diatomic molecule is $\frac{7}{2}R$. The equipartition value of $C_{V,m}$ for a triatomic molecule is $\frac{9}{2}R$. The equipartition value of $C_{V,m}$ for a polyatomic molecule is $\frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$.

Solutions to exercises

The thermal energy is given by $U = \frac{1}{2}k_B T$. When a molecule is in a state of thermal equilibrium with a reservoir at temperature T , the probability of finding it in a state of energy ϵ is given by $P(\epsilon) = \frac{e^{-\epsilon/k_B T}}{Z}$, where Z is the partition function.

$$P(\epsilon) = \frac{e^{-\epsilon/k_B T}}{Z}$$

For a diatomic molecule, the energy levels are given by $\epsilon_{v,J} = \frac{1}{2}h\nu + \frac{1}{2}h^2 B J(J+1)$, where ν is the vibrational frequency and B is the rotational constant.

$$Z = \sum_{v,J} e^{-\epsilon_{v,J}/k_B T} = \sum_{v,J} e^{-\frac{1}{2}h\nu/k_B T} e^{-\frac{1}{2}h^2 B J(J+1)/k_B T}$$

For a diatomic molecule, the energy levels are given by $\epsilon_{v,J} = \frac{1}{2}h\nu + \frac{1}{2}h^2 B J(J+1)$, where ν is the vibrational frequency and B is the rotational constant.

$$Z = \sum_{v,J} e^{-\epsilon_{v,J}/k_B T} = \sum_{v,J} e^{-\frac{1}{2}h\nu/k_B T} e^{-\frac{1}{2}h^2 B J(J+1)/k_B T}$$

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

For a diatomic molecule, $\nu_V = 1$.

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