

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 $\nu_V = 6$ for linear molecules and $\nu_V = 9$ for non-linear molecules. The total heat capacity is then

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

The equipartition limit is only valid when the temperature is well above the characteristic temperature of the mode. In the case of the vibrational modes, the characteristic temperature is often very high, and the vibrational modes are not active at room temperature. In this case, the vibrational modes contribute very little to the total heat capacity. The total heat capacity is then given by $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R$. In the case of the rotational modes, the characteristic temperature is often very low, and the rotational modes are active at room temperature. In this case, the rotational modes contribute significantly to the total heat capacity. The total heat capacity is then given by $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$.

Solutions to exercises

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

$$U = \frac{1}{2}k_B T \nu$$

For a diatomic molecule, the number of degrees of freedom is $\nu = 5$.

$$U = \frac{1}{2}k_B T \nu = \frac{1}{2}k_B T \times 5 = \frac{5}{2}k_B T$$

For a monatomic gas, the number of degrees of freedom is $\nu = 3$.

$$U = \frac{1}{2}k_B T \nu = \frac{1}{2}k_B T \times 3 = \frac{3}{2}k_B T$$

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

For a diatomic molecule, $\nu_R^\ddagger = 2$ and $\nu_V = 6$.

Physical Chemistry 9th Solution Manual

C. A. Trapp, M. P. Cady, Carmen Giunta



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