

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 heat capacity is often very small. In the case of the rotational modes, the characteristic temperature is often very low, and the rotational heat capacity is often very close to its equipartition value. In the case of the translational modes, the characteristic temperature is always very low, and the translational heat capacity is always very close to its equipartition value. The total heat capacity is then the sum of these three contributions.

Solutions to exercises

The vibrational heat capacity is given by $C_{V,m} = \frac{1}{2}R \sum_{j=1}^{\nu_V} \frac{\theta_{V,j}}{T} \frac{e^{-\theta_{V,j}/T}}{1 - e^{-\theta_{V,j}/T}}$. When the temperature is well above the characteristic temperature of the vibrational modes, the heat capacity is given by

$$C_{V,m} = \frac{1}{2}R \sum_{j=1}^{\nu_V} \frac{\theta_{V,j}}{T} \frac{e^{-\theta_{V,j}/T}}{1 - e^{-\theta_{V,j}/T}} \approx \frac{1}{2}R \sum_{j=1}^{\nu_V} \frac{\theta_{V,j}}{T} \frac{e^{-\theta_{V,j}/T}}{1 - e^{-\theta_{V,j}/T}}$$

which is the equipartition limit. In the case of the rotational modes, the characteristic temperature is often very low, and the rotational heat capacity is often very close to its equipartition value.

$$C_{V,m} = \frac{1}{2}R \sum_{j=1}^{\nu_V} \frac{\theta_{V,j}}{T} \frac{e^{-\theta_{V,j}/T}}{1 - e^{-\theta_{V,j}/T}} \approx \frac{1}{2}R \sum_{j=1}^{\nu_V} \frac{\theta_{V,j}}{T} \frac{e^{-\theta_{V,j}/T}}{1 - e^{-\theta_{V,j}/T}}$$

which is the equipartition limit.

$$C_{V,m} = \frac{1}{2}R \sum_{j=1}^{\nu_V} \frac{\theta_{V,j}}{T} \frac{e^{-\theta_{V,j}/T}}{1 - e^{-\theta_{V,j}/T}} \approx \frac{1}{2}R \sum_{j=1}^{\nu_V} \frac{\theta_{V,j}}{T} \frac{e^{-\theta_{V,j}/T}}{1 - e^{-\theta_{V,j}/T}}$$

$$C_{V,m} = \frac{1}{2}R \sum_{j=1}^{\nu_V} \frac{\theta_{V,j}}{T} \frac{e^{-\theta_{V,j}/T}}{1 - e^{-\theta_{V,j}/T}} \approx \frac{1}{2}R \sum_{j=1}^{\nu_V} \frac{\theta_{V,j}}{T} \frac{e^{-\theta_{V,j}/T}}{1 - e^{-\theta_{V,j}/T}}$$

which is the equipartition limit.

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G Thomas



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