

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

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

The equipartition limit is only valid when the temperature is high compared to the characteristic temperatures of the modes. If the temperature is lower than the characteristic temperature of a mode, then the energy of the mode is not enough to excite it, and $\nu_V = 0$ corresponding to all degrees of freedom in the mode being inactive. When $T = \theta_V$, the energy of vibration is on the order of kT , the average vibrational energy is $\frac{1}{2}kT$, and all vibrational degrees of freedom are contributing to the heat capacity. The average vibrational energy then becomes $\frac{1}{2}kT$ as $T \rightarrow \infty$ as each degree of freedom then has the equipartition energy of $\frac{1}{2}kT$ for each degree of freedom.

Solutions to exercises

The thermal energy is given by $\epsilon = \frac{1}{2}kT$ per molecule. When several modes are active, each mode contributes to the expression for ϵ .

$$\epsilon = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT$$

so that $\epsilon = 2kT$ for the equipartition limit, as above.

$$\epsilon = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = 2kT = 2(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K}) = 1.66 \times 10^{-21} \text{ J}$$

so that $\epsilon = 2kT$.

$$\epsilon = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = 2kT = 2(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K}) = 1.66 \times 10^{-21} \text{ J}$$

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

with $\nu_R^\ddagger = 2$ and $\nu_V = 6$.

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Keith James Laidler, John H. Meiser



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