

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

$$C_{V,m} = \frac{1}{2}R(3 + \nu_R^\ddagger + \nu_V^\ddagger)$$

The equipartition value of $C_{V,m}$ is $\frac{1}{2}R(3 + \nu_R^\ddagger + \nu_V^\ddagger)$ and is the value that would be obtained if all modes were active. In the limit of high temperature, all modes are active and the heat capacity approaches the equipartition value. In the limit of low temperature, only the translational modes are active and the heat capacity approaches $\frac{3}{2}R$. The vibrational heat capacity is zero at low temperature and approaches $\frac{1}{2}R$ at high temperature. The rotational heat capacity is zero at low temperature and approaches $\frac{1}{2}R$ at high temperature. The vibrational heat capacity is zero at low temperature and approaches $\frac{1}{2}R$ at high temperature. The rotational heat capacity is zero at low temperature and approaches $\frac{1}{2}R$ at high temperature.

Solutions to exercises

The vibrational heat capacity is given by $C_{V,m} = \frac{1}{2}R \sum_{i=1}^{\nu_V} \frac{\theta_{V,i}}{T} \left(\frac{\theta_{V,i}}{T} \right)^{-1} \left(\frac{\theta_{V,i}}{T} \right)^{-2} \left(\frac{\theta_{V,i}}{T} \right)^{-3} \dots$

$$= \frac{1}{2}R \sum_{i=1}^{\nu_V} \frac{\theta_{V,i}}{T} \left(\frac{\theta_{V,i}}{T} \right)^{-1} \left(\frac{\theta_{V,i}}{T} \right)^{-2} \left(\frac{\theta_{V,i}}{T} \right)^{-3} \dots$$

At high temperature, $\theta_{V,i}/T \ll 1$ and $\left(\frac{\theta_{V,i}}{T} \right)^{-1} \left(\frac{\theta_{V,i}}{T} \right)^{-2} \left(\frac{\theta_{V,i}}{T} \right)^{-3} \dots \approx 1$

$$C_{V,m} \approx \frac{1}{2}R \sum_{i=1}^{\nu_V} \frac{\theta_{V,i}}{T} \approx \frac{1}{2}R \nu_V = \frac{1}{2}R \nu_V^\ddagger$$

At low temperature, $\theta_{V,i}/T \gg 1$

$$C_{V,m} \approx \frac{1}{2}R \sum_{i=1}^{\nu_V} \frac{\theta_{V,i}}{T} \left(\frac{\theta_{V,i}}{T} \right)^{-1} \left(\frac{\theta_{V,i}}{T} \right)^{-2} \left(\frac{\theta_{V,i}}{T} \right)^{-3} \dots \approx \frac{1}{2}R \sum_{i=1}^{\nu_V} \frac{\theta_{V,i}}{T} \left(\frac{\theta_{V,i}}{T} \right)^{-1} = \frac{1}{2}R \nu_V^\ddagger$$

$$C_{V,m} = \frac{1}{2}R(3 + \nu_R^\ddagger + \nu_V^\ddagger)$$

At high temperature, $\theta_{V,i}/T \ll 1$

Physical Chemistry 9th Edition Solutions

Clemens Wendtner



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