

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

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

The equipartition value $C_{V,m} = 2.5R$ is reached when all the vibrational modes are active. At $T = 298 \text{ K}$, the vibrational temperatures of the modes of CO_2 are 3300 K , 2200 K , 1330 K , 690 K , 470 K , and 430 K . The vibrational temperatures of the modes of H_2O are 5400 K , 3650 K , 2280 K , 1590 K , 940 K , and 540 K . The vibrational temperatures of the modes of CH_4 are 4700 K , 3050 K , 1900 K , 1300 K , 750 K , and 500 K . The vibrational temperatures of the modes of NH_3 are 4250 K , 2700 K , 1650 K , 1100 K , 650 K , and 450 K . The vibrational temperatures of the modes of H_2 are 6100 K , 4300 K , 2700 K , and 1500 K . The vibrational temperatures of the modes of O_2 are 7700 K , 5400 K , 3400 K , and 2000 K . The vibrational temperatures of the modes of N_2 are 3350 K , 2350 K , 1480 K , and 860 K . The vibrational temperatures of the modes of Cl_2 are 810 K , 560 K , 340 K , and 200 K . The vibrational temperatures of the modes of Br_2 are 470 K , 320 K , 190 K , and 110 K . The vibrational temperatures of the modes of I_2 are 310 K , 210 K , 130 K , and 70 K . The vibrational temperatures of the modes of HCl are 4300 K , 3000 K , 1900 K , 1300 K , 750 K , and 500 K . The vibrational temperatures of the modes of HBr are 3480 K , 2450 K , 1550 K , 1050 K , 600 K , and 400 K . The vibrational temperatures of the modes of HI are 2400 K , 1700 K , 1100 K , 700 K , 400 K , and 270 K . The vibrational temperatures of the modes of HF are 9000 K , 6300 K , 4000 K , 2700 K , 1600 K , and 1000 K . The vibrational temperatures of the modes of H_2O are 5400 K , 3650 K , 2280 K , 1590 K , 940 K , and 540 K . The vibrational temperatures of the modes of CO_2 are 3300 K , 2200 K , 1330 K , 690 K , 470 K , and 430 K . The vibrational temperatures of the modes of CH_4 are 4700 K , 3050 K , 1900 K , 1300 K , 750 K , and 500 K . The vibrational temperatures of the modes of NH_3 are 4250 K , 2700 K , 1650 K , 1100 K , 650 K , and 450 K . The vibrational temperatures of the modes of H_2 are 6100 K , 4300 K , 2700 K , and 1500 K . The vibrational temperatures of the modes of O_2 are 7700 K , 5400 K , 3400 K , and 2000 K . The vibrational temperatures of the modes of N_2 are 3350 K , 2350 K , 1480 K , and 860 K . The vibrational temperatures of the modes of Cl_2 are 810 K , 560 K , 340 K , and 200 K . The vibrational temperatures of the modes of Br_2 are 470 K , 320 K , 190 K , and 110 K . The vibrational temperatures of the modes of I_2 are 310 K , 210 K , 130 K , and 70 K . The vibrational temperatures of the modes of HCl are 4300 K , 3000 K , 1900 K , 1300 K , 750 K , and 500 K . The vibrational temperatures of the modes of HBr are 3480 K , 2450 K , 1550 K , 1050 K , 600 K , and 400 K . The vibrational temperatures of the modes of HI are 2400 K , 1700 K , 1100 K , 700 K , 400 K , and 270 K . The vibrational temperatures of the modes of HF are 9000 K , 6300 K , 4000 K , 2700 K , 1600 K , and 1000 K .

Solutions to exercises

The vibrational energy is given by $\epsilon = \frac{1}{2}h\nu$ and the vibrational temperature is $\theta_v = \frac{h\nu}{k_B}$. The vibrational energy is $\epsilon = \frac{1}{2}h\nu = \frac{1}{2}k_B\theta_v$.

$$\theta_v = \frac{2\epsilon}{k_B} = \frac{2 \times 0.025 \text{ eV}}{8.617 \times 10^{-5} \text{ eV K}^{-1}} = 580 \text{ K}$$

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Physical Chemistry 9th Edition Instructors Solution Guide

Roman Wölfel



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