

Solutions to Homework Problem Set 19

1. The mean energy per particle is given by $\bar{\epsilon} = \frac{\sum_{m=-1}^{m=1} P_m \epsilon_m}{\sum_{m=-1}^{m=1} P_m}$, where $P_m = e^{-\epsilon_m/kT}$. Here $\epsilon_m(m = \pm 1) = \epsilon$ and $\epsilon_m(m = 0) = 0$. Therefore

$$\bar{\epsilon} = \frac{2\epsilon e^{-\frac{\epsilon}{kT}}}{2e^{-\frac{\epsilon}{kT}} + 1} = \epsilon \left(1 - \frac{1}{2e^{-\frac{\epsilon}{kT}} + 1}\right)$$

And the molar internal energy is given by

$$E(T) = N_a \bar{\epsilon} = N_a \epsilon \left(1 - \frac{1}{2e^{-\frac{\epsilon}{kT}} + 1}\right)$$

where N_a is the Avogadro number.

The expression above suggests that $E(T)$ monotonically increases with T . At the low temperature limit, the exponential function takes the value of zero, thus $E(T)$ approaches zero; at the high temperature limit, the exponential function takes the value of 1, thus $E(T) \approx \frac{2}{3} N_a \epsilon$, or the mean energy of the three states, which is no longer dependent on temperature. The heat capacity will gradually increase from zero as $E(T)$ rapidly increases with T increasing from $T = 0$ K, and then will decrease to zero as $E(T)$ is approaching the high temperature limit independent of T .

Using the expression of $\bar{\epsilon}$, the molar heat capacity is given as

$$c_V = \left(\frac{\partial E(T)}{\partial T}\right)_V = 2R \left(\frac{\epsilon}{kT}\right)^2 \frac{e^{-\frac{\epsilon}{kT}}}{(2e^{-\frac{\epsilon}{kT}} + 1)^2}$$

where R is the gas constant $R = N_a k$.

For very low temperatures, $e^{-\epsilon/kT}$ approaches zero much faster than $(1/T)^2$, so c_V approaches zero. For large values of T , the exponential function approaches 1, and

$$c_V \approx \frac{2}{9} R \left(\frac{\epsilon}{kT}\right)^2$$

or c_V is inversely proportional to T^2 , which tends to zero at large T .

Stowe 18.32

We use the partition function for each mode at very high temperatures given in Table 18.1.

For translational energy, at very high temperatures, the partition function of this mode is $Z = V(2\pi m kT/h^2)^{3/2} = V(2\pi m/\beta h^2)^{3/2} = C\beta^{-3/2}$, where $\beta = 1/(kT)$ and C is a constant including all other terms not related to the temperature. So the mean energy per particle is given by $\bar{\epsilon} = -\partial \ln Z / \partial \beta = -\partial (\ln C - 3/2 \ln \beta) / \partial \beta = 3/(2\beta) = 3/2kT$. Since a particle has 3 degrees of freedom related to the translational motion, so $\nu = 3$. According to equipartition, the mean energy of each degree of freedom is $1/2kT$. So the mean translational energy is $\bar{\epsilon} = \nu/2kT = 3/2kT$, consistent with the result above.

For rotational mode, at very high temperatures, the partition function is $Z = (2IkT/\hbar^2)^{2/2} = C\beta^{-1}$. So the mean rotational energy $\bar{\epsilon} = -\partial \ln Z / \partial \beta = -\partial(-\ln \beta) / \partial \beta = 1/\beta = kT$. For a diatomic gas, each molecule has 2 degrees of freedom related to rotational motion, so according to equipartition theorem the mean rotational energy $\bar{\epsilon} = \nu 1/2kT = kT$, consistent with the calculation.

For vibrational mode, at very high temperatures, the partition function is $Z = (kT/\hbar\omega)^{2/2} = C\beta^{-1}$. So the mean rotational energy $\bar{\epsilon} = -\partial \ln Z / \partial \beta = -\partial(-\ln \beta) / \partial \beta = 1/\beta = kT$. For a diatomic gas, each molecule has 2 degrees of freedom related to vibrational motion, so according to equipartition theorem the mean rotational energy $\bar{\epsilon} = \nu 1/2kT = kT$, consistent with the calculation.