Sept. 12, 2007
Chem. 1410
Problem Set 1, Solutions

(1) [4 points] Note: since \( \nu = c / \lambda \), then, given a small change in wavelength of \( \delta \lambda \) about a central value of \( \lambda \), the corresponding frequency change is \( \delta \nu = (d \nu / d \lambda)\delta \lambda = -(c / \lambda^2)\delta \lambda \). [If frequency increases, wavelength decreases: hence the – sign.] Thus, appealing to the equation in point (ii), i.e., \( D_\lambda (\lambda) \Delta \lambda = D_\nu (\nu) \Delta \nu \), we can write

\[
\frac{8\pi}{\lambda^2} \frac{\lambda^2}{c} \Delta \nu = D_\nu (\nu) \Delta \nu \quad [1]
\]

Note, either side of this equation gives the number of modes in the selected interval, and thus \( \Delta \nu \) and \( \Delta \lambda \) are the magnitudes of the (small) frequency and wavelength intervals, respectively. Finally, Eq. 1 above implies:

\[ D_\nu (\nu) = \frac{8\pi}{\lambda^2 c} = \frac{8\pi \nu^2}{c^3} \text{, QED} \]

(2) (a) [2 points] In general, the average of a property \( A \) over a discrete probability distribution is given by \( \langle A \rangle = \sum_j p_j A_j \), where \( p_j \) is the normalized probability to be in state \( j \), and \( A_j \) is the value of the property \( A \) in associated with state \( j \). In the case of interest here the states are labeled by \( j=0,1,2,\ldots\infty \) and the normalized probability to be in state \( j \) is the Boltzmann factor

\[ p_j = e^{-\frac{\nu j h}{k_B T}} / \sum_{j=0}^{\infty} e^{-\frac{j \hbar \nu}{k_B T}} \].

Furthermore, the energy of state \( j \) (corresponding to \( j \) photons in an electromagnetic mode of frequency \( \nu \)) is \( E_j = j \hbar \nu \). Thus:

\[ \langle E(\nu) \rangle = h\nu \sum_{j=0}^{\infty} j e^{-\frac{\nu j h}{k_B T}} / \sum_{j=0}^{\infty} e^{-\frac{j \hbar \nu}{k_B T}} \].

(b) (i) [1 point] The infinite geometric series \( 1 + x + x^2 + \ldots = \frac{1}{1-x} \) for \( |x|<1 \) (otherwise the series diverges). In the case of our series expression for \( D(\nu) \), we identify \( x = \exp(-\hbar \nu / k_B T) < 1 \), and thus:

\[ D(\nu) = [1 - e^{-\hbar \nu / k_B T}]^{-1} \text{, QED} \]

(ii) [2 points] Differentiating the series for \( D(\nu) \) term by term w.r.t. \( \nu \):


\[ \frac{\partial D}{\partial \nu} = \sum_{j=0}^{\infty} \frac{-j\hbar}{k_B T} e^{-j\hbar \nu/k_B T} \]

and thus:
\[ N(\nu) = \frac{-k_B T}{h} \frac{\partial D(\nu)}{\partial \nu}, \quad \text{QED.} \]

iii) [1 point] Given the expression in (ii) and the explicit form for \( D(\nu) \) in (i), we can evaluate:
\[ N(\nu) = \frac{e^{-\hbar \nu/k_B T}}{(1 - e^{-\hbar \nu/k_B T})^2} \]

and hence:
\[ <E(\nu)> = h\nu N(\nu) / D(\nu) = \frac{h\nu}{[e^{\hbar \nu/k_B T} - 1]}, \quad \text{QED.} \]
root mean square speed, \( v_{rms} = \langle v^2 \rangle^{1/2} = \sqrt{\frac{3kT}{m}} \), in which \( m \) is the molecular mass and \( k \) is the Boltzmann constant. Using this formula, calculate the de Broglie wavelength for He and Ar atoms at 100 and 500 K.

\[
\lambda = \frac{h}{mv_{rms}} = \frac{h}{\sqrt{3kT/m}} = \frac{6.626\times10^{-34} J\text{s}}{\sqrt{3\times1.381\times10^{-23} J \text{K}^{-1} \times 100 K \times 4.003 \text{amu} \times 1.661\times10^{-27} \text{kg amu}^{-1}}} = 1.26\times10^{-10} \text{m}
\]

for He at 100 K. \( \lambda = 5.65\times10^{-11} \text{m} \) for He at 500 K. For Ar, \( \lambda = 4.00\times10^{-11} \text{m} \) and \( 1.79\times10^{-11} \text{m} \) at 100 K and 500 K, respectively.

P1.7) Assume that water absorbs light of wavelength \( 3.00 \times 10^{-6} \text{m} \) with 100% efficiency. How many photons are required to heat 1.00 g of water by 1.00 K? The heat capacity of water is 75.3 J mol\(^{-1}\) K\(^{-1}\).

\[
E = Nh\nu = N \frac{hc}{\lambda} = n C_{p,m} \Delta T
\]

\[
N = \frac{m C_{p,m} \Delta T \lambda}{M \ h c} = \frac{1.00 \text{g} \times 75.3 \text{J K}^{-1} \text{mol}^{-1} \times 1.00 \text{K} \times 3.00 \times 10^{-6} \text{m}}{18.02 \text{g mol}^{-1} \times 6.626\times10^{-34} J\text{s} \times 2.998\times10^{8} \text{m s}^{-1}} = 6.31\times10^{16}
\]

P1.12) Show that the energy density radiated by a blackbody

\[
\frac{E_{\text{total}}(T)}{V} = \int_{0}^{\infty} \rho(\nu, T) d\nu = \int_{0}^{\infty} \frac{8\pi h \nu^3}{c^3 e^{h\nu/kT} - 1} d\nu
\]

depends on the temperature as \( T^4 \).

(Hint: Make the substitution of variables \( x = \nu/kT \).) The definite integral

\[
\int_{0}^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}
\]

Using your result, calculate the energy density radiated by a blackbody at 800 and 4000 K.

\[
\frac{E_{\text{total}}}{V} = \frac{8\pi^3 k^4 T^4}{15 h^2 c^3} = \frac{8\pi^3 (1.381\times10^{-23} J \text{K}^{-1})^4 \times (800 \text{ K})^4}{15 \times (6.626\times10^{-34} J \text{s}) \times (2.998\times10^{8} \text{m s}^{-1})^3} = 3.10\times10^{-2} \text{J m}^{-3}
\]

At 4000 K,

\[
\frac{E_{\text{total}}}{V} = \frac{8\pi^3 k^4 T^4}{15 h^2 c^3} = \frac{8\pi^3 (1.381\times10^{-23} J \text{K}^{-1})^4 \times (4000 \text{ K})^4}{15 \times (6.626\times10^{-34} J \text{s}) \times (2.998\times10^{8} \text{m s}^{-1})^3} = 0.194 \text{ J m}^{-3}
\]
P1.17) The observed lines in the emission spectrum of atomic hydrogen are given by
\[ \tilde{\nu} (\text{cm}^{-1}) = R_H (\text{cm}^{-1}) \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{cm}^{-1}, n > n_1. \]
In the notation favored by spectroscopists, \( \tilde{\nu} = \frac{1}{\lambda} = \frac{E}{hc} \) and \( R_H = 109,677 \text{cm}^{-1} \). The Lyman, Balmer, and Paschen series refers to \( n_1 = 1, 2, \) and \( 3 \), respectively, for emission from atomic hydrogen. What is the highest value of \( \tilde{\nu} \) and \( E \) in each of these series?

The highest value for \( \tilde{\nu} \) corresponds to \( \frac{1}{n} \to 0 \). Therefore,

\[ \tilde{\nu} = R_H \left( \frac{1}{1^2} \right) \text{cm}^{-1} = 109,667 \text{cm}^{-1} \text{ or } E_{\text{max}} = 2.18 \times 10^{-18} \text{ J for the Lyman series.} \]

\[ \tilde{\nu} = R_H \left( \frac{1}{2^2} \right) \text{cm}^{-1} = 27419 \text{cm}^{-1} \text{ or } E_{\text{max}} = 5.45 \times 10^{-19} \text{ J for the Balmer series, and} \]

\[ \tilde{\nu} = R_H \left( \frac{1}{3^2} \right) \text{cm}^{-1} = 12186 \text{cm}^{-1} \text{ or } E_{\text{max}} = 2.42 \times 10^{-19} \text{ J for the Paschen series.} \]

P1.19) If an electron passes through an electrical potential difference of 1 V, it has an energy of 1 electron-volt. What potential difference must it pass through in order to have a wavelength of 0.100 nm?

\[ E = \frac{1}{2} m_e v^2 = \frac{1}{2} m_e \left( \frac{h}{m_e \lambda} \right)^2 = \frac{h^2}{2m_e \lambda^2} \]

\[ = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{2 \times 9.109 \times 10^{-31} \text{ kg} \times (10^{-10} \text{ m})^2} = 2.41 \times 10^{-17} \text{ J} \times \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} = 150.4 \text{ eV} \]

The electron must pass through an electrical potential of 150.4 V.