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 λ, the corresponding frequency change is $\delta\nu = (d\upsilon/d\lambda)\delta\lambda$ = -(c/λ^2)$\delta\lambda$. [If frequency increases, wavelength decreases: hence the – sign.] Thus, appealing to the equation in point (ii), i.e., $D_\lambda(\lambda)\Delta\lambda = D_\nu(\upsilon)\Delta\nu$, we can write

$$\frac{8\pi}{\lambda^4}\cdot\frac{\lambda^2}{c}\Delta\upsilon = D_\nu(\upsilon)\Delta\nu \qquad [1]$$

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

$$D_\upsilon(\upsilon) = \frac{8\pi}{\lambda^2 c} = \frac{8\pi\nu^2}{c^3} \quad \text{, QED}$$

(2) (a) (2 points) In general, the average of a property A over a discrete probability distribution is given by $<A> = \sum_j p_j A_j$, 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,…*∞ and the normalized probability to be in state *j* is the Boltzmann factor $p_j = e^{-jh\nu/k_BT} / \sum_{j=0}^{\infty} e^{-jh\nu/k_BT}$. Furthermore, the energy of state *j* (corresponding to *j* photons in an electromagnetic mode of frequency υ) is $E_j = jh\upsilon$. Thus:

$$<E(\upsilon)> = h\nu\sum_{j=0}^{\infty} je^{-jh\nu/k_BT} / \sum_{j=0}^{\infty} e^{-jh\nu/k_BT} .$$

(b) (i) (1 point) The infinite geometric series $1 + x + x^2 + ... = \frac{1}{1-x}$ for $|x| < 1$ (otherwise the series diverges). In the case of our series expression for $D(\upsilon)$, we identify $x = \exp(-h\upsilon/k_BT) < 1$, and thus:

$$D(\upsilon) = [1 - e^{-h\nu/k_BT}]^{-1} \quad \text{, QED}$$

(ii) (2 points) Differentiating the series for $D(\upsilon)$ term by term w.r.t. υ:

$$\partial D / \partial \upsilon = \sum_{j=0}^{\infty} \frac{-jh}{k_B T} e^{-jh\nu / k_B T}$$

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

iii)(1 point) Given the expression in (ii) and the explicit form for $D(\upsilon)$ in (i), we can evaluate:

$$N(\upsilon) = \frac{e^{-h\upsilon / k_B T}}{(1 - e^{-h\upsilon / k_B T})^2}$$

and hence:

$$< E(\nu) >= h\nu N(\upsilon) / D(\upsilon) = \frac{h\nu}{[e^{h\nu / k_B T} - 1]} \quad \text{, QED.}$$

P1.2) 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 at 500 K.

$$\lambda = \frac{h}{m v_{rms}} = \frac{h}{\sqrt{3kTm}} = \frac{6.626\times10^{-34}\,\text{J s}}{\sqrt{3\times1.381\times10^{-23}\,\text{J K}^{-1}\times100K\times4.003\,\text{amu}\times1.661\times10^{-27}\,\text{kg amu}^{-1}}}$$

$= 1.26\times10^{-10}\,\text{m}$

for He at 100 K. $\lambda = 5.65\times10^{-11}$ m for He at 500 K. For Ar, $\lambda = 4.00\times10^{-11}$ m and 1.79×10^{-11} m at 100 K and 500 K, respectively.

P1.7) Assume that water absorbs light of wavelength 3.00×10^{-6} 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}.

$$E = Nh\nu = N\frac{hc}{\lambda} = nC_{P,m}\Delta T$$

$$N = \frac{m}{M}\frac{C_{P,m}\Delta T\lambda}{hc} = \frac{1.00\text{g}}{18.02\text{g mol}^{-1}}\cdot\frac{75.3\,\text{J K}^{-1}\,\text{mol}^{-1}\times1.00\,\text{K}\times3.00\times10^{-6}\,\text{m}}{6.626\times10^{-34}\,\text{J s}\times2.998\times10^{8}\,\text{m s}^{-1}} = 6.31\times10^{19}$$

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

$$\frac{E_{total}(T)}{V} = \int_0^\infty \rho(\nu,T)\,d\nu = \int_0^\infty \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}\,d\nu$$ depends on the temperature as T^4.

(*Hint:* Make the substitution of variables $x = h\nu/kT$.) 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.

$$\frac{E_{total}}{V} = \int_0^\infty \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}d\nu.\ \text{Let } x = \frac{h\nu}{kT};\ dx = \frac{h}{kT}d\nu$$

$$\int_0^\infty \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}d\nu = \frac{8\pi k^4T^4}{h^3c^3}\int_0^\infty \frac{x^3}{e^x-1}dx = \frac{8\pi^5k^4T^4}{15h^3c^3}$$

At 800 K, $\frac{E_{total}}{V} = \frac{8\pi^5k^4T^4}{15h^3c^3} = \frac{8\pi^5(1.381\times10^{-23}\text{J K}^{-1})^4\times(800\text{ K})^4}{15\times(6.626\times10^{-34}\text{J s})^3(2.998\times10^8\text{m s}^{-1})^3} = 3.10\times10^{-4}\text{J m}^{-3}$

At 4000, $\frac{E_{total}}{V} = \frac{8\pi^5\times(1.381\times10^{-23}\text{J K}^{-1})^4\times(4000\text{ K})^4}{15\times(6.626\times10^{-34}\text{J s})^3\times(2.998\times10^8\text{m s}^{-1})^3} = 0.194\text{ J m}^{-3}$

P1.17) The observed lines in the emission spectrum of atomic hydrogen are given by $\tilde{\nu}(\text{cm}^{-1}) = R_H\,(\text{cm}^{-1})\left(\frac{1}{n_1^2} - \frac{1}{n^2}\right)\text{cm}^{-1}, n > n_1$. In the notation favored by spectroscopists, $\tilde{\nu} = \frac{1}{\lambda} = \frac{E}{hc}$ and R_H = 109,677cm^{-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,

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

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

$\tilde{\nu} = R_H\left(\frac{1}{3^2}\right)\text{cm}^{-1} = 12186\text{cm}^{-1}$ or E_{max} = 2.42×10^{-19} 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?

$$E = \frac{1}{2}m_e\text{v}^2 = \frac{1}{2}m_e \times \left(\frac{h}{m_e\lambda}\right)^2 = \frac{h^2}{2m_e\lambda^2}$$

$$= \frac{(6.626\times10^{-34}\text{ J s})^2}{2\times9.109\times10^{-31}\text{ kg}\times(10^{-10}\text{ m})^2} = 2.41\times10^{-17}\text{ J}\times\frac{1\,\text{eV}}{1.602\times10^{-19}\text{ J}} = 150.4\,\text{eV}$$

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