

Physical Chemistry Cumulative Examination, October 6, 2016  
Professor Michael Trenary

1. (35 pts) The Maxwell-Boltzmann distribution function of molecular speeds is given by

$$f(s) = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} s^2 e^{-ms^2/2kT}$$

where  $m$  is the molecular mass,  $k$  is Boltzmann's constant, and  $T$  is the temperature in Kelvin. Since this is a probability distribution function, the integral from  $s = 0$  to  $s = \infty$  equals the total probability, which is unity:

$$\int_0^{\infty} f(s) ds = 1$$

The probability of the molecule having a speed between two values,  $s_1$  and  $s_2$ , is just the definite integral over that range:

$$\int_{s_1}^{s_2} f(s) ds$$

a) (5 pts) Sketch  $f(s)$  versus  $s$  and indicate on your sketch the position of the most probable speed,  $s_{mp}$ , and the average speed,  $s_{ave} = \langle s \rangle$ .

b) (10 pts) Derive an expression for the most probable speed,  $s_{mp}$ , in terms of  $m$  and  $kT$ .

c) (5 pts) Give an expression for the probability distribution in terms of  $s/s_{mp}$  such that  $m$ ,  $k$ , and  $T$  do not explicitly appear in the expression for  $f(s)$ .

d) (5 pts) Give an integral expression for the probability of a molecule having a speed less than or equal to the most probable speed, i.e. the probability of  $s$  being between 0 and  $s_{mp}$ . Reduce the integral to a simple form by defining the variable  $x = s/s_{mp}$ . Do not attempt to evaluate the integral for part d).

e) (10 pts) Give the probability of the molecule having a speed less than 1% of the most probable speed, i.e. the probability of  $s$  being in the interval  $0 \leq s \leq 0.01s_{mp}$ . In this range, the exponential function in the distribution can be simplified so that the integral can be evaluated.

2. (30 pts) For an ideal blackbody emitting radiation due to its temperature, the radiation energy density,  $\rho(\nu)$ , is given by Planck's distribution formula

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}$$

where  $c$  is the speed of light,  $h$  is Planck's constant, and  $k$  is Boltzmann's constant. Since  $\rho(\nu)$  is a distribution function, it can be integrated to find the energy density between any two values of the frequency. The total energy density associated with a blackbody is obtained from

$$\int_0^{\infty} \rho(\nu) d\nu = U_{total}$$

which integrates to give

$$U_{total} = \frac{8\pi^5 k^4 T^4}{15c^3 h^3}$$

a) (15 pts) Give an expression for the fraction of total energy density for frequencies given by  $h\nu/kT \geq 10$ . In this frequency range, the exponential in the denominator in the equation for  $\rho(\nu)$  will be much greater than 1, which will allow you to make a reasonable approximation for the integrand such that the definite integral can be evaluated using a standard form.

b) (15 pts) Planck's blackbody distribution can also be written in terms of the wavelength,  $\lambda$ , since  $\lambda\nu = c$ . Derive the quantity  $\rho(\lambda)d\lambda$  from the  $\rho(\nu)d\nu$  expression. In other words, given that

$$\int_{\nu_1}^{\nu_2} \rho(\nu) d\nu = \int_{\nu_1}^{\nu_2} \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} d\nu,$$

complete the equation

$$\int_{\lambda_1}^{\lambda_2} \rho(\lambda) d\lambda = ?,$$

where  $\nu_2 > \nu_1$  and  $\lambda_2 > \lambda_1$ .

3. (35 pts) The H atom wavefunctions,  $\psi_{n,l,m}(r,\theta,\phi)$ , can be factored into a radial part,  $R_{n,l}(r)$ , and an angular part,  $Y_{l,m}(\theta,\phi)$ , also known as a spherical harmonic. For  $n = 4$ , there are sixteen different wavefunctions for the H atom: 4s, 4p<sub>+1</sub>, 4p<sub>0</sub>, 4p<sub>-1</sub>, 4d<sub>-2</sub>, 4d<sub>-1</sub>, 4d<sub>0</sub>, 4d<sub>+1</sub>, 4d<sub>+2</sub>, 4f<sub>-3</sub>, 4f<sub>-2</sub>, 4f<sub>-1</sub>, 4f<sub>0</sub>, 4f<sub>1</sub>, 4f<sub>2</sub>, and 4f<sub>3</sub> (Tables of the  $R_{n,l}(r)$  and  $Y_{l,m}(\theta,\phi)$  functions are attached). Explicit forms for the  $\psi_{n,l,m}(r,\theta,\phi)$  functions are obtained by taking the product of the appropriate radial function and the appropriate spherical harmonic.

a)(10 pts) Choose one of the sixteen  $n = 4$  functions. Without doing any calculations, indicate if the average distance of the electron from the nucleus,  $\langle r \rangle$ , for the orbital you chose will be less than, greater than, or equal to  $\{\langle r^2 \rangle\}^{1/2}$ , the root mean square distance, for the same orbital. Briefly explain your reasoning.

b)(25 pts) For the orbital you chose in part a, calculate the average distance,  $\langle r \rangle$ , of the electron from the nucleus. Your answer should equal: (unitless number)( $a_0$ ), Hint: pick the function for which the integration is easiest. The only integration formula you should need is given below.

#### Miscellaneous Information

SI units: mass: kilograms (kg), distance: meters (m), time: seconds (s), energy: Joules (J)

$i = \sqrt{-1}$ ,  $c =$  speed of light  $= 2.998 \times 10^8 \text{ ms}^{-1}$ ,  $h = 6.626 \times 10^{-34} \text{ J s}$ ,  $k =$  Boltzmann's constant  $= 1.38 \times 10^{-23} \text{ J K}^{-1}$

Ave molecular speed:  $\langle s \rangle = \sqrt{\frac{8kT}{\pi m}}$ , RMS molecular speed:  $\sqrt{s^2} = \sqrt{\frac{3kT}{m}}$

$\exp(ax) = 1 + (ax) + \frac{1}{2}(ax)^2 + \dots = \sum (1/n!)(ax)^n$ ,  $\int_0^\infty r^n e^{-br} dr = \frac{n!}{b^{n+1}}$

## Hydrogen Atom Wavefunctions for n = 4

*Radial Functions*

$$\rho = \frac{r}{2a_0}$$

$$R_{4,0} = \frac{1}{96a_0^{3/2}} (24 - 36\rho + 12\rho^2 - \rho^3)e^{-\rho/2}$$

$$R_{4,1} = \frac{1}{32\sqrt{15}a_0^{3/2}} (20 - 10\rho + \rho^2)\rho e^{-\rho/2}$$

$$R_{4,2} = \frac{1}{96\sqrt{5}a_0^{3/2}} (6 - \rho)\rho^2 e^{-\rho/2}$$

$$R_{4,3} = \frac{1}{96\sqrt{35}a_0^{3/2}} \rho^3 e^{-\rho/2}$$

*Spherical Harmonics*

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{1,0} = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta, \quad Y_{1,1} = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}(\sin\theta)e^{i\phi}, \quad Y_{1,-1} = \frac{1}{2}\sqrt{\frac{3}{2\pi}}(\sin\theta)e^{-i\phi}$$

$$Y_{2,0} = \frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1), \quad Y_{2,1} = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}(\cos\theta\sin\theta)e^{i\phi}, \quad Y_{2,-1} = \frac{1}{2}\sqrt{\frac{15}{2\pi}}(\cos\theta\sin\theta)e^{-i\phi}$$

$$Y_{2,2} = -\frac{1}{4}\sqrt{\frac{15}{2\pi}}(\sin^2\theta)e^{i2\phi}, \quad Y_{2,-2} = \frac{1}{4}\sqrt{\frac{15}{2\pi}}(\sin^2\theta)e^{-i2\phi}$$

$$Y_{3,0} = \frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$$

$$Y_{3,1} = -\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)e^{i\phi}, \quad Y_{3,-1} = \frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)e^{-i\phi}$$

$$Y_{3,2} = -\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta(\cos\theta)e^{i2\phi}, \quad Y_{3,-2} = \frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta(\cos\theta)e^{-i2\phi}$$

$$Y_{3,3} = -\frac{1}{8}\sqrt{\frac{35}{\pi}}(\sin^3\theta)e^{i3\phi}, \quad Y_{3,-3} = \frac{1}{8}\sqrt{\frac{35}{\pi}}(\sin^3\theta)e^{-i3\phi}$$