Chemistry 331 **Assignment #1** (due Monday, September 20, in class)

Q1. This question refers to quantum oscillators with energy levels 0, $h\nu$, $2h\nu$, $3h\nu$, …

a) Explain why the average oscillator energy at temperature T is given by the equation

$$< h\nu > \; = \; \frac{h\nu e^{-h\nu/kT} + 2h\nu e^{-2h\nu/kT} + 3h\nu e^{-3h\nu/kT} + 4h\nu e^{-4h\nu/kT} + \cdots}{1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + e^{-3h\nu/kT} + e^{-4h\nu/kT} + \cdots}$$

[3] **b)** Starting with the equation in part **a**, show the average oscillator energy is

$$< h\nu > \; = \; \frac{h\nu}{e^{h\nu/kT} - 1}$$

(*Hint*: define $x = e^{-h\nu/kT}$ and use the identity $1 + x + x^2 + x^3 + \cdots = \frac{1}{1-x}$)

c) If the energy-level spacing is very small compared to the available thermal energy ($h\nu \ll kT$), show $<h\nu> = kT$, in agreement with **classical equipartition theory**.

Q2. Thermal radiation reaches maximum intensity at the frequency

$$\nu_{\max} = 2.821 \frac{kT}{h} \qquad \textbf{Wien's law}$$

For each of the following temperatures, calculate $\nu_{\max}$ and the corresponding wavelength $\lambda_{\max}$.

a) 4 K (the background temperature of the universe)

[3] **b)** 293 K (room temperature)

c) 10^8 K (the approximate temperature at the center of a thermonuclear explosion)

Also give the region of the electromagnetic spectrum (radio, infrared, visible, ultraviolet, X-ray, or gamma rays) corresponding to each $\nu_{\max}$.

Q3. **a)** **Classical equipartition theory** predicts RT for the molar vibrational energy of N_2 molecules ($RT/2$ for kinetic energy plus $RT/2$ for potential energy). *But wait*! Calorimetry shows N_2 molecules have ≈ zero vibrational energy at ambient temperatures! Why?

The N_2 vibration frequency is $\nu = 6.988 \times 10^{13}\ \mathrm{s}^{-1}$ and the vibrational energy levels are $E_0 = 0$, $E_1 = h\nu$, $E_2 = 2h\nu$, $E_3 = 3h\nu$, … Use this information to explain why N_2 molecules
[2] have negligible vibration energy at 300 K. (*Suggestion*: show $P_1/P_0 \approx 0$.)

b) But classical equipartition theory *correctly* predicts $3RT/2$ and RT for the respective molar translational and rotational energies of N_2. Explain.

Q4. The work function of chromium is 4.40 eV. Calculate the maximum kinetic energy of photoelectrons emitted from chromium irradiated with ultraviolet light at 200 nm. Also give the
[2] stopping potential (in volts) for these electrons.

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Q5. **a)** Explain how the **photoelectric effect** led to the surprising conclusion that electromagnetic waves can behave as particles.

[2] **b)** Describe an experiment that shows electrons can behave as waves.

Q6. **H-alpha radiation**, a crimson-colored line at 656.281 nm in the spectrum of atomic hydrogen, is used by astronomers to study gas clouds, nebulas, and detailed features of the solar atmosphere.

[2] **a)** Give the initial and final quantum numbers (n_i and n_f) for the emission of Hα radiation.

b) Give the frequency of Hα radiation in wavenumbers (cm^{-1}).

Q7. According to the **virial theorem**, the electric potential energy of the hydrogen atom (V_n) is twice as large as the kinetic energy (T_n): $E_n = V_n/2 = -T_n$.

For a ground-state hydrogen atom ($E_1 = -13.60$ eV), calculate:

a) the electric potential energy in eV
b) the kinetic energy in eV
[3] **c)** the de Broglie wavelength of the electron (assume all of the kinetic energy is due to electron motion)

Q8. Show the kinetic energy T of a particle with linear momentum p and mass m is $p^2/2m$. [1]

Q9. Bohr's equation $E_n = -\dfrac{\mu e^4}{8\varepsilon_0^2 h^2}\dfrac{1}{n^2}$ for the energy levels of the hydrogen atom was developed by assuming angular momentum is quantized. Is there a more intuitive way to understand this famous result?

[2] Rearrange Bohr's equation to show

$$E_n = -\frac{1}{2\mu}\frac{h^2}{(2\pi a_0 n)^2} = -\frac{1}{2\mu}\frac{h^2}{\lambda_n^2} = -\frac{p_n^2}{2\mu} = -T_n$$

where a_0 is the Bohr radius $a_0 = \dfrac{\varepsilon_0 h^2}{\pi\mu e^2}$

Why do this? For constructive interference, and a stable resonance orbit, the electron must be in phase with itself after completing one orbit. As a result, the circumference of a stable orbit equals the de Broglie wavelength of the electron ($\lambda_n = n2\pi a_0$):

$$\lambda = 2\pi a_0,\ 4\pi a_0,\ 6\pi a_0,\ 8\pi a_0,\ \ldots$$