Chemistry 331 **Assignment #1** (due Monday, September 16, in class)

Q1. For one-dimensional quantum-mechanical oscillators with energy levels

$$E_0 = 0 \qquad E_1 = h\nu_0 \qquad E_2 = 2h\nu_0 \qquad E_3 = 3h\nu_0 \quad \ldots$$

the probability P_n of finding an oscillator with energy E_n is proportional to $e^{-E_n/kT}$ which gives

$$P_n = \frac{e^{-nh\nu_0/kT}}{1 + e^{-h\nu_0/kT} + e^{-2h\nu_0/kT} + e^{-3h\nu_0/kT} + \ldots}$$

and

$$\langle E \rangle = \sum_{n=0}^{\infty} P_n E_n = \frac{0 + h\nu_0 e^{-h\nu_0/kT} + 2h\nu_0 e^{-2h\nu_0/kT} + 3h\nu_0 e^{-3h\nu_0/kT} + \ldots}{1 + e^{-h\nu_0/kT} + e^{-2h\nu_0/kT} + e^{-3h\nu_0/kT} + \ldots} \qquad (1)$$

[6]

for the average oscillator energy.

a) Starting with equation 1, derive the important result

$$\langle E \rangle = \frac{h\nu_0}{e^{h\nu_0/kT} - 1}$$

for the analysis of thermal radiation and heat capacities.

Hints. Define $x = e^{-h\nu_0/kT}$ to give

$$\langle E \rangle = h\nu_0 \frac{x + 2x^2 + 3x^3 + \ldots}{1 + x + x^2 + x^3 + \ldots}$$

and use $\dfrac{1}{1-x} = 1 + x + x^2 + x^3 + \ldots$

b) In the limit $h\nu_0/kT \ll 1$ (small energy level spacing $h\nu_0$ compared to kT), show that the average oscillator energy is the **classical value** $\langle E \rangle = kT$.

c) In the limit $h\nu_0/kT \gg 1$ (large energy level spacing $h\nu_0$ compared to kT), show the average oscillator energy is the **non-classical value** $\langle E \rangle = 0$.

… page 2

Q2. **a)** Calculate the vibrational energy of one mole of N_2 gas ($\nu_0 = 7.075 \times 10^{13}\ s^{-1}$) at 300 K.

[3] **b)** How does the result from part **a)** account for the fact the molar heat capacity of N_2 is $C_{V\text{m}} = 5R/2$ at room temperature, instead of the predicted classical value $C_{V\text{m}} = 7R/2$?

Q3. The energy levels of the hydrogen atom are

$$E_n = -\frac{2.178674 \times 10^{-18}\ \text{J}}{n^2} = -\frac{13.5982\ \text{eV}}{n^2} \qquad n = 1, 2, 3, 4, \ldots$$

a) The $n = 3$ to $n = 2$ transitions gives an intense red line ("H-alpha" radiation) in the emission spectrum of atomic hydrogen. Give the wavelength of this radiation.

b) Calculate the minimum frequency of radiation required to ionize ground-state ($n = 1$) hydrogen atoms.

[3]

c) Calculate the ionization energy for one mole of ground-state hydrogen atoms. Give your answer in units of kJ mol^{-1}.

Q4. **a)** The work function of chromium is 4.40 eV. Calculate the threshold frequency for the emission of photoelectrons from chromium.

[3] **b)** Will photoelectrons be emitted if chromium is exposed to 150 nm ultraviolet radiation? If so, give the maximum kinetic energy of the photoelectrons.

Q5. A laser pointer produces a 300 milliwatt beam of green photons ($\lambda = 532$ nm).

a) How many photons are emitted per second? (1 milliwatt $=$ 0.001 J s^{-1})

[3]

b) Each photon carries momentum h/λ. As a result, the emitted photons exert a force on the pointer (*photon propulsion*!). Calculate the magnitude of this force. *Hint*: From Newton's laws, the force equals the rate of change of momentum.

Chem 331 <u>Assignment #1</u>

Q1 The average energy of a quantum-mechanical oscillator with energy levels $0, h\nu_0, 2h\nu_0, 3h\nu_0, \ldots$

$$E_n = nh\nu_0$$

$$\langle E \rangle = \sum_{n=0}^{\infty} E_n P_n \qquad \left(P_n = \frac{e^{-E_n/kT}}{\sum_{i=0}^{\infty} e^{-E_i/kT}} = \frac{e^{-nh\nu_0/kT}}{\sum_{i=0}^{\infty} e^{-ih\nu_0/kT}} \right)$$

$$= \sum_{n=0}^{\infty} nh\nu_0 P_n$$

$$= \frac{\sum_{n=0}^{\infty} nh\nu_0 e^{-nh\nu_0/kT}}{\sum_{i=0}^{\infty} e^{-ih\nu_0/kT}}$$

$$= \frac{0 + h\nu_0 e^{-h\nu_0/kT} + 2h\nu_0 e^{-2h\nu_0/kT} + 3h\nu_0 e^{-3h\nu_0/kT} + \cdots}{e^0 + e^{-h\nu_0/kT} + e^{-2h\nu_0/kT} + e^{-3h\nu_0/kT} + \cdots}$$

Convenient to define $x = e^{-h\nu_0/kT}$, and from the helpful hints provided:

$$\langle E \rangle = \frac{0 + h\nu_0 x + 2h\nu_0 x^2 + 3h\nu_0 x^3 + \cdots}{1 + x + x^2 + x^3 + \cdots}$$

$$= h\nu_0 \frac{x + 2x^2 + 3x^3 + \cdots}{1 + x + x^2 + x^3 + \cdots}$$

$$= h\nu_0 \frac{x + 2x^2 + 3x^3 + \cdots}{\frac{1}{1-x}}$$

(Q1 a) cont.)

average oscillator energy

$$\langle E \rangle = h\nu_0 (x + 2x^2 + 3x^3 + \cdots)(1 - x)$$

$$= h\nu_0 (x + 2x^2 + 3x^3 + \cdots - x^2 - 2x^3 - 3x^4 - \cdots)$$

$$= h\nu_0 (x + x^2 + x^3 + \cdots)$$

$$= h\nu_0 (-1 + 1 + x + x^2 + x^3 + \cdots)$$

$$= h\nu_0 \left(-1 + \frac{1}{1-x}\right)$$

$$= h\nu_0 \left(\frac{-1+x}{1-x} + \frac{1}{1-x}\right)$$

$$= h\nu_0 \frac{x}{1-x}$$

$$\left(\frac{1}{x} = \frac{1}{e^{-h\nu_0/kT}} = e^{h\nu_0/kT}\right)$$

$$= h\nu_0 \frac{x/x}{\frac{1}{x} - \frac{x}{x}}$$

$$= h\nu_0 \frac{1}{\frac{1}{x} - 1}$$

$$\boxed{\langle E \rangle = h\nu_0 \frac{1}{e^{h\nu_0/kT} - 1}}$$

(Q1 cont.)

b) Average oscillator energy at high temperatures?

$$(h\nu_0 << kT)$$

$$\lim_{T\to\infty} \langle E\rangle = \lim_{T\to\infty} \frac{h\nu_0}{e^{h\nu_0/kT}-1}$$

$$= \lim_{T\to\infty} kT \frac{\frac{h\nu_0}{kT}}{e^{h\nu_0/kT}-1}$$

$$= \lim_{y\to 0} kT \frac{y}{e^y-1} \qquad \left(\begin{array}{c}\text{define} \\ y \equiv \frac{h\nu_0}{kT}\end{array}\right)$$

$$= \lim_{y\to 0} kT \frac{y}{1+y+\frac{y^2}{2!}+\frac{y^3}{3!}+\ldots-1}$$

$$= \lim_{y\to 0} kT \frac{y}{y+\frac{y^2}{2!}+\frac{y^3}{3!}+\ldots}$$

$$= \lim_{y\to 0} kT \frac{1}{1+\frac{y}{2!}+\frac{y^2}{3!}+\ldots}$$

$$\boxed{\langle E\rangle = kT} \text{ as } T\to\infty$$

(or, use l'Hopital's rule:

$$\lim_{y\to 0} kT \frac{y}{e^y-1} = \lim_{y\to 0} kT \frac{\frac{dy}{dy}}{\frac{d(e^y-1)}{dy}} = \lim_{y\to 0} kT \frac{1}{e^y} = kT$$)

(Q1 cont.)

c) Average oscillator energy at very low temperatures?

$$(h\nu_0 >> kT)$$

$$\lim_{T \to 0} \langle E \rangle = \lim_{T \to 0} \frac{h\nu_0}{e^{h\nu_0/kT} - 1}$$

$$= \lim_{y \to \infty} \frac{h\nu_0}{e^{y} - 1}$$

$$= \frac{h\nu_0}{\infty - 1}$$

$$\boxed{\langle E \rangle = 0} \quad \text{as } T \to 0$$

Q2 a) Vibrational energy of one mole of N_2

$$\langle E_m \rangle = N_A \langle E \rangle \qquad (N_A = \text{Avogadro's number})$$

$$= N_A \frac{h\nu_0}{e^{h\nu_0/kT} - 1} = N_A kT \frac{h\nu_0/kT}{e^{h\nu_0/kT} - 1}$$

$$= RT \frac{y}{e^{y} - 1} \qquad \left(y = \frac{h\nu_0}{kT}\right)$$

$$y = \frac{h\nu_0}{kT} = \frac{(6.626 \times 10^{-34})(7.075 \times 10^{13})}{(1.381 \times 10^{-23})(300)} = 11.32$$

(Q2 a) cont.)

$$\langle E_m \rangle = RT \frac{y}{e^y - 1} = (8.314)(300) \frac{11.32}{e^{11.32} - 1}$$

$$= 0.000138\ RT$$

$$\boxed{\langle E_m \rangle = 0.344\ J\ mol^{-1}}$$

b) The classical vibrational energy of one mole of N_2 is $RT = (8.314\ J\ K^{-1} mol^{-1})(300\ K)$
$= 2494\ J\ mol^{-1}$

The actual (quantum-mechanical) vibrational energy (from a) is only $0.000138\ RT$

(only 0.0138 % of the classical value)

⇒ N_2 molecules are "not vibrating" at 300 K!

⇒ the vibrational heat capacity is ≈ zero.

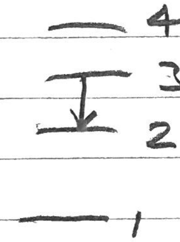
⇒ the actual (quantum-mechanical) heat capacity is

from 3 translations
from 2 rotations
from vibration

$$C_{Vm} = \frac{3}{2}R + \frac{2}{2}R + 0$$

$$= \frac{5}{2}R$$ (missing R from vibration)

(Q3) a) Wavelength of the radiation from the $n=3 \rightarrow n=2$ transition for atomic hydrogen:



photon energy $\quad h\nu = E_{n=3} - E_{n=2}$

$$= -2.178674 \times 10^{-18}\left(\frac{1}{9} - \frac{1}{4}\right) J$$

$$h\nu = 3.025936 \times 10^{-19} J$$

$$\nu = \text{frequency} = \frac{3.025936 \times 10^{-19} J}{6.62607004 \times 10^{-34} J\,s}$$

$$\nu = 4.566713 \times 10^{14}\ s^{-1}$$

wavelength $\quad \lambda = \frac{c}{\nu}$

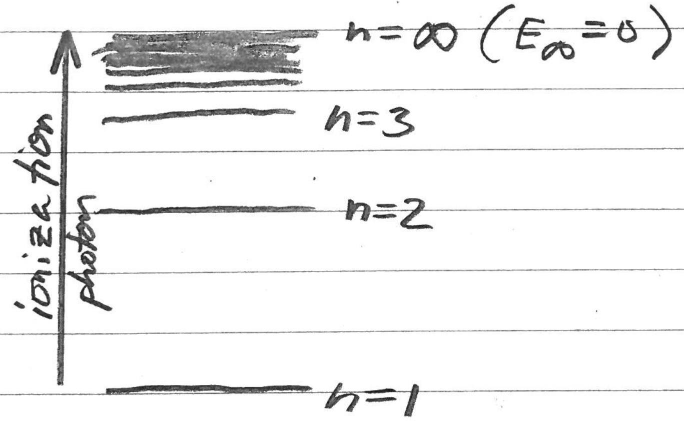
$$= \frac{2.9979246 \times 10^{8}\ m\,s^{-1}}{4.566713 \times 10^{14}\ s^{-1}}$$

$$= 6.564732 \times 10^{-7}\ m$$

$$\boxed{\lambda = 656.4732\ nm}$$

(Q3 cont.)

b) Ionizing a ground-state hydrogen atom requires raising the energy of the atom from $n=1$ (ground state) to $n=\infty$ (dissociated state)



$$E_n = -\frac{2.178674 \times 10^{-18}\ \mathrm{J}}{n^2}$$

ionization energy for one groundstate H atom

$$h\nu = E_\infty - E_1 = -2.178674 \times 10^{-18}\ \mathrm{J}\left(\frac{1}{\infty^2} - \frac{1}{1^2}\right)$$

$$h\nu = 2.178674 \times 10^{-18}\ \mathrm{J}$$

$$\nu = \frac{2.178674 \times 10^{-18}\ \mathrm{J}}{6.62607004 \times 10^{-34}\ \mathrm{J\,s^{-1}}} = \boxed{3.288033 \times 10^{15}\ \mathrm{s}}$$

(91.1768 nm)
(ultraviolet)

c) molar ionization $= N_A h\nu$

$$= (6.0221408 \times 10^{23}\ \mathrm{mol^{-1}})(2.178674 \times 10^{-18}\ \mathrm{J})$$

$$= 1.31203 \times 10^{6}\ \mathrm{J\,mol^{-1}} = \boxed{1312.03\ \mathrm{kJ\,mol^{-1}}}$$

(Q4) a) The maximum kinetic energy of ejected photo electrons is

$$\frac{1}{2}mv^2 = \text{photon energy} - \text{work function}$$

$$= h\nu - \phi$$

At the threshold frequency ν^*, the photon energy is just sufficient to overcome the work function:

$$0 = h\nu^* - \phi \qquad h\nu^* = \phi$$

$$\nu^* = \frac{\phi}{h}$$

$$= \frac{(4.40\,\text{eV})\ 1.602\times10^{-19}\,\text{J eV}^{-1}}{6.626\times10^{-34}\,\text{J s}}$$

$$\boxed{\nu^* = 1.06\times10^{15}\,\text{s}^{-1}} \qquad (\lambda^* = 282\ \text{nm})$$

b) Will 150 nm ultraviolet photons eject photoelectrons from Cr? yes! $150\ \text{nm} < \lambda^*$

max. electron kinetic energy $= h\nu - \phi$

$$= \frac{hc}{\lambda} - \phi = \frac{6.626\times10^{-34}\,\text{J s}(2.998\times10^{8}\,\text{m s}^{-1})}{150\times10^{-9}\,\text{m}} - 4.40(1.602\times10^{-19})$$

$$= \boxed{6.19\times10^{-19}\,\text{J} = 3.87\ \text{eV}}$$

(300 mW = 0.300 J/s)

Q5 a) How many photons are emitted per second from a 300 mW laser?

energy of one photon = $h\nu$

number of photons per second

$$P = \text{beam power} = h\nu\left(\frac{dN}{dt}\right)$$

$$\frac{dN}{dt} = \frac{P}{h\nu} = \frac{P}{h\frac{c}{\lambda}}$$

$$= \frac{0.300\ \frac{J}{s}}{6.626\times10^{-34}\ J\,s\left(\frac{2.998\times10^{8}\ \frac{m}{s}}{532\times10^{-9}\ m}\right)}$$

$$\boxed{\frac{dN}{dt} = 8.03\times10^{17}\ s^{-1}}$$

b) force generated by the emitted beam? (proposed for interstellar travel using "light sails")

force = rate of change of momentum

= (momentum per photon)(number of photons emitted per second)

$$= \left(\frac{h}{\lambda}\right)\left(\frac{P}{h\frac{c}{\lambda}}\right) = \frac{\text{laser power}}{c}$$

$$= \frac{0.300\ J\,s^{-1}}{2.998\times10^{8}\ m\,s^{-1}} = \boxed{1.00\times10^{-9}\ N}$$