Chem 3502/4502 **Physical Chemistry II (Quantum Mechanics)** 3 Credits

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Christopher J. Cramer

Answers to Homework Set 1

From lecture 2: What is the maximum number of electrons that can be emitted if a potassium surface of work function 2.40 eV absorbs 3.25 x 10^{-3} J of radiation at a wavelength of 300 nm? What is the kinetic energy and velocity of the emitted electrons?

Frequency ν is related to wavelength λ by the equation

$$c = \lambda\nu$$

where c is the speed of light (2.998 x 10^8 m sec^{-1}). Thus, the frequency of the incident light is

$$\begin{aligned}\nu &= \frac{c}{\lambda}\\ &= \frac{\left(2.998\times10^{8}\ \mathrm{m\,sec^{-1}}\right)}{\left(300\times10^{-9}\ \mathrm{m}\right)}\\ &= 9.99\times10^{14}\ \mathrm{sec^{-1}}\end{aligned}$$

The energy of photons having this frequency is computed from the equation

$$E = h\nu$$

where h is Planck's constant (6.626 x 10^{-34} J s). Carrying out the relevant multiplication gives E = 6.62 x 10^{-19} J. Using the conversion factor 1 J = 6.24 x 10^{18} eV gives an energy of 4.13 eV. If the work function is 2.40 eV, this leaves 1.73 eV (2.77 x 10^{-19} J) of energy that is converted into electron kinetic energy. To determine the velocity of the electrons, we use

$$\begin{aligned}v &= \sqrt{\frac{2T}{m_e}}\\ &= \sqrt{\frac{2\times2.77\times10^{-19}\ \mathrm{J}}{9.109\times10^{-31}\ \mathrm{kg}}}\\ &= 7.80\times10^{5}\ \mathrm{m\,s^{-1}}\end{aligned}$$

So, those electrons are ripping right along.

Now, if the total energy absorbed was 3.25 mJ, that would correspond to a number of electrons n_e

$$
\begin{aligned}
n_e &= \frac{3.25 \times 10^{-3}\ \mathrm{J}}{6.62 \times 10^{-19}\ \mathrm{J}\ e^{-1}} \\
&= 4.91 \times 10^{15}\ e
\end{aligned}
$$

if every photon's energy led to emission of an electron.

As a note of historical interest, eV is usually the unit of choice in these matters because one does *not* want to try to measure the kinetic energy of an electron! Instead, one would like to do the much simpler experiment of just seeing if there are electrons there or not. So, one applies a biasing voltage to the metal and measures the voltage at which electrons no longer escape. The energy of interaction between one electron and a potential in volts is 1 eV (hence the name…), so when one finds the voltage V that turns off the electrons, one immediately knows that the electrons would have had the same value of kinetic energy, now in <u>e</u>V, if there *were* no retarding voltage.

From lecture 3: For Li^{2+}, what is the longest wavelength that can be emitted by an electron ending in the n = 3 state?

Using eq. 3-17 for transition frequencies, we recall

$$
\begin{aligned}
\nu &= \frac{\Delta E_{m \to n}}{h} \\
&= \frac{m_e Z^2 e^4}{8 \varepsilon_0^2 h^3} \left(\frac{1}{n^2} - \frac{1}{m^2} \right)
\end{aligned}
$$

where for Li^{2+} Z = 3. The *longest* wavelength emission corresponds to the *least* energy difference between the initial state and the final state. As the final state is n = 3, the nearest initial state is m = 4.

This can be solved by looking up all of the relevant physical constants and getting the units right. I'll do it in a slightly quicker fashion (at least for me). Hydrogen has an ionization potential of 13.605 eV. Ionization potential corresponds to the difference between state n = 1 and state m = infinity, which makes the quantity in parentheses above 1. So, the mess of constants out front times h corresponds to the energy 13.605 eV when Z = 1. For Li, Z = 3, so the prefactor will be 9 times larger in Li^{2+}, corresponding to 122.45 eV. Converting from this energy to frequency involves division by h (4.14×10^{-15} eV s) which gives a frequency of $2.96 \times 10^{16}\ \mathrm{s}^{-1}$ for the prefactor. For the transition itself, we must multiply this constant by (1/9 – 1/16) = 0.0486 which gives a frequency for the transition of $1.44 \times 10^{15}\ s^{-1}$.

To compute wavelength λ we divide c by the last quantity to obtain (2.998×10^{8} m s^{-1} / $1.38 \times 10^{15}\ s^{-1}$) = 209 nm.

For those who prefer the direct approach, the relevant physical constants are:

$m_e = 9.109 \times 10^{-31}$ kg
$e = 1.602 \times 10^{-19}$ C
$\varepsilon_0 = 8.857 \times 10^{-12}$ F m^{-1}
$h = 6.626 \times 10^{-34}$ J s

From Lecture 4: Which of the following functions are eigenfunctions of the operator d^2/dx^2, and what are their corresponding eigenvalues if they are? (a) $ae^{-3x} + be^{-3ix}$, (b) $\sin^2 x$, (c) e^{-x}, (d) $\cos(ax)$, (e) $\sin x + \cos x$.

For these functions to be eigenfunctions they must satisfy the following equation for all values of the independent variable x

$$\frac{d^2}{dx^2} f(x) = Cf(x)$$

where C is a constant. So, to answer the question we simply need to apply the second derivative operator. For the five functions listed, this gives

$$\frac{d^2}{dx^2}\left(ae^{-3x} + be^{-3ix}\right) = 9ae^{-3x} - 9be^{-3ix}$$

$$\frac{d^2}{dx^2}\left(\sin^2 x\right) = 2\left(1 - 2\sin^2 x\right)$$

$$\frac{d^2}{dx^2}\left(e^{-x}\right) = e^{-x}$$

$$\frac{d^2}{dx^2}\left[\cos(ax)\right] = -a^2\cos(ax)$$

$$\frac{d^2}{dx^2}\left[\sin(x) + \cos(x)\right] = -\left[\sin(x) + \cos(x)\right]$$

Evidently, the first two functions are *not* eigenfunctions of the second derivative operator, while the last three are, with eigenvalues of 1, $-a^2$, and –1, respectively.