

Chem 6 sample Exam 2 solutions

1. (a) $(1/2)mv^2 = hv - \phi$. Since 274 nm is the maximum wavelength that will eject electrons, $E = hc/\lambda = \phi$

$$= (6.626 \times 10^{-34} \text{Js}) (3 \times 10^8 \text{ms}^{-1}) / (274 \text{ nm}) (1 \text{m} / 10^9 \text{ nm}) = 7.25 \times 10^{-19} \text{J}$$

Convert to kJ/mol

$$(7.25 \times 10^{-19} \text{J}) (1 \text{kJ} / 1000 \text{J}) (6.02 \times 10^{23} / \text{mol}) = \mathbf{437 \text{ kJ/mol}}$$

(b) $(1/2)mv^2 = hv - \phi$

$$= hc/\lambda - \phi = (6.626 \times 10^{-34} \text{Js}) (3 \times 10^8 \text{ms}^{-1}) / (100 \text{ nm}) (1 \text{m} / 10^9 \text{ nm})$$

$$= 1.99 \times 10^{-18} \text{J} - 7.25 \times 10^{-19} \text{J} = \mathbf{1.26 \times 10^{-18} \text{J}}$$

(c) $\text{KE} = 1/2mv^2 = 1.26 \times 10^{-18} \text{J}$

$$v = [2 (1.26 \times 10^{-18} \text{J}) / m_e]^{1/2}$$

where $m_e = \text{electron mass} = 9.11 \times 10^{-31} \text{kg}$

$$\text{so } v = \mathbf{1.66 \times 10^6 \text{ms}^{-1}}$$

This is less than the speed of light, as it should be, which provides a useful check on the magnitude of the answer.

2. The Heisenberg Uncertainty Principle states that

$$\Delta x \Delta p \geq h/4\pi$$

In this problem, the uncertainty in position, Δx , is 2 times the radius of the nucleus, $2 \times 10^{-15} \text{m}$.

$$\text{Then } \Delta p \geq (h/4\pi)(1/2 \times 10^{-15} \text{m}) = 2.64 \times 10^{-20} \text{kgms}^{-1}$$

Find the uncertainty in the kinetic energy of the electron ΔE

$$\Delta E \geq (\Delta p)^2 / 2m$$

Plug in the electron mass $m_e = 9.11 \times 10^{-31} \text{kg}$ and the value for Δp to get

$$\Delta E \geq 3.82 \times 10^{-10} \text{ J}$$

This **uncertainty** in the energy is greater than the potential energy barrier supposedly holding the electron inside the nucleus! Therefore, the electron cannot really be held inside the nucleus.

[Note: another way of looking at this problem is to find the uncertainty in the electron's velocity, Δv . Since $p=mv$, then $\Delta p = m\Delta v$ or $\Delta v = (\Delta p)/m$

$$= (2.64 \times 10^{-20} \text{ kgms}^{-1}) / 9.11 \times 10^{-31} \text{ kg} = 2.9 \times 10^{10} \text{ ms}^{-1}.$$

The uncertainty in the velocity is thus larger than the speed of light, which is again physically unreasonable. Thus, same conclusion as above -- the electron can't be stuck inside the nucleus.]

3. This is the photoelectric effect applied to an atom instead of a metal surface. Therefore, instead of the work function ϕ (the energy required to remove the electron from the metal surface), you need to use the ionization energy IE (the energy required to remove an electron from the atom.)

$$E = hv = IE + 1/2mv^2$$

Here the energy will be the combined energy of the 2 light beams, since there will be zero kinetic energy (as you are asked for the maximum wavelength)

$$E = hv_1 + hv_2 = hc/\lambda_1 + hc/\lambda_2$$

$$= (418.8 \text{ kJ/mol})(1 \text{ mol}/6.02 \times 10^{23}) (1000 \text{ J/kJ}) = 6.96 \times 10^{-19} \text{ J}$$

Plug in the given wavelength λ_1 and values for h and c to solve for hc/λ_2 :

$$hc/\lambda_2 = 6.96 \times 10^{-19} \text{ J} - (6.626 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ m/s}) / (650 \text{ nm})(1 \text{ m}/10^9 \text{ nm})$$

$$= 3.90 \times 10^{-19} \text{ J}$$

$$\lambda_2 = (6.626 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ m/s}) / (3.90 \times 10^{-19} \text{ J})$$

$$= 5.09 \times 10^{-7} \text{ m} (10^9 \text{ nm/m}) = \mathbf{509 \text{ nm}}$$

4. (a) the de Broglie wavelength is defined as $\lambda = h/p$, so we need to find the momentum $p=mv$ of the electron

Find mv from the quantization of angular momentum for the Bohr atom

$$mvr = nh/2\pi$$

$$mv = nh/2\pi r$$

$$\lambda = h/p = h/mv = 2\pi r/n$$

To find the radius r , use $r_n = (n^2/Z)a_0$

Plug in $n=2$ (first excited state) and $Z=4$ (for Be) and a_0 (Bohr radius) = 0.530\AA

to get

$$r_n = (4/4)a_0 = 0.530\text{\AA} \quad (1\text{m}/10^{10}\text{\AA}) = 5.3 \times 10^{-11}\text{m}. \quad \text{Plug this in to get}$$

$$\lambda = h/p = h/mv = 2\pi r/n$$

$$= 2\pi(5.3 \times 10^{-11}\text{m})/2 = 1.67 \times 10^{-10}\text{m}$$

$$= \mathbf{0.167 \text{ nm}}$$

(b) This is very similar to part (a).

$$mvr = nh/2\pi$$

$$v = nh/2\pi mr$$

$$\text{plug in } r = (n^2/Z)a_0$$

$$v = nh/(2\pi m)((n^2/Z)a_0)$$

$$= nhZ/2\pi mn^2 a_0 \quad \text{Plug in } n=1 \text{ for the ground state}$$

$$\mathbf{v = hZ/2\pi ma_0}$$

So as atomic number Z increases, the velocity of the electron will increase.

5. The key to this problem is to understand that the spectral lines are due to transitions between different energy levels (stationary states). The frequencies of the spectral lines are given by

$$\mathbf{v = C(1/n_f^2 - 1/n_i^2)}$$

where n_f is the quantum number for the final state, n_i is the quantum number for the initial state, and C is a constant, $C = 3.29 \times 10^{15} \text{s}^{-1} Z^2$ [constant since the atomic number Z doesn't change].

Since you are given that the emission lines terminate at the **2nd** excited level of the atom, **$n_f = 3$** .

In order to get the shortest wavelength, you need to maximize the frequency (energy) of the transition, ie **n_i must be infinity** (the transition of interest is the **series limit**.) If you find the constant C from the wavelength of one of the given lines, you can plug it into the frequency equation above, along with $n_i = \text{infinity}$, and find the frequency for the transition. Convert this to the wavelength and you're all done.

For example, the first line is due to the transition $n_i = 4 \rightarrow n_f = 3$. For it,
 $4690 \text{ \AA} (1 \text{ m} / 10^{10} \text{ \AA}) = 4.69 \times 10^{-7} \text{ m}$

$$\text{so } \nu = 3 \times 10^8 \text{ ms}^{-1} / 4.69 \times 10^{-7} \text{ m} = \mathbf{6.40 \times 10^{14} \text{ s}^{-1}}$$

Plug the value for C into the frequency equation to get

$$\nu_1 = 6.40 \times 10^{14} \text{ s}^{-1} = C (1/9 - 1/16)$$

$$\text{to obtain } \mathbf{C = 1.32 \times 10^{16} \text{ s}^{-1}}$$

[You should get similar results for the other 2 lines, which correspond to

$$n_i = 5 \rightarrow n_f = 3 \quad \text{and} \quad n_i = 6 \rightarrow n_f = 3.]$$

Plug this back in with $n_i = \text{infinity}$ to get:

$$\nu_{\text{limit}} = 1.32 \times 10^{16} \text{ s}^{-1} (1/9 - 1/[\text{infinity}]^2) = 1.46 \times 10^{15} \text{ s}^{-1}$$

Convert to wavelength by $\nu = c/\lambda$

$$\text{so } \lambda = 3 \times 10^8 \text{ ms}^{-1} / 1.46 \times 10^{15} \text{ s}^{-1} = 2.05 \times 10^{-7} \text{ m}$$

Convert to \AA [$10^{-10} \text{ m} = 1 \text{ \AA}$] to get **2050 \AA** .

Note, this is smaller than the given wavelengths, so the answer makes sense!

Additional note -- you didn't need to find Z to solve this problem, as shown above. [That's why you were explicitly told not to assume a value for Z]. If you found Z, you should get $Z=2$.

6. (a) The **maxima** correspond to the distances r from the nucleus where the probability of finding the electron is the greatest. The **minima** correspond to the distances r from the nucleus where the probability of finding the electron is the least, zero.

(b) For the correct plots, **see the lecture handout**. These probability distributions should have $n - \ell - 1$ nodes:

for the 3s, $3 - 0 - 1 = 2$ nodes,

for the 3p, $3 - 1 - 1 = 1$ nodes (this fits the plot given)

for the 3d, $3 - 2 - 1 = 0$ nodes

The probability distribution should go to zero at $r=0$ and at large r .

The positions of the largest maxima should be $r(\text{max})_{3d} < r(\text{max})_{3p} < r(\text{max})_{3s}$

The probability of the electron being very close to the nucleus (penetration) should follow the order $s > p > d$.

7. (a) **3d** (b) $m_\ell = 2, 1, 0, -1, -2$

(c) You could draw any of these five d-orbitals. The d_{xz} , d_{xy} , d_{yz} , $d_{x^2-y^2}$, d_{z^2} , which are illustrated in the textbook. Each has 2 angular nodes (nodal planes) since $\ell = 2$.

8. (a) **Be** has the larger first ionization energy because its 2s valence electron is closer to the nucleus (and therefore held more tightly Coulombically) than the Ba 6s one. [The numbers are 899.4 kJ/mol for Be and 502.9 kJ/mol for Ba.]

(b) **I** has a larger electron affinity than **Te**, since it has a larger Z_{eff} -- it has greater nuclear charge, which is inefficiently shielded by the additional 5p electron. [The numbers are 190.15 kJ/mol for **Te** and 295.2 kJ/mol for **I**.]

(c) **K > F⁻ > Na⁺**

K should be the largest of these species, since, unlike the other atoms and ions, it has an additional electron in the 4s orbital, which has greater radial extent than the 3p orbital, which is the valence orbital for the other atoms and ions.

The **F⁻** and **Na⁺** are isoelectronic, so their relative sizes should be governed by the effective nuclear charge, which is in the order **Na⁺** ($Z=11$) > **F⁻** ($Z=9$). The larger Z_{eff} should pull the electrons in closer to the nucleus to give the observed size order.

[The numbers are **K** (atomic radius = 2.27 Å); **Na⁺** (ionic radius = 0.98 Å); **F⁻** (ionic radius = 1.33 Å)]

9. (a) **(ii)** or **both (ii) and (iii)** were acceptable

(b) **(iv)**

(c) **(iii)**

(d) **(ii)**