Solutions of Problem sheet PHY6014- CHEM 6111

1. The volume, $V$, of a sphere is given by:

$$ V = \frac{4}{3}\pi R^3 \quad (1) $$

where $R$ is the radius of the sphere.

The diameter, $D$, of a sphere is:

$$ D = 2R $$

We can write the volume as a function of the diameter, $D$:

$$ V = \frac{4}{3}\pi R^3 = \frac{4}{3}\pi \left(\frac{D}{2}\right)^3 = \frac{\pi D^3}{6} \quad (2) $$

The density of a material, $\rho$, is defined as its mass, $m$, per unit volume, $V$:

$$ \rho = \frac{m}{V} \quad (3) $$

Replacing the volume, given by (2), in (3) and rearranging the equation in order to $m$:

$$ \rho = \frac{m}{V} = \frac{m}{\frac{\pi D^3}{6}} = \frac{6m}{\pi D^3} \Rightarrow $$

$$ m = \frac{\pi D^3 \rho}{6} \quad (4) $$

The Avogadro constant, $N_A$, is by definition the number of atoms in one mol, i.e.:

1 mole_______________________$N_A$ atoms
n mole per nanoparticle_______N atoms per nanoparticle

Thus, the number of atoms per nanoparticle, $N$, is equal to the number of moles per nanoparticle, $n$, multiplied by the Avogadro constant, $N_A$

$$ N = nN_A \quad (5) $$
The molecular weight, $M_w$, is:

$$M_w = \frac{m}{n} \quad (6)$$

we can rearrange and write:

$$n = \frac{m}{M_w} \quad (7)$$

replacing the number of moles per nanoparticle, given by (7), in (5) we have:

$$N = nN_A = \frac{m}{M_w}N_A \quad (8)$$

Using the mass, given by (4), in (8) we can write the number of atoms per nanoparticle as:

$$N = \frac{m}{M_w}N_A = \frac{\pi D^3 \rho}{6M_w}N_A \quad (9)$$

2. The concentration of nanoparticles, $C$, is given by:

$$C = \frac{n}{V} \quad (10)$$

where, $n$ is the number of moles of each nanoparticle and $V$ is the volume of the nanoparticle.

The number of moles per nanoparticle, $n$, is equal to the ratio between the total number of moles of gold atoms in solution, $n_T$, and the number of atoms per nanoparticles, $N$:

$$n = \frac{n_T}{N} \quad (11)$$

replacing (11) in (10):

$$C = \frac{n_T}{NV} \quad (12)$$
Thus, the number of atoms per nanoparticle, $N_T$, is equal to the number of moles of gold atoms in solution, $n_T$, multiplied by the Avogadro constant, $N_A$:

$$N_T = n_T N_A \iff n_T = \frac{N_T}{N_A} \quad (13)$$

Replacing (13) in (12), we can write:

$$C = \frac{n_T}{N_V} = \frac{N_T}{N_A N_V}$$

$$C = \frac{N_T}{N_V N_A} \quad (14)$$

3. Combining the following equations:

$$T = \frac{I}{I_0} = 10^{-\alpha l} = 10^{-\varepsilon lc}$$

$$A = -\log_{10}(T)$$

and using the definition of logarithms, we can write:

$$A = -\log_{10}\left(\frac{I}{I_0}\right)$$

$$A = -\log_{10}\left(\frac{I}{I_0}\right) = -\log_{10}(10^{-\varepsilon lc}) = \varepsilon lc$$
3.1. using the Beer-Lambert equation we have:

\[ A_1 = \varepsilon_1 l c_1 \quad (15) \]

\[ A_2 = \varepsilon_1 l c_1 \quad (15) \]

Dividing (15) by (16):

\[ \frac{A_1}{A_2} = \frac{\varepsilon_1 l c_1}{\varepsilon_2 l c_2} \]

Since nanoparticles in both solutions have the same size, \( \varepsilon_1 = \varepsilon_2 \), and thus:

\[ \frac{A_1}{A_2} = \frac{c_1}{c_2} \Leftrightarrow c_2 = c_1 \frac{A_2}{A_1} \]

Knowing that \( c_1 = 5 \) nM and using the given values for \( A_1 \) and \( A_2 \):

\[ A_1 = 3.7 \]
\[ A_2 = 4.1 \]

\[ c_2 = c_1 \frac{A_2}{A_1} = 5.0 \times \frac{4.1}{3.7} = 5.5 \text{ nM} \]

4. Knowing that:

\[ \Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \quad (15) \]

\[ r = r^* \Rightarrow \frac{d\Delta G}{dr} = 0 \]
The derivative of (15) is:

\[
\frac{d\Delta G}{dr} = \frac{4}{3} 3\pi r^2 \Delta G_v + 4 \times 2\pi r \gamma = 4\pi r^2 \Delta G_v + 8\pi r \gamma = 0 \Leftrightarrow \frac{r^*(4\pi r^2 \Delta G_v + 8\pi r \gamma)}{\Delta G_v} = 0 \Leftrightarrow r^* = 0 \lor r^* = -2 \frac{\gamma}{\Delta G_v}
\]

and thus the critical radius is:

\[
r^* = -2 \frac{\gamma}{\Delta G_v} \quad (16)
\]

Replacing (16) in (15) we have:

\[
\Delta G^* = \frac{4}{3} \pi \left(-2 \frac{\gamma}{\Delta G_v}\right)^3 \Delta G_v + 4\pi \left(-2 \frac{\gamma}{\Delta G_v}\right)^2 \gamma
\]

\[
= \frac{4}{3} \pi \left(-8 \frac{\gamma^3}{\Delta G_v^3}\right) \Delta G_v + 4\pi \left(4 \frac{\gamma^2}{\Delta G_v^2}\right) \gamma = -\frac{32}{3} \pi \frac{\gamma^3}{\Delta G_v^2} + 16\pi \frac{\gamma^3}{\Delta G_v^2} = \frac{16\pi \gamma^3}{3\Delta G_v^2}
\]

\[
\Delta G^* = \frac{16\pi \gamma^3}{3\Delta G_v^2}
\]

5. Knowing that:

\[
E_g(d) = E_g(bulk) + \frac{h^2}{2m_e^*d^2} - 1.8 \frac{e^2}{2\pi \varepsilon \varepsilon_0 d} \quad (17)
\]

\[
h = 6.6261 \times 10^{-34} \text{ J.s}
\]
\[
e = 1.6021 \times 10^{-19} \text{ C}
\]
\[
\varepsilon_{\text{CdSe}} = 5.8
\]
\[
\varepsilon_0 = 8.854 \times 10^{-12} \text{ C}^2/N/ \text{ m}^2
\]
\[
m_e = 0.13m_0
\]
\[
m_h = 0.40m_0
\]
we can calculate the reduced mass of the exciton, \( m^* \):

\[
\frac{1}{m^*} = \frac{1}{m_e} + \frac{1}{m_h} = \frac{1}{0.13m_0} + \frac{1}{0.40m_0} = \frac{0.53}{0.052m_0} \Rightarrow m^* = 0.098 m_0
\]

\[m_0 = 9.1095 \times 10^{-31} \text{ kg}\]

\[m^* = 0.098 m_0 = 0.098 \times 9.1095 \times 10^{-31} = 8.927 \times 10^{-32} \text{ Kg}\]

Using \( eV = 1.602 \times 10^{-19} \text{ J} \), we can calculate the bulk value for the energy gap for CdSe quantum dots in J:

\[E_g (bulk) = 1.74 \text{ eV} = 1.74 \times 1.602 \times 10^{-19}J = 2.79 \times 10^{-19} J\]

Replacing in (17), we can calculate the energy gap of a spherical semiconductor quantum dot with 5 nm of diameter:

\[E_g(5\text{ nm}) = E_g(bulk) + \frac{\hbar^2}{2m^* d^2} - 1.8 \frac{e^2}{2\pi\varepsilon\varepsilon_0 d}
\]

\[= 2.79 \times 10^{-19} + \frac{(6.6261 \times 10^{-34})^2}{2 \times 8.9364 \times 10^{-32} \times (5 \times 10^{-9})^2}
\]

\[-1.8 \frac{(1.6021 \times 10^{-19})^2}{2\pi \times 5.8 \times 8.854 \times 10^{-12} \times 5 \times 10^{-9}} =
\]

\[= 2.79 \times 10^{-19} + 9.83 \times 10^{-20} - 2.86 \times 10^{-20} =
\]

\[= 3.49 \times 10^{-19}J =
\]

\[= \frac{3.49 \times 10^{-18}}{1.602 \times 10^{-19}} \text{ eV} = 2.18 \text{ eV}\]
Identically to a spherical semiconductor quantum dot with 3 nm of diameter, the energy gap is:

\[
E_g(3\text{nm}) = E_g(\text{bulk}) + \frac{\hbar^2}{2m^*d^2} - 1.8 \frac{e^2}{2\pi\epsilon\epsilon_0d}
\]

\[
= 2.79 \times 10^{-19} + \frac{(6.6261 \times 10^{-34})^2}{2 \times 8.9364 \times 10^{-32} \times (3 \times 10^{-9})^2}
\]

\[
-1.8 \frac{(1.6021 \times 10^{-19})^2}{2\pi \times 5.8 \times 8.854 \times 10^{-12} \times 3 \times 10^{-9}} =
\]

\[
= 2.79 \times 10^{-19} + 2.73 \times 10^{-19} - 4.77 \times 10^{-20} =
\]

\[
= 5.04 \times 10^{-19} J =
\]

\[
= \frac{5.04 \times 10^{-19}}{1.602 \times 10^{-19}} \text{eV} = 3.15 \text{eV}
\]

Units’ verification:

\[
E_g(d) = E_g(\text{bulk}) + \frac{\hbar^2}{2m^*d^2} - 1.8 \frac{e^2}{2\pi\epsilon\epsilon_0d}
\]

\[
E_g(d) \propto J
\]

\[
E_g(\text{bulk}) \propto J
\]

Taking into account that: \( J = N. m = \frac{Kg.m^2}{s^2} \)

\[
\frac{\hbar^2}{2m^*d^2} \propto \frac{(J.s)^2}{Kg.m^2} = \frac{J^2s^2}{Kg.m^2} = \frac{J^2}{Kg.m^2} = \frac{J^2}{s^2} = J
\]

\[
-1.8 \frac{e^2}{2\pi\epsilon\epsilon_0d} \propto \frac{C^2}{N.m^\gamma m} = \frac{1}{N.m} = N. m = J
\]
6. The surface energies of the low-index crystallographic facets are:

\[ \gamma_{\{100\}} = 4 \left( \frac{\epsilon}{a^2} \right) \quad (18) \]

\[ \gamma_{\{110\}} = 3\sqrt{2} \left( \frac{\epsilon}{a^2} \right) \quad (19) \]

\[ \gamma_{\{111\}} = 2\sqrt{3} \left( \frac{\epsilon}{a^2} \right) \quad (20) \]

Dividing (19) by (18):

\[ \frac{\gamma_{\{110\}}}{\gamma_{\{100\}}} = \frac{3\sqrt{2} \left( \frac{\epsilon}{a^2} \right)}{4 \left( \frac{\epsilon}{a^2} \right)} = 1.06 \iff \gamma_{\{110\}} = 1.06 \gamma_{\{100\}} \Rightarrow \gamma_{\{110\}} > \gamma_{\{100\}} \]

Dividing (18) by (20):

\[ \frac{\gamma_{\{100\}}}{\gamma_{\{111\}}} = \frac{4 \left( \frac{\epsilon}{a^2} \right)}{2\sqrt{3} \left( \frac{\epsilon}{a^2} \right)} = 1.15 \iff \gamma_{\{100\}} = 1.15 \gamma_{\{111\}} \Rightarrow \gamma_{\{100\}} > \gamma_{\{111\}} \]

If \( \gamma_{\{110\}} > \gamma_{\{100\}} \) and \( \gamma_{\{100\}} > \gamma_{\{111\}} \).

Thus, the energetic sequence is:

\[ \gamma_{\{110\}} > \gamma_{\{100\}} > \gamma_{\{111\}} \]