Solutions of Problem sheet PHY6014- CHEM 6111

1. the volume, *V*, of a sphere is given by:

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

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*:

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

The density of a material, ρ, is defined as its mass, m, per unit volume, *V*:

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

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

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

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

$$N = nN_A \qquad (5)$$

The molecular weight, M_w, is:

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

we can rearrange and write:

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

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

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

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

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

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

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

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:

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

replacing (11) in (10):

$$C = \frac{n_T}{NV} \qquad (12)$$

1 mole________________________N_A atoms
n_T moles in solution_________N_T atoms in solution

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:

$$N_T = n_T N_A \Leftrightarrow n_T = \frac{N_T}{N_A} \qquad (13)$$

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

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

$$C = \frac{N_T}{NVN_A} \qquad (14)$$

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:

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

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

3.1. using the Beer-Lambert equation we have:

$$A_1 = \varepsilon_1 l c_1 \qquad (15)$$

$$A_2 = \varepsilon_1 l c_1 \qquad (15)$$

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:

$$\frac{A_1}{A_2} = \frac{\varepsilon_1 l c_1}{\varepsilon_2 l c_2} = \frac{c_1}{c_2} \Leftrightarrow c_2 = c_1 \frac{A_2}{A_1}$$

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

$$A_1 = 3.7$$

$$A_2 = 4.1$$

$$c_2 = c_1 \frac{A_2}{A_1} = 5.0 \times \frac{4.1}{3.7} = 5.5\, nM$$

4. Knowing that:

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \qquad (15)$$

$$r = r^* \Rightarrow \frac{d\Delta G}{dr} = 0$$

The derivative of (15) is:

$$\frac{d\Delta G}{dr} = \frac{4}{3}3\pi r^{*2}\Delta G_v + 4 \times 2\pi r\gamma = 4\pi r^{*2}\Delta G_v + 8\pi r\gamma = 0 \Leftrightarrow$$

$$r^*(4\pi r^{*2}\Delta G_v + 8\pi r\gamma) = 0 \Leftrightarrow r^* = 0 \vee r^* = -2\frac{\gamma}{\Delta G_v}$$

and thus the critical radius is:

$$r^* = -2\frac{\gamma}{\Delta G_v} \qquad (16)$$

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:

$$E_g(d) = E_g(bulk) + \frac{h^2}{2m^*d^2} - 1.8\frac{e^2}{2\pi\varepsilon\varepsilon_0 d} \qquad (17)$$

h ≈ 6.6261×10^{-34} J.s
$e = 1.6021\times10^{-19}$ C
$\varepsilon_{CdSe} = 5.8$
$\varepsilon_0 = 8.854\times10^{-12}$ $C^2/N/m^2$
$m_e = 0.13m_0$
$m_h = 0.40m_0$

we can calculate the reduced mass of the exciton, m^*:

$$\frac{1}{m^*} = \frac{1}{m_e} + \frac{1}{m_h} = \frac{1}{0.13m_0} + \frac{1}{0.40m_0} = \frac{0.53}{0.052m_0} \Leftrightarrow m^* = 0.098\, m_0$$

$m_0 = 9.1095 \times 10^{-31}$ kg

$$m^* = 0.098\, m_0 = 0.098 \times 9.1095 \times 10^{-31} = 8.927 \times 10^{-32}\ \mathrm{Kg}$$

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

$$Eg\ (bulk) = 1.74\ eV = 1.74 \times 1.602 \times 10^{-19} J = 2.79 \times 10^{-19}\ J$$

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

$$E_g(5nm) = E_g(bulk) + \frac{h^2}{2m^* d^2} - 1.8\frac{e^2}{2\pi\varepsilon\varepsilon_0 d}$$

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

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

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

$$= 3.49 \times 10^{-19}\mathrm{J} =$$

$$= \frac{3.49 \times 10^{-18}}{1.602 \times 10^{-19}}\ \mathrm{eV} = 2.18\ \mathrm{eV}$$

Identically to a spherical semiconductor quantum dot with 3 nm of diameter, the energy gap is:

$$E_g(3nm) = E_g(bulk) + \frac{h^2}{2m^*d^2} - 1.8\frac{e^2}{2\pi\varepsilon\varepsilon_0 d}$$

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

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

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

$$= 5.04 \times 10^{-19}\mathrm{J} =$$

$$= \frac{5.04 \times 10^{-19}}{1.602 \times 10^{-19}}\ \mathrm{eV} = 3.15\ \mathrm{eV}$$

Units' verification:

$$E_g(d) = E_g(bulk) + \frac{h^2}{2m^*d^2} - 1.8\frac{e^2}{2\pi\varepsilon\varepsilon_0 d}$$

$$E_g(d) \propto\ J$$

$$E_g(bulk) \propto\ J$$

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

$$\frac{h^2}{2m^*d^2} \propto \frac{(J.s)^2}{Kg.m^2} = \frac{J^2s^2}{Kg.m^2} = \frac{J^2}{\frac{Kg.m^2}{s^2}} = \frac{J^2}{J} = J$$

$$-1.8\frac{e^2}{2\pi\varepsilon\varepsilon_0 d} \propto \frac{C^2}{\frac{C^2}{N.m^2}m} = \frac{1}{\frac{1}{N.m}} = N.m = J$$

6. The surface energies of the low-index crystallographic facets are:

$$\gamma_{\{1\,0\,0\}} = 4\left(\frac{\varepsilon}{a^2}\right) \qquad (18)$$

$$\gamma_{\{1\,1\,0\}} = 3\sqrt{2}\left(\frac{\varepsilon}{a^2}\right) \qquad (19)$$

$$\gamma_{\{1\,1\,1\}} = 2\sqrt{3}\left(\frac{\varepsilon}{a^2}\right) \qquad (20)$$

Dividing (19) by (18):

$$\frac{\gamma_{\{1\,1\,0\}}}{\gamma_{\{1\,0\,0\}}} = \frac{3\sqrt{2}\left(\frac{\varepsilon}{a^2}\right)}{4\left(\frac{\varepsilon}{a^2}\right)} = 1.06 \Leftrightarrow \gamma_{\{1\,1\,0\}} = 1.06\,\gamma_{\{1\,0\,0\}} \Rightarrow \gamma_{\{1\,1\,0\}} > \gamma_{\{1\,0\,0\}}$$

Dividing (18) by (20):

$$\frac{\gamma_{\{1\,0\,0\}}}{\gamma_{\{1\,1\,1\}}} = \frac{4\left(\frac{\varepsilon}{a^2}\right)}{2\sqrt{3}\left(\frac{\varepsilon}{a^2}\right)} = 1.15 \Leftrightarrow \gamma_{\{1\,0\,0\}} = 1.15\,\gamma_{\{1\,1\,1\}} \Rightarrow \gamma_{\{1\,0\,0\}} > \gamma_{\{1\,1\,1\}}$$

If $\gamma_{\{1\,1\,0\}} > \gamma_{\{1\,0\,0\}}$ and $\gamma_{\{1\,0\,0\}} > \gamma_{\{1\,1\,1\}}$.

Thus, the energetic sequence is:

$\gamma_{\{1\,1\,0\}} > \gamma_{\{1\,0\,0\}} > \gamma_{\{1\,1\,1\}}$