| HW 3 | Inorganic Materials <br> Chemistry | Name: |  |
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| Points: | C7780 | Date: |  |
| Max. 100 points | Fall 2014 | A |  |

1. (20 pts) Mixed metal oxides could be prepared by sol-gel reactions from aqueous solutions of metal salts.
a) (10 pts.) Order these ions $\mathrm{Al}^{3+}, \mathrm{Ba}^{2+}, \mathrm{Cs}^{+}, \mathrm{H}^{+}, \mathrm{Li}^{+}, \mathrm{Mg}^{2+}$ according to the increasing value of hydration enthalpy: $\mathrm{M}^{2+}+\mathrm{n} \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{M}\left(\mathrm{H}_{2} \mathrm{O}\right)_{\mathrm{n}}\right]^{2+} \quad \Delta \mathrm{H}_{\text {hydration }}$
b) (10 pts.) For a hydrolytic reaction $\left[\mathrm{M}\left(\mathrm{H}_{2} \mathrm{O}\right)_{\mathrm{N}}\right]^{2+}+\mathrm{h}_{\mathrm{H}_{2} \mathrm{O}} \rightarrow\left[\mathrm{M}(\mathrm{OH})_{\mathrm{h}}\left(\mathrm{H}_{2} \mathrm{O}\right)_{\mathrm{N}-\mathrm{h}}\right]^{(z-\mathrm{h})+}+\mathrm{h} \mathrm{H}_{3} \mathrm{O}^{+}$
$\Delta \mathrm{H}^{\circ}=(75.2-9.6 \mathrm{z}) \mathrm{kJ} \mathrm{mol}^{-1}$ and $\Delta \mathrm{S}^{\circ}=(-148.4+73.1 \mathrm{z}) \mathrm{J} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$
Write equation that gives a measure of spontaneity of reaction. (Write a formula relating this function to $\Delta \mathrm{H}^{\circ}$ and $\Delta \mathrm{S}^{\circ}$ ). Calculate, for which of the above listed ions is this reaction spontaneous?
2. (20 pts) Green light-emitting diodes can be made from solid solution of GaP and AlP. These two compounds have band gaps of 2.26 and 2.43 eV , respectively. What composition would be needed to prepare $\mathrm{Ga}_{1-\mathrm{x}} \mathrm{Al}_{\mathrm{x}} \mathrm{P}$ with emitted light wavelength of 520 nm ? Band gap varies linearly with composition. Name the law governing this case.
$1 \mathrm{eV}=1.60210^{-19} \mathrm{~J}$. Show your calculation.
3. (20 pts) Mesoporous material MCM-41 consists of regular cylindrical pores of uniform diameter. Relate its total pore volume $\mathrm{V}_{\mathrm{p}}$ to its surface area SA and pore radius r .
4. (20 pts) Alkaline precipitation method for the preparation of mixed ferrites $\left(\mathrm{Mn}_{\mathrm{x}} \mathrm{Zn}_{1-\mathrm{x}}\right) \mathrm{Fe}_{2} \mathrm{O}_{4}$ presents difficulties due to the varying solubilities of the metal hydroxides. $\mathrm{Fe}(\mathrm{OH})_{3}$ starts to precipitate early at pH 2.6 , while $\mathrm{Mn}(\mathrm{OH})_{2}$ precipitates at a much higher pH of 9.4. The $\mathrm{Zn}^{2+}$ cations precipitate at pH 7.6 , but begin to redissolve at pH 9 .
a) Write chemical equations for the precipitation and dissolution of $\mathrm{Zn}^{2+}$ cations.
b) What pH should be used to obtain homogeneous precipitate of mixed hydroxides?
5. (20 pts) What is the relation between the diameter of a spherical nanocrystal ( $\mathrm{D}_{\mathrm{c}}$, large spheres) and the size of tetrahedral pores ( $\mathrm{D}_{\mathrm{p}}$, small sphere). Nanocrystals touch each other, they are close packed. Show your calculation.

