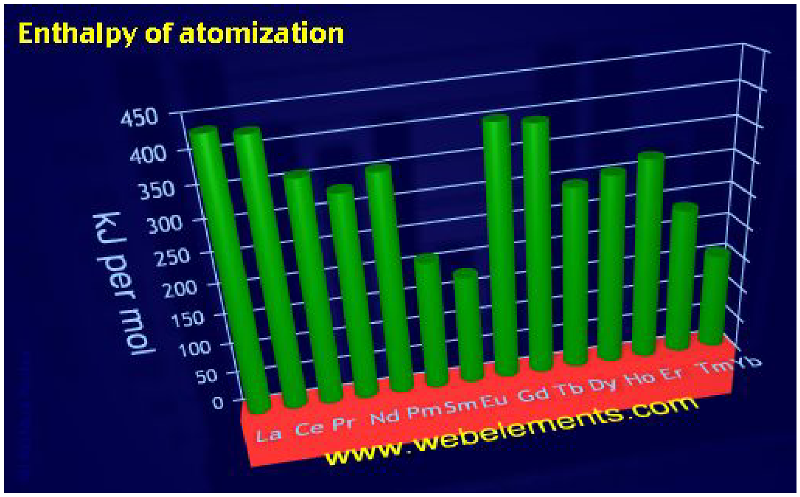
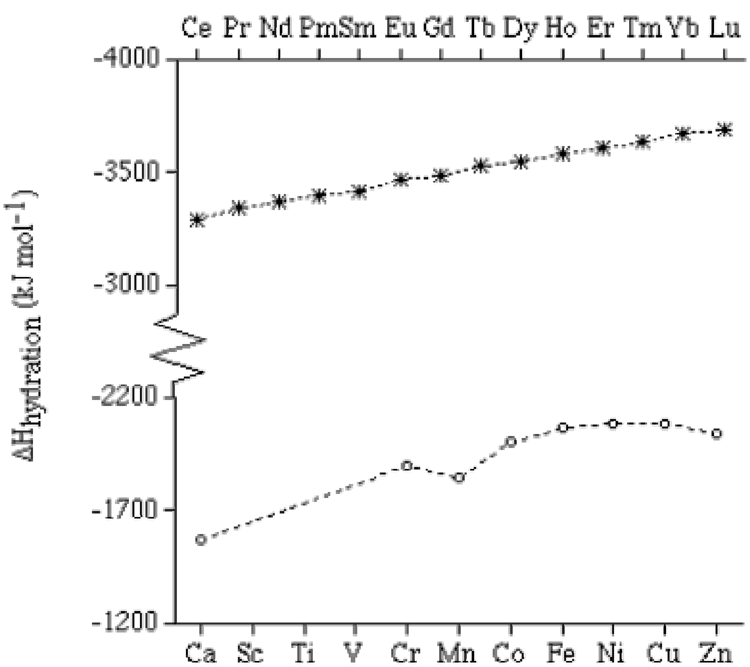
Assignment 2 (5%) due 9.30 am Tuesday 24th February

(a) Plot the atomization energies of the elements La – Lu (use www.webelements.com for the data; plot the data yourself or attach a figure from the site), and account for the shape of your graph (5 marks).



The graph is essentially the inverse of the plot of the 3rd ionization energy. Recall that the Ln metals can be thought of as Ln^{3+} with the 3 electrons delocalized into the conduction band; this generates the metallic bonding but comes at a cost expressed by the ionization energies.

(b) The enthalpies of hydration for Ln^{3+} and M^{2+} (M = 3d metal) ions are shown on the graph below.



Account for

(i) the slope of the lines

Increasing Z_{eff} reduces the size of the ions, increasing charge density and strength of the $H_2O\text{-}M^{n+}$ interaction (according to the Born equation, ΔH_{hyd} is proportional to 1/r).

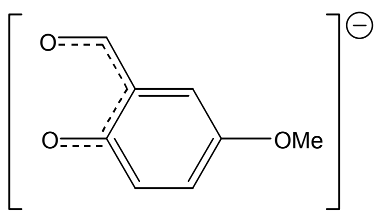
(ii) the shape of the lines

The Ln^{3+} line is straight because the Ln ions decrease steadily in size. The characteristic "double-hump" of the M^{2+} line is due to the effect of ligand field stabilization energy.

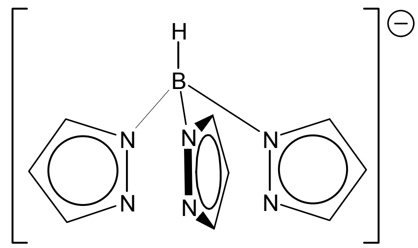
(iii) the relative values of ΔH_{hyd} for Ln^{3+} compared to M^{2+} (7 marks)

Higher charge density (again, Born equation, ΔH_{hyd} is proportional to z_+^2).

(c) To a solution of Eu^{3+} was added three equivalents of each of the ligands shown below:



A



B

A has a solid angle factor of 0.200 and **B** 0.284. Predict which neutral complex Eu$\mathbf{A}_{3-n}\mathbf{B}_n$ (n = 0–3) will precipitate from solution (3 marks).

Calculate which will come out closest to 0.75; this is Eu$\mathbf{AB}_2$ (0.200 + 2 × 0.284 = 0.768). Higher than 0.75 will tend to dissociate a ligand, lower will tend to associate another. 0.75 most closely fulfils the steric requirements of the Ln^{3+} ion.

(d) Complete Table L.4, from your lanthanides handout (2 marks).

Table L.4. Summary of the properties of Ln^{III} ions.

Ln^{3+}	$4f^n$	ground level	color	$g\,[J(J+1)]^{1/2}$	Observed
La	0	$^1S_0$	colorless	0	0
Ce	1	$^2F_{5/2}$	colorless	2.54	2.3-2.5
Pr	2	$^3H_4$	green	3.58	3.4-3.6
Nd	3	$^4I_{9/2}$	lilac	3.62	3.5-3.6
Pm	4	$^5I_4$	pink	2.68	-
Sm	5	$^6H_{5/2}$	yellow	0.85	1.4-1.7
Eu	6	$^7F_0$	pale pink	0	3.3-3.5
Gd	7	$^8S_{7/2}$	colorless	7.94	7.9-8.0

Tb	8	$^{7}F_{6}$	pale pink	9.72	9.5-9.8
Dy	9	$^{6}H_{15/2}$	yellow	10.65	10.4-10.6
Ho	10	$^{5}I_{8}$	yellow	10.60	10.4-10.7
Er	11	$^{4}I_{15/2}$	rose-pink	9.58	9.4-9.6
Tm	12	$^{3}H_{6}$	pale green	7.56	7.1-7.5
Yb	13	$^{2}F_{7/2}$	colorless	4.54	4.3-4.9
Lu	14	$^{1}S_{0}$	colorless	0	0

(e) Using Figure L1 from your lanthanides handout, predict the equilibrium constant for the formation of the 1:1 Y^{3+}:$EDTA^{4-}$ complex in aqueous solution (1 mark).

The atomic radius of Y^{3+} is about the same as Ho^{3+}, so log K ~ 18.5.

(f) Bastnaesite, MCO_3F, contains a mixture of lanthanide and Group 3 metals. Explain why these metals are found together (2 marks).

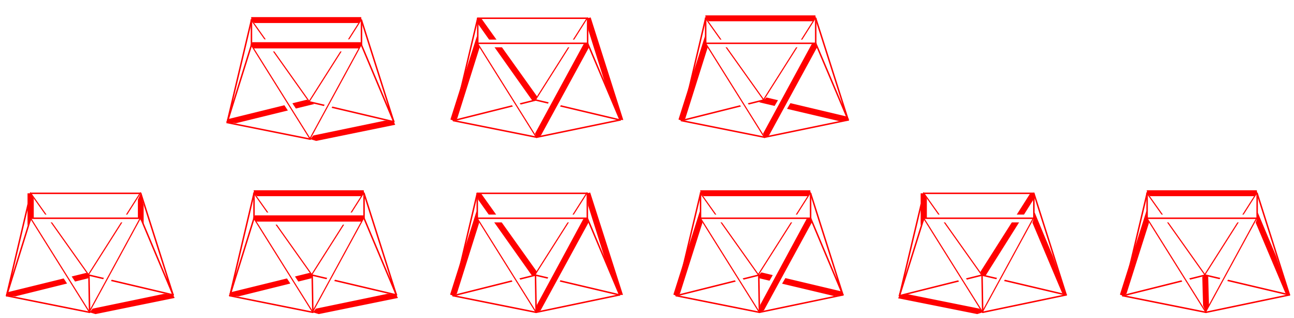
Similar atomic radius, and both are found in the +3 oxidation state. Close similarity in chemistry reflected in geochemistry.

(g) Roasting bastnaesite in air forms a mixture of M_2O_3 and $\mathbf{A}O_2$. Treatment with dilute HCl provides a solution of MCl_3, but $\mathbf{A}O_2$ does not dissolve. The solution may be treated with a reducing agent, which allows separation of another element as $\mathbf{B}SO_4$. The remaining elements are immobilized on an ion-exchange column then eluted with $EDTA^{4-}$. The first complex to elute from the column contains **C**, the last **D**.

Identify **A**, **B**, **C** and **D**, giving your reasoning (6 marks).

A = Ce. Only Ln with water-stable +4 oxidation state.
B = Eu. Only Ln with water-stable +2 oxidation state.
C = Lu. Smallest ion.
D = La. Largest ion.

(h) Draw all the possible isomers for $[M(oxalate)_4]^{4-}$ for both square antiprismatic and bicapped trigonal prismatic coordination geometries (5 marks).



(i) Zr and Hf form ions of formula $[M(BH_4)_5]^{-}$ which appear to be 10 coordinate. Suggest a plausible binding mode for the BH_4^{-} ligand, and compare with the structure of $M(BH_4)_4$ (4 marks).

In $M(BH_4)_4$, each BH_4^- forms 3 B-H-M 3c-2e bonds. The H's are arranged icosahedrally around M. In $[M(BH_4)_5]^-$, each BH_4^- forms 2 B-H-M 3c-2e bonds. The H's are arranged in a bicapped square antiprism about M.

(j) NbF_5 is a volatile solid, whose ^{19}F NMR spectrum shows the presence of three distinct fluorine environments. $NbCl_4$ has a high melting point and is diamagnetic. "$NbBr_{2.33}$" is also diamagnetic, is soluble in water and upon addition of Ag^+, only one-seventh of the bromide precipitates as AgBr. Rationalize this data by describing the structures of these halides (4 marks).

NbF_5 forms tetramers, with octahedrally coordinated Nb linked by linear Nb-F-Nb bridges.
$NbCl_4$ is octahedrally coordinated, forms an ionic lattice in which the Nb atoms are distorted towards each other in pairs, forming Nb-Nb bonds and pairing electrons.
"$NbBr_{2.33}$" is actually Nb_6Br_{14}, which contains $[Nb_6Br_{12}]^{2+}$ clusters linked by bridging Br^- ions (these ions precipitate on addition of Ag^+). It is diamagnetic again because of Nb-Nb bonding.

(k) "Chevrel phases" have the general formula $M_xMo_6Q_8$. Using textbooks or *reliable* internet sources, find out what the structure is, what M_x and Q refer to, why Chevrel phases are of research interest, and what relationship they bear to the metal halide clusters we studied in Special Topic B (6 marks).

M_x = a vacancy, a rare earth element, a transition or main group element
Q = S, Se, Te
Research interest primarily due to superconductivity in presence of strong magnetic fields.
Very similar to metal halide clusters – Mo form octahedron with Mo-Mo bonding, Q cap each face.

(l) Nitrogenase has another metal-containing site not described in class, the "P-cluster". Find out its structure and probable function (5 marks).

The P-cluster pair consists of two $[Fe_4S_4]$ clusters bridged by two Cys thiol ligands and a disulfide bond. It is involved in the electron transfer cascade from ATP to N_2.

(TOTAL: 50 marks)