- Here are short answers to some of the exercise questions, but not those requiring longer verbal answers
- Note that these are not necessarily complete model answers, but rather short answers enough for you to be able to judge whether your own answers are correct or not
- On the last page you can find the evaluation table; please let me know if you find some mistakes e.g. in summing up the points
- Note that even though you have got the full “2” points, your answer may not be perfectly correct; the evaluation scale was roughly as follows:

2 points: all questions addressed with reasonable and mostly correct answers

1.5 points: questions mostly answered but several clear mistakes

1 point: answer sheet returned but only partly answered/a number of mistakes

QUESTIONS: Lecture 1

Which element(s) was/were discovered

- **As a result of huge interest in burning reactions in 1700s: O, N**
- **Based on accurate measurements of air in 1890s: Ar, Kr, Ne, Xe**
- **Thanks to the progress in electrochemical techniques in 1800-1810: alkali and alkaline earth metals**
- **Thanks to the progress in spectroscopy techniques in 1860s: Cs, Rb, Tl, In, He**
- **For the first time from outside of the Earth (1868): He**
- **Much earlier in South America by native Indians than in Europe (in 1750~1850): platinum metals**
- **Based on quantum chemical considerations: Hf (first, several others later)**
- **By a Finnish professor: Y (and Pm from the nature for the first time)**
- **The discovery was rewarded by a Nobel prize in 1906: F**

QUESTIONS: Lecture 2

1. Why copper readily exists in the oxidation state +I ? Give the electron configuration for Cu. **Valence electron configuration: $4s^1 3d^{10}$**

2. How many f electrons (in neutral atom) the following elements have: La, Eu, Lu ?
   La 0 ($6s^2 5d^1$), Eu 7 ($6s^2 5d^0 4f^7$), Lu 14 ($6s^2 5d^1 4f^{14}$)

3. How many f electrons the following ions have: La^{3+}, Eu^{3+}, Eu^{2+} ?
   La^{3+} 0, Eu^{3+} 6, Eu^{2+} 7

4. How many unpaired electrons the following ions have: V^{5+} **(0)**, Cr^{3+} **(3)**, Cu^{2+} **(1)**, Eu^{3+} **(6)**, Tb^{3+}**(6 or 8)**, Yb^{3+}**(1)**, Lu^{3+} **(0)**?

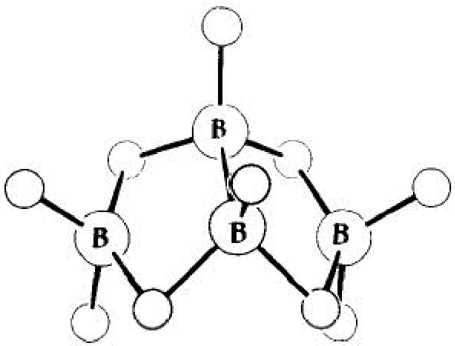
5. Indicate for each of the following pairs the **larger** atom/ion, or state that they are of the same size if that is the case: Na–**K**, **K**–Ca, **Fe^{2+}**–Fe^{3+}, **Ti^{3+}**–Ti^{4+}, Ti^{4+}–**Zr^{4+}**, **Zr^{4+}–Hf^{4+} (same size)**, **La**–Lu

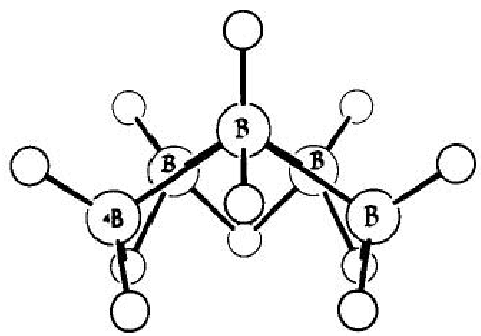
QUESTIONS: Lecture 3

1. **Name four main group elements which you consider to be most unique; also give the most characteristic property for each of these elements.**

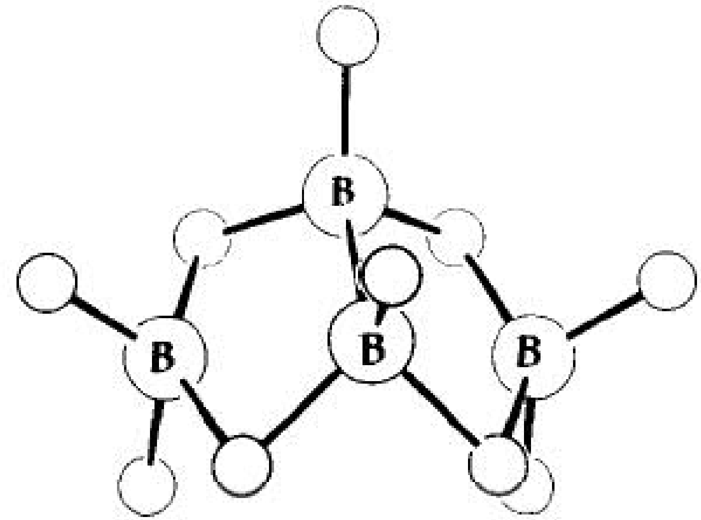
2. **Draw semitopological diagrams for the following boranes: B_4H_{10} and B_5H_{11}**

See the following slides





B_4H_{10}

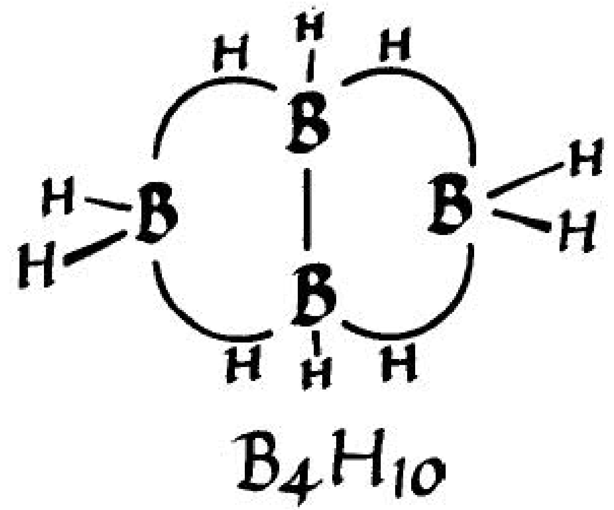


Valence electrons:

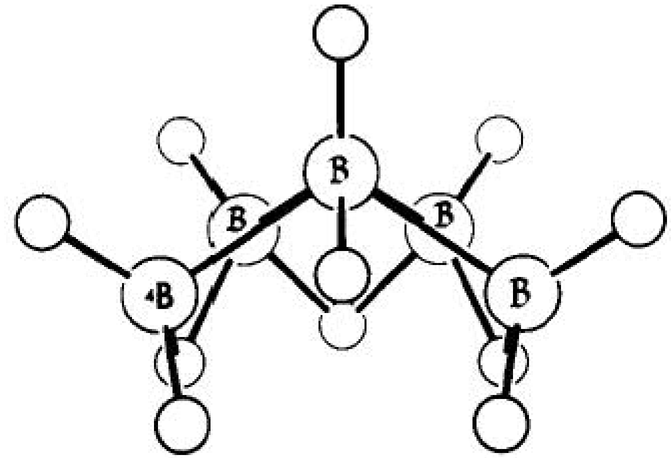
4 x 3e + 10 e = 22 e

Bonds:

6	**2c-2e**	**B-H**	**12 e**
4	**3c-2e**	**B-H-B**	**8 e**
1	**2c-2e**	**B-B**	**2 e**



B_5H_{11}

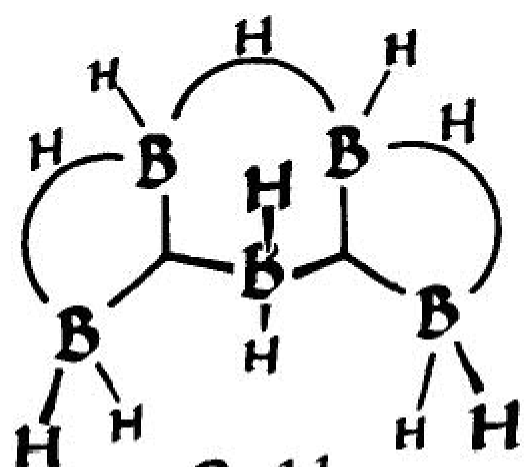


Valence electrons:

5 x 3e + 11 e = 26 e

Bonds:

8	2c-2e	B-H	16 e
3	3c-2e	B-H-B	6 e
2	3c-2e	B-B-B	4 e



B_5H_{11}

QUESTIONS: Lecture 5

Below are Latimer diagrams for bromine in acidic and basic conditions:

Acidic: $BrO_4^- \xrightarrow{+1.82\ V} BrO_3^- \xrightarrow{+1.49\ V} HBrO \xrightarrow{+1.59\ V} Br_2 \xrightarrow{+1.07\ V} Br^-$

Basic: $BrO_4^- \xrightarrow{+0.99\ V} BrO_3^- \xrightarrow{+0.54\ V} HBrO \xrightarrow{+0.45\ V} Br_2 \xrightarrow{+1.07\ V} Br^-$

Draw the corresponding Frost diagrams and answer to the following questions:

see the next slide

(a) Which of the species tend to disproportionate?

Acidic: HBrO

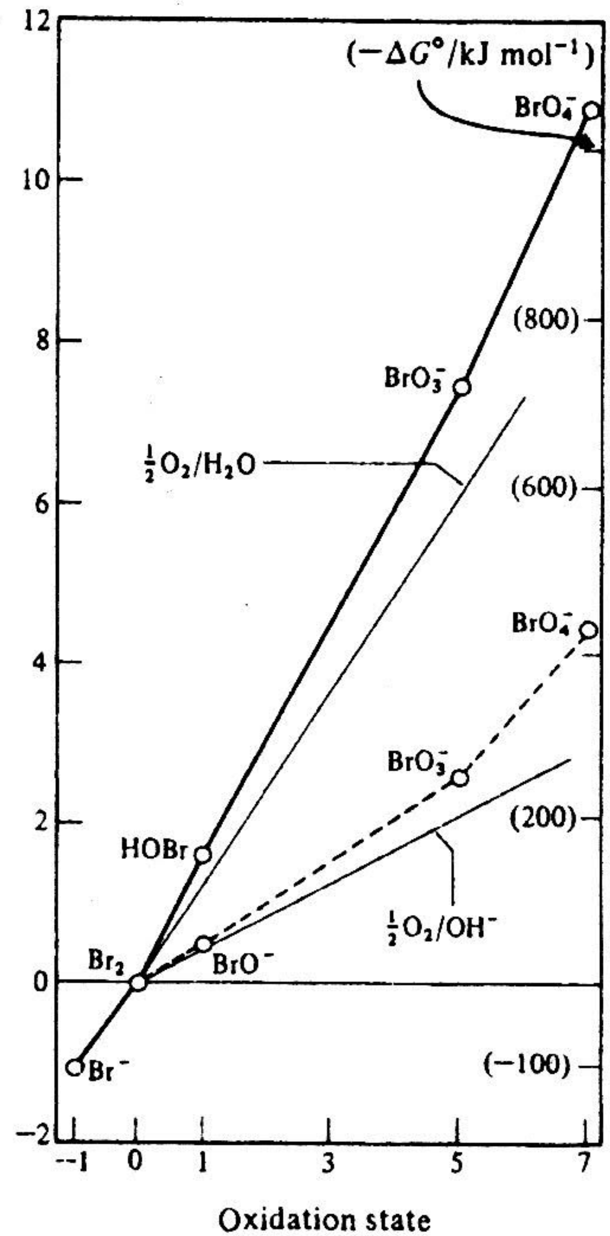
Basic: Br_2

(b) Calculate E^0_{red} for the reduction of BrO_3^- ion to bromine.

For example in acidic: [(4∗1.49)+(1∗1.59)] V / 5 = 1.51 V

(c) Why the last reduction potential is the same in acidic and basic conditions?

This reaction does not involve H or O atoms



(−ΔG°/kJ mol⁻¹)
BrO₄⁻
BrO₃⁻
½O₂/H₂O
(800)
(600)
BrO₄⁻
BrO₃⁻
(200)
HOBr
½O₂/OH⁻
Br₂
BrO⁻
Br⁻
(−100)
12
10
8
6
4
2
0
−2
−1
0
1
3
5
7
Oxidation state

QUESTIONS: Lecture 6

- **In octahedral crystal field, transition metal cations with the electron configurations of d^4, d^5, d^6 and d^7 have the possibility for two spin states. Give the electron configurations for which the same applies in tetrahedral crystal field.**

  d^3, d^4, d^5, d^6

- **How many unpaired electrons the following ions have (assume high spin) in (a) octahedral, and (b) tetrahedral crystal fields: Cr^{3+} (3,3), Mn^{2+} (5,5), Fe^{2+} (4,4), and Co^{+2} (3,3) ?**

- **Which of the following ions is/are (a) colourless (Cu^{+}; d^{10}), (b) lightly coloured (Fe3^{+}; d^5), (c) strongly coloured (Co^{2+}; d^7): Fe^{3+}, Co^{2+}, Cu^{+}?**

QUESTIONS: Lecture 7

- Why Zr and Hf are of the same size ? Give an example of the consequence of the same size ?

- Which of the four elements (Zn, Ti, Zr, Hf) forms compounds at oxidation state +III ?
  Ti

- Coordination number preferences of Zn, Ti, Zr and Hf in their oxides ?
  Zn 4, Ti 6, Zr 7, Hf 7

- Which element can be used as a substituent to enhance electrical conductivity of ZnO ? Would the conductivity be of n- or p-type ? Al^{3+} for Zn^{2+} → n-type

- Which element can be used as a substituent to create oxygen vacancies in ZrO_2 ? Why ? Y^{3+} for Zr^{4+} (charge is balanced through creation of oxygen vacancies; these are needed for the compound to be a good oxide ion conductor)

- How thin is a thin film ?

- Why in ALD technique: - film thickness control is straightforward ?
  - conformal coating is readily achieved ?

QUESTIONS: Lecture 8

1. Explain shortly:

Perovskite

MOF

MLD

2. Name the following metal complexes:

$K_3[Fe(CN)_6]$	potassium hexacyanoferrate(III)
$[CoN_3(NH_3)_5]SO_4$	penta-ammine atsido cobalt(III)sulphate
$NH_4[Cr(NCS)_4(NH_3)_2]$	ammonium diamine tetrakis(isothiocyanato)chromate(III)
$[Cr(H_2O)_6]Cl_3$	hexa-aqua chromium(III)chloride
$[Al(OH)(H_2O)_5]^{2+}$	penta-aqua hydroxo aluminium(III)ion

QUESTIONS: Lecture 9

1. Explain why K_2CrO_4 is colorful even though hexavalent Cr does not have d electrons. Give two other examples of the same phenomenon.

   Electron transfer from O to Cr → Cr^{+V} & O^{-I}

   Similar examples: $KMnO_4$, CrO_3

2. Give three examples of typical 2D materials.

3. Explain the concept of "layer-engineering".

QUESTIONS: Lecture 10

1. **Most stable oxidation state in acidic conditions: Mn (+2), Fe (+2), Co (+2), Ni (+2), Cu (0) (you can see these e.g. from Frost diagrams) ?**

2. **In which condition (acidic or basic) Cu^{+} tends to disproportionate ?**

3. **How many unpaired 3d electrons (oct./hs): Fe^{2+} (4), Fe^{3+} (5), Co^{2+} (3), Co^{3+} (4)?**

4. **Which one of the iron oxides, FeO, Fe_3O_4 and Fe_2O_3, is:**
   - mixed valent Fe_3O_4
   - antiferromagnetic Fe_2O_3
   - ferrimagnetic Fe_3O_4
   - electrically conducting Fe_3O_4 (because mixed valent)

5. **Give the abbreviated name for $HgBa_2Ca_2Cu_3O_8$: Hg-1223**

QUESTIONS: Lecture 11

- Give three examples of seriously critical elements

- Explain three chemistry approaches to solve the problems related to the CRMs

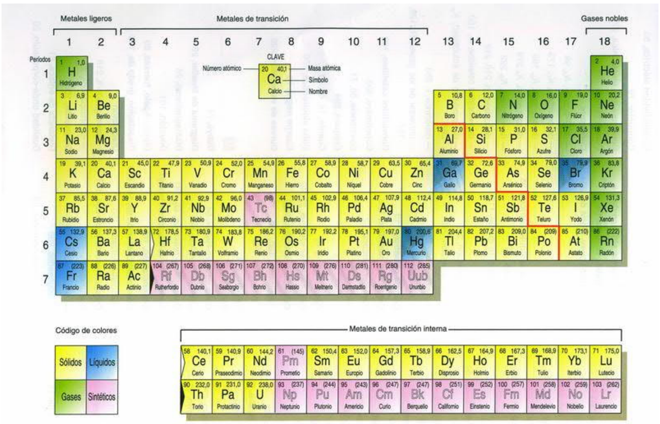
QUESTIONS: Lecture 12

- **List all the possible lanthanoid ions that have 7 f electrons: Eu^{2+}, Gd^{3+}, Tb^{4+}**

- **List all the possible lanthanoid ions that have 14 f electrons: Yb^{2+}, Lu^{3+}**

- **Why Eu has so low melting point? Eu: $6s^2\ 5d^0\ 4f^7$; only two (for lanthanides typically three) electrons per atom participate in metal bond → weaker metal bond → easier to break → lower melting point**

- **Which way you prefer to place the rare earth elements in the periodic table ? Why ?**



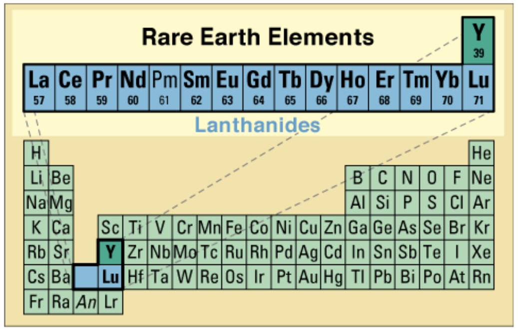
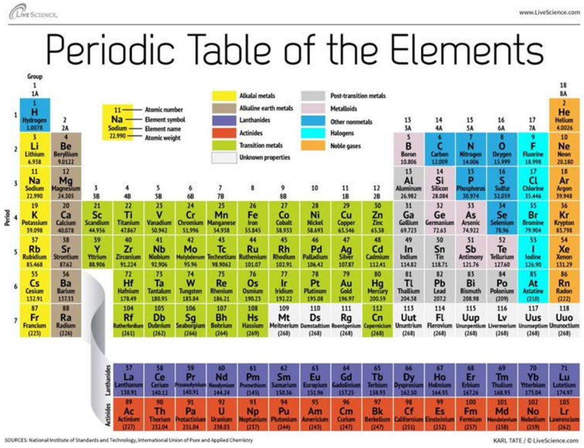


Figure 2. Chemical periodic table delineating the 16 rare earth elements (REE): the lanthanides, La through Lu, plus Y, whose geochemical behavior is virtually identical to that of the heavier lanthanides. Promethium has no long-lived isotopes and occurs naturally on Earth only in vanishingly small quantities. An represents the first 14 actinide elements; Lr is the last actinide.



QUESTIONS: Lecture 13

1. Give the abbreviated name for $HgBa_2Ca_2Cu_3O_8$: Hg-1223

2. Oxidation state of Cu in La_2CuO_4 (+2.0), $La_2CuO_{4.1}$ (+2.2) and $(La_{0.9}Ba_{0.1})_2CuO_4$ (+2.2) ?

3. Are the above copper oxides superconducting ?
Superconductivity requires V(Cu) > +2 → $La_2CuO_{4.1}$ (+2.2) and $(La_{0.9}Ba_{0.1})_2CuO_4$ (+2.2) superconducting

4. Why multilayered structure is important for high-T_c superconductors ?
Non-superconducting metal oxide layers help the compound to form (charge balance) and work for adjusting the Cu valence in the CuO2 layers to be > +2.

5. Why multilayered structure is useful for thermoelectric materials ?
Multilayered structure increases the structural complexity which is important to decrease thermal conductivity without decreasing electrical conductivity.

No	1	2	3	4	5	6	7	8	9	10	11	12	13	∑
528333	2	2	-	-	0.75	-	1.5	1.75	1.25	-	1.75	2	1.75	14.75
876276	2	2	1	2	1.5	0.5	1.5	1.75	2	1.5	1.75	1	1.75	20.25
655206	2	2	2	2	1.5	1.5	2	1.75	2	1.5	2	2	2	24.25
437686	2	2	0.75	2	-	1.5	2	2	1.75	2	2	2	-	18
612760	2	2	2	2	2	-	2	2	2	2	2	-	2	22
652267	2	2	1.75	1.5	1.5	1.5	1.75	1.75	2	1.75	2	1	1.75	22.25
587413	2	2	2	2	2	2	2	2	2	2	2	2	-	24
913605	2	2	2	1.5	1.5	1.5	1.5	1.5	-	1.25	1	0.5	1	17.25
593261	2	1.75	1.75	-	-	-	1.75	-	2	1	1.75	1.75	1.75	15.5
899949	2	2	1.75	2	1.75	1.75	2	1.75	2	1.5	1.5	2	-	22
480235	2	1.75	-	1.5	-	-	-	-	-	-	-	-	-	5.25
606080	2	2	2	2	2	2	2	2	2	2	2	2	2	26
894737	2	2	2	2	-	1	-	-	2	-	-	2	-	13
879561	2	2	1.75	2	2	1	2	2	2	1.5	1.75	1.5	2	23.5
657356	2	2	2	2	2	2	2	2	2	2	2	2	2	26