Chemistry of Elements

CHEM-E4130

2022

- **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 were correct or not.**
- **If you find some mistakes in these answers, please let me know.**

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**
- **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**
- **Based on quantum chemical considerations: Hf (first, several others later)**

QUESTIONS: Lecture 2

1. Give the outer electron configuration for the following neutral atoms: Sc, Mn, Cu. Based on these configurations predict (with short explanation !) the most favourable oxidation states(s) of these elements.

   Sc: $4s^2 3d^1$ → 3+

   Mn: $4s^2 3d^5$ → 2+

   Cu: $4s^1 3d^{10}$ → 1+, 2+

2. How many unpaired electrons the following ions have (please explain shortly !): Mn^{2+}, Fe^{3+}, Ni^{2+}

   Mn^{2+}: $3d^5$ → 5 unpaired electrons

   Fe^{3+}: $3d^5$ → 5 unpaired electrons

   Ni^{2+}: $3d^8$ → 2 unpaired electrons

3. Indicate (with short explanation !) for each of the following pairs the **larger** atom/ion:

   Na–**K**, **K**–Ca, **Fe^{2+}**–Fe^{3+}, **Ti^{3+}**–Ti^{4+}, Ti^{4+}–**Zr^{4+}**, **La**–Lu

QUESTIONS: Lecture 3

1. Each of the following main group elements is specific/unique among all the elements, regarding at least one chemical or physical feature: B, F, He. Explain which feature.

   B: electron-deficient bonds

   F: most electronegative element; only one (-1) possible oxidation state

   He: does not exist in solid state even at temperatures approaching 0 K

2. For a hypothetical group of elements (Aa – Ff) in Periodic Table, the following melting points have been reported: Aa 30 ^{o}C, Bb 100 ^{o}C, Cc 400 ^{o}C, Dd 550 ^{o}C, Ee 500 ^{o}C, Ff 250 ^{o}C. Based on this information, predict (with short explanations) the metallic versus non-metallic nature of each element.
   When combined with OH groups, do you expect Bb to form acidic or basic compound?

   Aa, Bb, Sc non-metals (melting point increases when going downward in the group)

   Ee, Ff metals (melting point decreases when going downward in the group)

   Dd possibly metalloid

   Since Bb is non-metal, its OH compound should be acidic

3. Name the following boron compound, list the types of bonds it has, and draw the so-called semitopological diagram for it: B4H10 : **See next page**

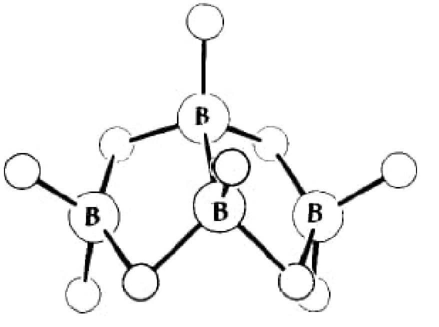
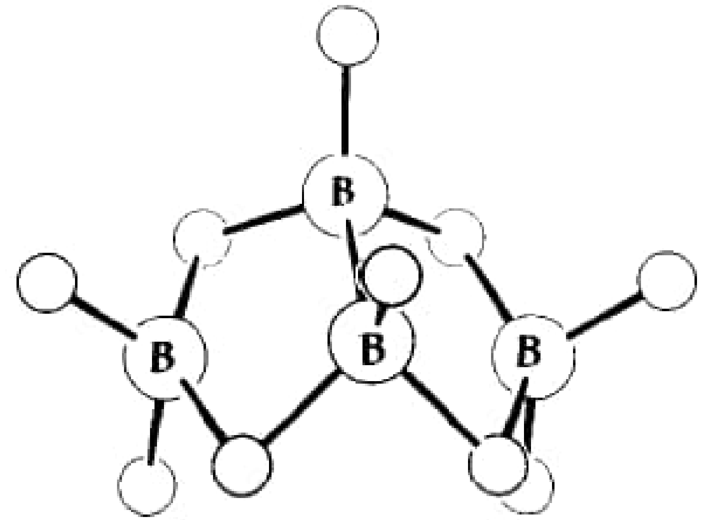


Fig. 6. B_4H_{10}.

B_4H_{10}

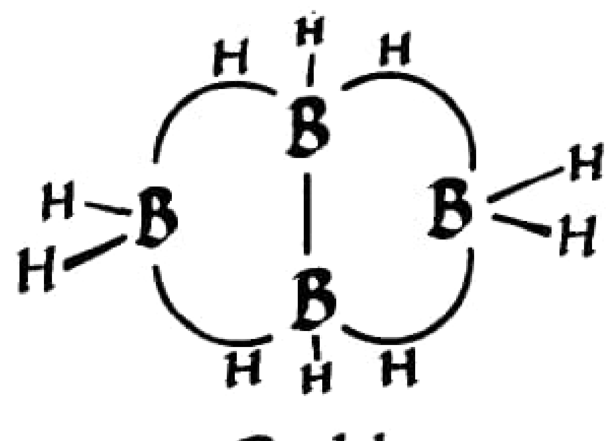


Valence electrons:

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_4H_{10}

QUESTIONS: Lecture 4

1. Among the following four elements, Zn, Ti, Zr, and Hf, only one forms compounds at +III oxidation state. Just by looking at the Periodic Table, predict which element this is. Most importantly, explain why you predicted so. **Ti**

2. Hf is mostly found in nature in trace amounts in Zr minerals. Why it is so easy for Hf to replace some of the Zr in these minerals? **Zr and Hf are of the same size**

3. Which element is commonly used as a substituent to create oxygen vacancies in ZrO_2 ? Why ? **Y ($Y^{3+} \rightarrow Zr^{4+}$; due to charge balance, oxygen content decreases)**

4. Why in ALD technique:
   (a) Film thickness control is straightforward?
   (b) Conformal coating is readily achieved?

QUESTIONS: Lecture 5

1. Give plausible explanations for the following melting point (ºC) comparisons:

Cu 1083 & Zn 420 **(Cu is transition metal, and d electrons may also participate in metal bonds)**

Cr 1860 & Mn 1245 & Fe 1535 **(for Mn $3d^5$ d electrons participate only weakly in metal bonds)**

Fe 1535 & Ru 2282 & Os 3045 **(downward in a group d electron participation in metal bonding increases)**

2. Select among the following ions those which you assume would be color-less or very weakly colored: Ti^{4+}, Ti^{3+}, Mn^{4+}, Mn^{3+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Cu^{+}. Most importantly, motivate your answer with short explanations. **Color-less: Ti^{4+} (d^0), Cu^{+} (d^{10}); Weakly coloured: Fe3^{+} (d^5), Mn^{2+} (d^5)**

3. Why pigments may appear different under sunlight and under fluorescent lighting?

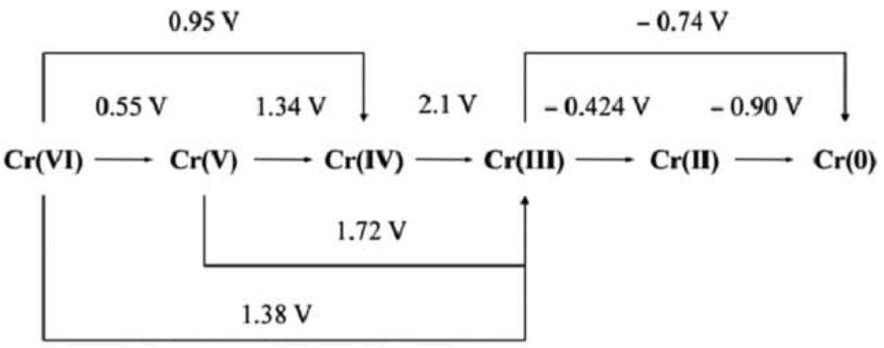
QUESTIONS: Lecture 6

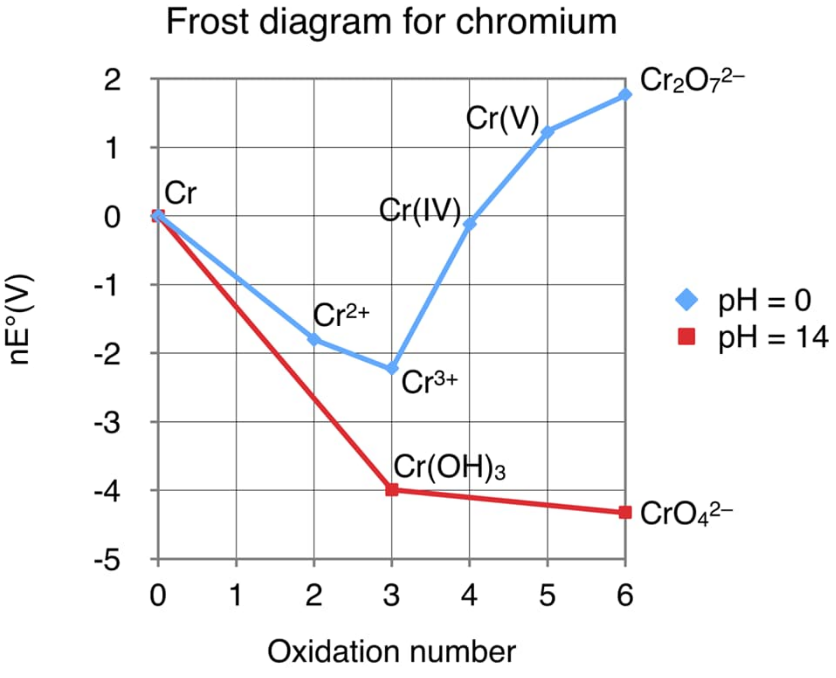
1. Among the following elements, select two, for which disproportionation reaction is not possible: K, Mn, Fe, Cu, Br, Cl, F, O. Explain why!: **K, F (for these elements, only one oxidation state is possible)**

2. Below is the Latimer diagram for chromium in acidic conditions; Draw the corresponding Frost diagram /with some explanations!) and answer to the following questions: See the blue line in the Frost diagram below

   - What is the most stable oxidation state? **+III**

   - For which oxidation states disproportionation tend to occur **? +IV and +V**





QUESTIONS: Lecture 7

1. In octahedral crystal field, transition metal cations with the electron configurations of d^4, d^5, d^6 and d^7 have the choice of showing two different spin states, high-spin state or low-spin state. Give the electron configurations for which the same applies in tetrahedral crystal field. **d^3, d^4, d^5 and d^6**

2. 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)** ?

3. For which of the following ions (assume high-spin) would you expect to see (strong) Jahn-Teller distortion: Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Cu^{2+}. Explain why! **Mn^{3+} (d^4) and Cu^{2+} (d^9)**

QUESTIONS: Lecture 8

1. Which one(s) of the followings may involve both inorganics and organics: **Perovskite**, POM, **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 another example 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 interesting 2D materials; motivate your answers.

3. From your opinion, what is the main advantage of the ALD/MLD technique over solution-based techniques in precise “layer-engineering” of inorganic-organic multi-layer structures? Please elaborate your answer with few sentences of explanation.

QUESTIONS: Lecture 12

- List all the possible lanthanide ions that have 7 f electrons: **Eu^{2+}, Gd^{3+}, Tb^{4+}**
- List all the possible lanthanide ions that have 14 f electrons: **Yb^{2+}, Lu^{3+}**
- Why Eu has so low melting point? Which other lanthanide has exceptionally low melting point ? **$4f^7$ configuration stable, hence only (mostly) the two $6s^2$ electrons participate in metal bonding for Eu. Similar case for Yb.**

QUESTIONS: Lecture 13

1. Most stable oxidation state(s) for (in acidic conditions):

   Mn **(+2)**, Fe **(+2)**, Co **(+2)**, Ni **(+2)**, Cu **(0) (see Frost diagrams)**.

2. How many unpaired 3d electrons in metals: Mn, Fe, Co, Ni, Cu ?

3. Propose a (simple-minded) reason why Mn is not ferromagnetic.

4. Propose a (simple-minded) reason why Cu is not ferromagnetic.

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

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

QUESTIONS: Lecture 14

Select two examples of critical elements, and describe why the element is critical, and how you think would be the best way to mitigate the criticality.

QUESTIONS: Lecture 15

Explain shortly why ZnO:organic superlattice thin films are better thermoelectric materials than ZnO thin films, especially for future wearable applications., and why the ALD/MLD technique is an highly advantageous technique for the fabrication of these films.