

Chemistry of Elements

CHEM-E4130

2023

- **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)**

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

Na–**K**, **K**–Ca, **Fe²⁺**–Fe³⁺, **Ti³⁺**–Ti⁴⁺, Ti⁴⁺–**Zr⁴⁺**, **La**–Lu

QUESTIONS: Lecture 2

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 °C, Bb 100 °C, Cc 400 °C, Dd 550 °C, Ee 500 °C, Ff 250 °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, Cc 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

QUESTIONS: Lecture 3

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 ($\text{Y}^{3+} \rightarrow \text{Zr}^{4+}$; 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 4

1. Give plausible explanations for the following melting point ($^{\circ}\text{C}$) 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: Fe^{3+} (d^5), Mn^{2+} (d^5)**

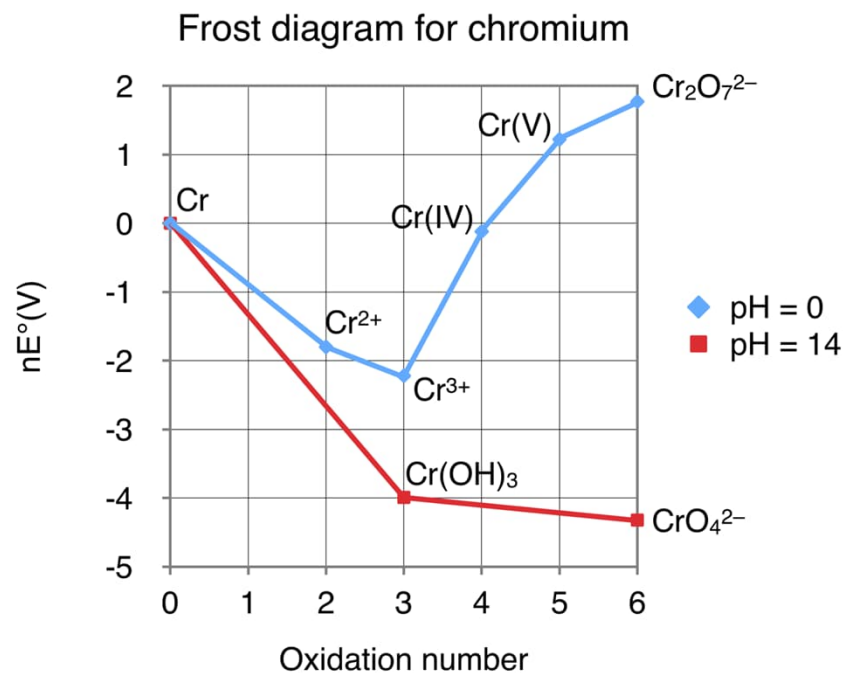
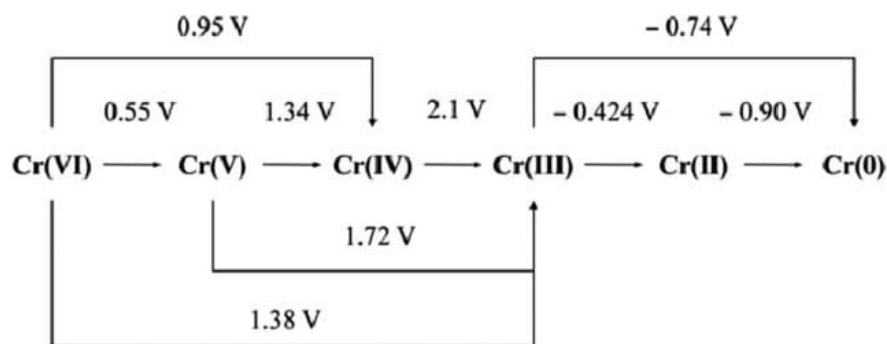
3. Why pigments may appear different under sunlight and under fluorescent lighting?

QUESTIONS: Lecture 5

- 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)**
- 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 6

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 7

1. Which one(s) of the followings may involve both inorganics and organics: **Perovskite**, POM, **MOF**, MLD

2. Name the following metal complexes:



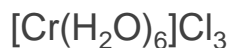
potassium hexacyanoferrate(III)



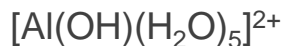
penta-ammine atside cobalt(III)sulphate



ammonium diamine tetrakis(isothiocyanato)chromate(III)



hexa-aqua chromium(III)chloride



penta-aqua hydroxo aluminium(III)ion

QUESTIONS: Lecture 8

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 \rightarrow 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 9

1. How many unpaired 3d electrons in metals:
Mn **(5)**, Fe **(4)**, Co **(3)**, Ni **(2)**, Cu **(0)** ?
2. Propose a (simple-minded) reason why Mn is not ferromagnetic.
3. Propose a (simple-minded) reason why Cu is not ferromagnetic.
4. How many unpaired 3d electrons (oct./hs): Fe²⁺ **(4)**, Fe³⁺ **(5)**
5. Which one(s) of the iron oxides, FeO, Fe₃O₄ and Fe₂O₃, is/are:
 - mixed valent **Fe₃O₄**
 - antiferromagnetic **FeO, Fe₂O₃**
 - ferrimagnetic **Fe₃O₄**
 - electrically conducting **Fe₃O₄ (because mixed valent)**

QUESTIONS: Lecture 10

Which one(s) of the following materials are **superconducting** ? Most importantly, explain/motivate each of your choices !

- **Hg**

- Cu

- CuO

- La_2CuO_4

- **$\text{La}_2\text{CuO}_{4.1}$**

- **$(\text{La}_{0.9}\text{Ba}_{0.1})_2\text{CuO}_4$**

- **$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.2}$**

QUESTIONS: Lecture 12

- ▶ List all the possible lanthanide ions that have 7 f electrons: **Eu²⁺, Gd³⁺, Tb⁴⁺**
- ▶ List all the possible lanthanide ions that have 14 f electrons: **Yb²⁺, Lu³⁺**
- ▶ Why Eu has so low melting point? Which other lanthanide has exceptionally low melting point ? **4f⁷ configuration stable, hence only (mostly) the two 6s² electrons participate in metal bonding for Eu. Similar case for Yb.**

QUESTIONS: Lecture 13

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.