LECTURE SCHEDULE

	Date		Topic
1.	Wed	28.10.	Course Introduction & Short Review of the Elements
2.	Fri	30.10.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	06.11.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Wed	11.11.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
5.	Fri	13.11.	Redox Chemistry
6.	Mon	16.11.	Transition Metals: General Aspects & Crystal Field Theory
7.	Wed	18.11.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
8.	Fri	20.11.	V, Nb, Ta & Metal Complexes and MOFs
9.	Mon	23.11.	Cr, Mo, W & 2D materials
10	Wed	25.11.	Mn, Fe, Co, Ni, Cu & Magnetism and Superconductivity
11.	Fri	27.11.	Resources of Elements & Rare/Critical Elements & Element Substitutions
12.	Mon	30.11.	Lanthanoids + Actinoids & Pigments & Luminescence & Upconversion
13.	Wed	02.12.	Inorganic Materials Chemistry Research

EXAM: Thu Dec 10, 9:00-12:00 Ke1

PRESENTATION TOPICS/SCHEDULE

Wed	**18.11.**	**Ti: Ahonen & Ivanoff**
Mon	**23.11.**	**Mo: Kittilä & Kattelus**
Wed	**25.11.**	**Mn: Wang & Tran**
		Ru: Mäki & Juopperi
Fri	**27.11.**	**In: Suortti & Räsänen**
		Te: Kuusivaara & Nasim
Mon	**30.11.**	**U: Musikka & Seppänen**

INSTRUCTIONS for SEMINAR PRESENTATIONS

- Presentation (15 ~ 20 min) is given in a group of two persons
- It will be evaluated in the scale: 10 ~ 25 points
- The presentation is given in English, and the slides will be put up in MyCourses afterwards
- Content of the presentation:

- ELEMENT: discovery, origin of name, abundancy, world production, special features if any, etc.

- CHEMISTRY: position in Periodic Table, electronic configuration, oxidation states, metal and ionic sizes, reactivity, etc.

- COMPOUNDS: examples of important compounds, their properties and applications, etc.

- SPECIFIC FUNCTIONALITIES/APPLICATIONS: Two or three examples of exciting functionalities/applications/special consideration of the element or its compounds. Here the meaning is to discuss why this specific topic is important /unique to the element in focus. You will be given one or two scientific articles for a reference (you can use these papers but it is not mandatory), and you should search for couple of more (recent) articles to be discussed in the presentation.

QUESTIONS: Lecture 5

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

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

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

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

(a) Which of the species tend to disproportionate?

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

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

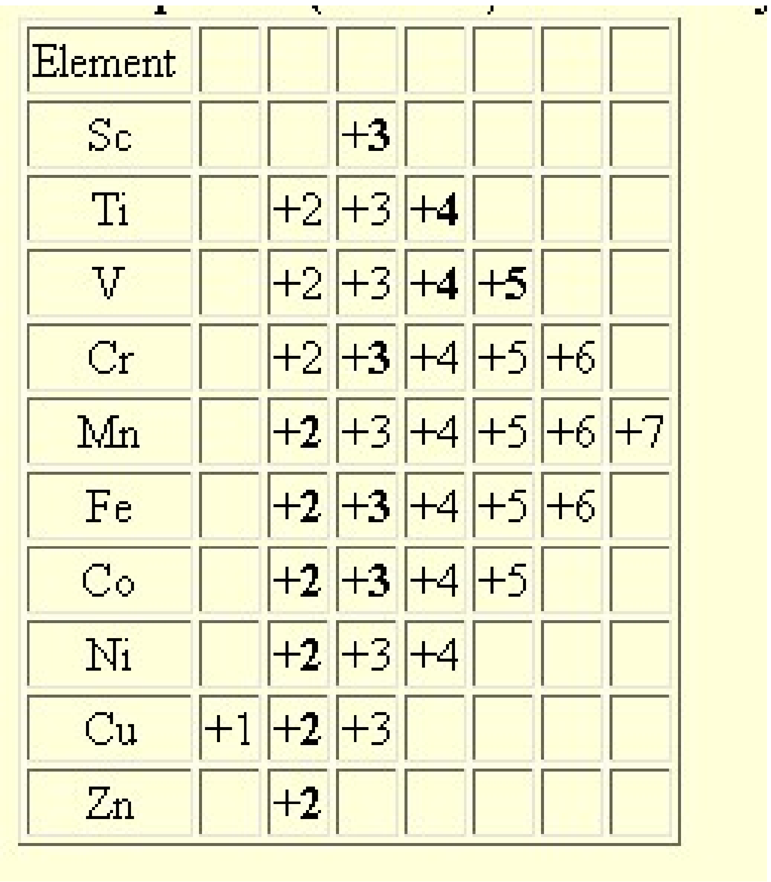
REDOX CHEMISTRY

- Electron configuration
- Oxidation/valence states & ion charge
- Latimer diagram
- Frost diagram — in SOLUTION
- [Pourbaix diagram (corrosion)]
- Ellingham diagram (metal/oxide)
- Oxygen (non)stoichiometry
- Mixed valency — in SOLID
- Disproportionation
- Valence separation
- Charge ordering

REF: CHEM-E4100 Laboratory projects in chemistry

Electron configurations of 3d metals: $1s^22s^22p^63s^23p^64s^23d^x$

			3d				4s
Scandium (Sc)	↑						↑↓
Titanium (Ti)	↑	↑					↑↓
Vanadium (V)	↑	↑	↑				↑↓
Chromium (Cr)	↑	↑	↑	↑	↑		↑
Manganese (Mn)	↑	↑	↑	↑	↑		↑↓
Iron (Fe)	↑↓	↑	↑	↑	↑		↑↓
Koboltti (Co)	↑↓	↑↓	↑	↑	↑		↑↓
Nikkeli (Ni)	↑↓	↑↓	↑↓	↑	↑		↑↓
Kupari (Cu)	↑↓	↑↓	↑↓	↑↓	↑↓		↑
[Sinkki (Zn)]	↑↓	↑↓	↑↓	↑↓	↑↓		↑↓



Element							
Sc			**+3**				
Ti		+2	+3	**+4**			
V		+2	+3	**+4**	**+5**		
Cr		+2	**+3**	+4	+5	+6	
Mn		**+2**	+3	+4	+5	+6	+7
Fe		**+2**	**+3**	+4	+5	+6	
Co		**+2**	**+3**	+4	+5		
Ni		**+2**	+3	+4			
Cu	+1	**+2**	+3				
Zn		**+2**					

OXIDATION STATES

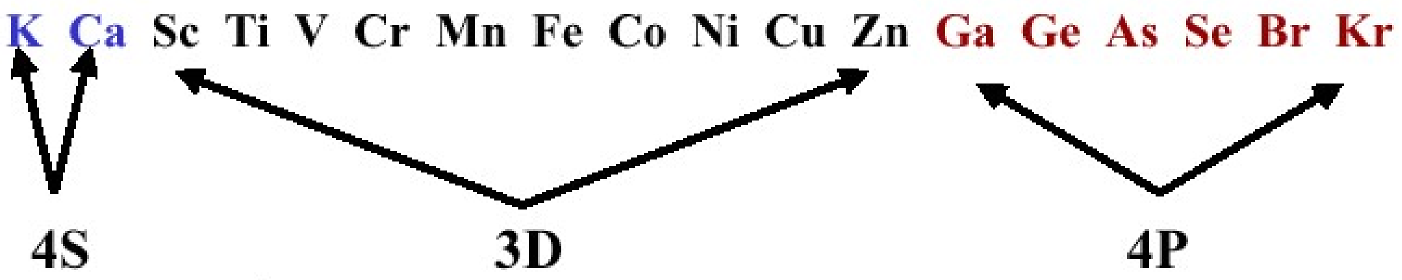
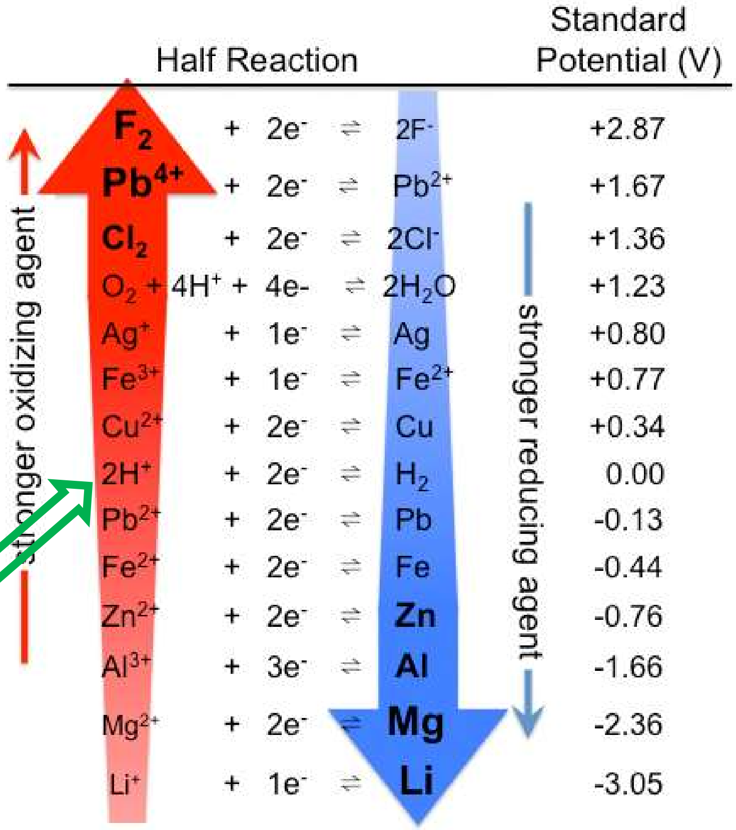


Figure 1. The 4th row of the periodic table. The transition metals are the elements that range from Sc (Scandium) to Zn (Zinc).

Standard reduction potentials (E^0_{red})



Half Reaction	Standard Potential (V)
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.67
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Ag^+ + 1e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$	+0.77
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.36
$Li^+ + 1e^- \rightleftharpoons Li$	-3.05

REDOX REACTIONS

- **Separated into two half-reactions**
- **E^0: standard electrode potential**
  [$2H^+(aq) + 2e^- \rightarrow H_2(g)$; $E^0 = 0.00\,V$]
- **Nernst: $E = E^0 - RT/nF \times \ln [prod]/[react]$**
- **Gibbs free energy: $\Delta G^0 = -nFE^0$**
- **NOTE: E^0_{red} values are not directly additive, but ΔG^0 values are !!!**

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $\quad E^0_{red} = +0.77\,V$

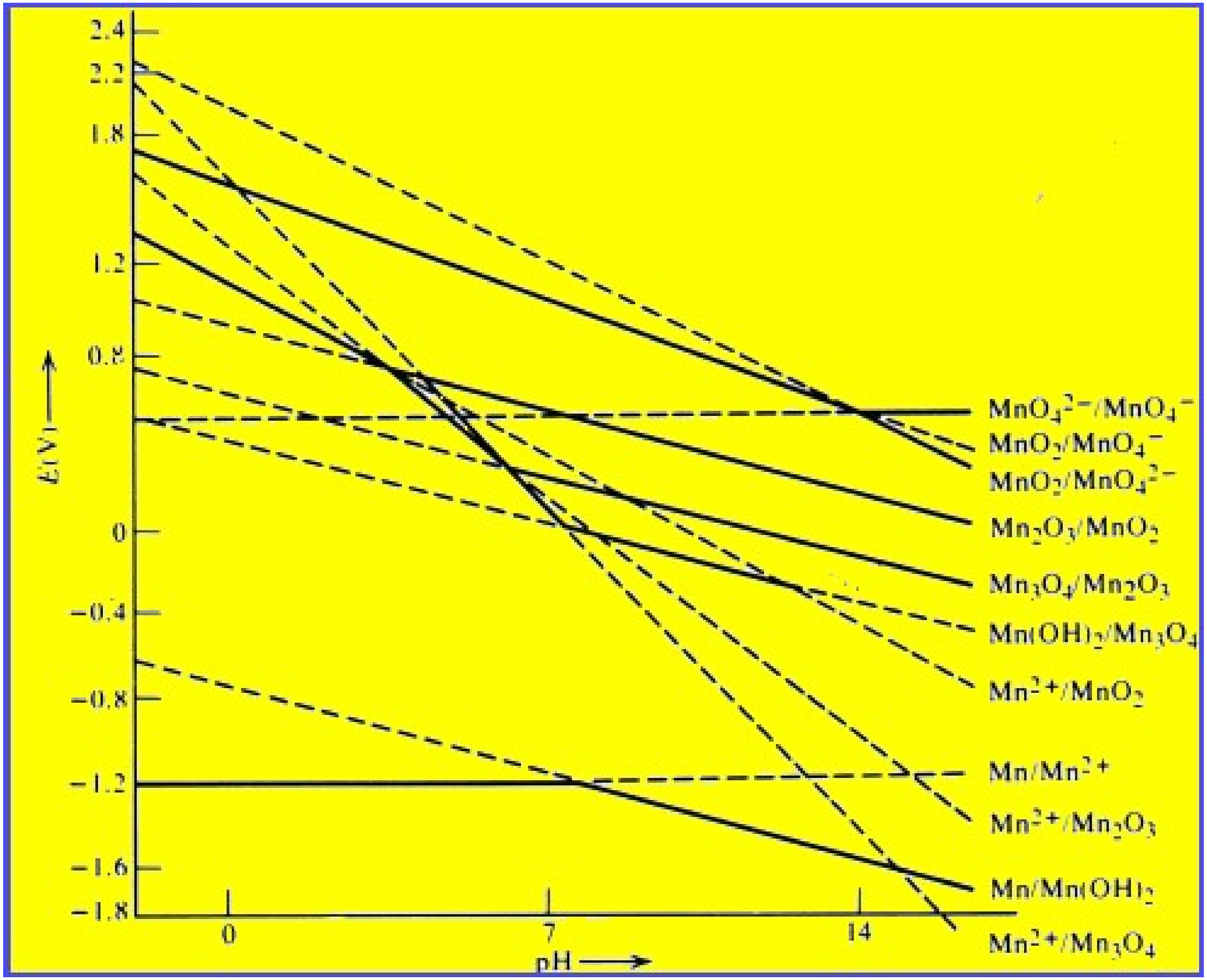
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $\quad E^0_{red} = -0.44\,V$

$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$ $\quad E^0_{red} = 1/3(1 \times 0.77 - 2 \times 0.44)\,V = -0.04\,V$

R: Gas constant = 8.314 J·mol⁻¹·K⁻¹

F: Faraday constant (magnitude of electric charge per mole of electrons) = 96 485 C mol⁻¹

Redox potentials may depend on pH STRONGLY !!!



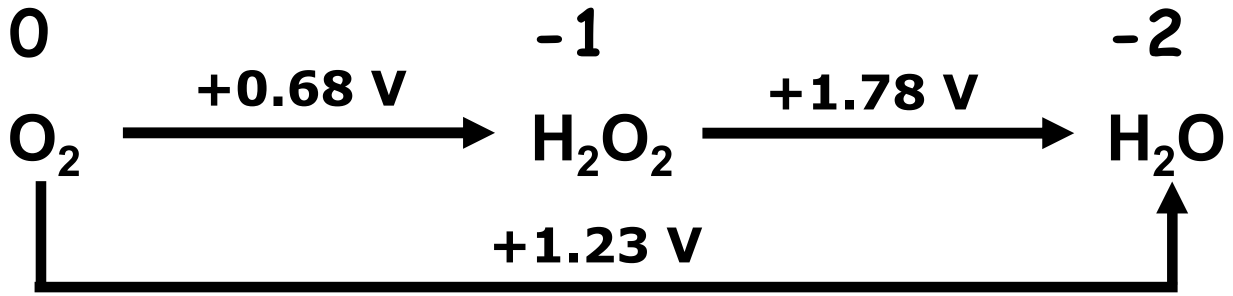
LATIMER DIAGRAM

- Simple visual representation of the standard reduction potentials (E^0_{red}) between different oxidation states of an element
- Involves: metal, cations, oxo-ions, hydroxides & oxides
- OFTEN: Highest oxidation state is on the left, lowest on the right
- More positive E^0_{red} → more readily the species on the left is reduced to the species on the right

$$\begin{tikzcd}
+6 & +3 & +2 & 0 \\
FeO_4^{2-} \arrow[r, "+2.20\ V"] & Fe^{3+} \arrow[r, "+0.77\ V"] \arrow[rr, bend right, "-0.04\ V"] & Fe^{2+} \arrow[r, "-0.44\ V"] & Fe
\end{tikzcd}$$

Disproportionation: EXAMPLE: oxygen

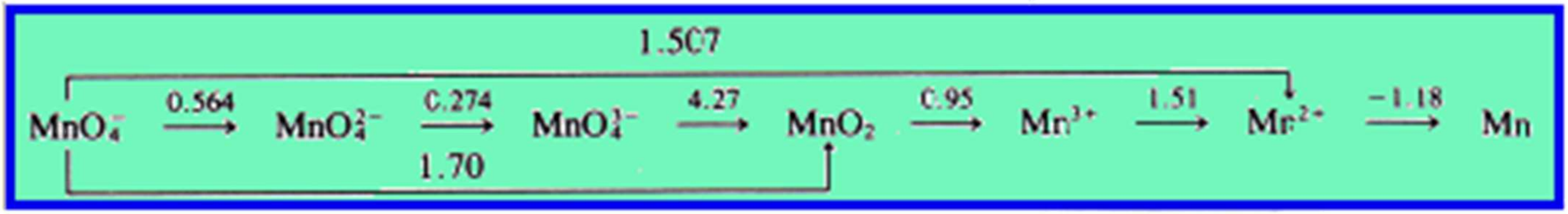
- H_2O_2 is readily reduced to H_2O
- H_2O_2 is NOT so readily oxidized to O_2
- However: +1.78 V > +0.68 V
- H_2O_2 disproportionates into oxygen and water:
  - in practice the reaction is slow without a catalyst



$$O_2 \xrightarrow{+0.68\ V} H_2O_2 \xrightarrow{+1.78\ V} H_2O$$

DISPROPORTIONATION:
chemical redox reaction where the same species (atom/ion/molecule) is simultaneously oxidized and reduced

Which manganese species tend to disportionate ?



$$\begin{tikzcd}
MnO_4^- \arrow[r, "0.564"] \arrow[rrrrr, bend left, "1.507"] \arrow[rrr, bend right, "1.70"'] & MnO_4^{2-} \arrow[r, "0.274"] & MnO_4^{3-} \arrow[r, "4.27"] & MnO_2 \arrow[r, "0.95"] & Mn^{3+} \arrow[r, "1.51"] & Mn^{2+} \arrow[r, "-1.18"] & Mn
\end{tikzcd}$$

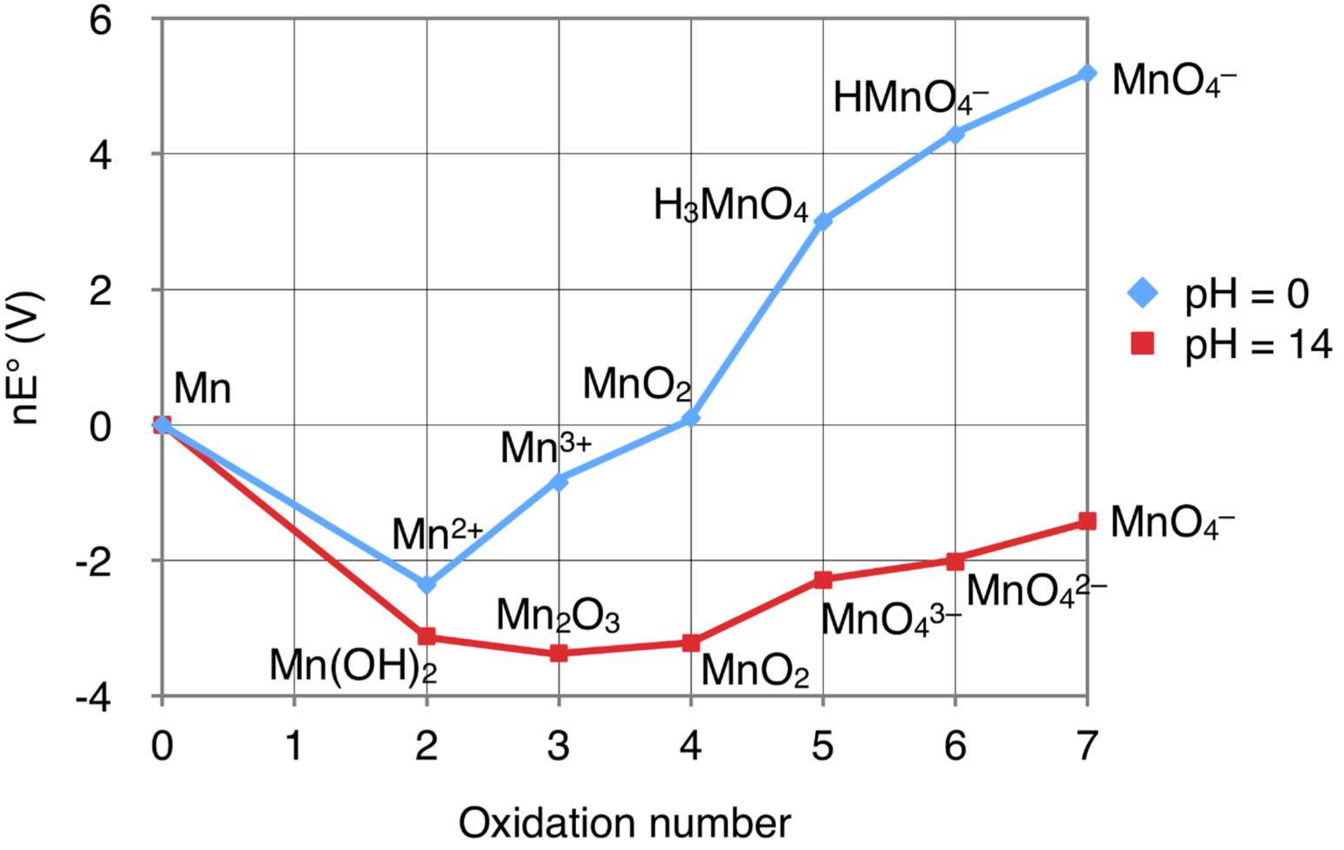
FROST DIAGRAM

- **2D version of the Latimer diagram**
- **The number of moving electrons is taken into account ($-n \times E^0_{red}$)**
- **x-axis: oxidation state**
- **y-axis: ΔG (in F)**
- **For pure metal: y = 0 V**
- **From the diagram we can see:**
  relative stabilities of the species with different oxidation states

Gibbs free energy: $\Delta G^0 = -nFE^0$

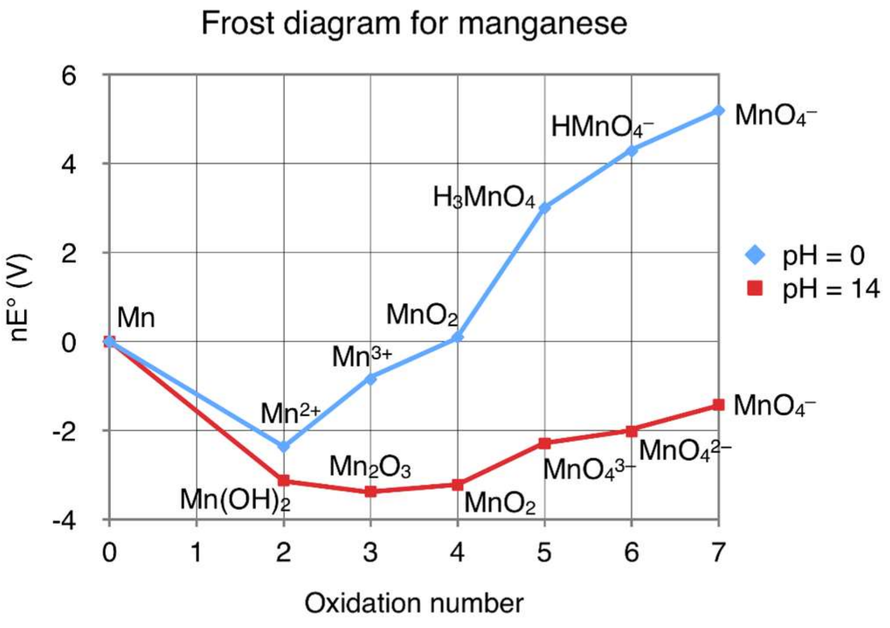
Latimer diagram (acidic conditions)

Frost diagram for manganese



What can we see from the Frost diagram

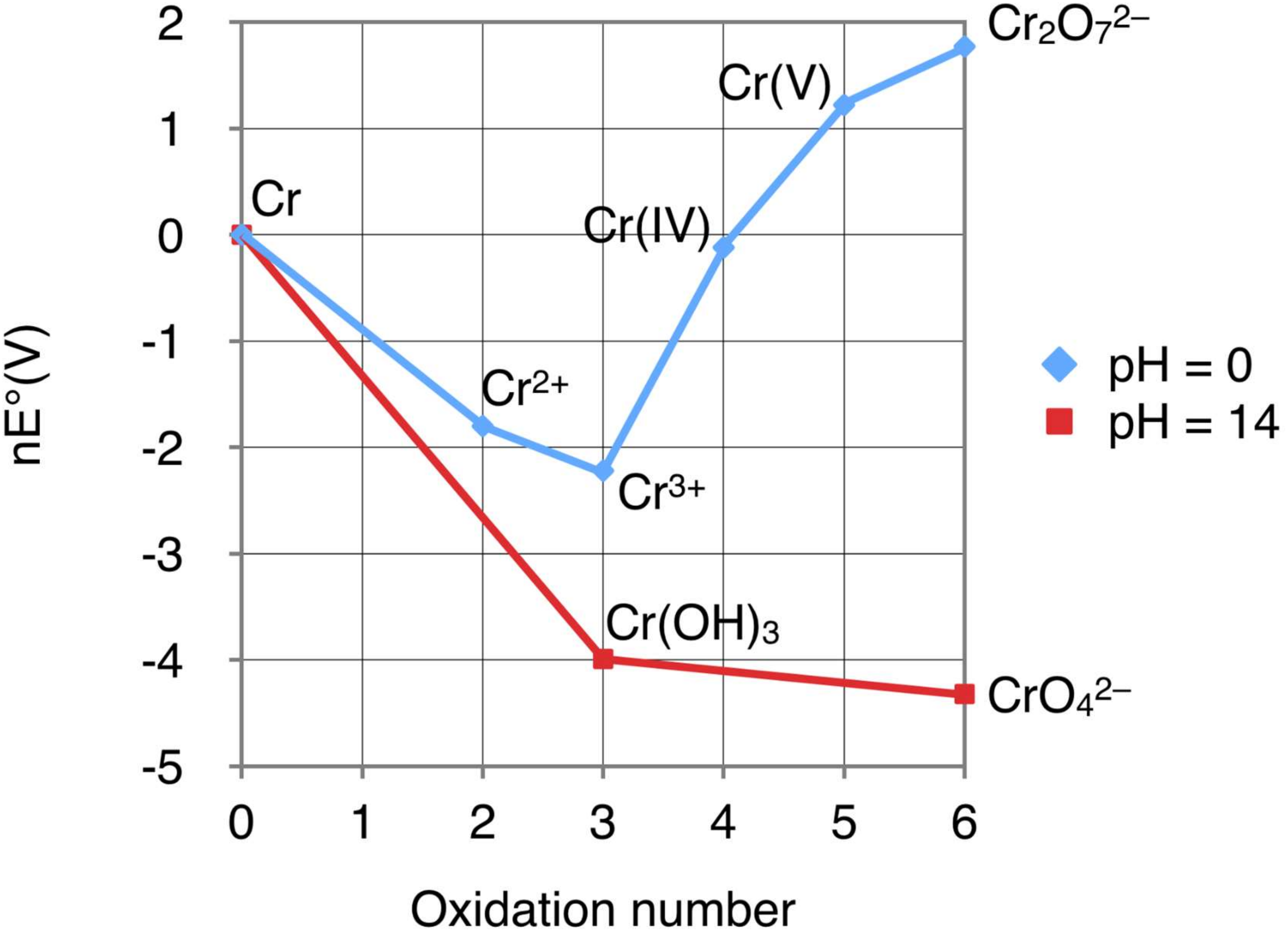
- **The lower the position of the species in the diagram is, the more stable (in terms of redox behavior) the species is**
- **A species that is on a convex (*kupera*) curve (compared to its neighbors) tends to disproportionate**
- **A species that is on a concave (*kovera*) curve (compared to its neighbors) does not disproportionate**

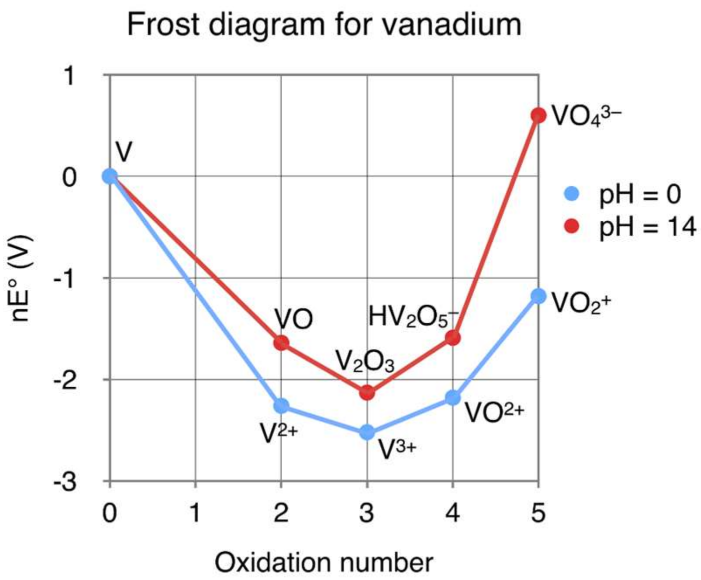


Manganese (acidic cond)

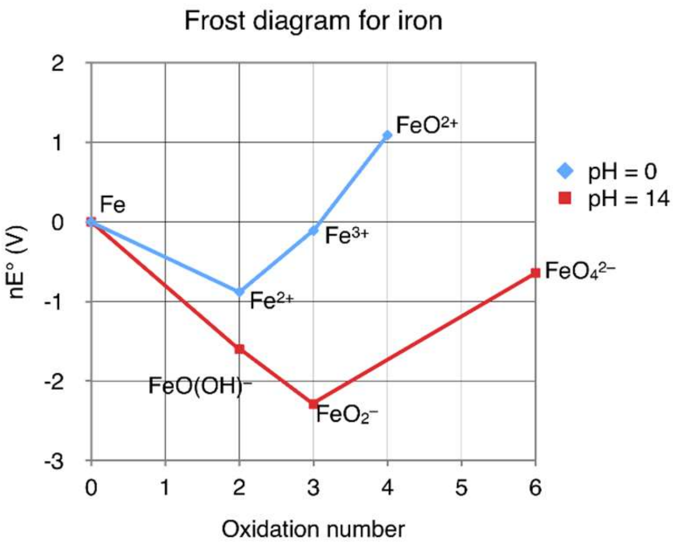
- Mn^{2+}: most stable
- MnO_4^-: strong oxidizer
- Mn^{3+} and MnO_4^{3-} tend to disproportionate
- MnO_2: does not disproportionate
- NOTE: According to thermodynamics MnO_4^- should be reduced to Mn^{2+}; this reaction is however slow without catalyst, explaining why MnO_4^- solutions can be stored in laboratory

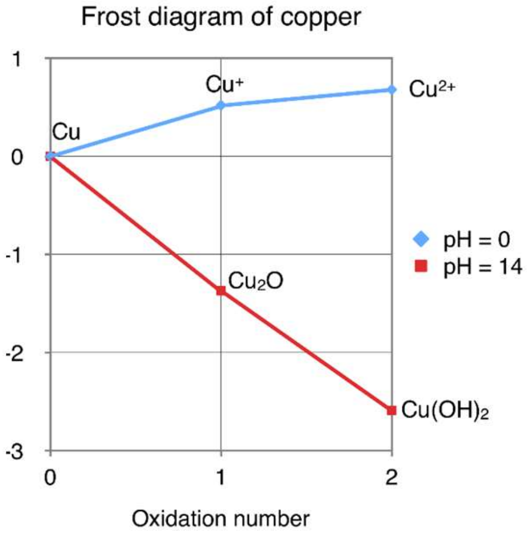
Frost diagram for chromium

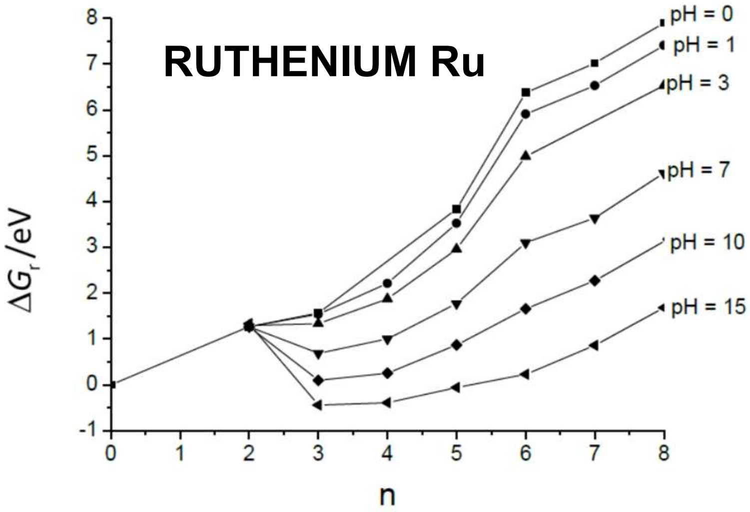



Frost diagram for vanadium
nE° (V)
Oxidation number
1
0
-1
-2
-3
0
1
2
3
4
5
V
VO
V2+
V2O3
V3+
HV2O5−
VO2+
VO4 3−
VO2+
● pH = 0
● pH = 14

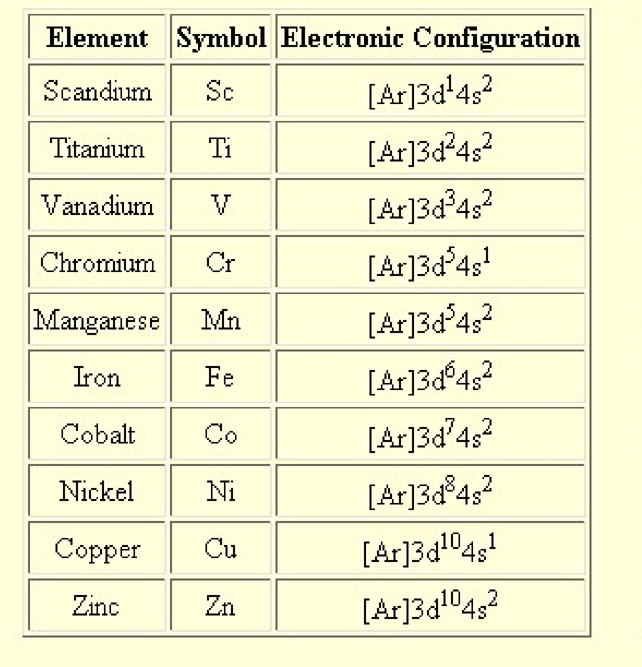
V^{2+} V^{3+} VO^{2+} VO_2^+


Frost diagram for iron
nE° (V)
Oxidation number
2
1
0
-1
-2
-3
0
1
2
3
4
5
6
Fe
Fe2+
Fe3+
FeO2+
FeO(OH)−
FeO2−
FeO4 2−
◆ pH = 0
■ pH = 14

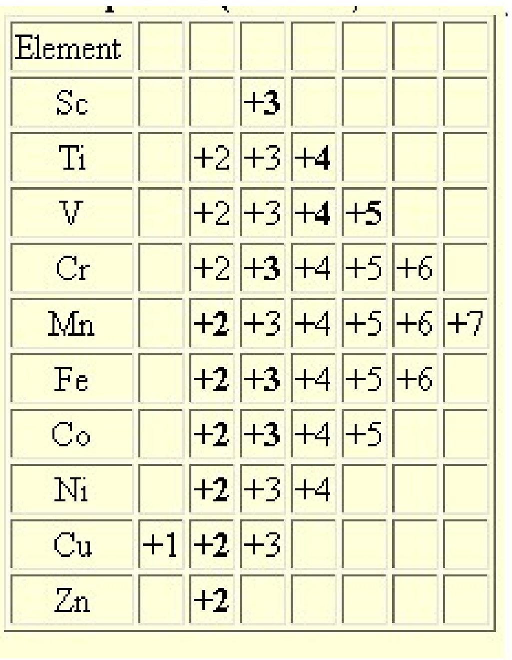

Frost diagram of copper
Oxidation number
1
0
-1
-2
-3
0
1
2
Cu
Cu+
Cu2+
Cu2O
Cu(OH)2
◆ pH = 0
■ pH = 14


RUTHENIUM Ru
ΔGr /eV
n
8
7
6
5
4
3
2
1
0
-1
0
1
2
3
4
5
6
7
8
pH = 0
pH = 1
pH = 3
pH = 7
pH = 10
pH = 15

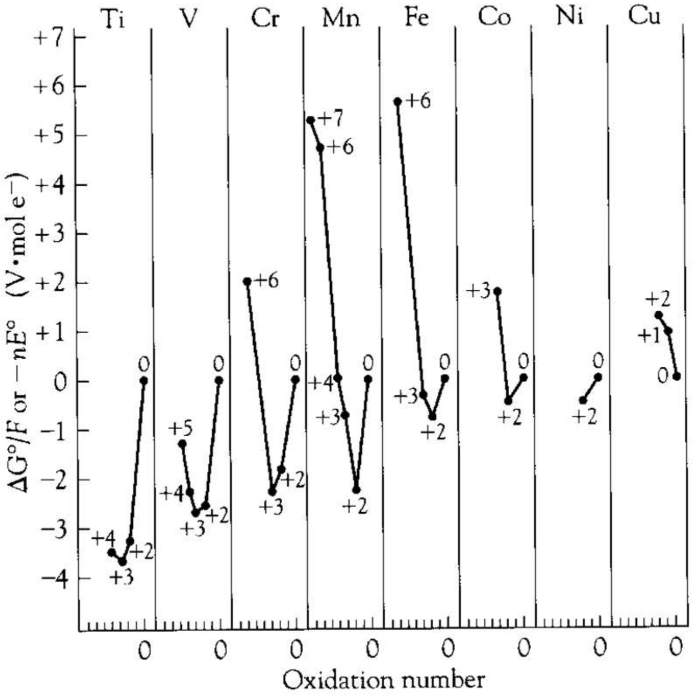
FROST DIAGRAMS



Element	Symbol	Electronic Configuration
Scandium	Sc	$[Ar]3d^14s^2$
Titanium	Ti	$[Ar]3d^24s^2$
Vanadium	V	$[Ar]3d^34s^2$
Chromium	Cr	$[Ar]3d^54s^1$
Manganese	Mn	$[Ar]3d^54s^2$
Iron	Fe	$[Ar]3d^64s^2$
Cobalt	Co	$[Ar]3d^74s^2$
Nickel	Ni	$[Ar]3d^84s^2$
Copper	Cu	$[Ar]3d^{10}4s^1$
Zinc	Zn	$[Ar]3d^{10}4s^2$



Element							
Sc			**+3**				
Ti		+2	+3	**+4**			
V		+2	+3	**+4**	**+5**		
Cr		+2	**+3**	+4	+5	+6	
Mn		**+2**	+3	+4	+5	+6	+7
Fe		**+2**	**+3**	+4	+5	+6	
Co		**+2**	**+3**	+4	+5		
Ni		**+2**	+3	+4			
Cu	+1	**+2**	+3				
Zn		**+2**					



OXIDATION STATES (slightly depending on conditions !)

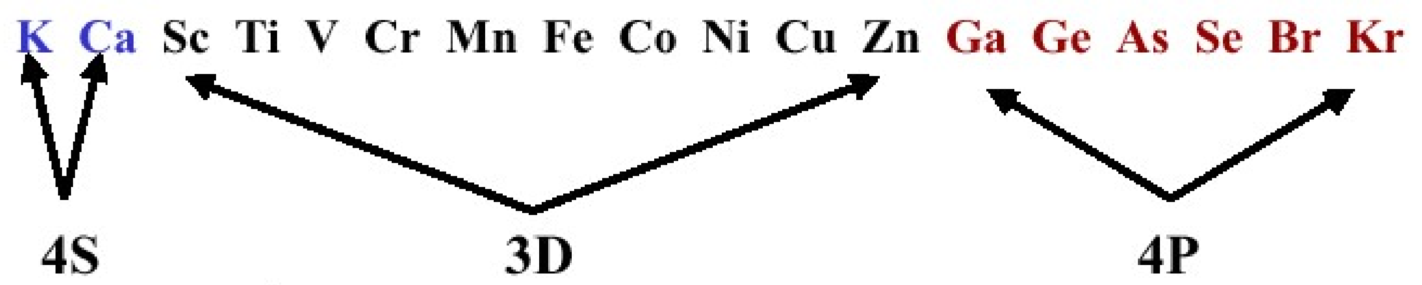
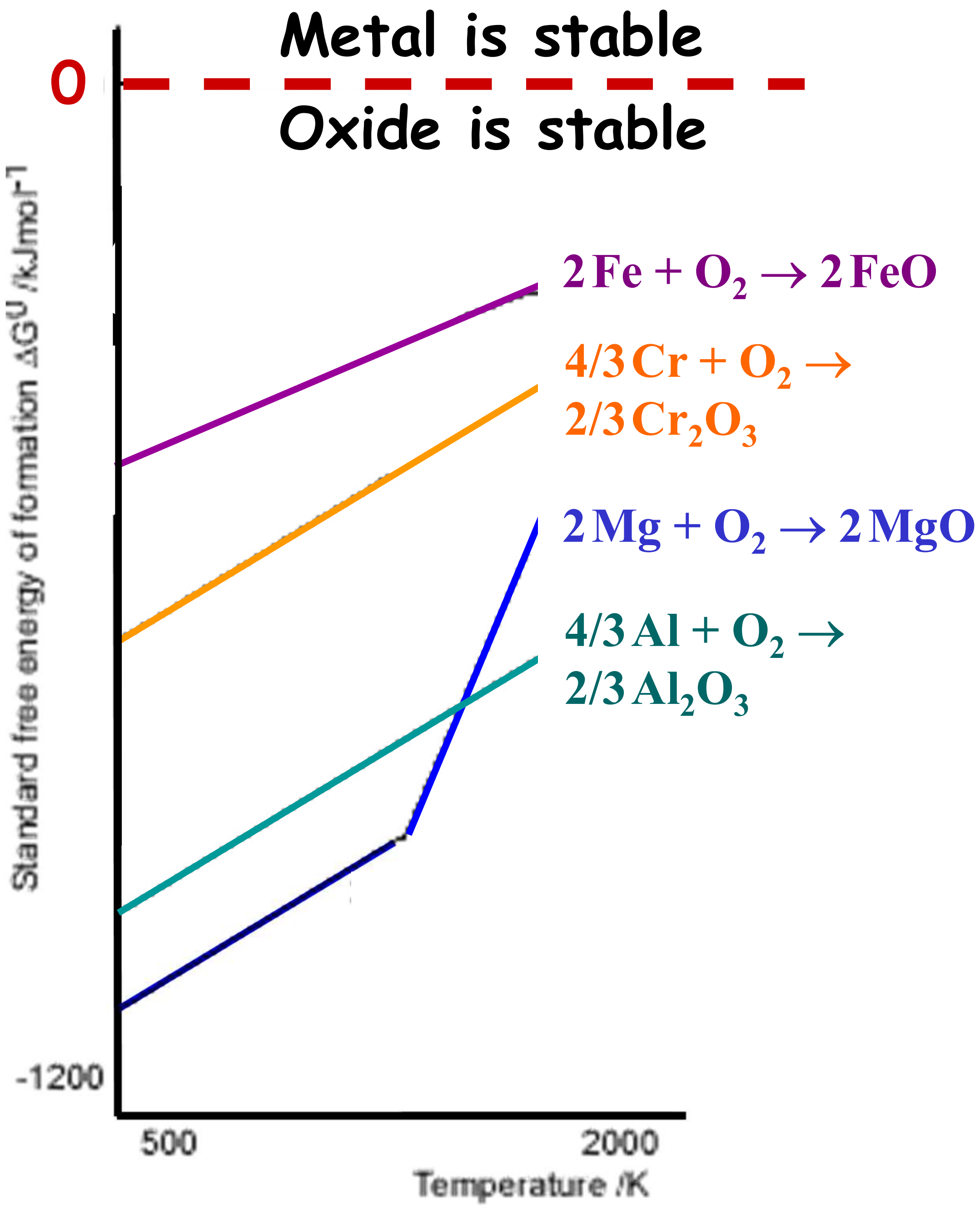
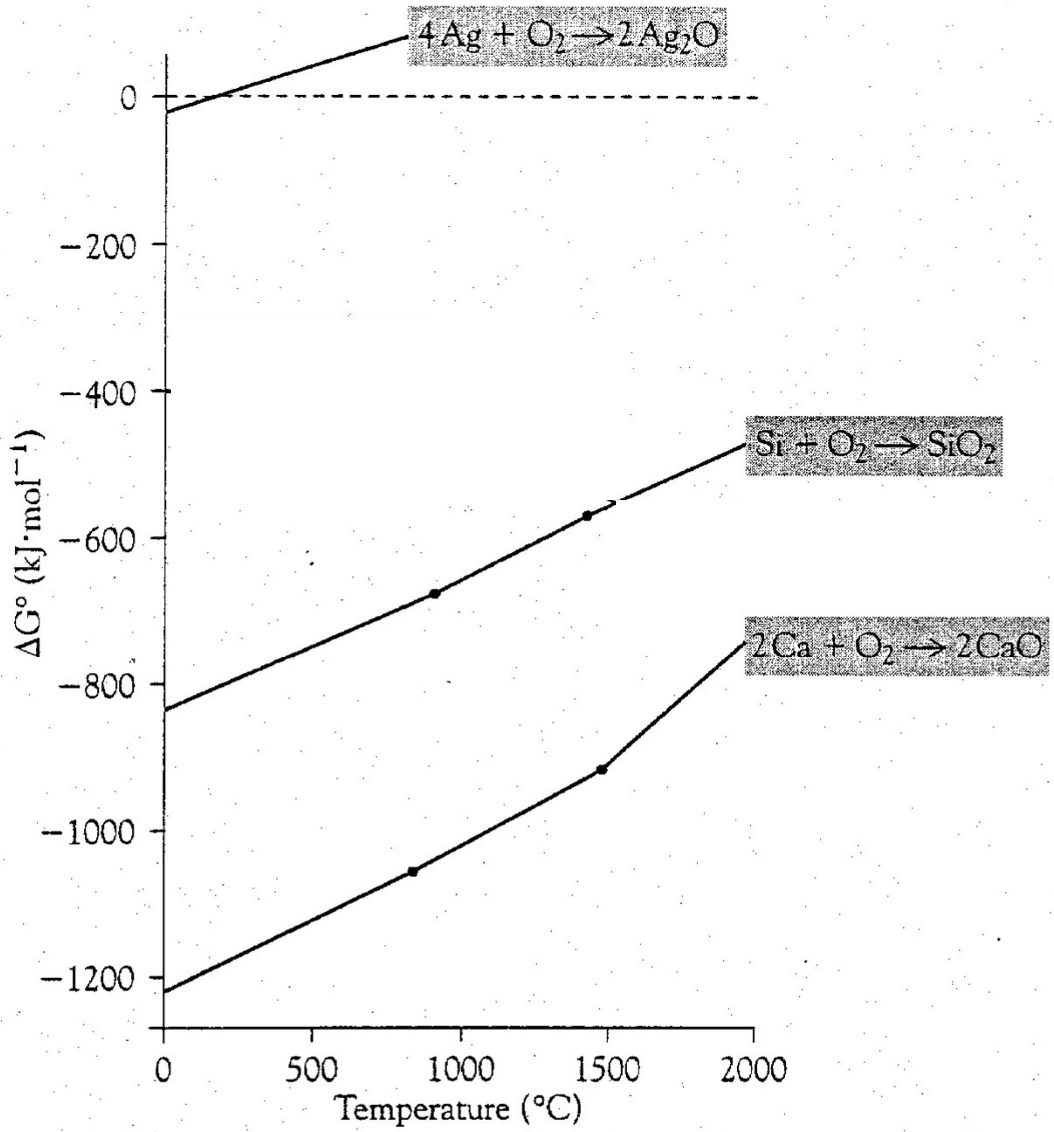


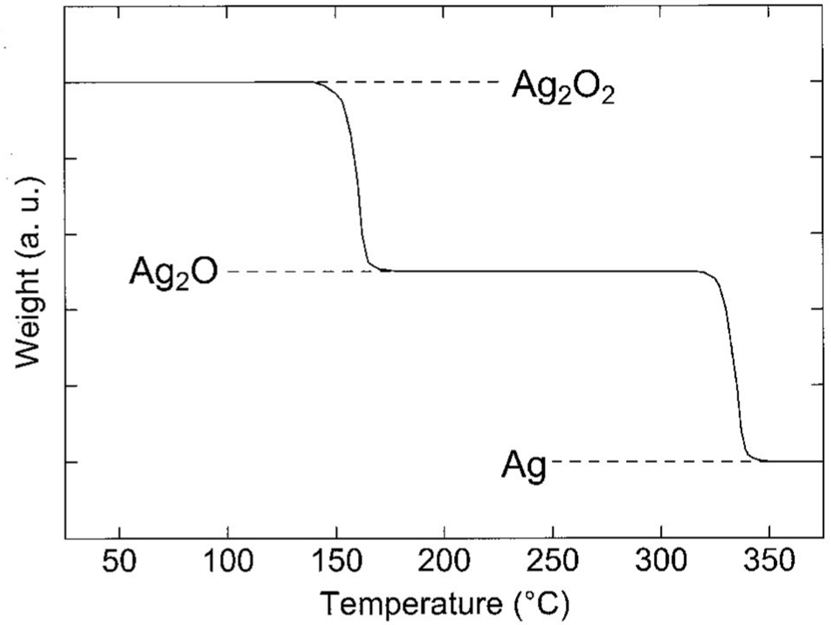
Figure 1. The 4th row of the periodic table. The transition metals are the elements that range from Sc (Scandium) to Zn (Zinc).

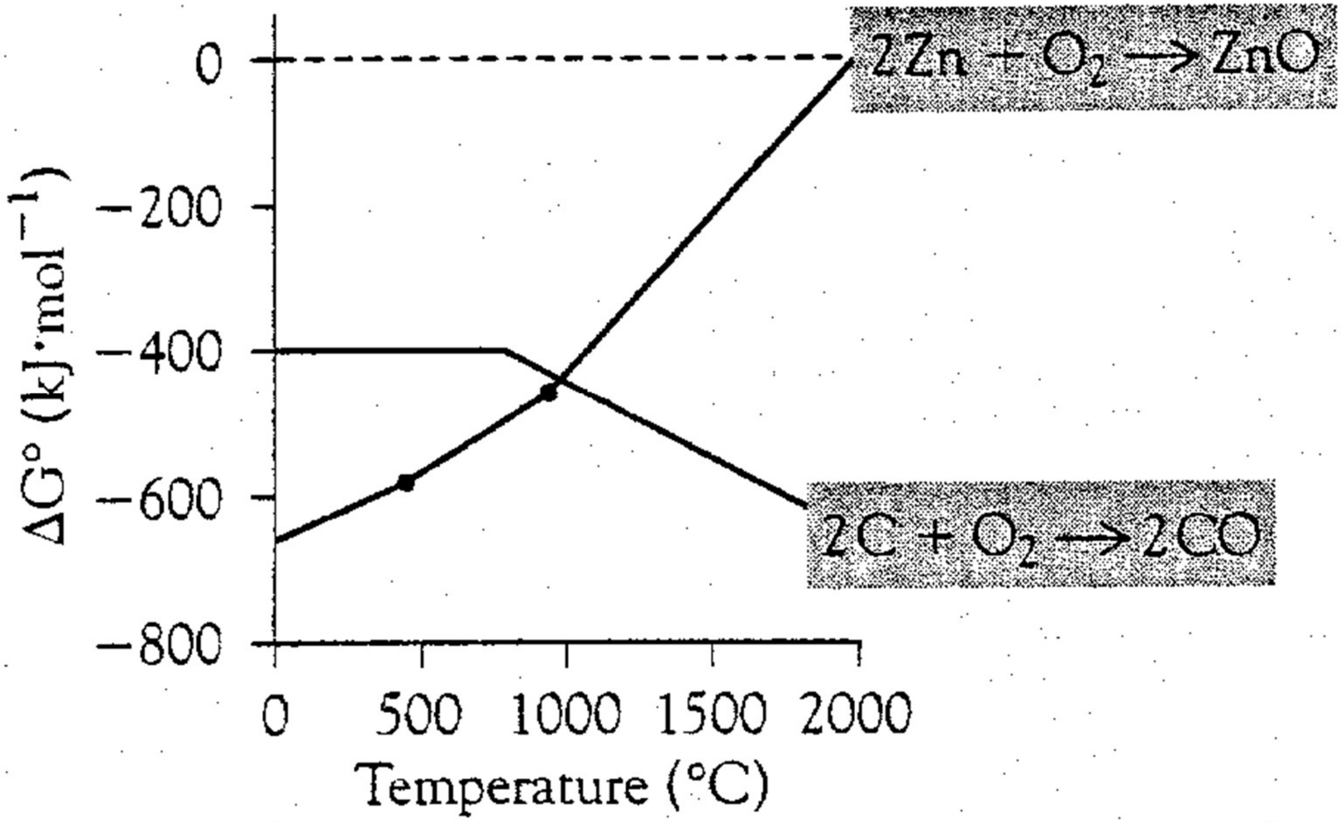
Ellingham diagram

- Gibb's free energy of formation versus temperature for metal oxides
- Temperature at which a metal oxide is spontaneously (ΔG^0 becomes positive) reduced to a metal



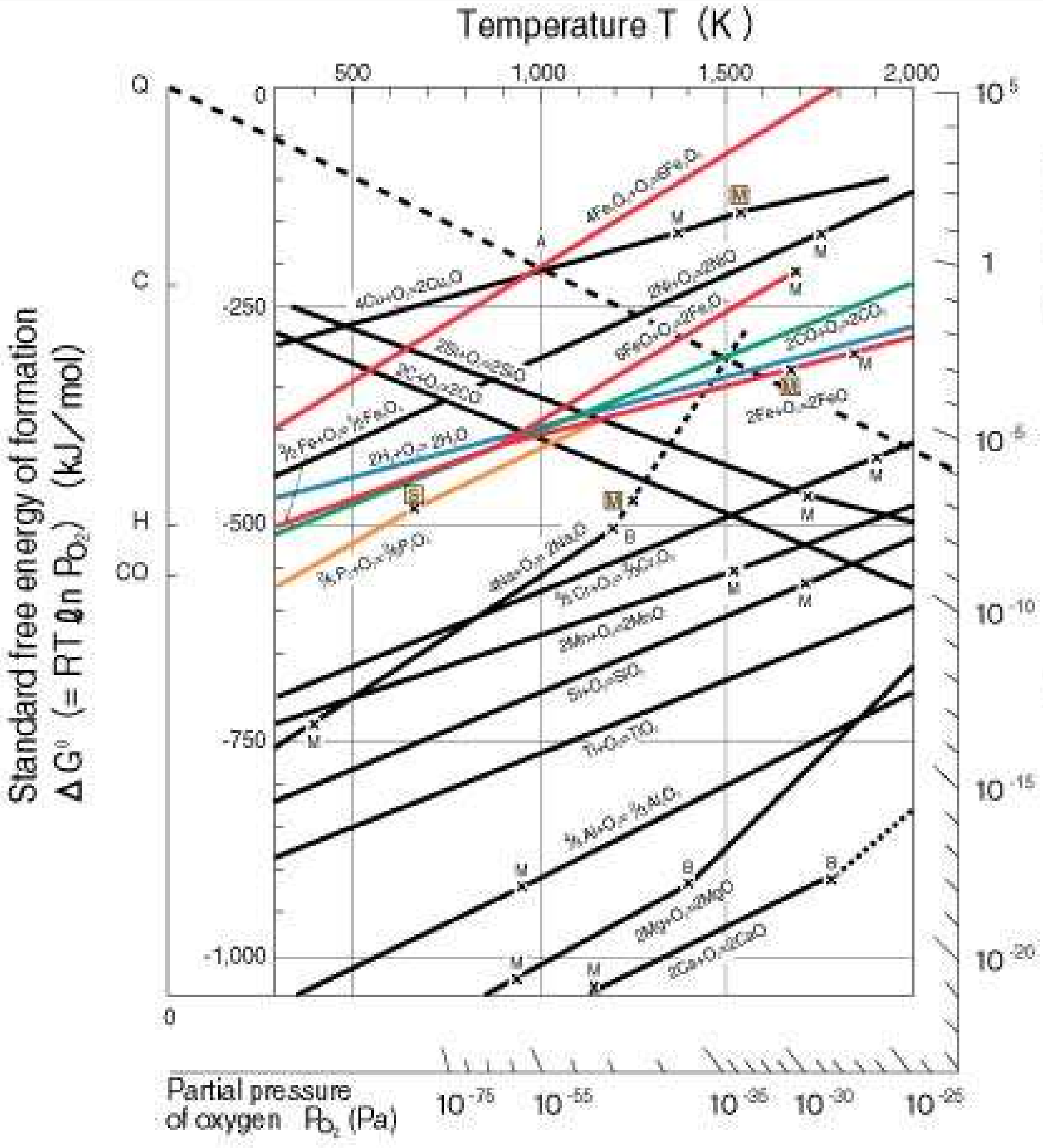

$4Ag + O_2 \rightarrow 2Ag_2O$
$Si + O_2 \rightarrow SiO_2$
$2Ca + O_2 \rightarrow 2CaO$
ΔG° (kJ·mol^{-1})
0
−200
−400
−600
−800
−1000
−1200
0
500
1000
1500
2000
Temperature (°C)


Ag_2O_2
Ag_2O
Ag
Weight (a. u.)
50
100
150
200
250
300
350
Temperature (°C)



Above 900 ^{o}C ZnO can be reduced to Zn by carbon

2**B**(1) Standard Free Energy of Formation of Oxides



	Element	Oxide
Melting point	M	M
Boiling point	B	
Sublimation point	S	S

$Me+O_2=MeO_2$ (1)

$\Delta G^{\circ}=RT\ \ell n\ P_{O_2}$ (2)

Ref.: F.D.Richardson, JISI (1948)

Oxygen Release

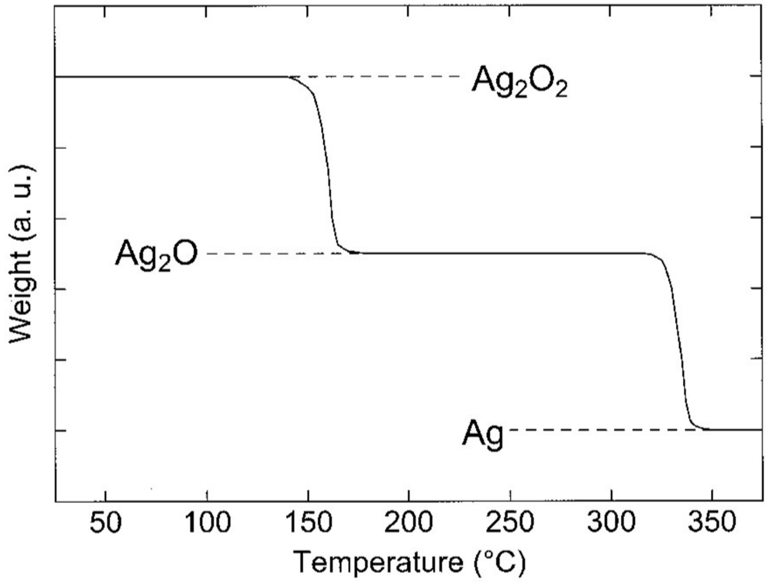
Oxygen Engineering !

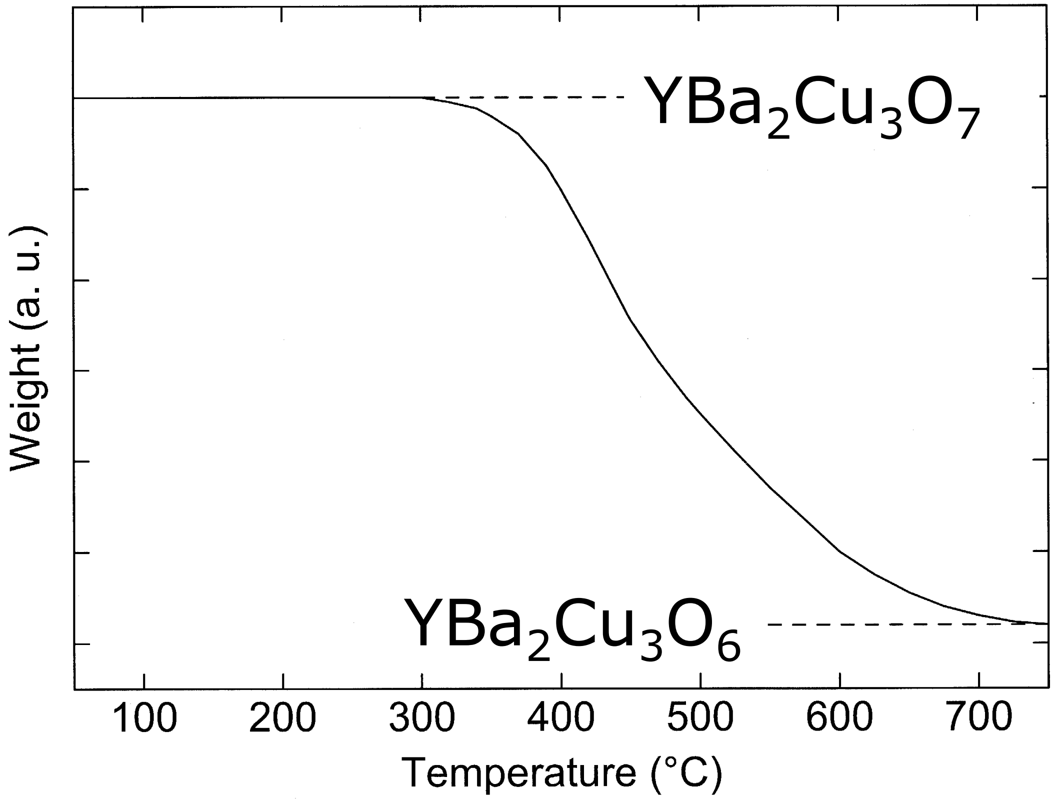
Ag_2O_2 :

in two discrete steps

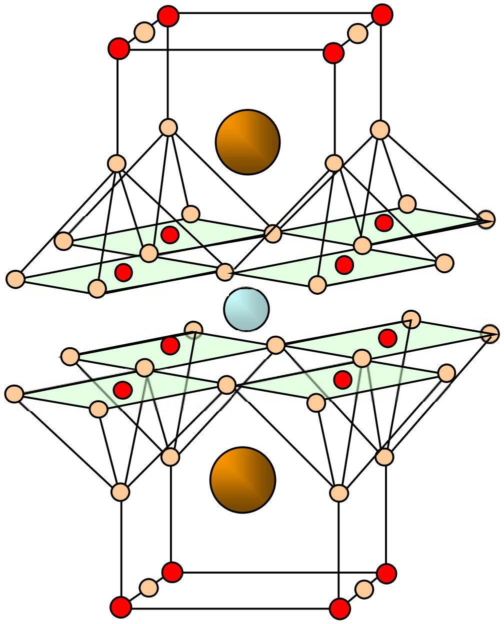
$YBa_2Cu_3O_{7-\delta}$:

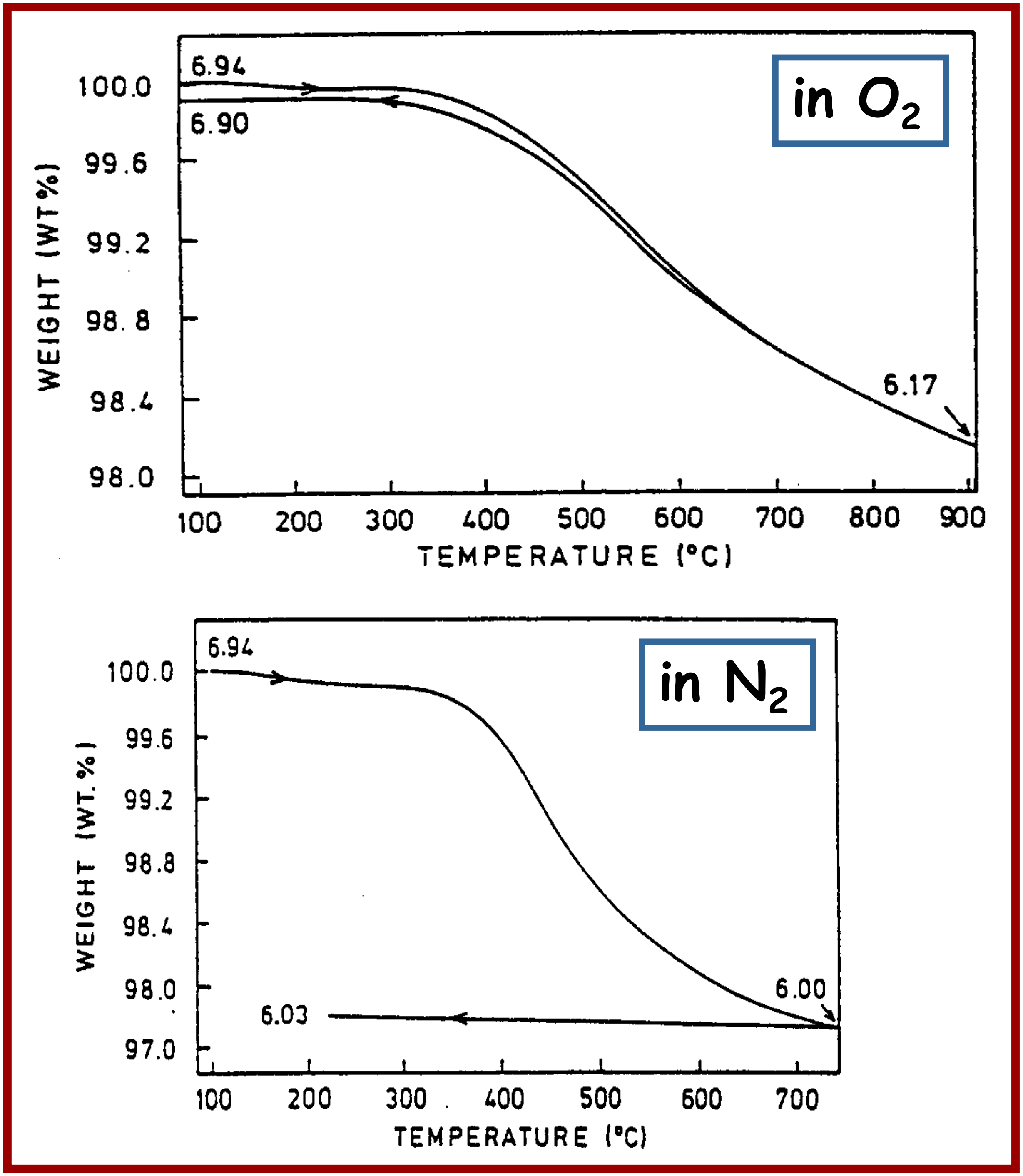
Gradually → mixed-valent Cu



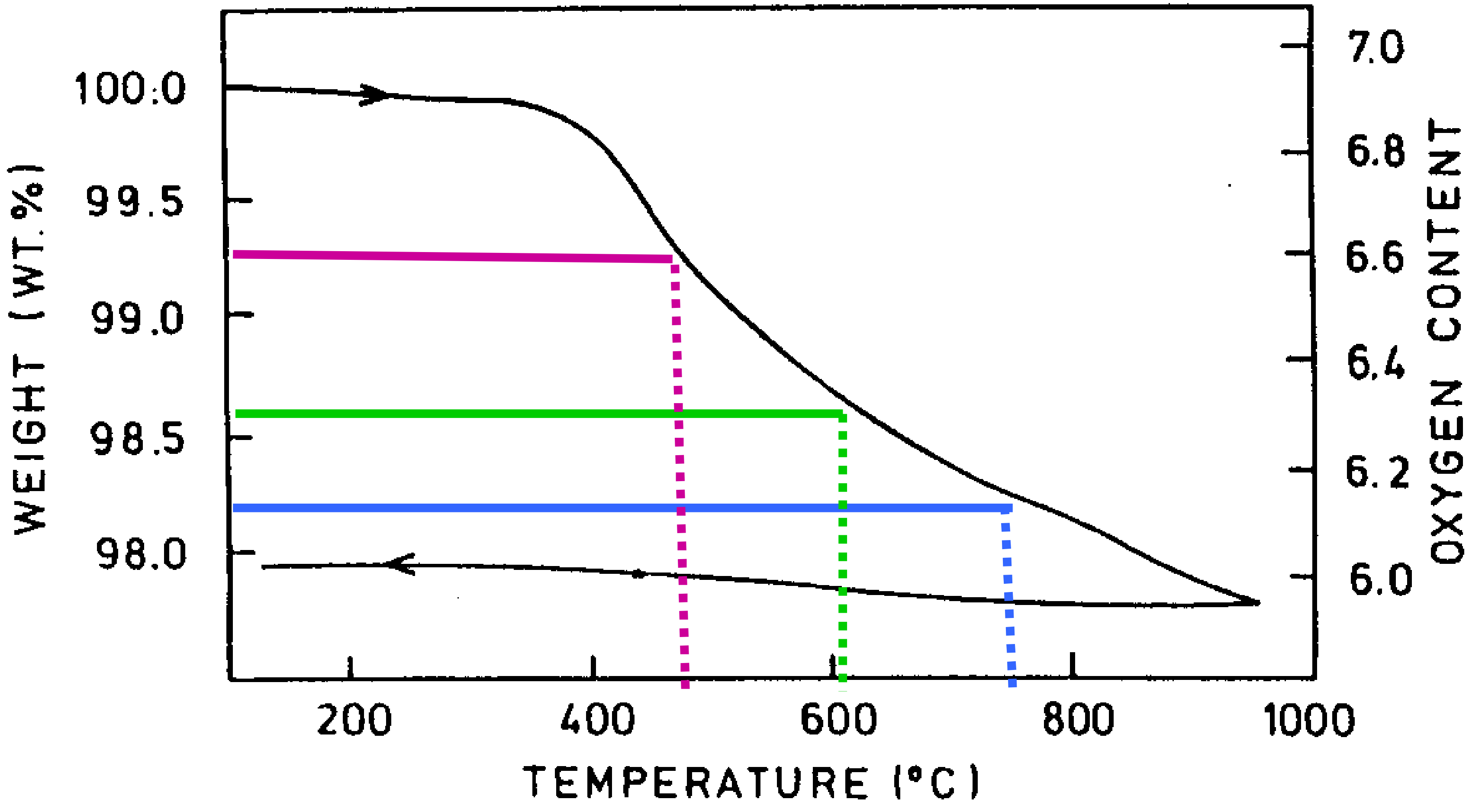


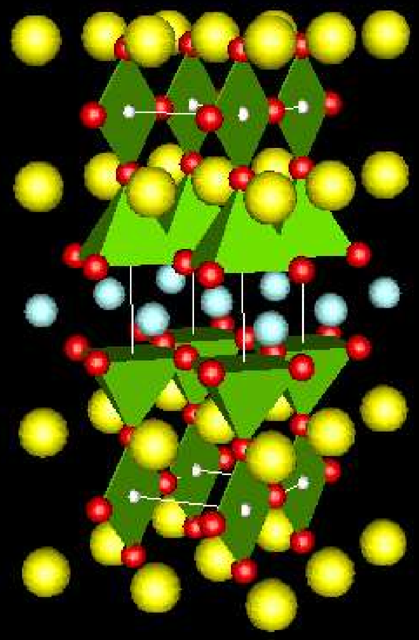
$YBa_2Cu_3O_{7-\delta}$





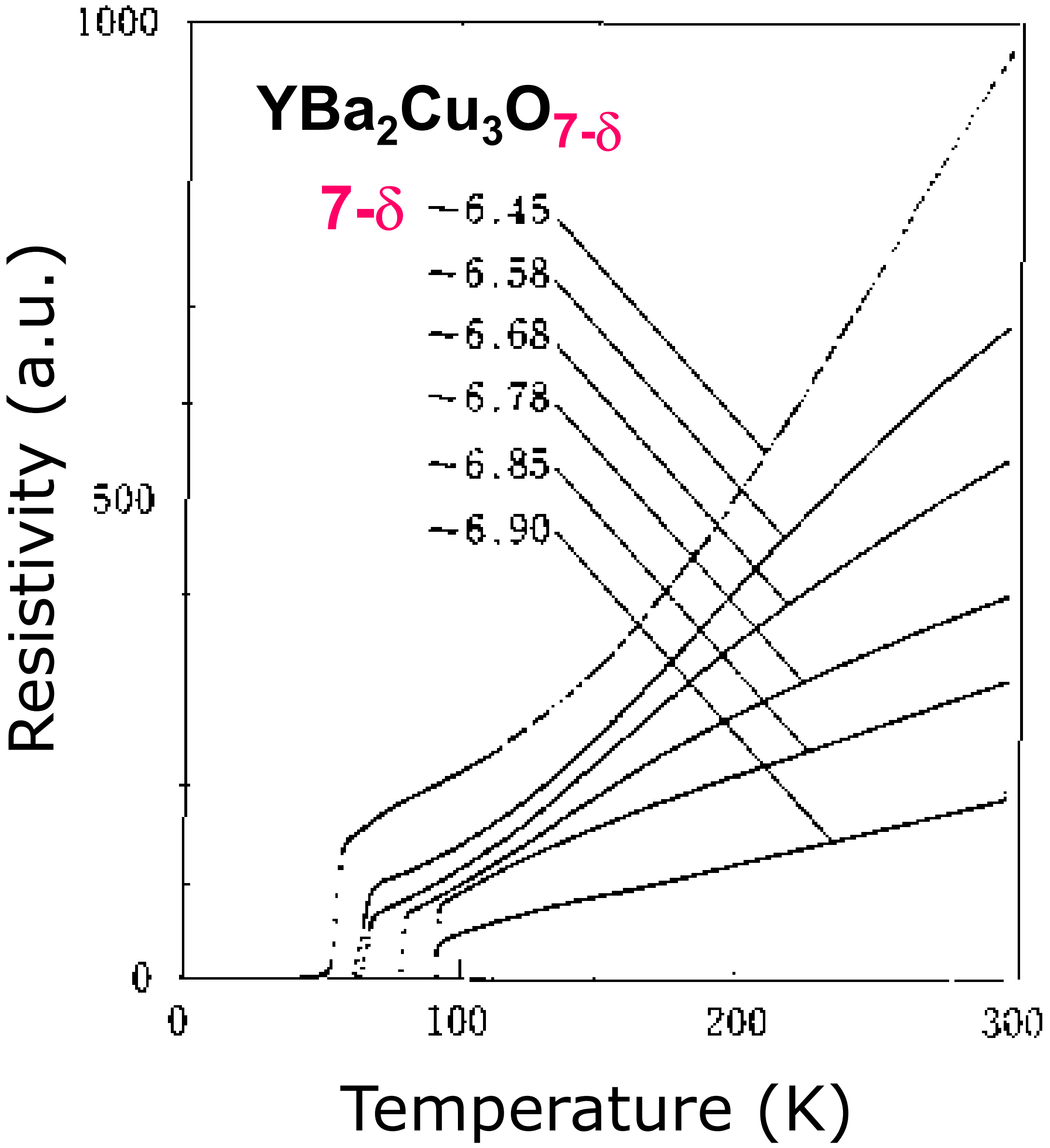
OXYGEN-DEFICIENT SAMPLES





$YBa_2Cu_3O_{7-\delta}$

High-T_c
Superconductor



OXYGEN NONSTOICHIOMETRY

(1) Oxygen vacancies

- $YBa_2Cu_3O_{7-\delta}$

(2) Interstitial oxygen atoms

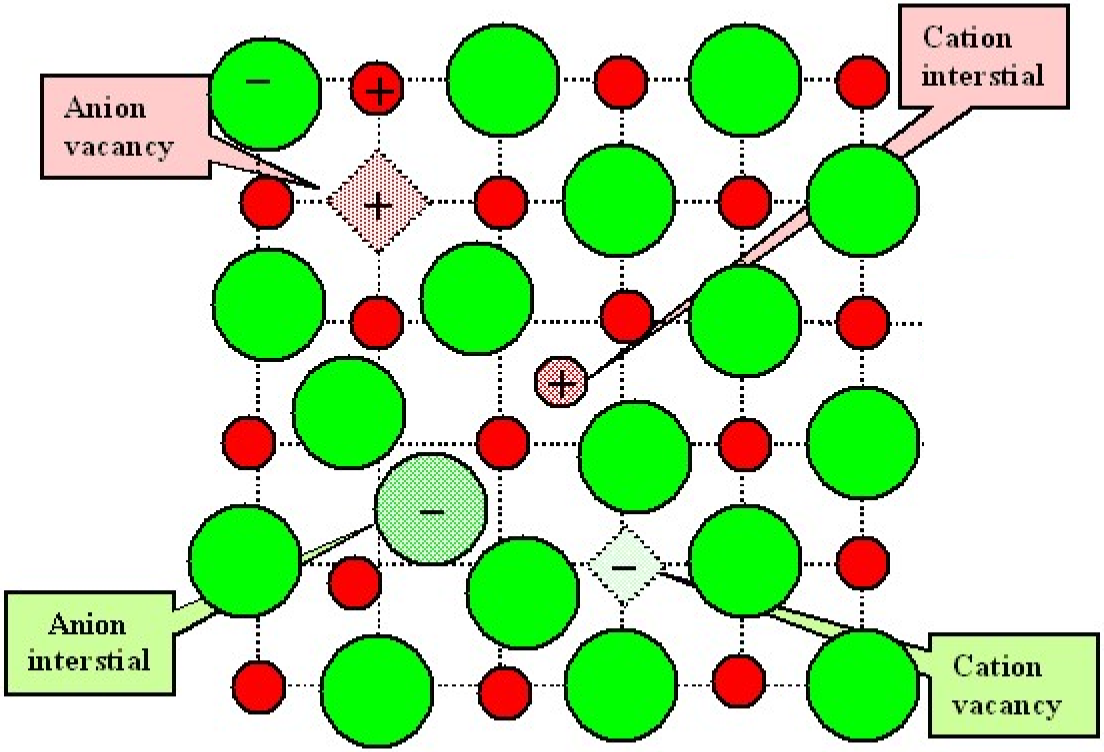
- $La_2CuO_{4+\delta}$

(3) Cation vacancies

- $La_{1-x}Mn_{1-x}O_3$

(4) Interstitial cations

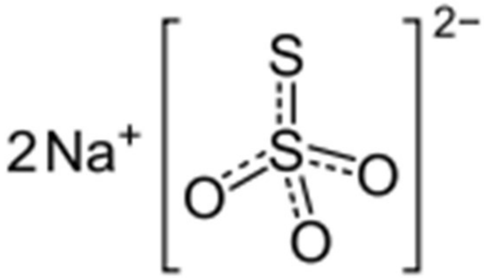
- $Zn_{1+x}O$



Definition of MIXED VALENCY: TWO POSSIBILITIES

(1) **the formal oxidation state for** (at least) **one of the elements is fractional**

(2) (at least) **one of the elements is at two different** (integer) **oxidation states**



CLASSIFICATION OF MIXED-VALENCE COMPOUNDS

M.B. Robin & P. Day, Adv. Inorg. Chem. Radiochem. 10, 247 (1967).

Class-I

- e.g. $Na_2S_2O_3$ (S^{-II} & S^{VI})
- clearly different environments for the two different atoms
- large energy required for electron transfer between these atoms → no interaction → no special properties

Class-II

- e.g. Ag_2O_2 (Ag^{I} & Ag^{III})
- different but sufficiently similar environments → only a small energy required for electron transfer between the different atoms → semiconducting

Class-III

- e.g. Ag_2F ($Ag^{0.5}$) & $YBa_2Cu_3O_{7-\delta}$
- all mixed-valence atoms have identical environments → electrons delocalized → metallic conductivity

VALENCE SEPARATION (Verwey-type)

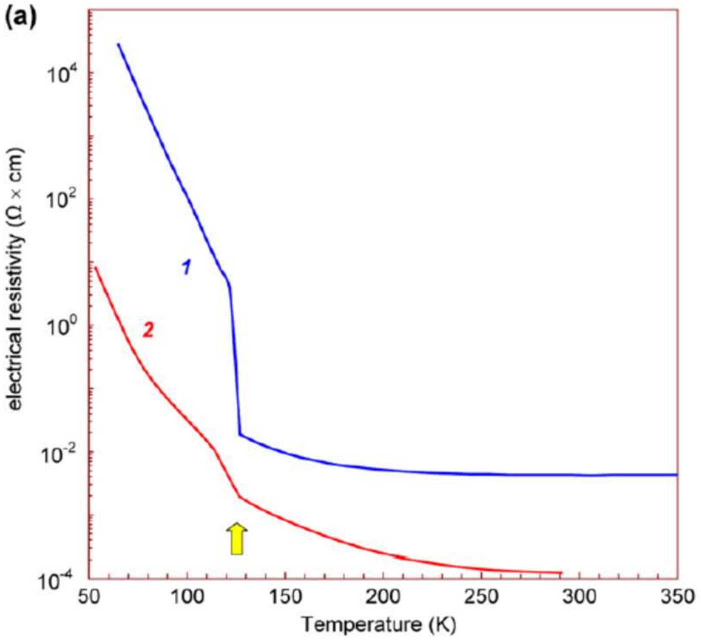
$$2\,M^{m+0.5} \rightarrow M^{m} + M^{m+1}$$

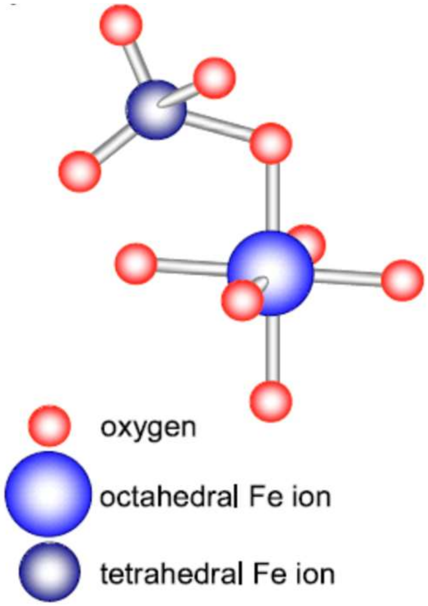
(mixed valence state) → (valence-separated state)

Example: Magnetite Fe_3O_4

- Inverse spinel structure: $Fe^{III}_{tet}[Fe^{2.5}]_{oct}O_4$
- Verwey transition (around 125 K): $2\,Fe^{2.5} \rightarrow Fe^{II} + Fe^{III}$

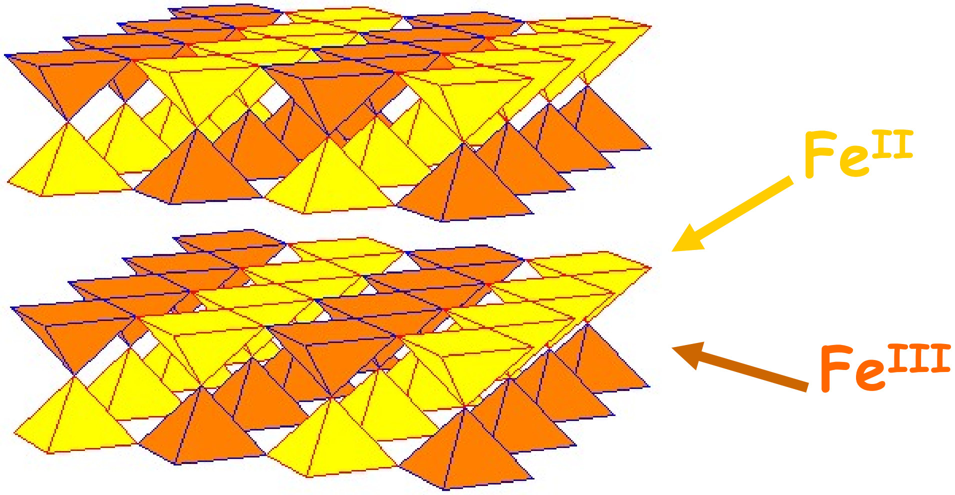
1 single crystal
2 thin film





CHARGE ORDERING (CO)

Example: $Ba^{II}Ln^{III}Fe_2O_{5.0}$ at low temperatures



P. Karen et al., PRB 64, 214405 (2001).

CHARGE DISPROPORTIONATION (CD)

$$2\,M^{m} \rightarrow M^{m-1} + M^{m+1}$$

Examples:

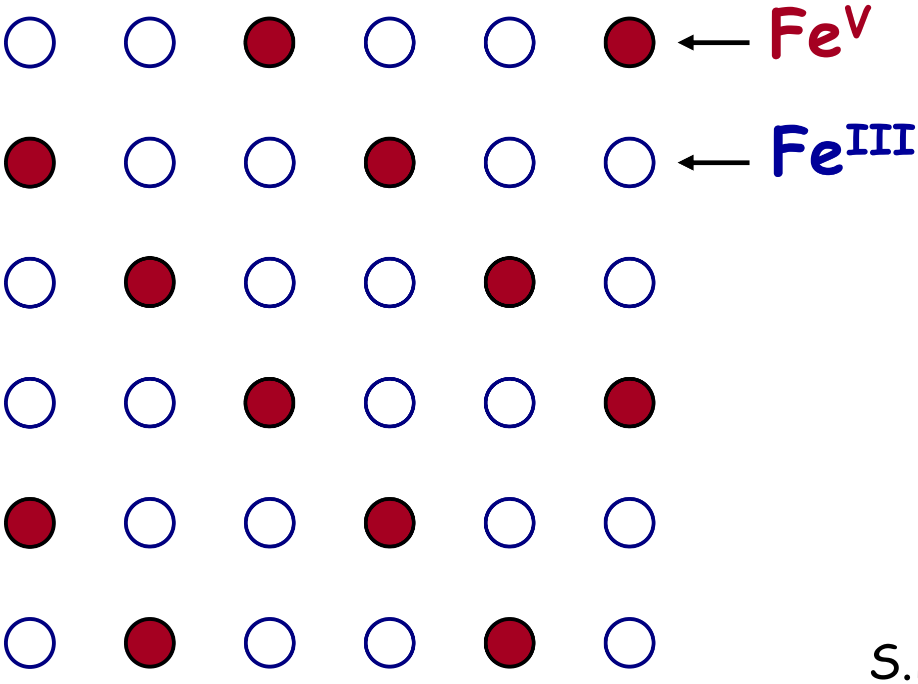
- d^6 & d^8: Pt^{IV}-Pt^{II}
- d^8 & d^{10}: Au^{III}-Au^{I}
- d^9 & $d^{10}s^1$: Cu^{II}-Cu^{0}
- d^{10} & $d^{10}s^2$: Sb^{V}-Sb^{III}, Hg^{II}-Hg^{0}

Example: CD & CO

Perovskite: $(La^{III}_{1/3}Sr^{II}_{2/3})Fe^{3.67}O_3$

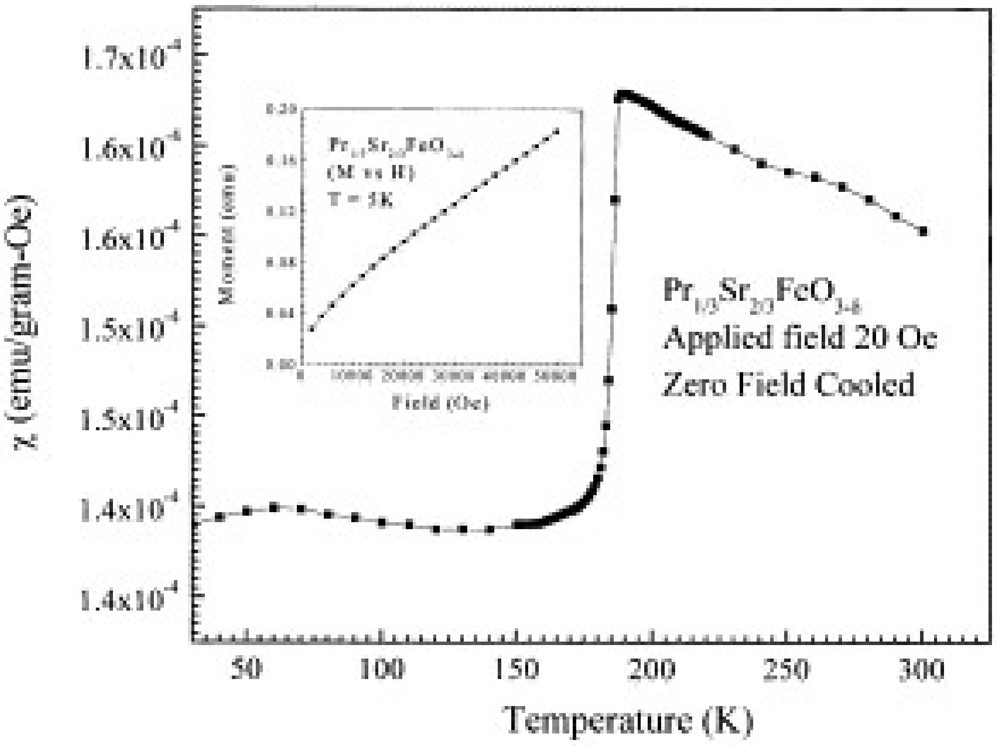
$Fe^{III} + 2\ Fe^{IV} \rightarrow Fe^{III} + Fe^{III} + Fe^{V}$

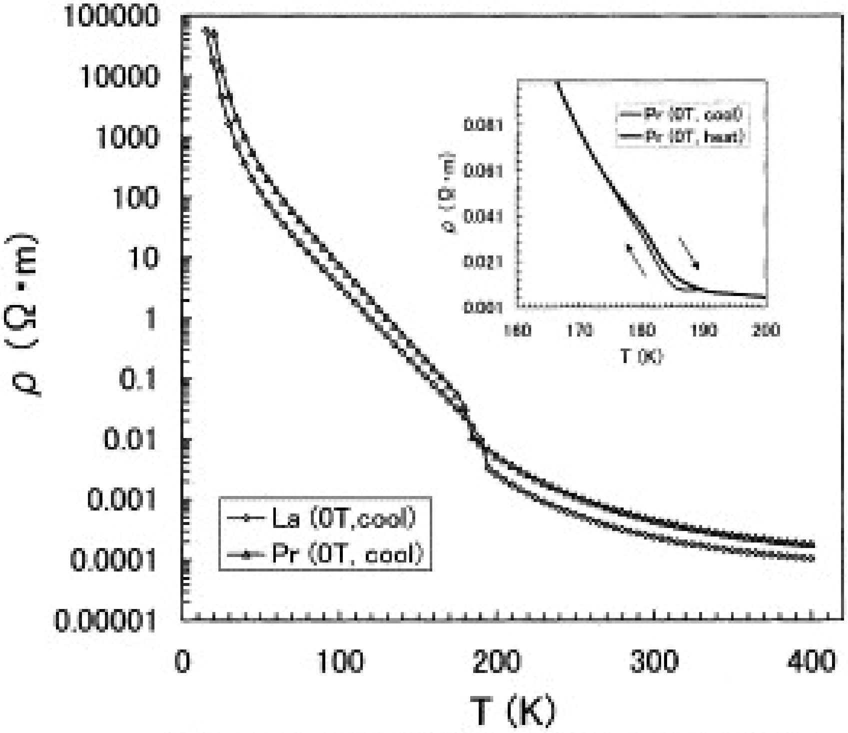
$T_{CO} = T_{CD} = 198\ K$

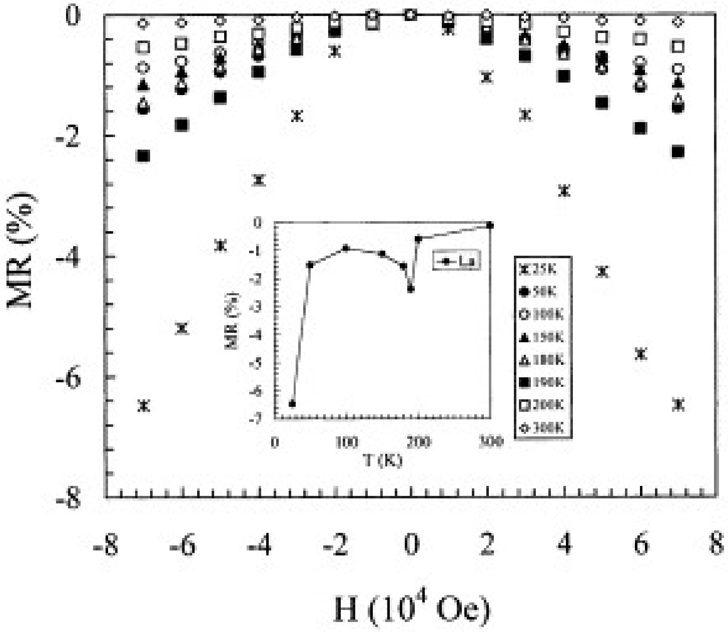


S.K. Park et al., PRB 60, 10788 (1999).

$(Ln_{1/3}Sr_{2/3})FeO_3$







V.P.S. Awana, J. Nakamura, J. Lindén,
M. Karppinen & H. Yamauchi,
Solid State Commun. 119, 159-162 (2001).