TENTATIVE LECTURE SCHEDULE

		Date	Topic
1.	Mon	13.09.	Course Introduction & Short Review of the Elements
2.	Wed	15.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	17.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Mon	20.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Wed	22.09.	Transition Metals: General Aspects & Pigments
6.	Mon	27.09.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
7.	Wed	29.09.	Redox Chemistry
8.	Mon	04.10.	Crystal Field Theory
9.	Wed	06.10.	V, Nb, Ta & Metal Complexes & MOFs
10.	Fri	08.10.	Cr, Mo, W & 2D materials
11.	Mon	11.10.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
12.	Wed	13.10.	EXTRA
13.	Fri	15.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Mon	18.10.	Lanthanoids + Actinoids & Luminescence (Down/Upconversion)
15.	Wed	20.10.	Inorganic Materials Chemistry Research

EXAM: Thu Oct. 28, 2021

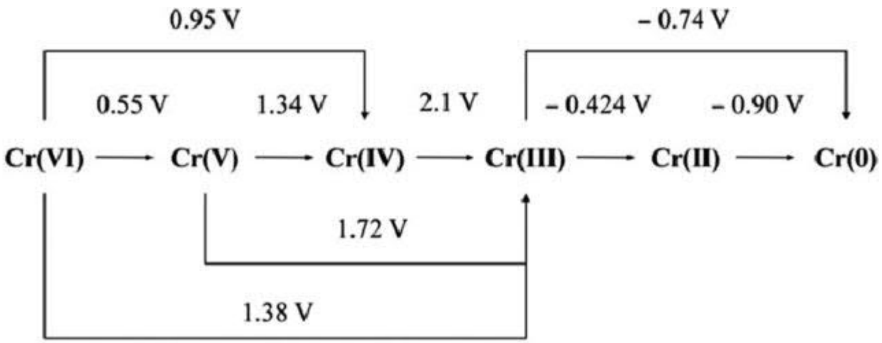
PRESENTATION TOPICS/SCHEDULE

Wed	06.10.	Nb:	Toivonen
Fri	08.10.	Mo:	Ahmed, Shamshad, Svinhufvud
Mon	11.10.	Mn:	Majaniemi, Thakur, Ahkiola
		Ru:	Ichanson, Locqueville
Wed	13.10.	Co:	Ekholm, Olander, Syväniemi
		Cu:	Kolawole, Nguyen, Munib
Fri	15.10.	In:	Kovanen, Ogunyemi
		Te:	Huhtakangas, Wallin, Kaarne
Mon	18.10.	Eu:	Sonphasit, Tuisku
		Nd:	Jussila, Siuro, Perttu
		U:	Sinkkonen, Wennberg, Partanen

QUESTIONS: Lecture 7

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

2. **Below is the Latimer diagram for chromium in acidic conditions:**



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

- What is the most stable oxidation state?

- For which oxidation states disproportionation tend to occur?

REDOX CHEMISTRY

- Electron configuration
- Oxidation/valence states & ion charge
- Latimer diagram
- Frost diagram

in SOLUTION

- Ellingham diagram (metal/oxide)
- Oxygen (non)stoichiometry
- Mixed valency

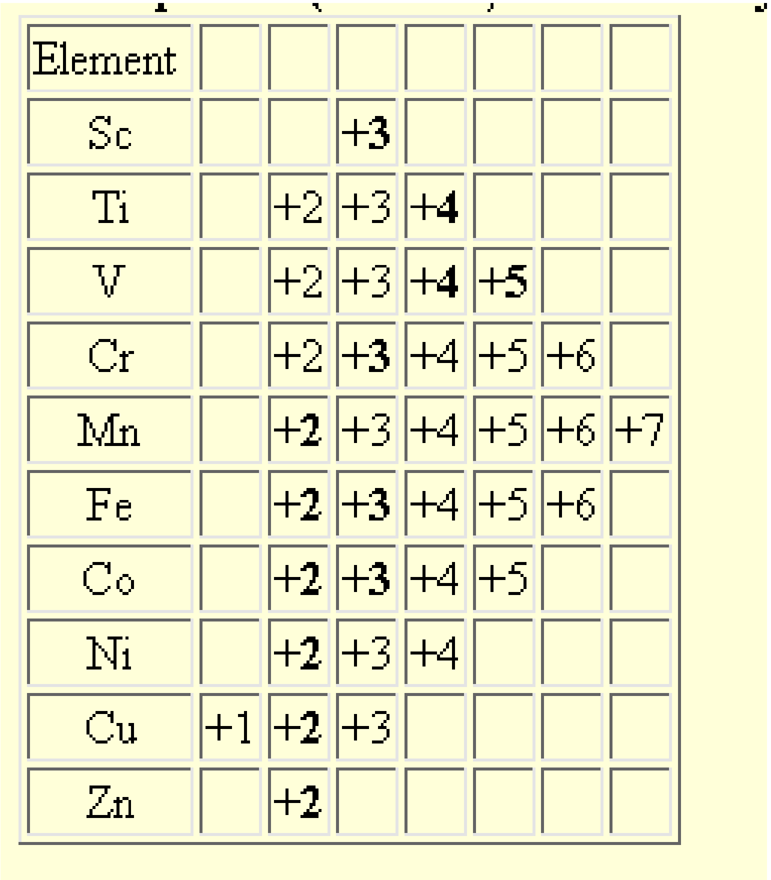
in SOLID

- Disproportionation
- Valence separation

Electron configurations of 3d metals: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^x$

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

OXIDATION STATES



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**					

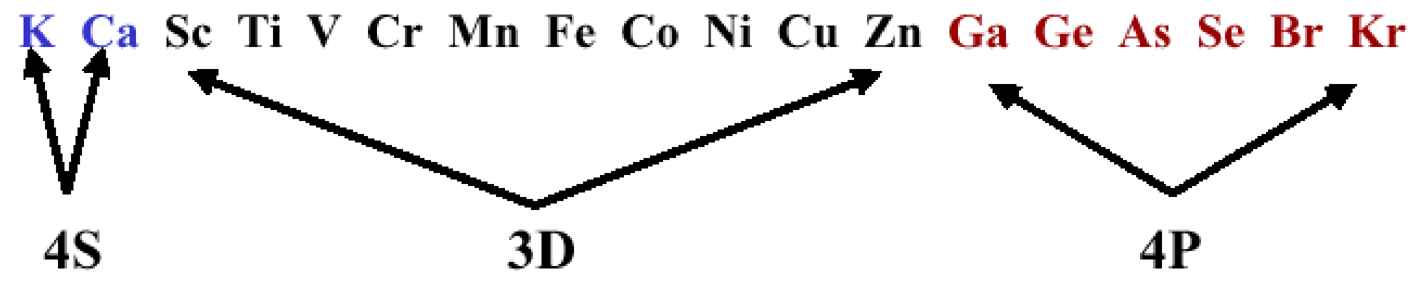
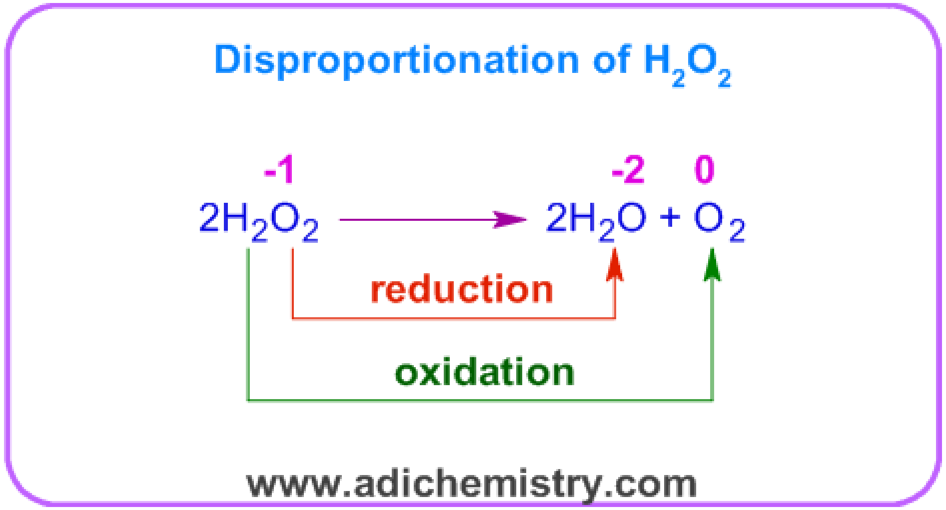
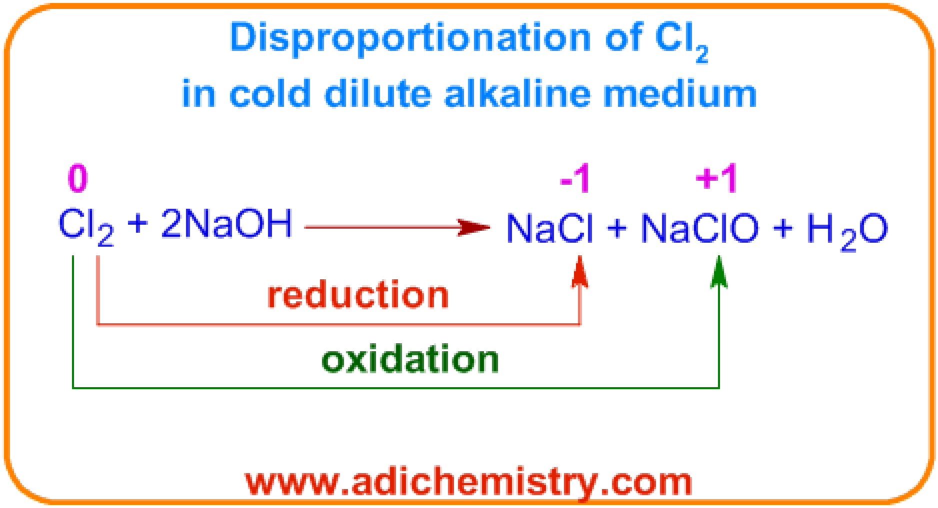


Figure 1. The 4th row of the periodic table. The transition metals are the elements that range from Sc (Scandium) to Zn (Zinc).

DISPROPORTIONATION

Redox reaction in which atoms of an element from one oxidation state are simultaneously oxidized and reduced.

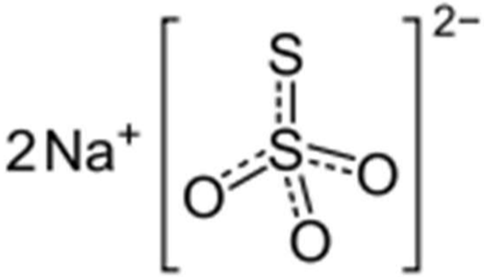




MIXED VALENCY (mixed oxidation state)

(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**

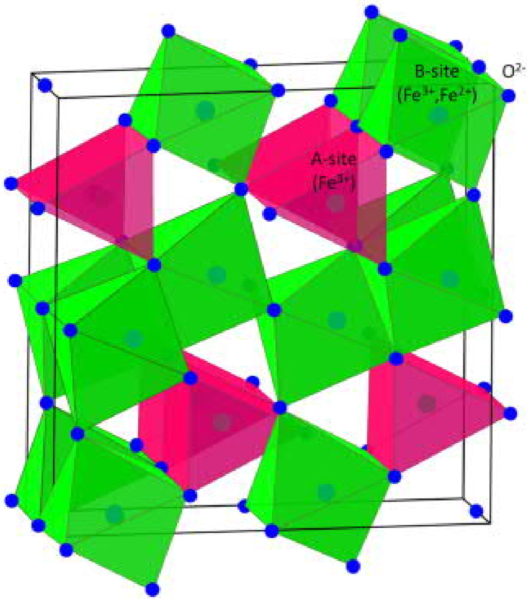
VALENCE SEPARATION (Verwey-type)

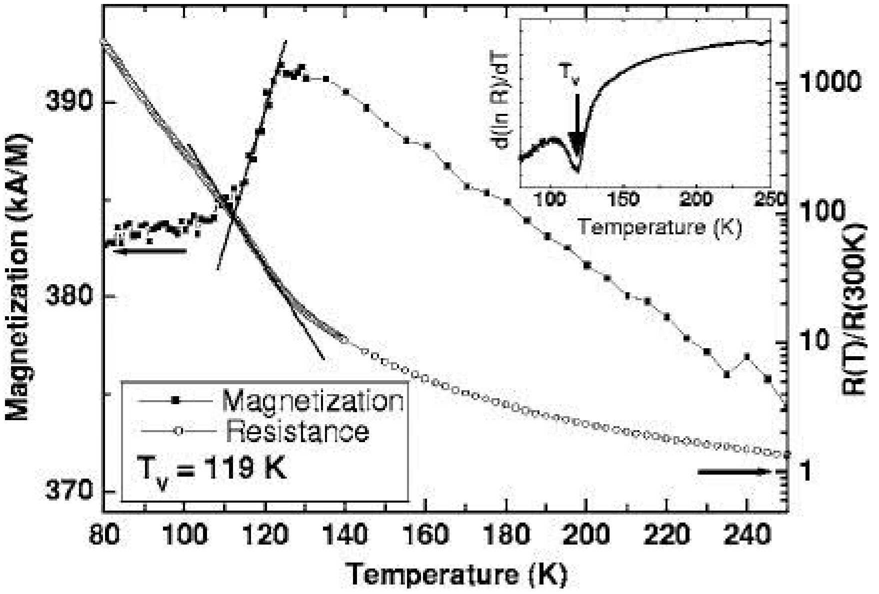
$$2\,M^{m+0.5} \rightarrow M^{m} + M^{m+1}$$

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

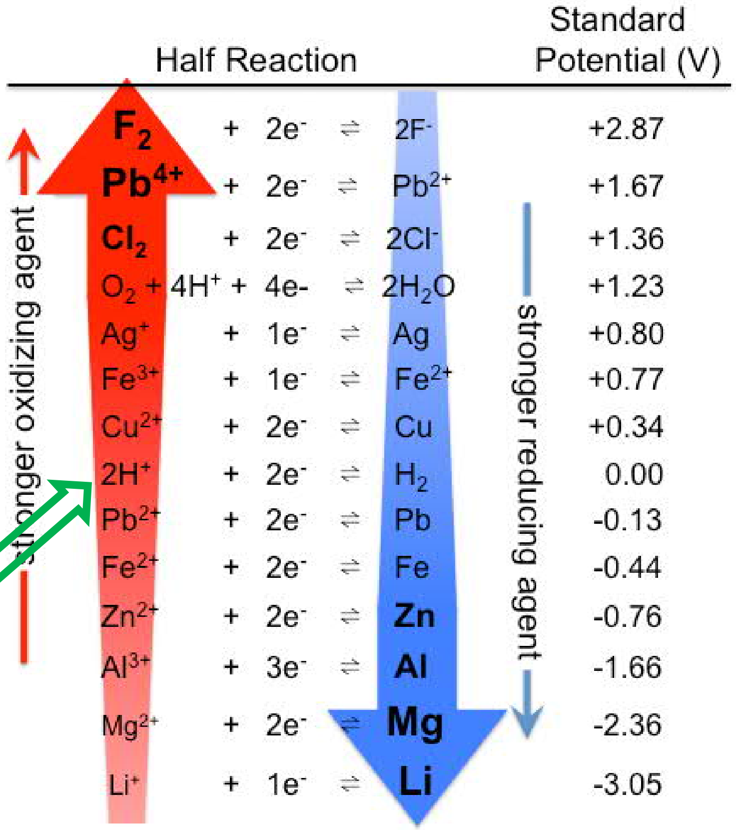
Example: Magnetite Fe_3O_4 (

- **Inverse spinel structure: $^{tet}[Fe^{III}]\ ^{oct}[Fe^{2.5}]_2\,O_4$**
- **Verwey transition (around 125 K): $2\,Fe^{2.5} \rightarrow Fe^{II} + Fe^{III}$**





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 !!!**

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

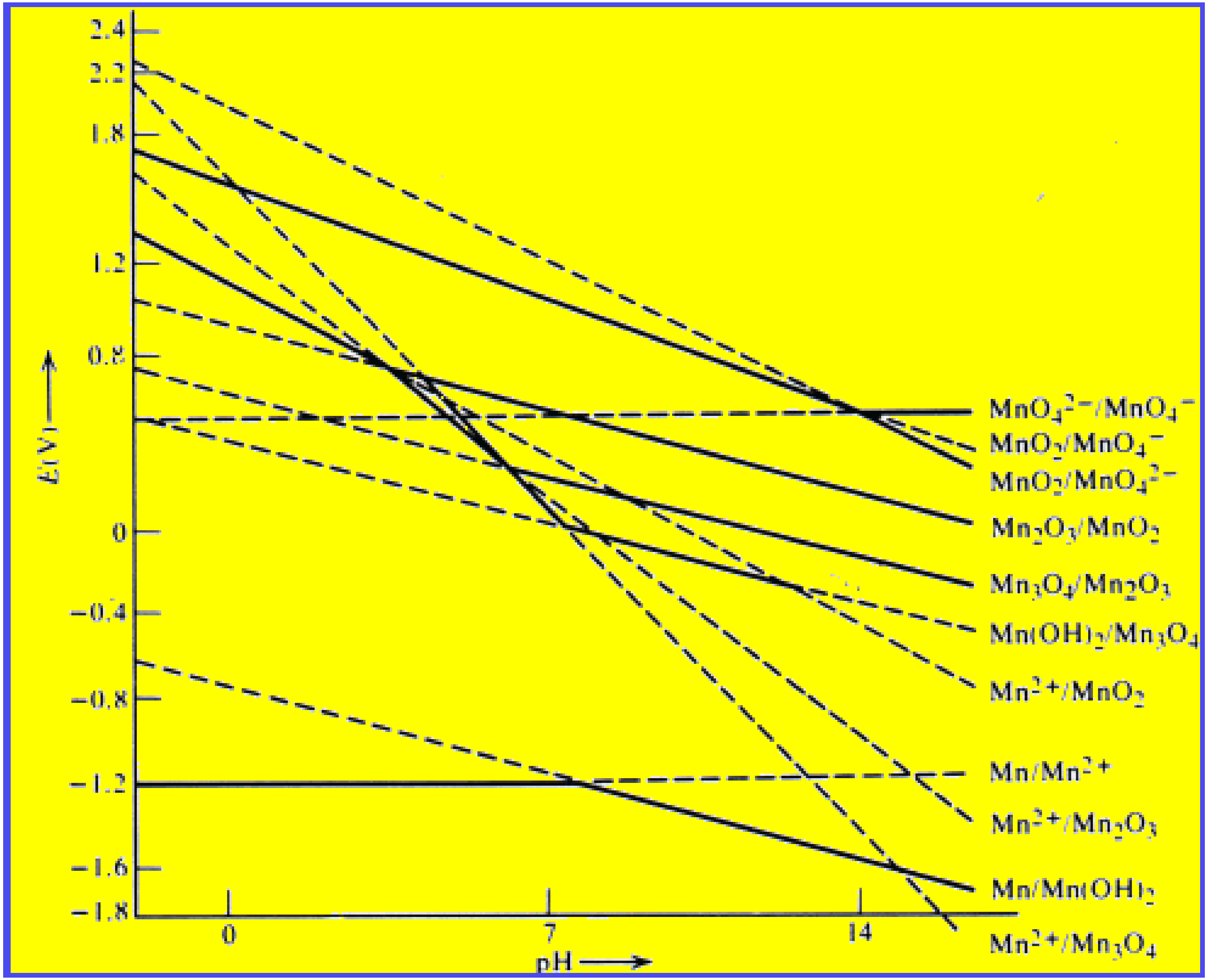
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $E^0_{red} = -0.44$ V

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

R: Gas constant = 8.314 $J \cdot mol^{-1} \cdot K^{-1}$

F: Faraday constant (magnitude of electric charge per mole of electrons) = 96 485 C mol^{-1}

Redox potentials may depend on pH STRONGLY !!!



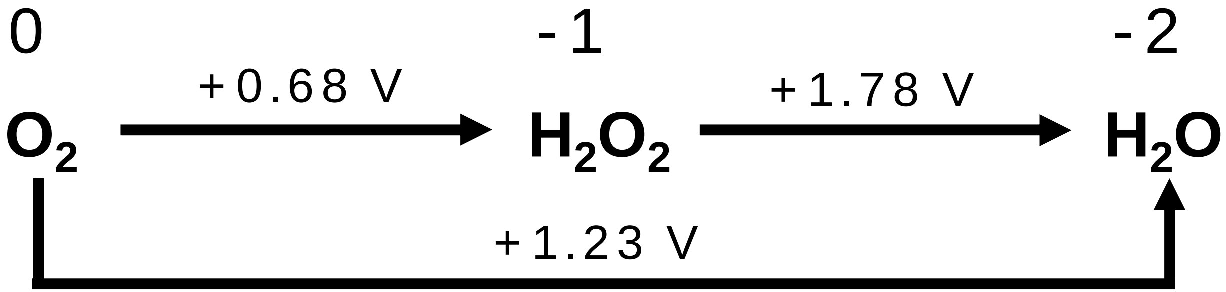
LATIMER DIAGRAM

- **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

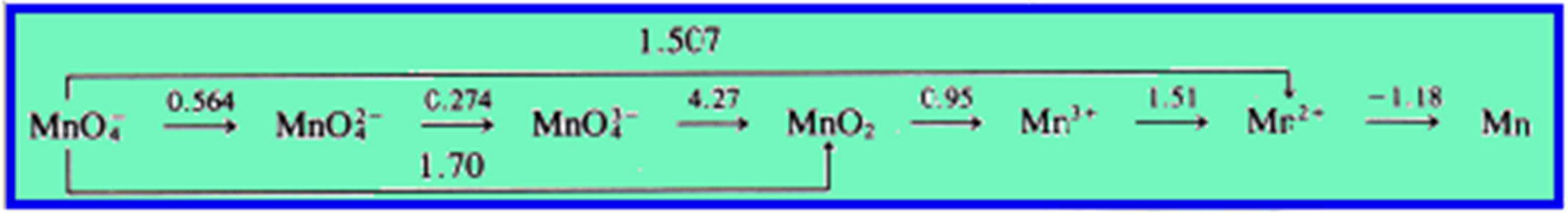
- H_2O_2 is readily reduced to H_2O
- H_2O_2 is NOT so readily oxidized to O_2
- However: +1.78 V > +0.68 V
- H_2O_2 disproportionates into oxygen and water:
  - in practice the reaction is slow without a catalyst



$$\begin{tikzcd}
0 & -1 & -2 \\
O_2 \arrow[r, "+0.68\ V"] \arrow[rr, bend right, "+1.23\ V"'] & H_2O_2 \arrow[r, "+1.78\ V"] & H_2O
\end{tikzcd}$$

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

Which manganese species tend to disportionate ?



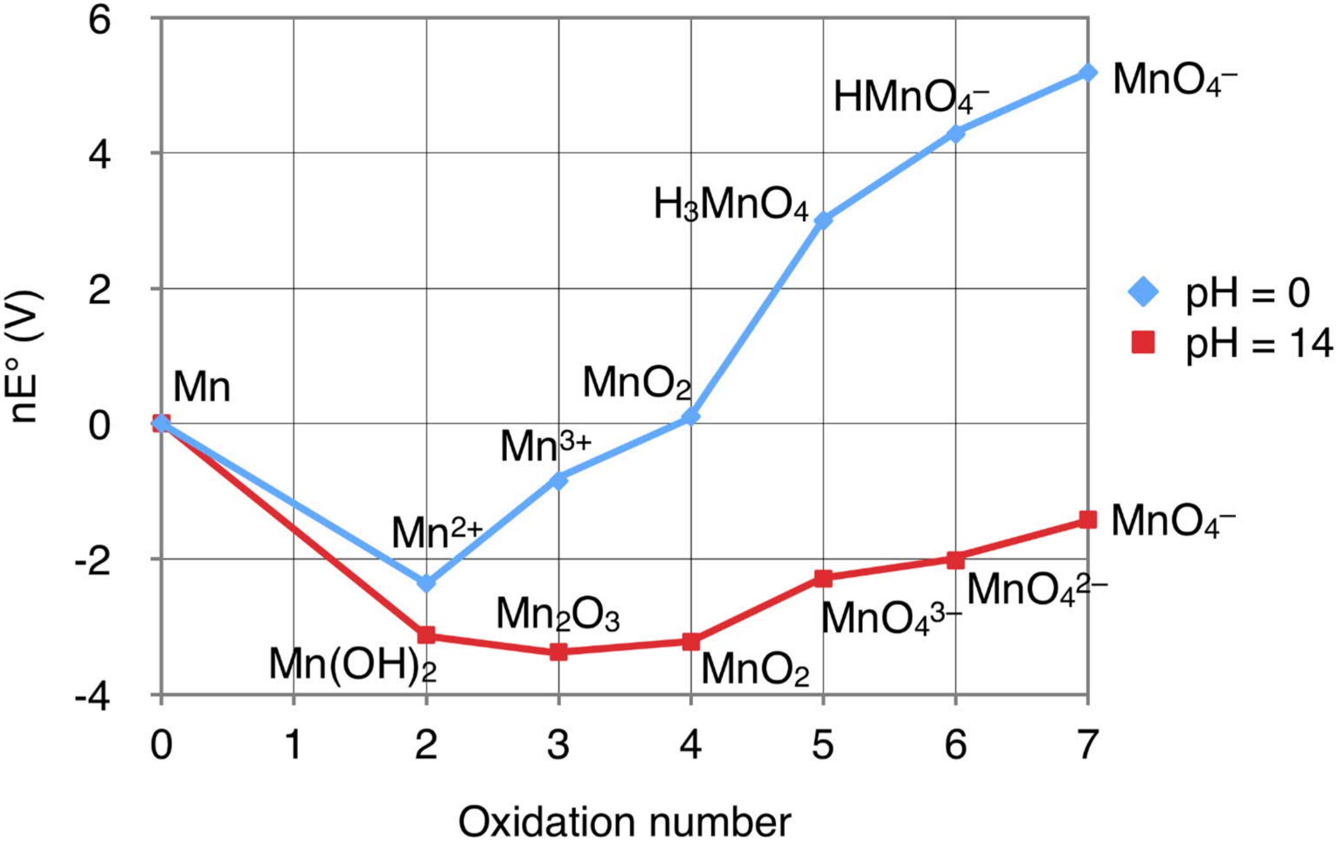
FROST DIAGRAM

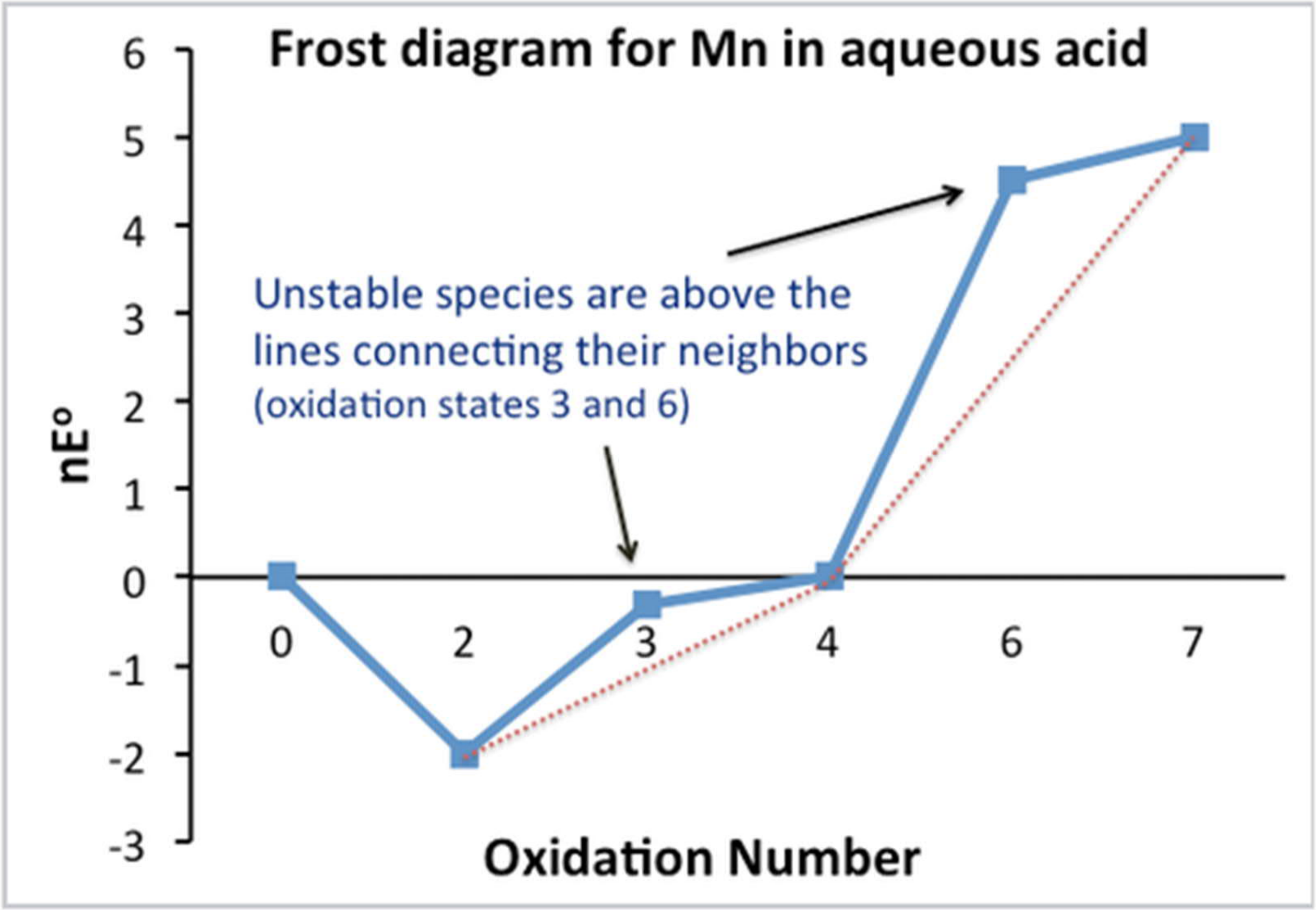
- 2D version of the Latimer diagram
- The number of moving electrons is taken into account ($-n \times E^0_{red}$)
- x-axis: oxidation state
- y-axis: ΔG (in F)
- For pure metal: y = 0 V
- From the diagram we can see:
  relative stabilities of the species with different oxidation states

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

Latimer diagram (acidic conditions)

Frost diagram for manganese



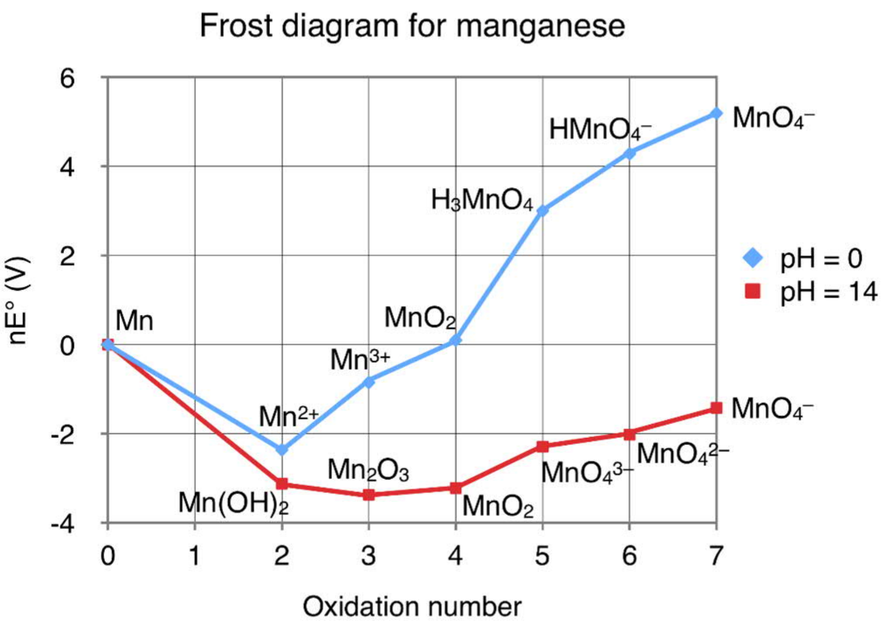


Frost diagram for Mn in aqueous acid

Unstable species are above the lines connecting their neighbors (oxidation states 3 and 6)

What can we see from the Frost diagram

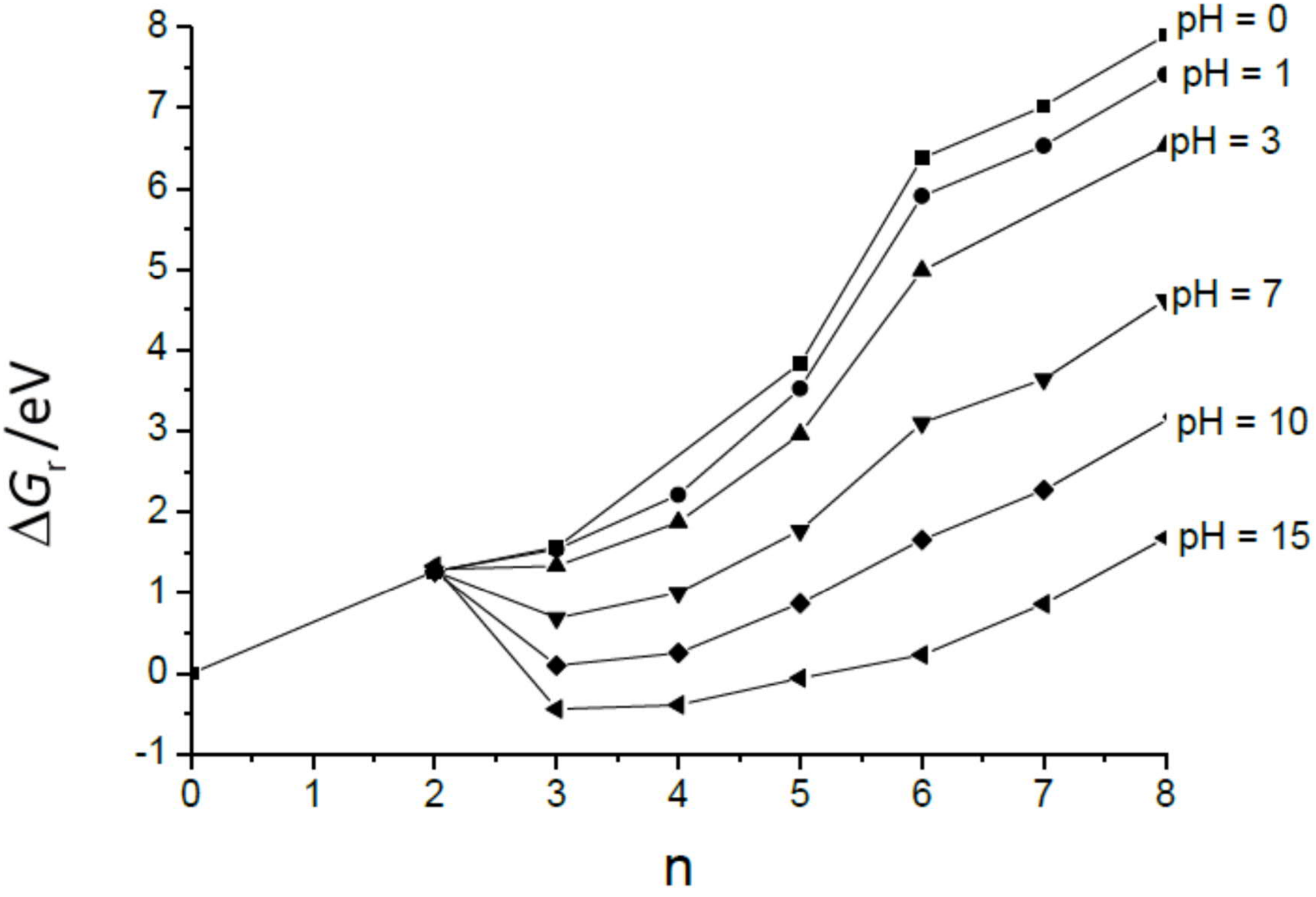
- **The lower the position of the species in the diagram is, the more stable (in terms of redox behavior) the species is**
- **A species that is on a convex (*kupera*) curve (compared to its neighbors) tends to disproportionate**
- **A species that is on a concave (*kovera*) curve (compared to its neighbors)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

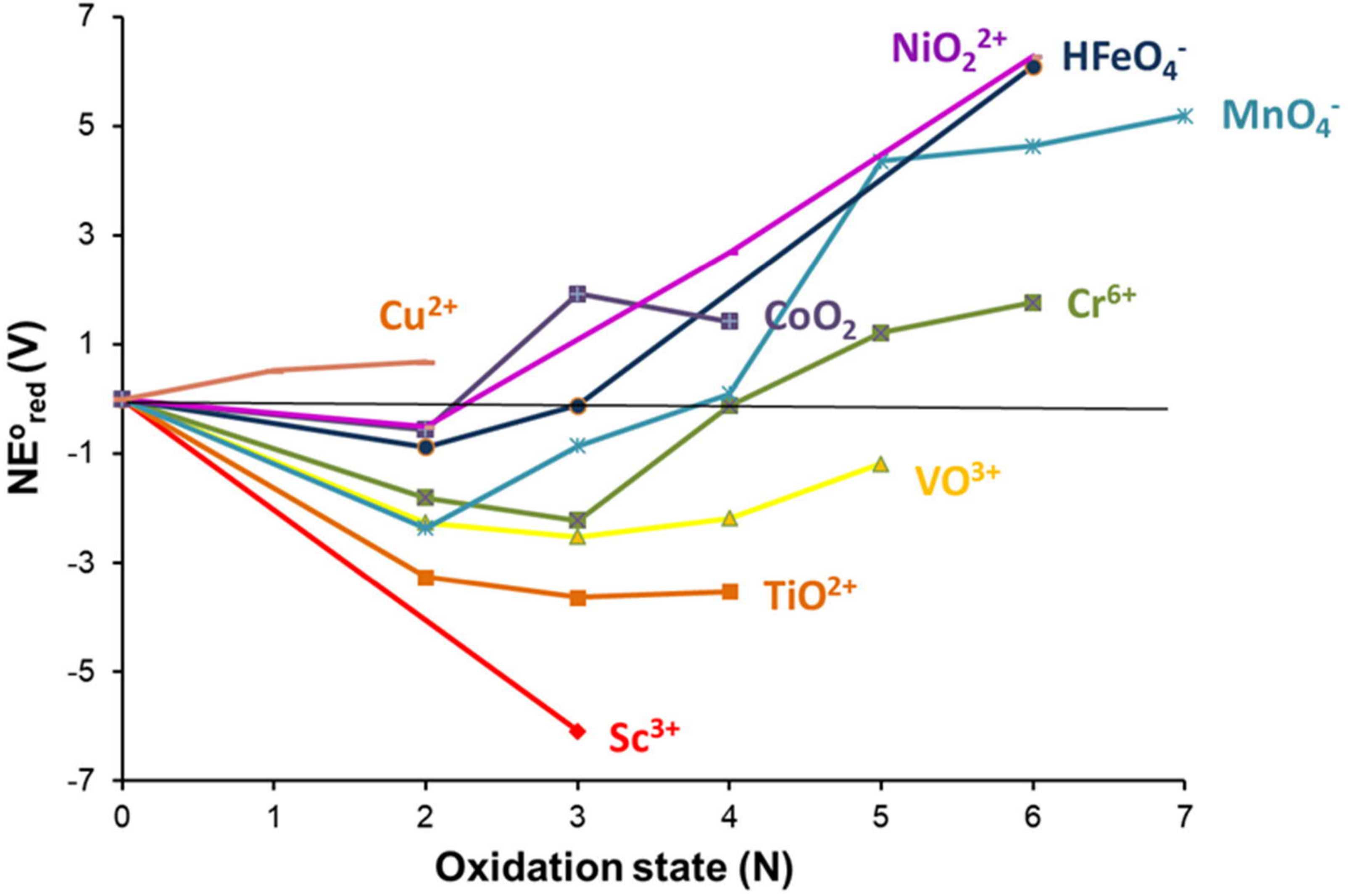


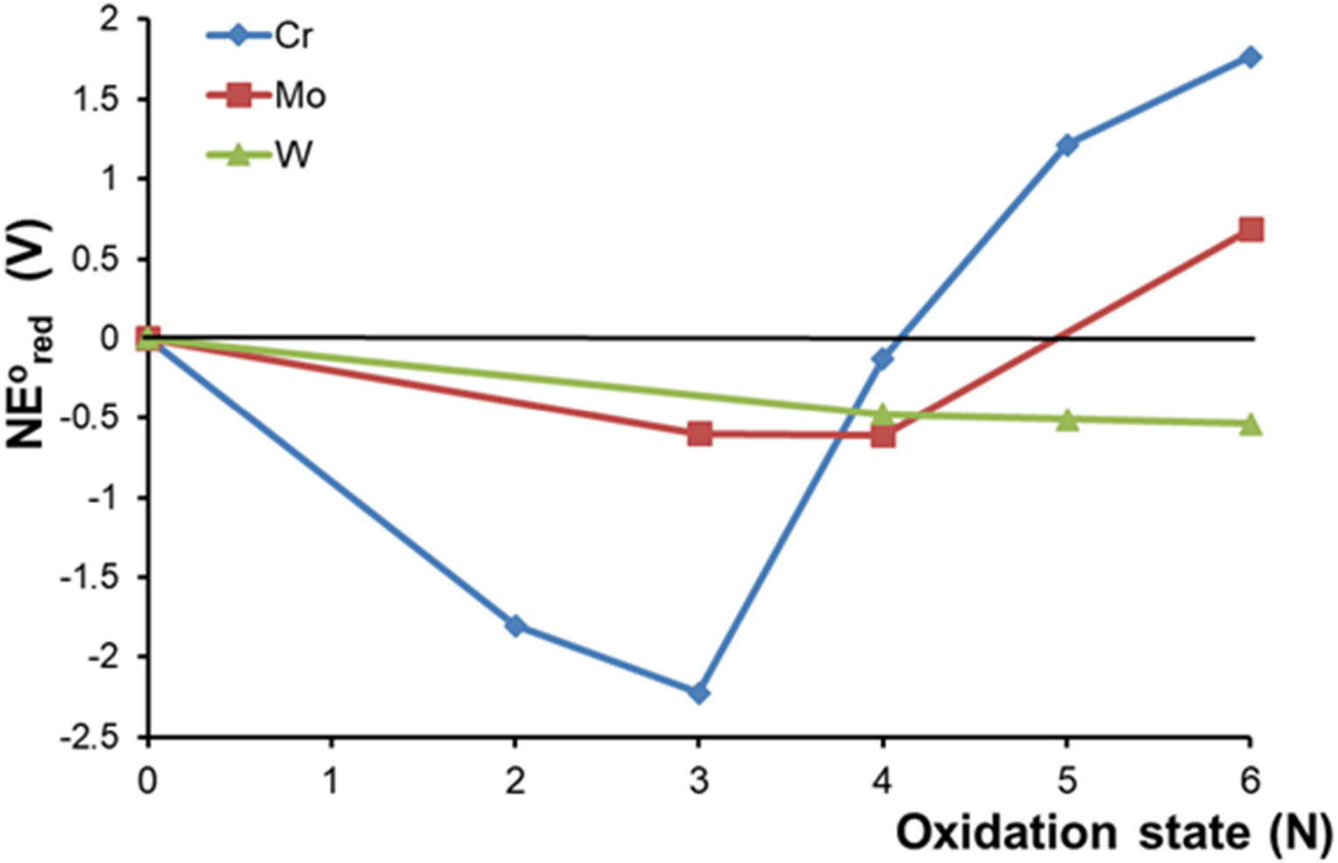
Manganese (acidic cond)

- 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

RUTHENIUM Ru

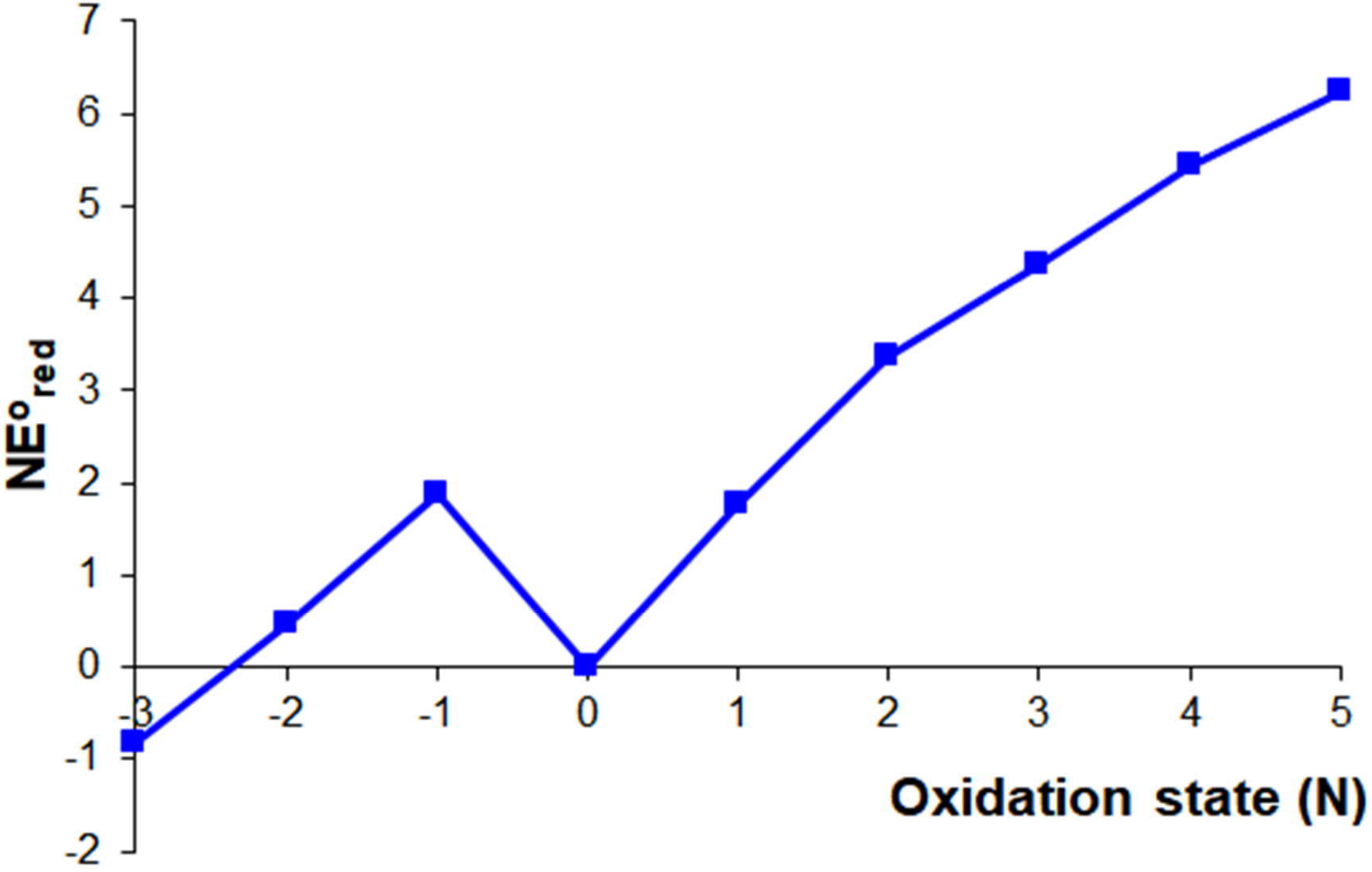


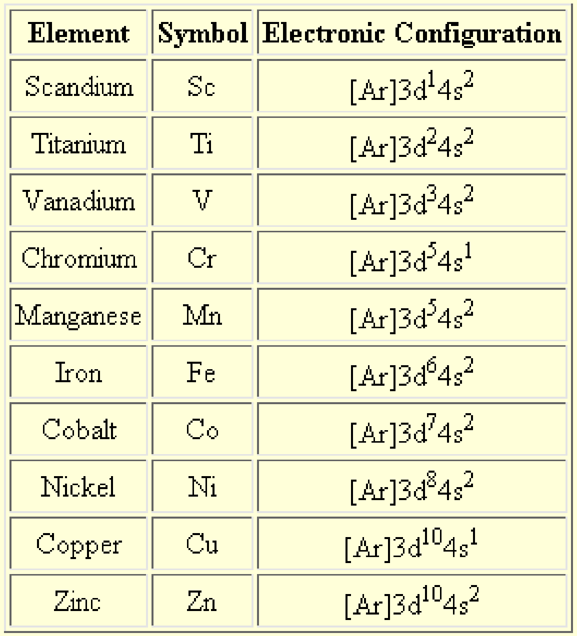

NE°red (V)
Oxidation state (N)
7
5
3
1
-1
-3
-5
-7
0
1
2
3
4
5
6
7
NiO2 2+
HFeO4 -
MnO4 -
Cu2+
CoO2
Cr6+
VO3+
TiO2+
Sc3+


Cr
Mo
W
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
NE^o_{red} (V)
0
1
2
3
4
5
6
Oxidation state (N)

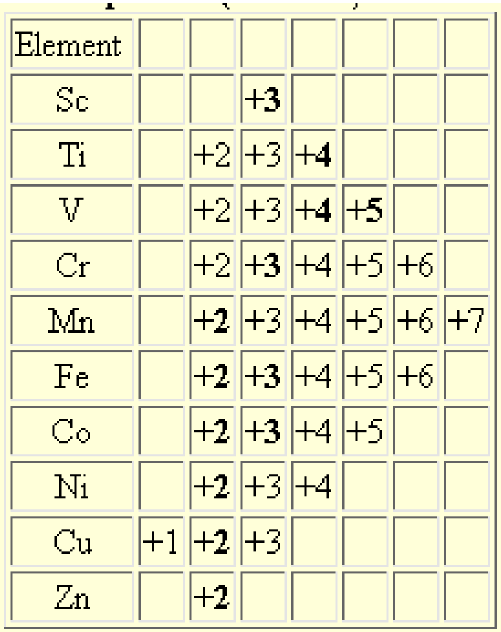
+5 **+4** **+3** **+2** **+1** **0** **-1** **-2** **-3**

$$NO_3^- \xrightarrow{0.803\ V} N_2O_4 \xrightarrow{1.07\ V} HNO_2 \xrightarrow{0.996\ V} NO \xrightarrow{1.59\ V} N_2O \xrightarrow{1.77\ V} N_2 \xrightarrow{-1.87\ V} NH_3OH^+ \xrightarrow{1.41\ V} N_2H_5^+ \xrightarrow{1.275\ V} NH_4^+$$



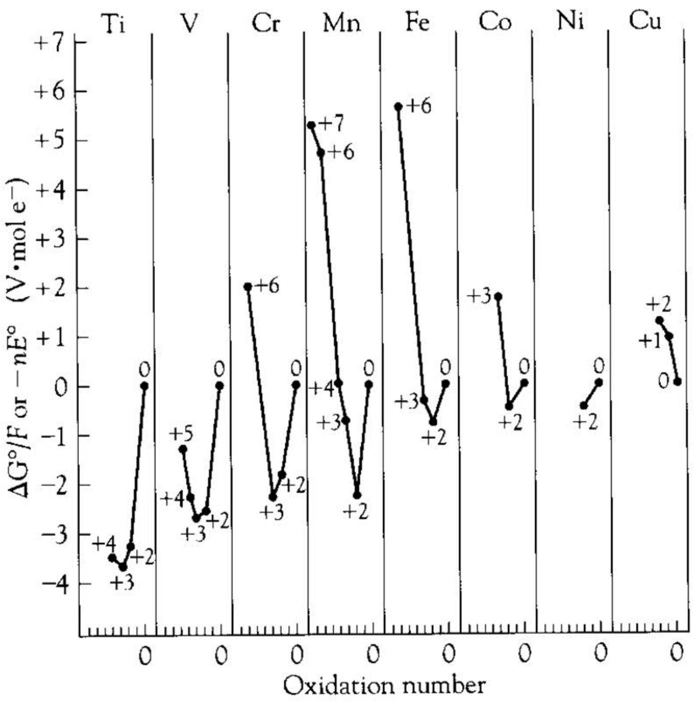


Element	Symbol	Electronic Configuration
Scandium	Sc	$[Ar]3d^14s^2$
Titanium	Ti	$[Ar]3d^24s^2$
Vanadium	V	$[Ar]3d^34s^2$
Chromium	Cr	$[Ar]3d^54s^1$
Manganese	Mn	$[Ar]3d^54s^2$
Iron	Fe	$[Ar]3d^64s^2$
Cobalt	Co	$[Ar]3d^74s^2$
Nickel	Ni	$[Ar]3d^84s^2$
Copper	Cu	$[Ar]3d^{10}4s^1$
Zinc	Zn	$[Ar]3d^{10}4s^2$



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**					

FROST DIAGRAMS



OXIDATION STATES (slightly depending on conditions !)

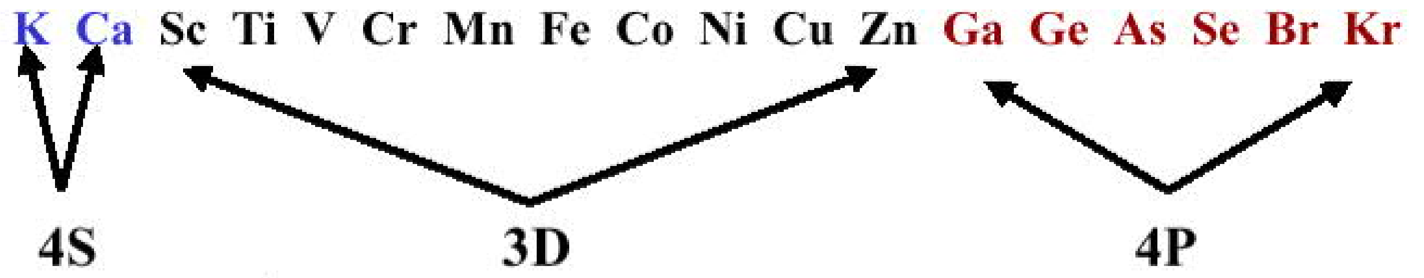
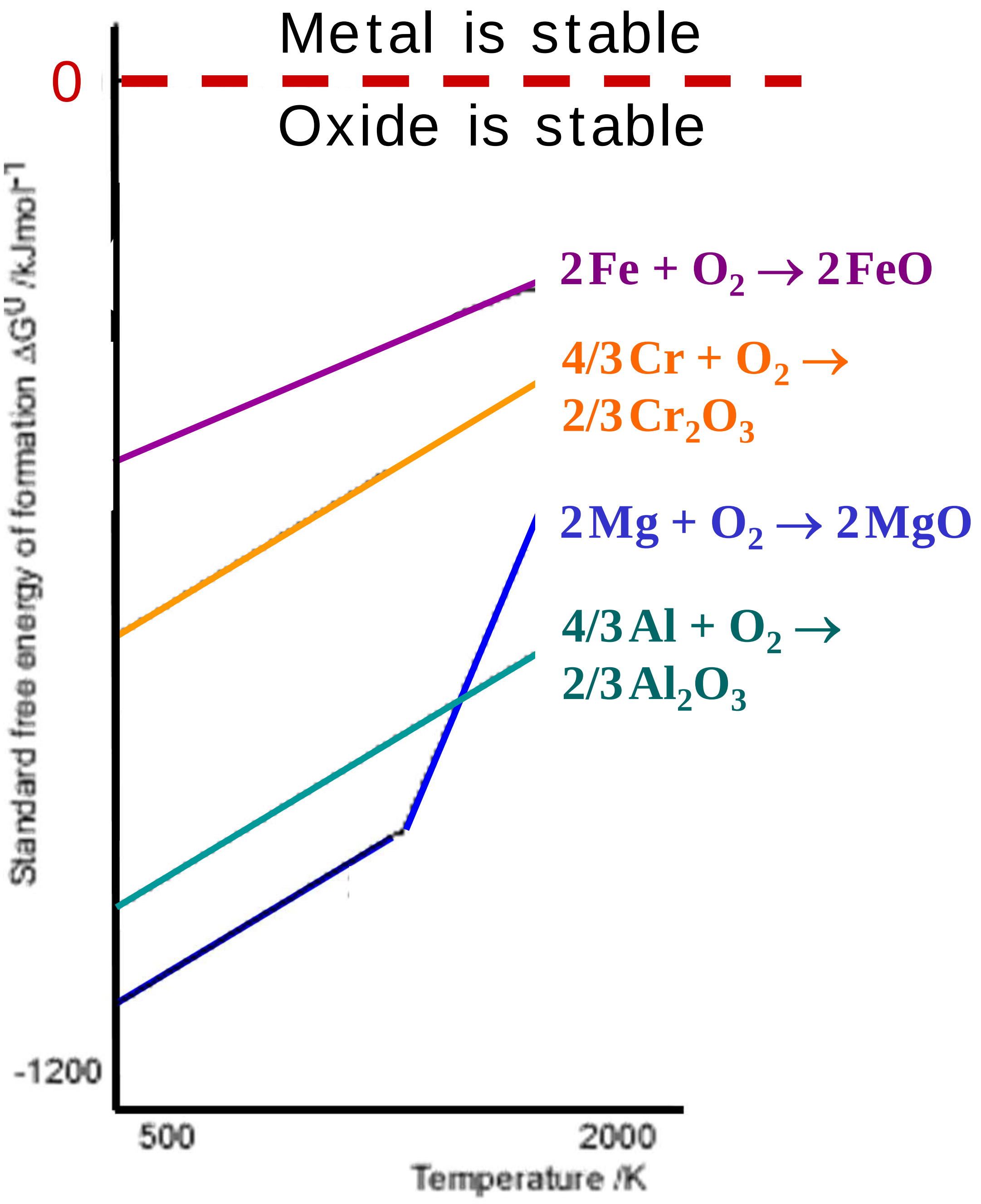
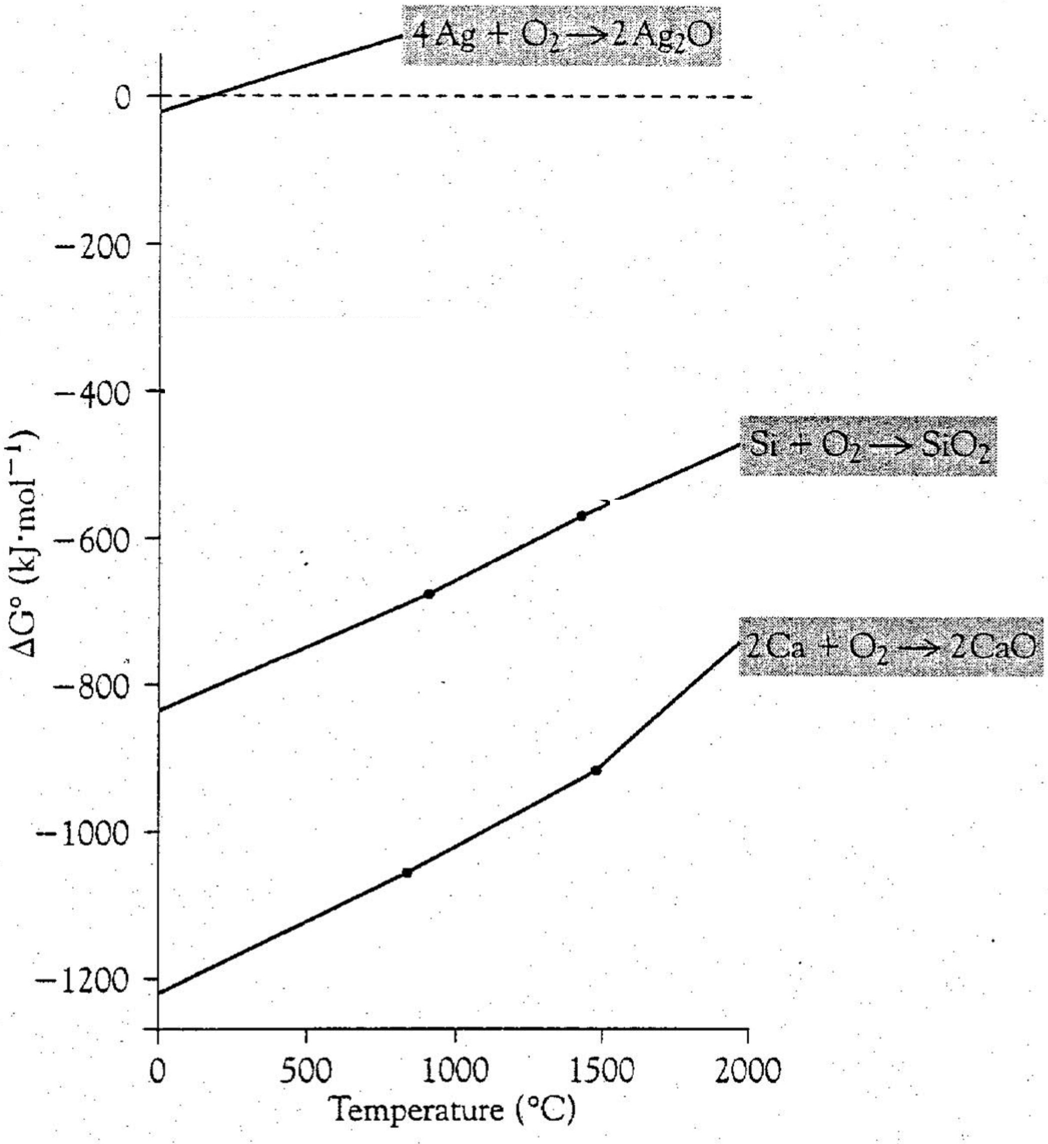


Figure 1. The 4th row of the periodic table. The transition metals are the elements that range from Sc (Scandium) to Zn (Zinc).

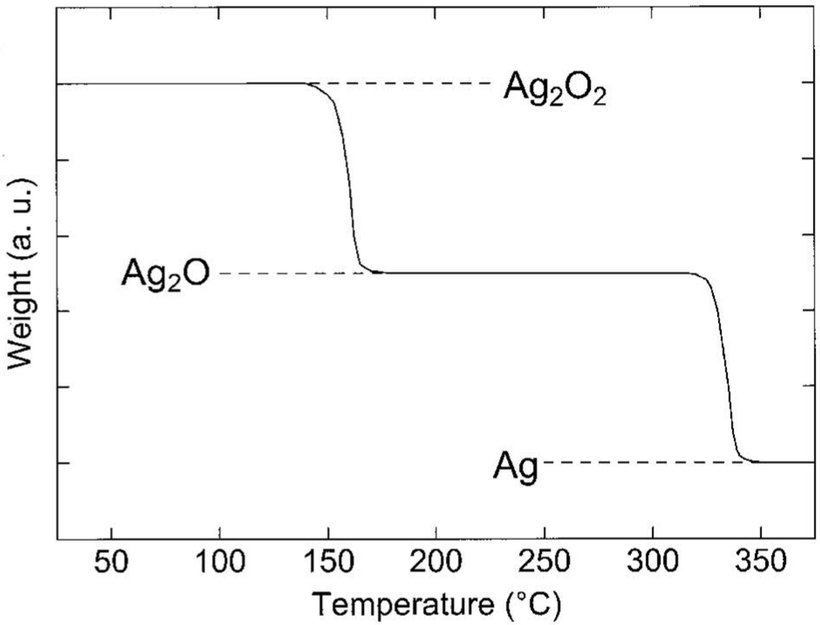
Ellingham diagram

- 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

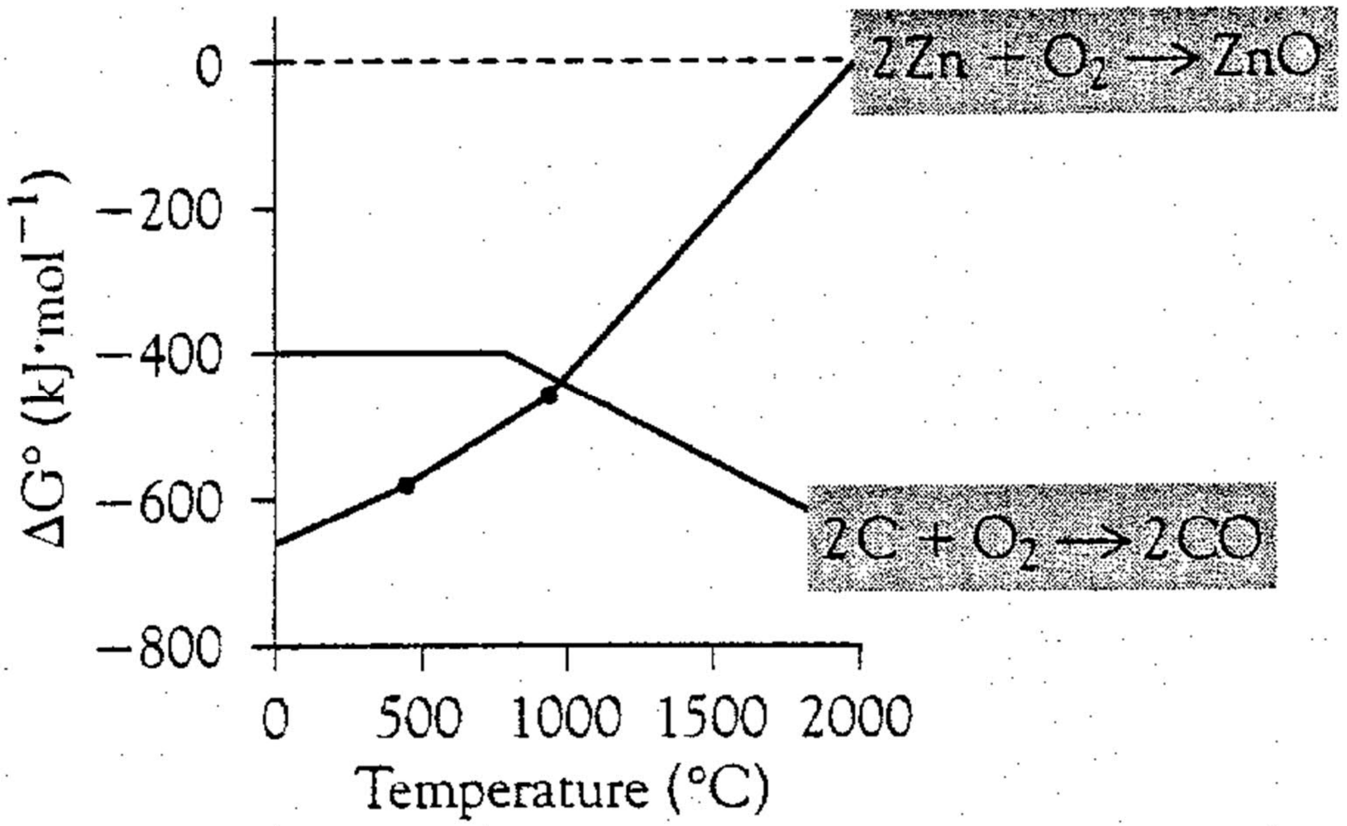




$4Ag + O_2 \rightarrow 2Ag_2O$
$Si + O_2 \rightarrow SiO_2$
$2Ca + O_2 \rightarrow 2CaO$
ΔG° (kJ·mol⁻¹)
0
−200
−400
−600
−800
−1000
−1200
0
500
1000
1500
2000
Temperature (°C)

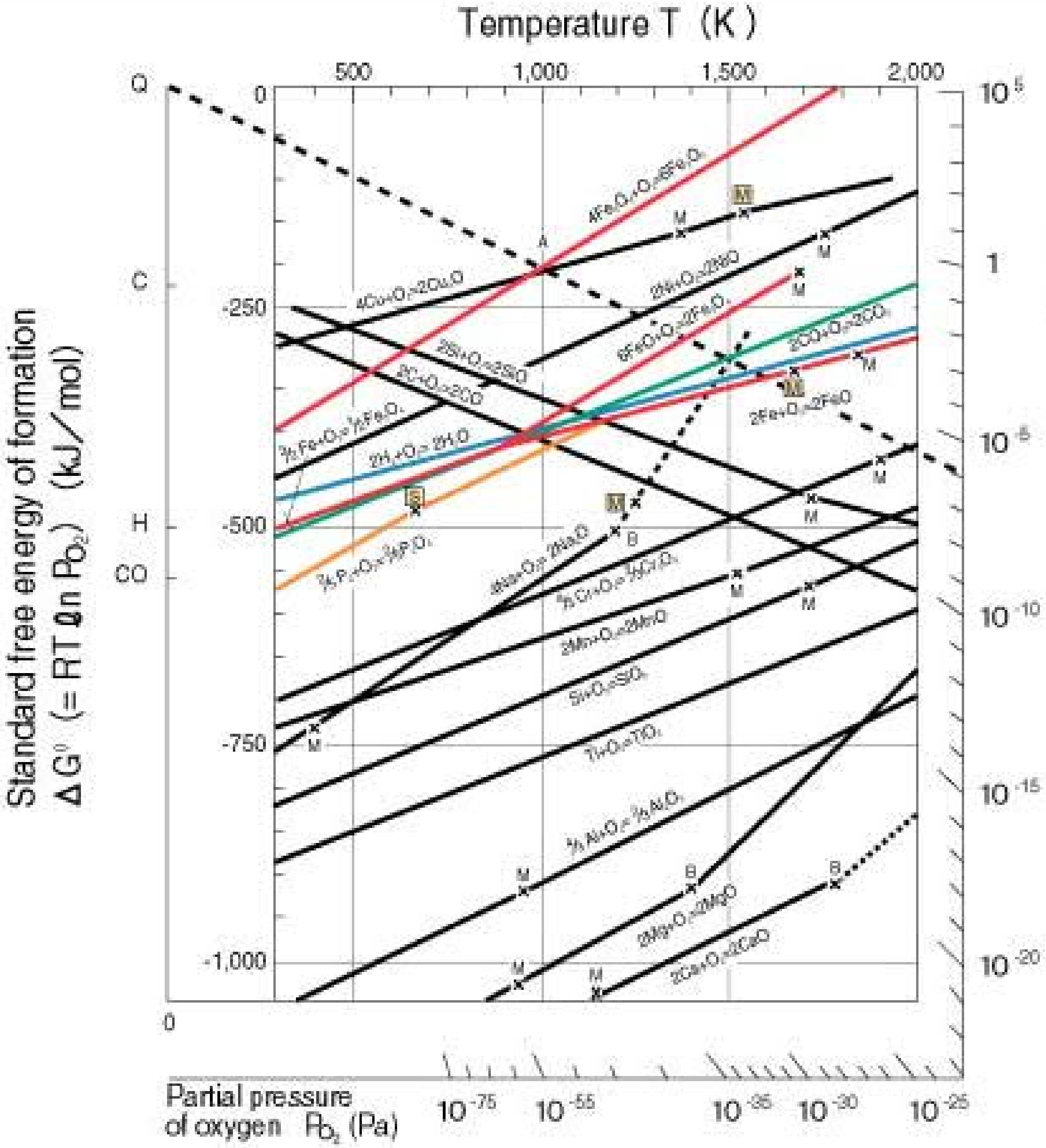


Ag_2O_2
Ag_2O
Ag
Weight (a. u.)
50
100
150
200
250
300
350
Temperature (°C)



Above 900 ^oC ZnO can be reduced to Zn by carbon

2B(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)

$\Delta G^0=RT\ \ell n\ P_{O_2}$ (2)

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

Oxygen Release

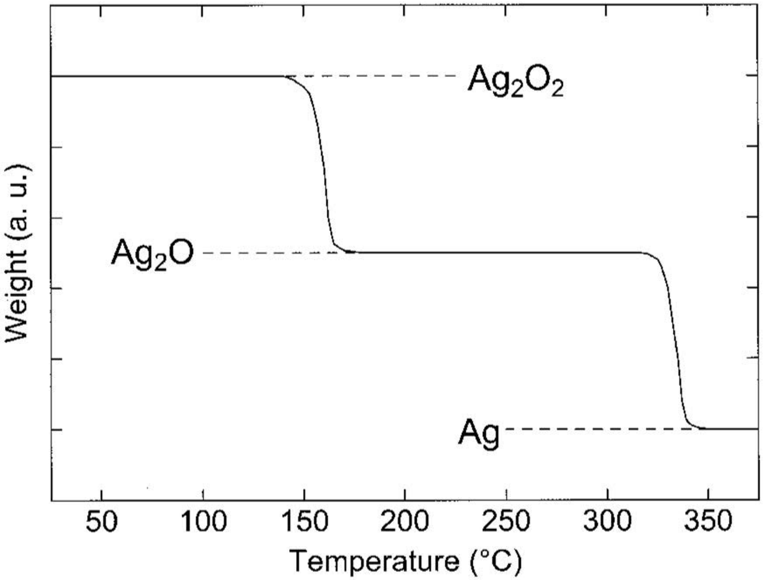
Oxygen Engineering !

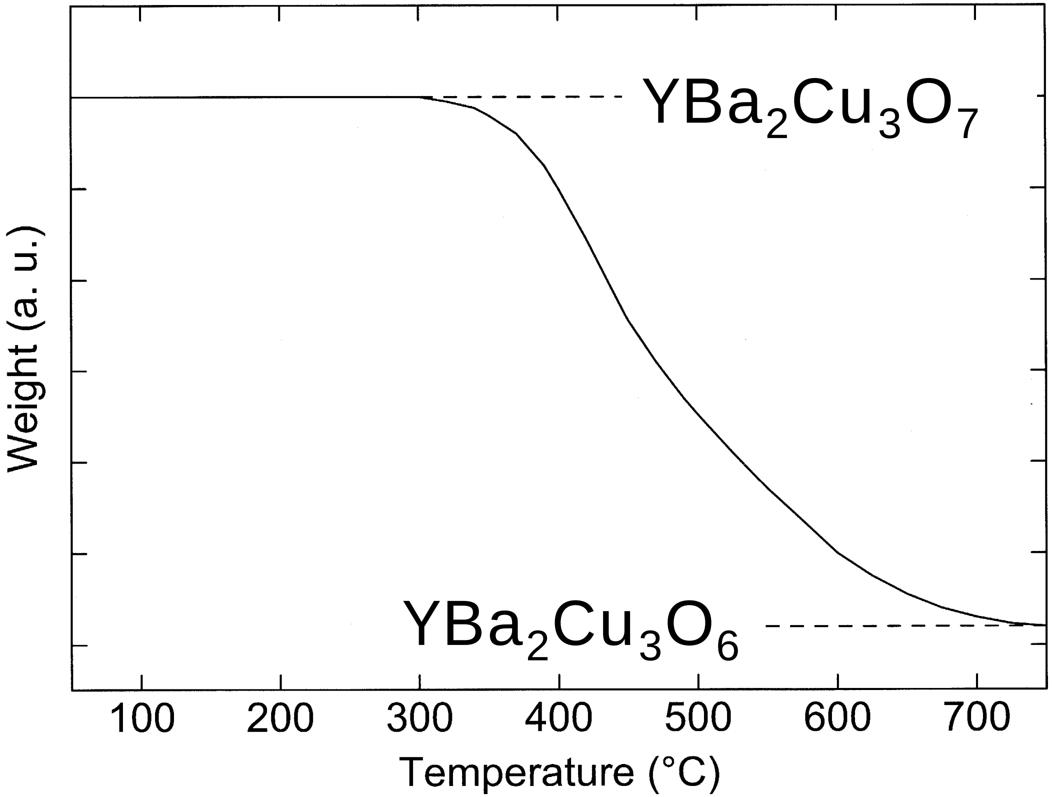
Ag_2O_2 :

in two discrete steps

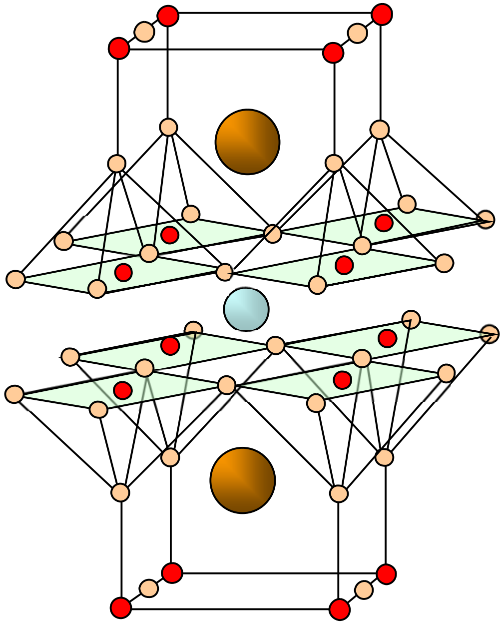
$YBa_2Cu_3O_{7-\delta}$:

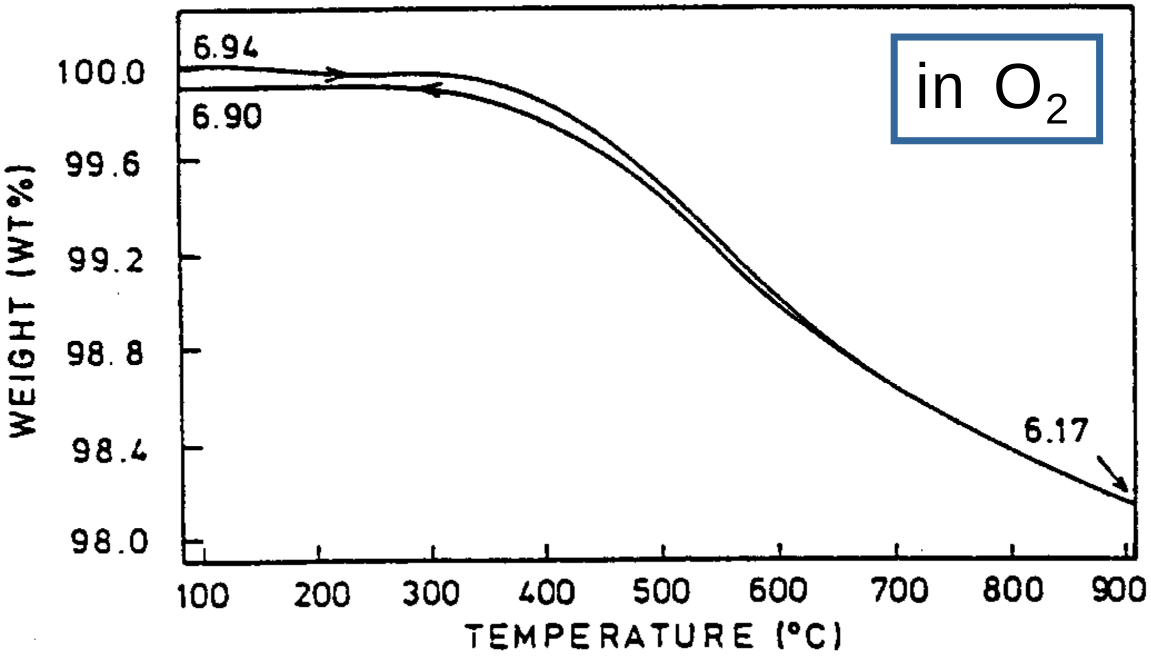
Gradually → mixed-valent Cu

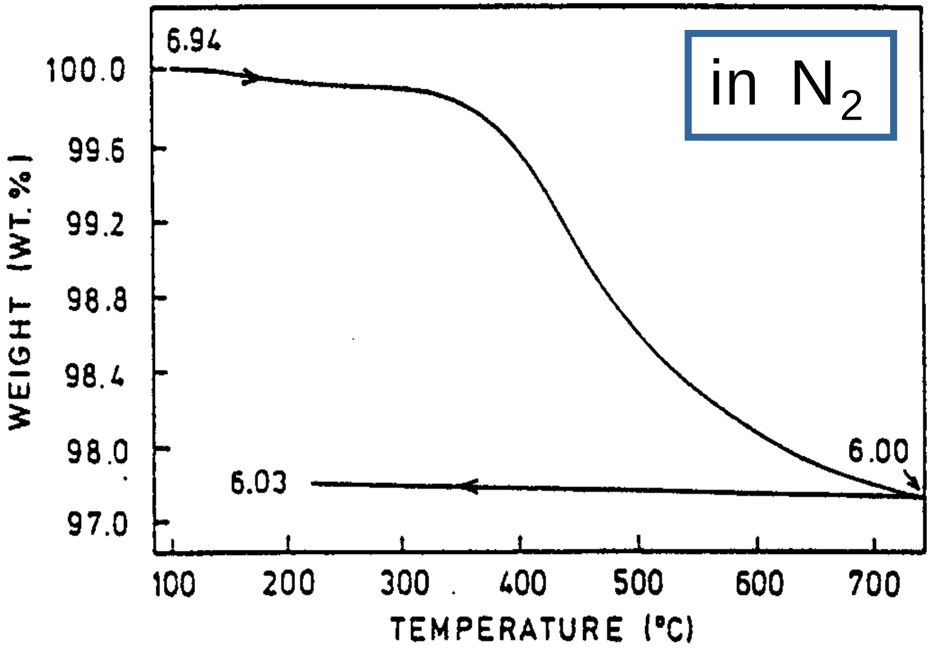




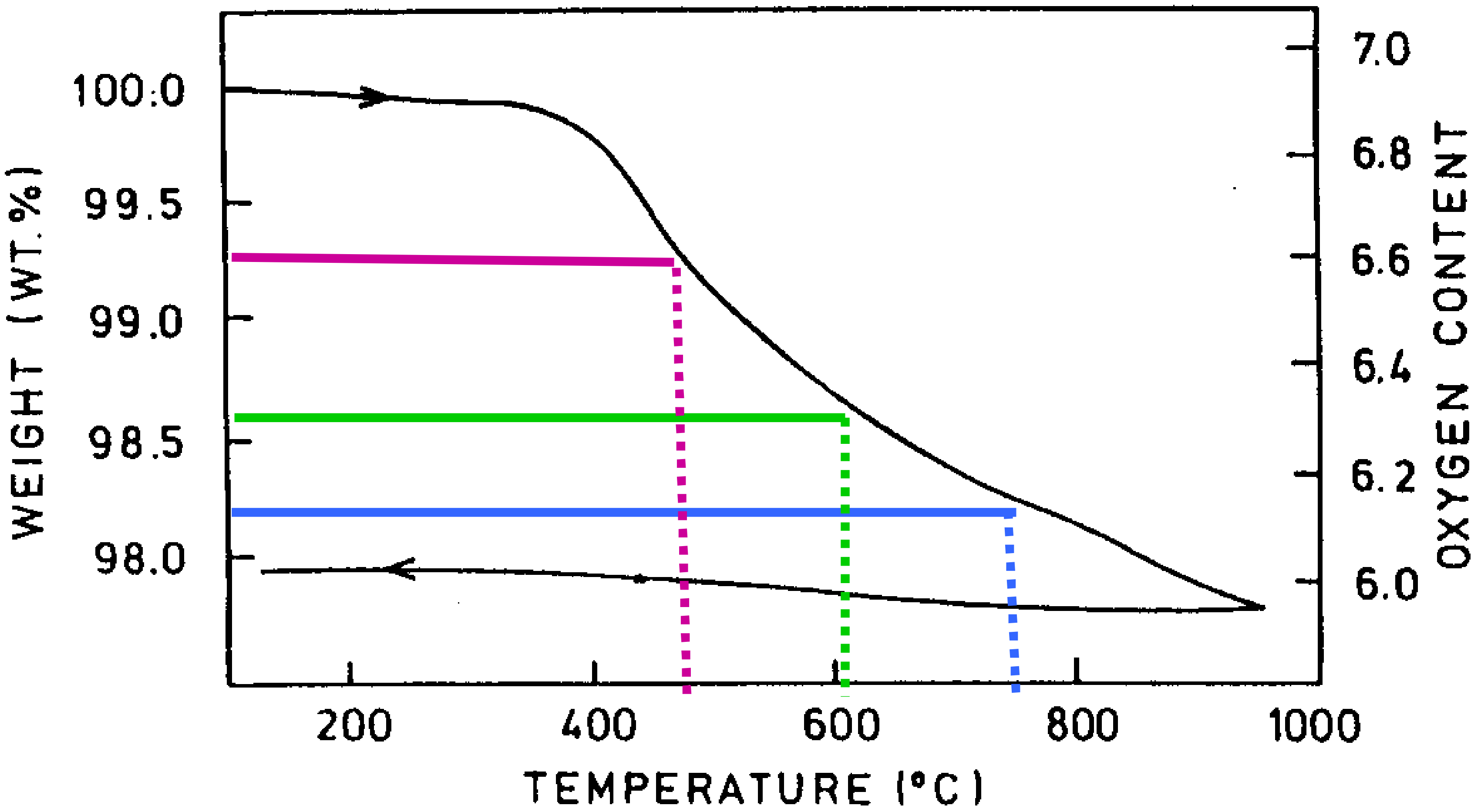
$YBa_2Cu_3O_{7-\delta}$

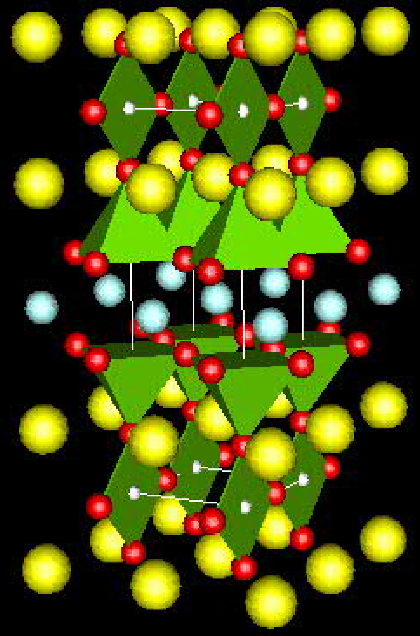






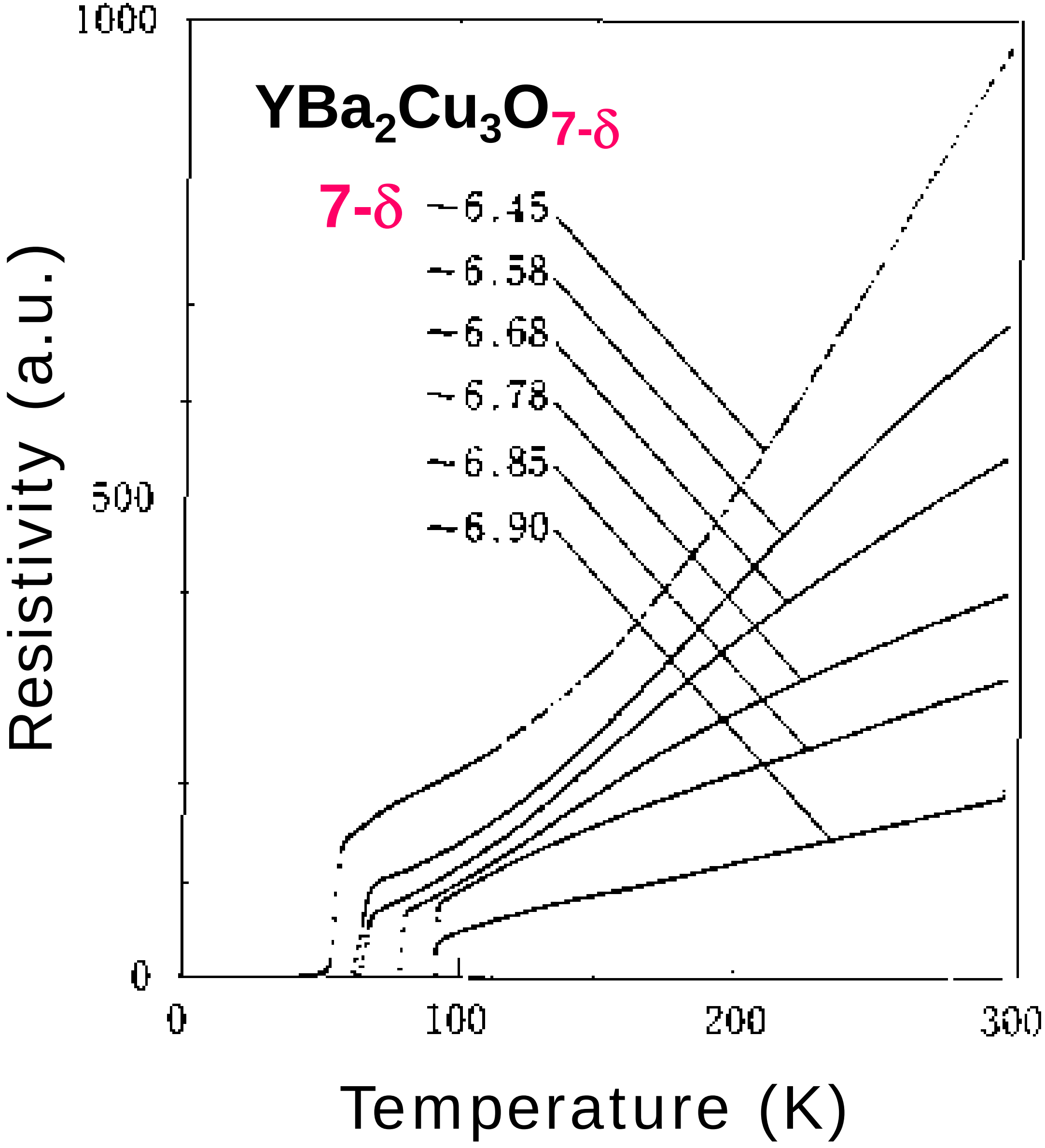
OXYGEN-DEFICIENT SAMPLES





$YBa_2Cu_3O_{7-\delta}$

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

- $Zn_{1+x}O$