

Topic I

Basic principles of extraction of metals from ores & purification

Extraction of Metals -the chemistry within

Iron Pillar of Delhi



- ❖ The History of metallurgy in the Indian subcontinent dates back to 1700 BC.
- ❖ Metals and related concepts were mentioned in various early Vedic age texts.
- ❖ The Rig-Veda already uses the Sanskrit term **Ayas** (metal).

Composition: Iron Pillar of Delhi

[Fe(O)(OH)]

Published composition analyses of DIP iron

	Hadfield [25] (1912)	Ghosh [5] (1963)		Lahiri et al. [27] (1963)	Lal [26] (1945)
		Above	Under		
C	0.08	0.23	0.03	0.26	0.90
Si	0.046	0.026	0.004	0.056	0.048
S	0.006	trace	0.008	0.003	0.007
P	0.114	0.280 ^a	0.436–0.48	0.155	0.174
Mn	Nil	Nil	Nil	Nil	Nil
N	–	0.0065			
Fe	99.720	Diff			99.67
Others	0.246				0.011
Specific gravity	7.81	7.672–7.747		7.5	

Oxygen	46.71	1774	92 %	99.5 %	All other elements = 0.03 %	
Silicon	27.69	1824				
Aluminum	8.07	1825				
Iron	5.05	ancient				
Calcium	3.65	1808				
Sodium	2.75	1807	99.97 %			Need for efficient separation techniques
Potassium	2.58	1807				
Magnesium	2.08	1755				
Titanium	0.62	1791				
Hydrogen	0.14	1776				
Phosphorus	0.13	1669				
Carbon	0.094	ancient				
Manganese	0.09	1774				
Sulfur	0.052	ancient				
Barium	0.05	1808				
Chlorine	0.045	1774				
Chromium	0.035	1797				
Fluorine	0.029	1886				
Zirconium	0.025	1789				
Nickel	0.019	1751				

Methods of Separation / Extraction

1. Mechanical separation

2. Thermal decomposition

3. Displacement

4. High temperature chemical reduction

5. Electrolytic reduction

And so on

(i) Mechanical Separation

Free elemental form – unreactive elements

Coinage & Pt metals

Gold; 19.3 g/cm^{-3} , separated by *panning*



(ii) Thermal Decomposition

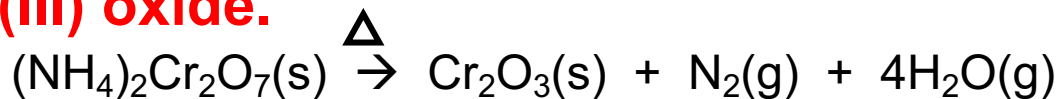
Unstable compounds \rightarrow Constituent elements



Marsh test: As, Sb salt + Zn/H₂SO₄ \rightarrow As/SbH₃ \rightarrow Silver mirror of the metal

Decomposition of ammonium compounds

Ammonium dichromate on heating yields nitrogen, water and chromium(III) oxide.



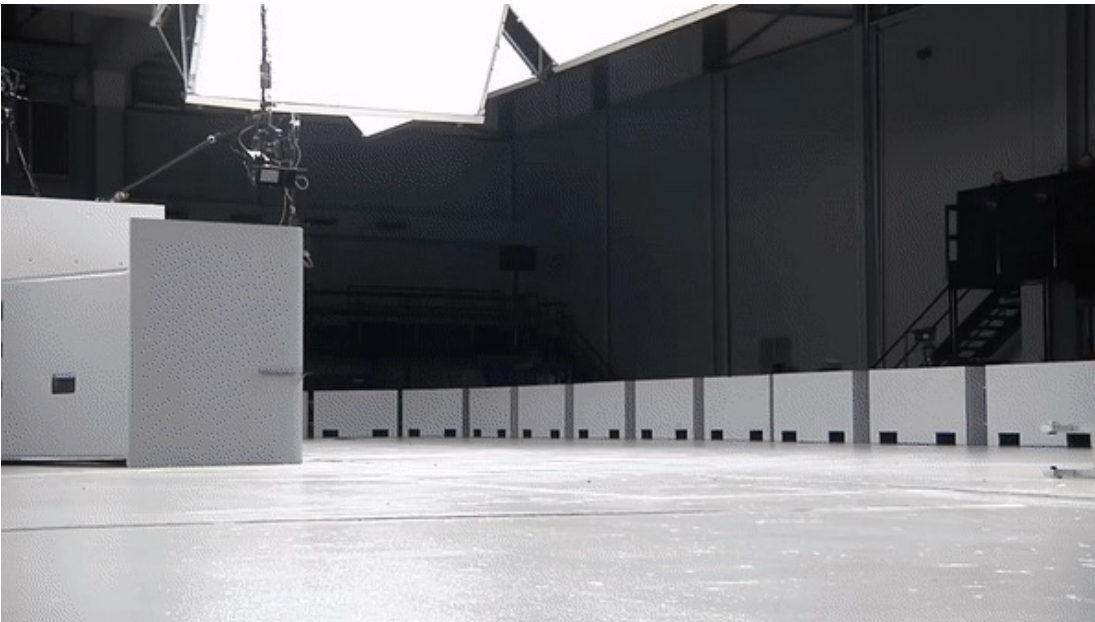
Please refer to text book or other resources for more examples of thermal decomposition reactions: **Self study**

Thermal Decomposition of Carbonate and Azide

Carbonate decomposition



Azide decomposition / Life saving reaction

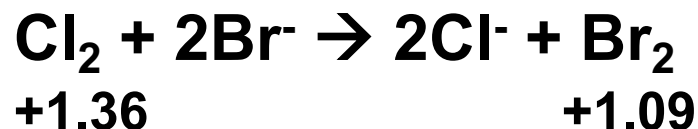
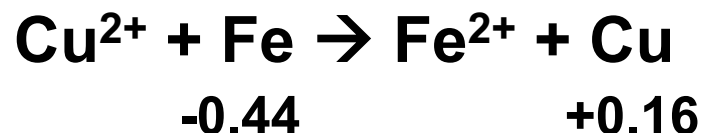


0.03 SECOND is all it takes to inflate an air bag.

130 g. needed (~ Rs. 100)

(iii) Displacement Of One Element By Other

In principle, any element may be displaced by another element which has more negative E° in electrochemical series.





How does this work?



$$\text{Total} = +0.78$$

Exothermic reaction...

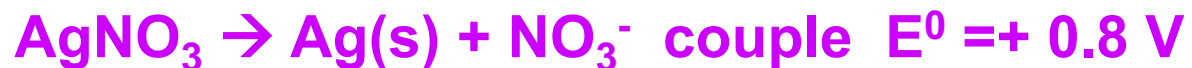
	Half Reaction	Standard Potential (V)
	$\text{F}_2 + 2\text{e}^- \rightleftharpoons 2\text{F}^-$	+2.87
	$\text{Pb}^{4+} + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+}$	+1.67
	$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36
	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.23
	$\text{Ag}^+ + 1\text{e}^- \rightleftharpoons \text{Ag}$	+0.80
	$\text{Fe}^{3+} + 1\text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
	$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$	+0.34
	$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.00
	$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$	-0.13
	$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$	-0.44
	$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	-0.76
	$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}$	-1.66
	$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}$	-2.36
	$\text{Li}^+ + 1\text{e}^- \rightleftharpoons \text{Li}$	-3.05
		

Demonstration !!!



Demonstration II

Which one can oxidize Cu then?



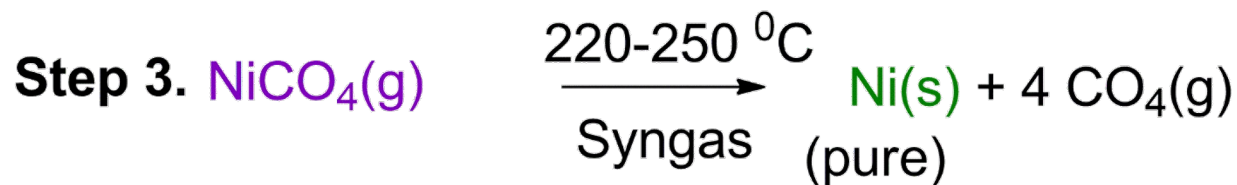
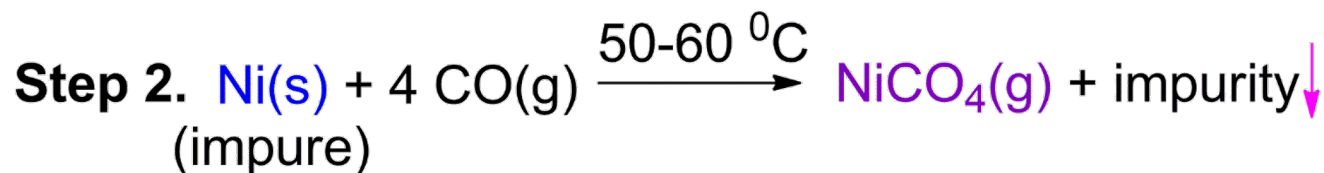
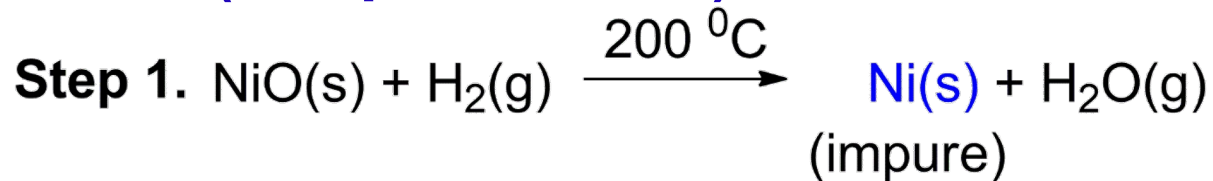
High Temperature Chemical Reduction

1. Many metals are found as their oxides
2. Oxide Ores: Directly reduced (smelted) to the metal. General reducing agents: C , Al, Si, H₂. Carbon is the most widely used reducing agent (can form carbide)
3. Sulfide Ores: First roasted to convert them to oxide and then reduced to the metal (for thermodynamic reasons oxides rather than sulfides used) (SELF REDUCTION)
4. Other metals as reducing agents

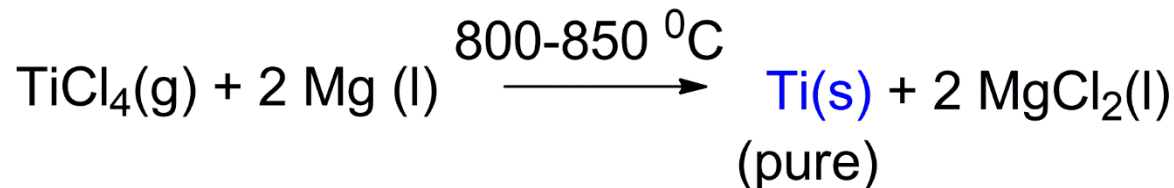
(all points will be elaborated)

Chemical Reduction

Mond's Process (For pure nickel):

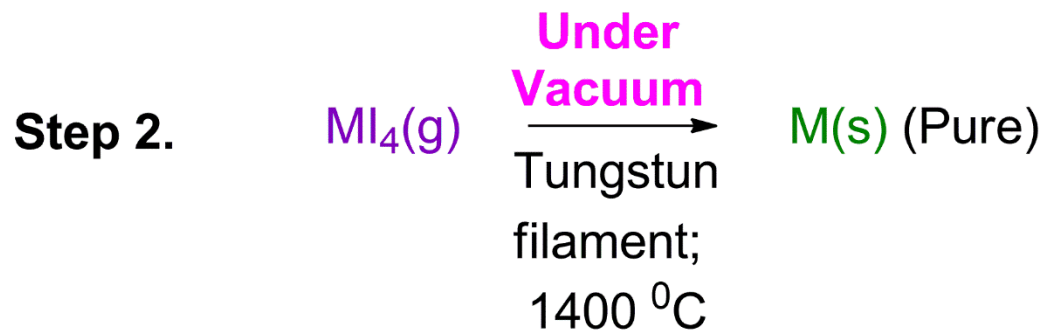
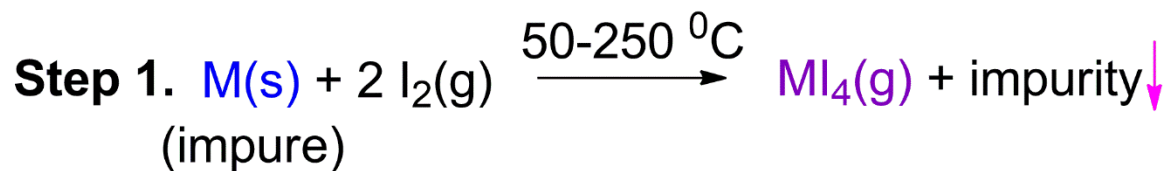


Kroll's Process (for pure titanium):



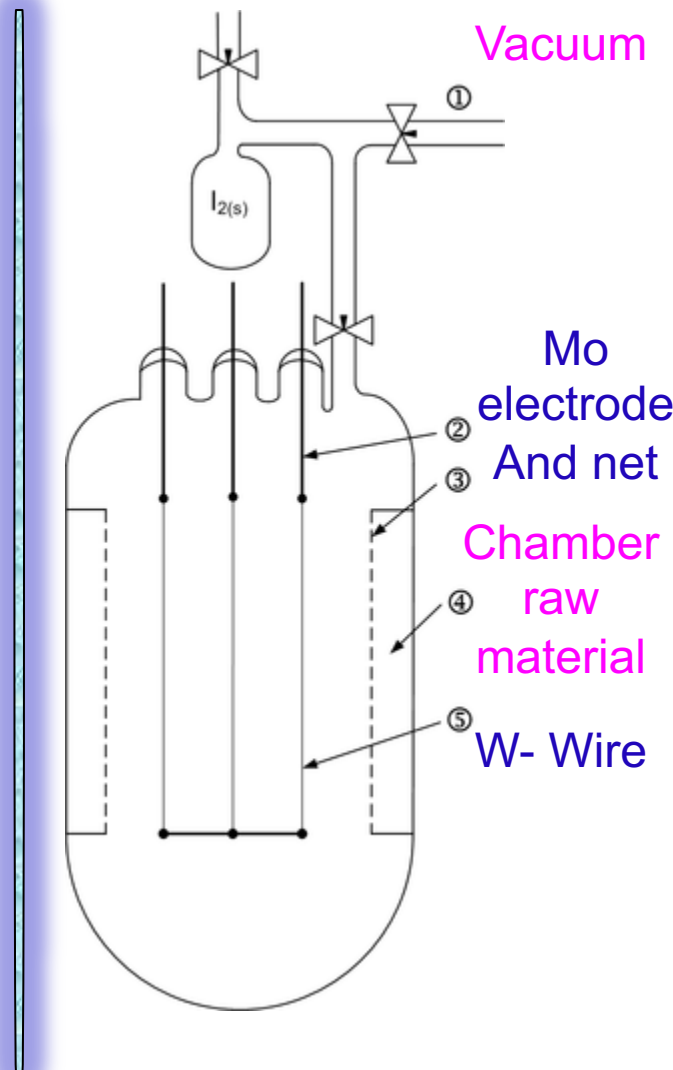
First Industrial Process For Zr and Ti

Van Arkel-deBoer's Process (for metallic Zr / Ti):



Where M = **Ti**, **Zr**, Hf, V, Th

MI_4	MP ($^{\circ}\text{C}$)	BP ($^{\circ}\text{C}$)
Ti	150	377
Zr	499	600



Electrolytic Reduction

- 1. Electron – the strongest known reducing agent.**
- 2. Highly electropositive metals, e.g. alkaline earth metals are produced this way (Electrolytic reduction of their fused halides)**
- 3. Ionic materials (salts) are electrolyzed – reduction at cathode**
- 4. Excellent method, gives pure metal, but expensive**

Methods of Separation / Extraction

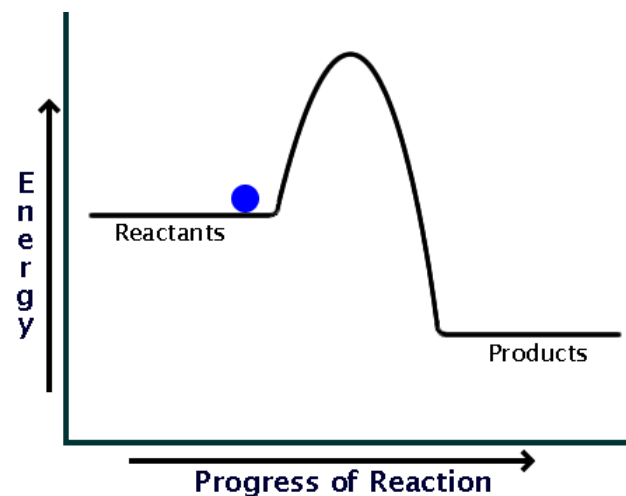
- 1. Mechanical separation**
 - 2. Thermal decomposition**
 - 3. Displacement of one element by other**
 - 4. High temperature chemical reduction**
 - 5. Electrolytic reduction**
- And so on**

High –T Chemical Reduction- Thermodynamic Considerations....

1. Used to identify which reactions are spontaneous under the prevailing conditions.
2. To choose most economical reducing agent and reaction condition

Criterion for spontaneity

$$\Delta G^{\circ} = - RT \ln K$$



- Negative ΔG° corresponds to $K > 1$; favorable reaction
- Kinetics is not important as reductions are done at high. temp & fast

High –T Chemical Reduction- Thermodynamic Considerations....

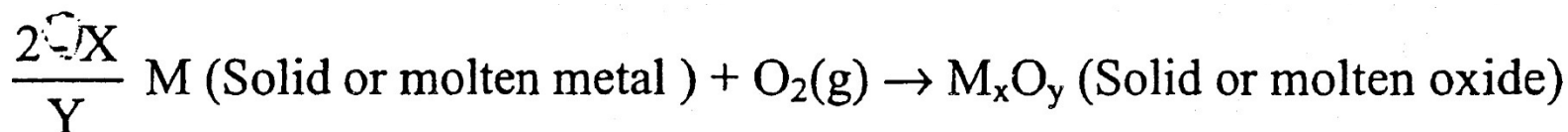
$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S$$

For the formation of metal oxide,
 $2M(s) + O_2(g) \rightarrow 2MO(s)$

- ΔS is negative; because oxygen gas is used up.
- If temperature is raised, $T\Delta S$ becomes more negative & hence $(-T\Delta S)$ is more positive
- Thus the free energy change (ΔG°) increases with increase in the temperature

Table-1 : Heats of formation of some metal oxides

Oxide	ΔH_f (per mole of O_2 (g))	$E^\circ (M_{aq} / M)$
M_gO	-288 Kcal	-2.37 volts
Al_2O_3	-266 Kcal	-1.66 volts
ZnO	-166 Kcal	-0.76 volts
NiO	-177 Kcal	-0.25 volts
CuO	-74 Kcal	+0.34 volts
Ag_2O	-15 Kcal	+0.78 volts



$$\Delta G^\circ = \Delta H^\circ - T\Delta S$$

The free energy changes that occur when one gram molecule of a common reactant (O_2) is used, is plotted against temperature.

This graph is called Ellingham Diagram

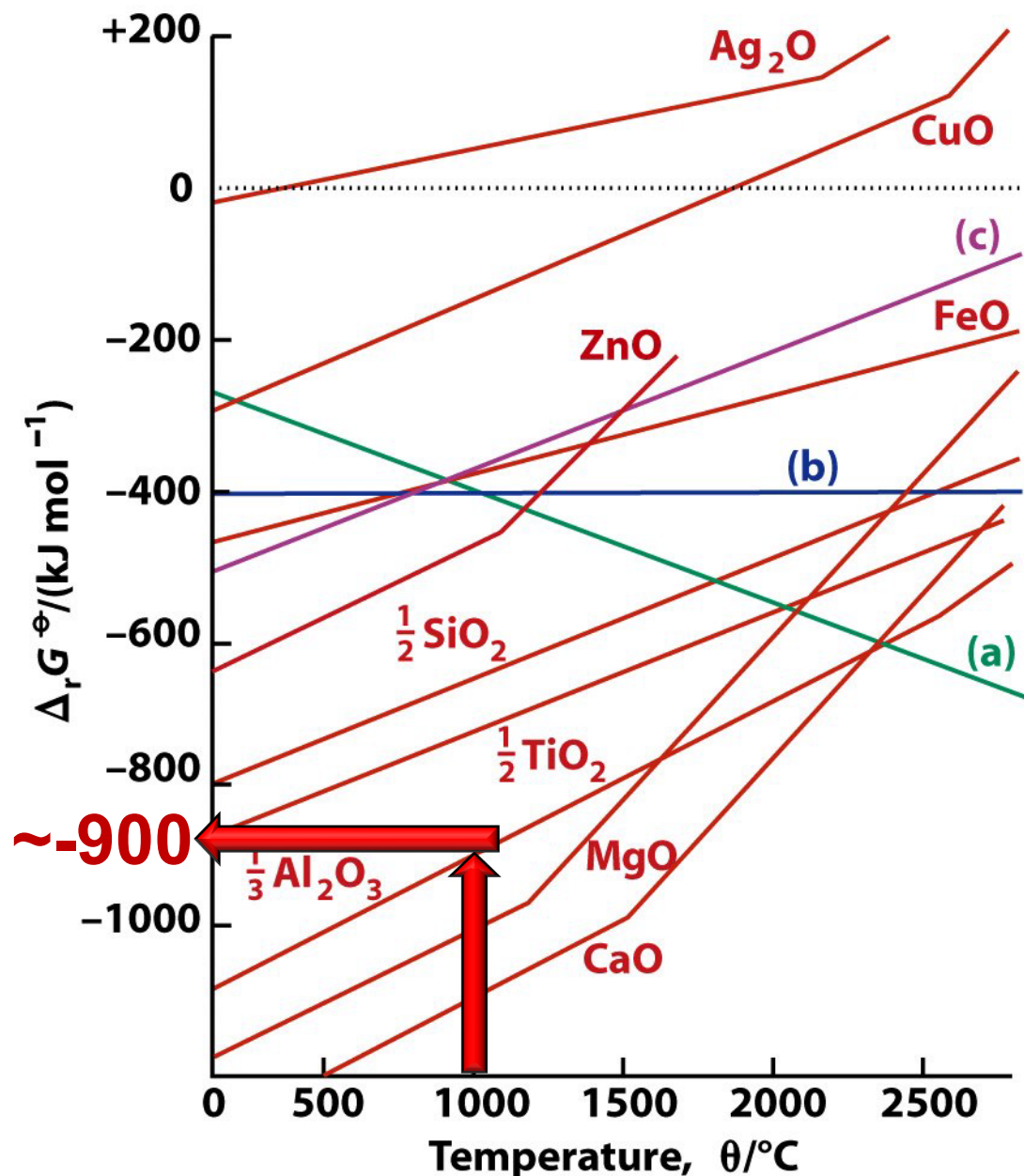


Figure 5-16

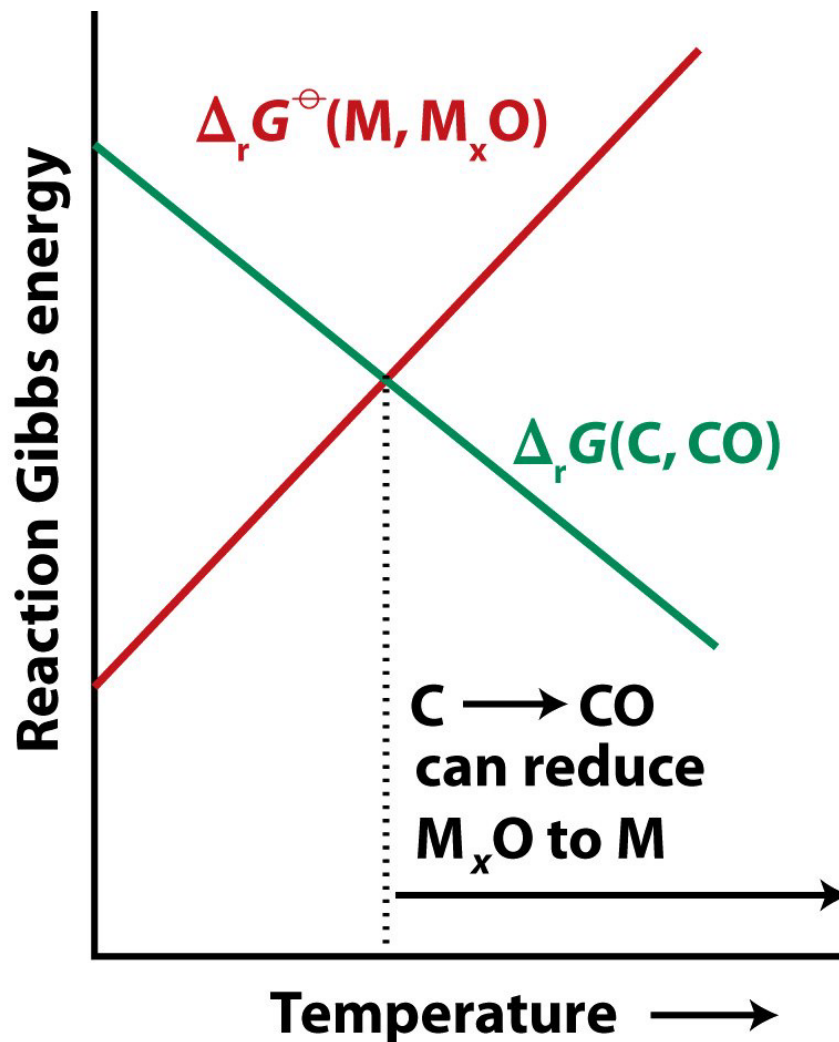
Shriver & Atkins Inorganic Chemistry, Fourth Edition

© 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

Properties of Ellingham Diagram!

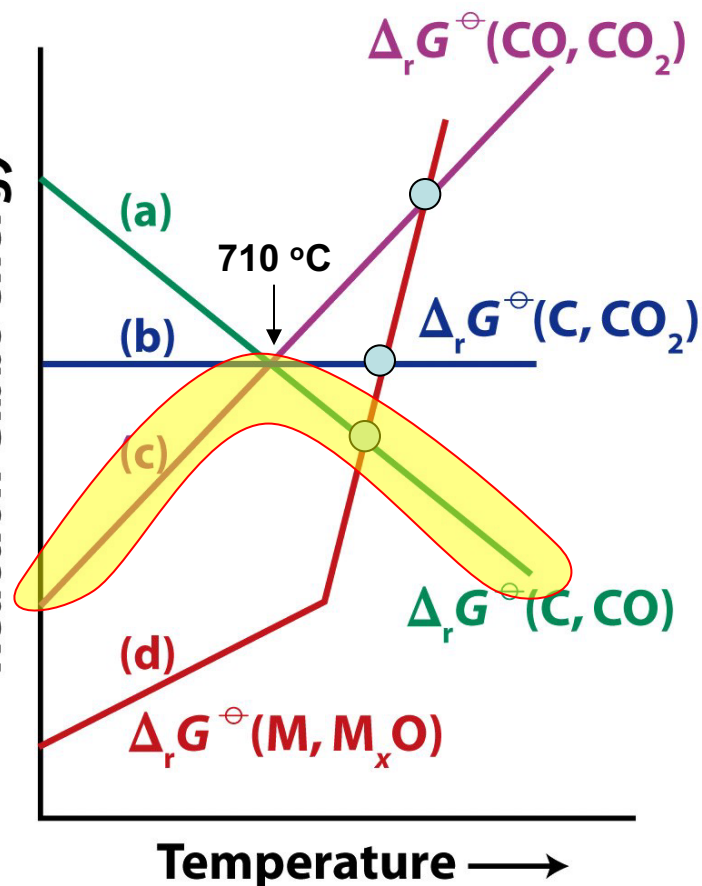
- ✓ All metal oxide curves slop upwards
- ✓ If materials melt / vaporize, the slope changes
- ✓ When the curve crosses $\Delta G^\circ = 0$, decomposition of oxide begins (Ag, Au, Hg)
- ✓ Electropositive metal curves are at the bottom of the diagram
- Any metal will reduce the oxide of other metal which is above in Ellingham diagram (the ΔG° will become more negative by an amount equal to the difference between the two graphs at a particular temperature)

Carbon As The Reducing Agent



$$\Delta G^\ominus = \Delta G^\ominus(C, CO) - \Delta G^\ominus(M, MO)$$

Reaction Gibbs energy



When $\text{C} \rightarrow \text{CO}$ line is below $\text{M} \rightarrow \text{MO}$ line, C reduces the MO and produces CO.

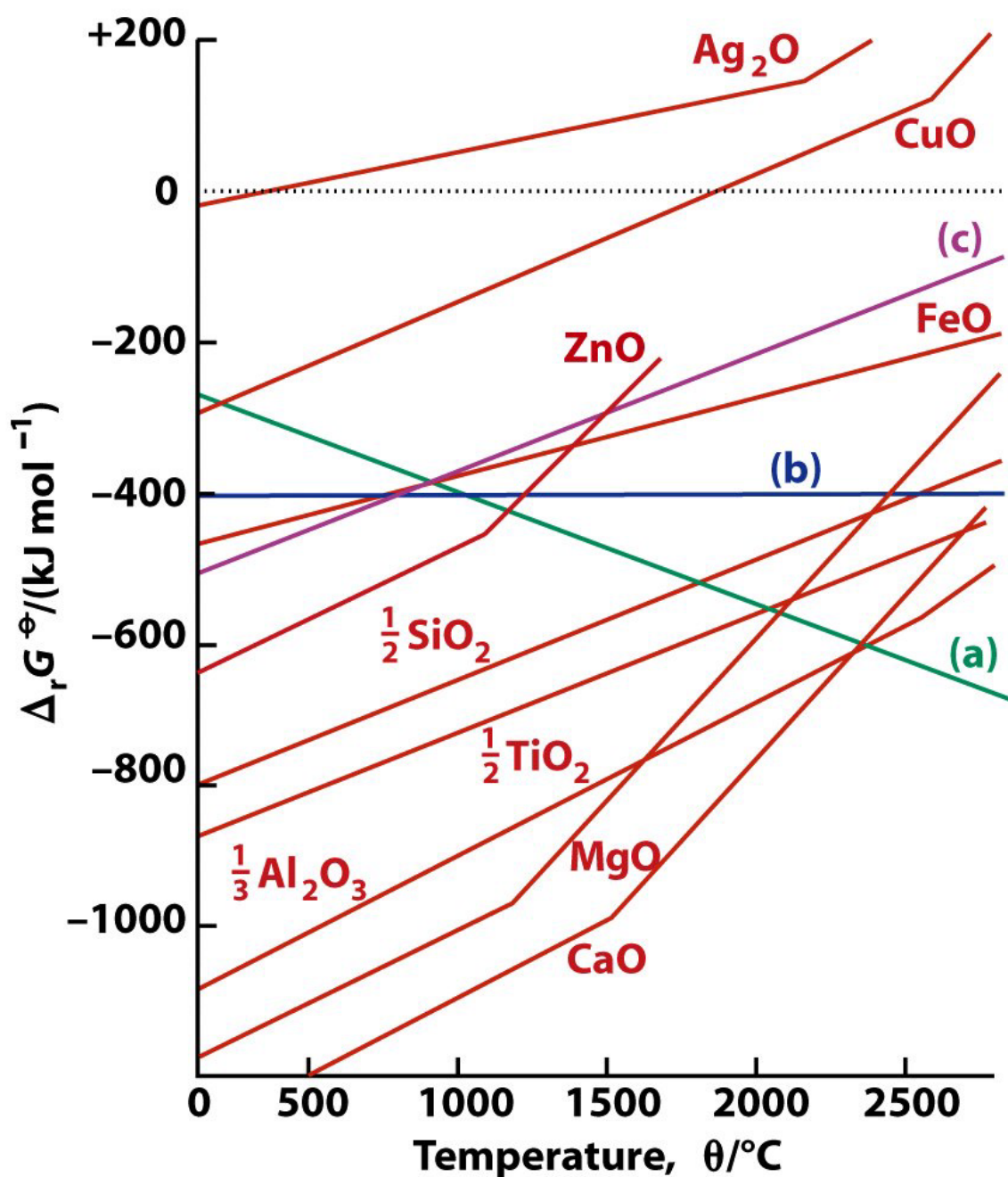
When $\text{C} \rightarrow \text{CO}_2$ line is below $\text{M} \rightarrow \text{MO}$ line, C reduces the MO and produces CO_2 .

When $\text{CO} \rightarrow \text{CO}_2$ line is below $\text{M} \rightarrow \text{MO}$ line, CO reduces the MO and produces CO_2 .

The three curves intersect at 710 °C

Below 710 °C, CO is better reducing agent.

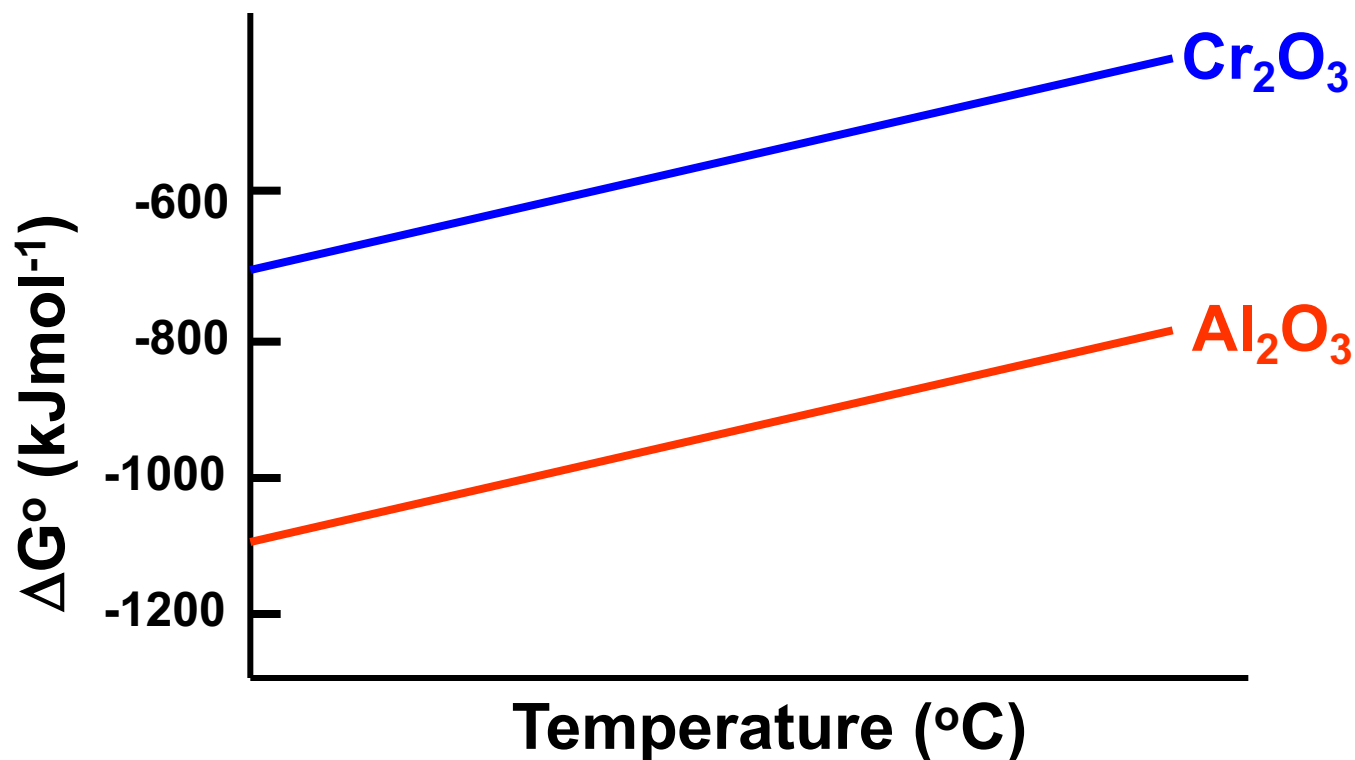
Above 710 °C, carbon is better reducing agent.



Using ED, find out what is the lowest temp. at which ZnO can be reduced to Zn by carbon. What is the overall reaction?

What is the minimum temp. required for the reduction of MgO by carbon?

Thermit Process – Sacrificial Method



$$\Delta H = -266 \text{ Kcal/mol}$$



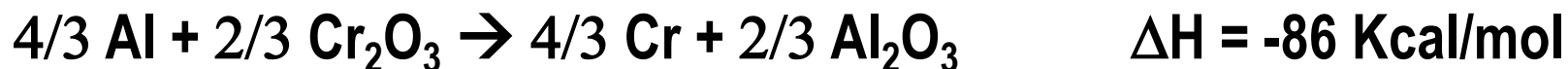
$$\Delta H = -180 \text{ Kcal/mol}$$



$$\Delta H = -86 \text{ Kcal/mol}$$

$\Delta G \approx \Delta H$ (since ΔS is similar)

Thermit Process – Details



ΔG is negative at all temperatures.

ΔS is very small since there are no gaseous products

Hence, ΔG is approximately same at different temperatures

However Al reduction requires higher temperature to trigger off.

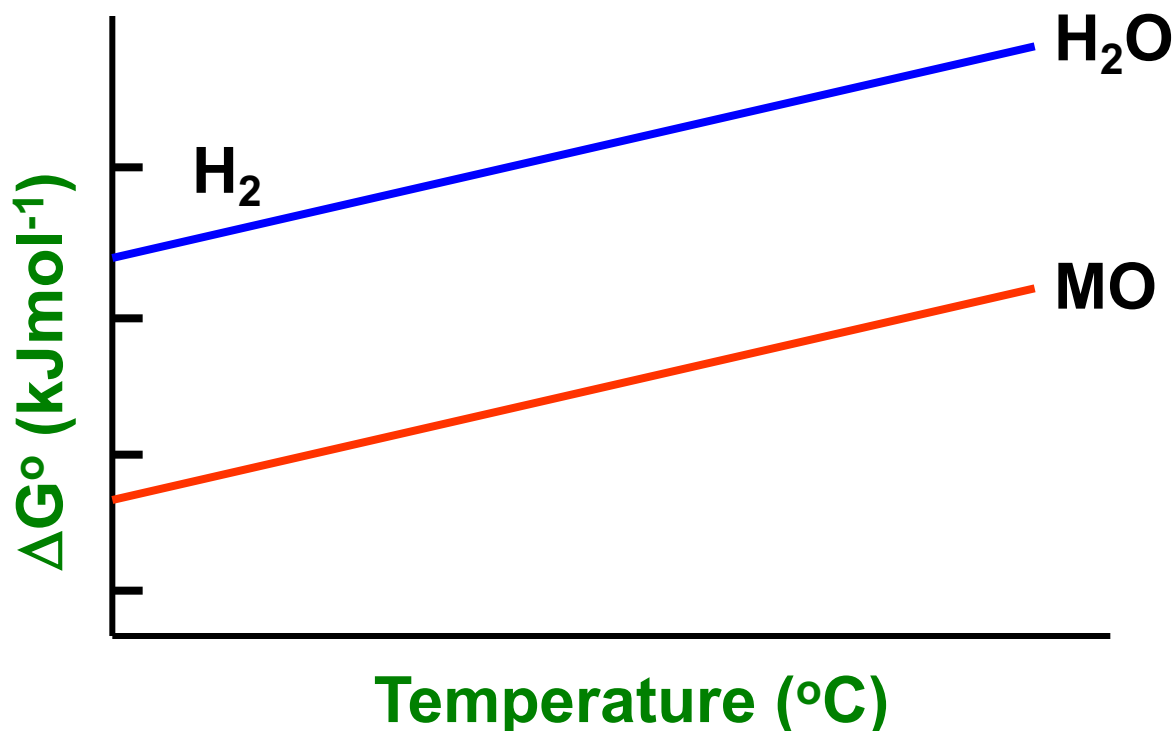
Kinetic factor: Activation energy

Priming the reaction with Mg-ribbon and barium peroxide / a $\text{KNO}_3 + \text{S} + \text{Al}$ pellet is necessary.

The reduction is usually exothermic. Once initiated, the whole mass gets reduced spontaneously.

Alloy formation with Al can take place in some cases.

H₂- A Poor Reducing Agent



- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}$; entropy decreases
- points upwards and runs parallel to many MO curves.
- Up above in the diagram
- Metal hydride formation
- Dissolved (interstitial) hydrogen – poor properties

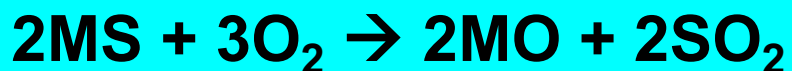
Reduction of Metal Sulfides

Many metals, which are chemically soft, occur as sulfide ores. e.g. Cu, Hg, Zn, Fe, etc.

Carbon is not a good reducing agent to for sulfide ores.

$MS + C \rightarrow CS_2$ has no slope in ED.

First roasted to MO and
then reduced to metal

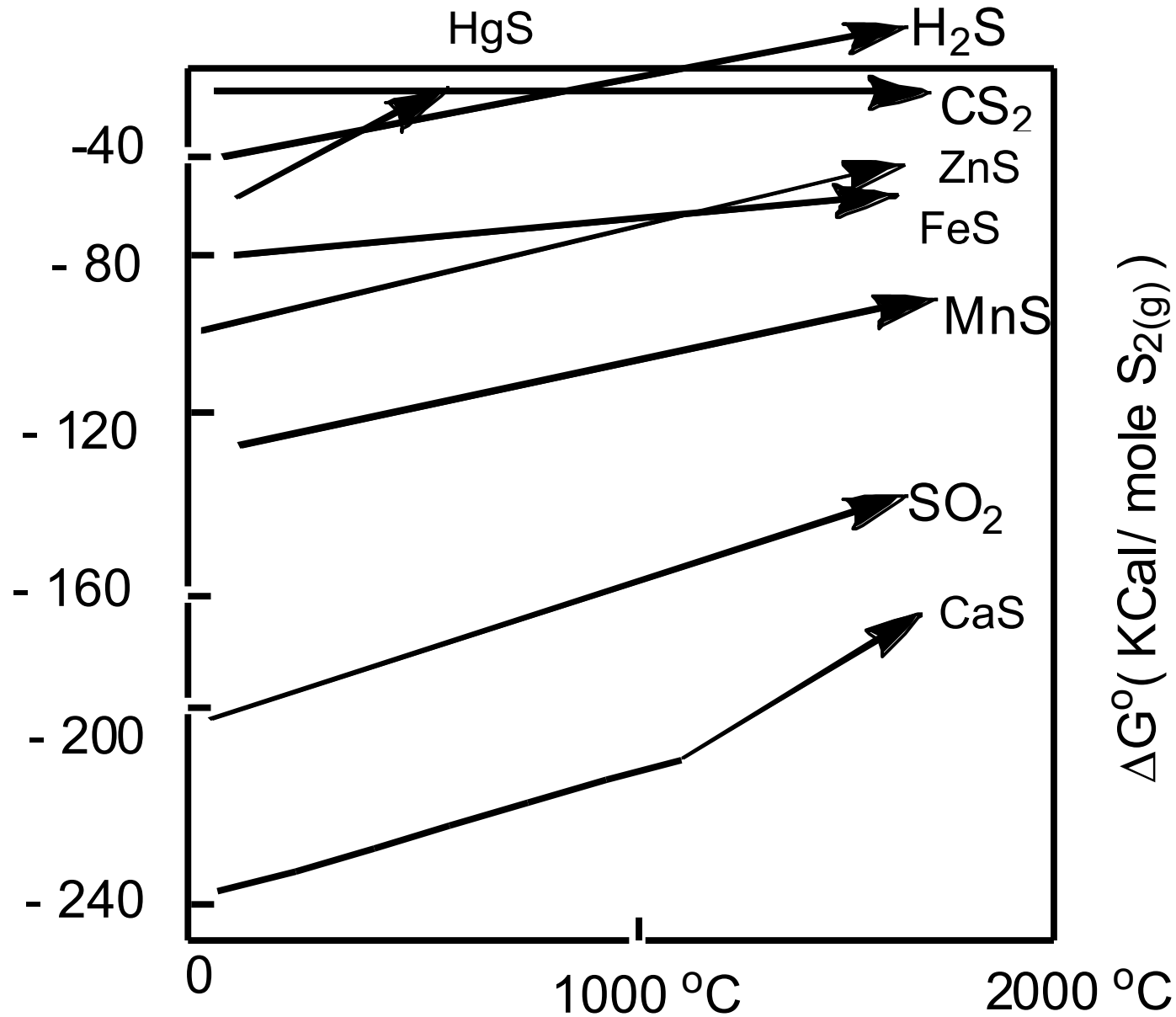


Self reduction:

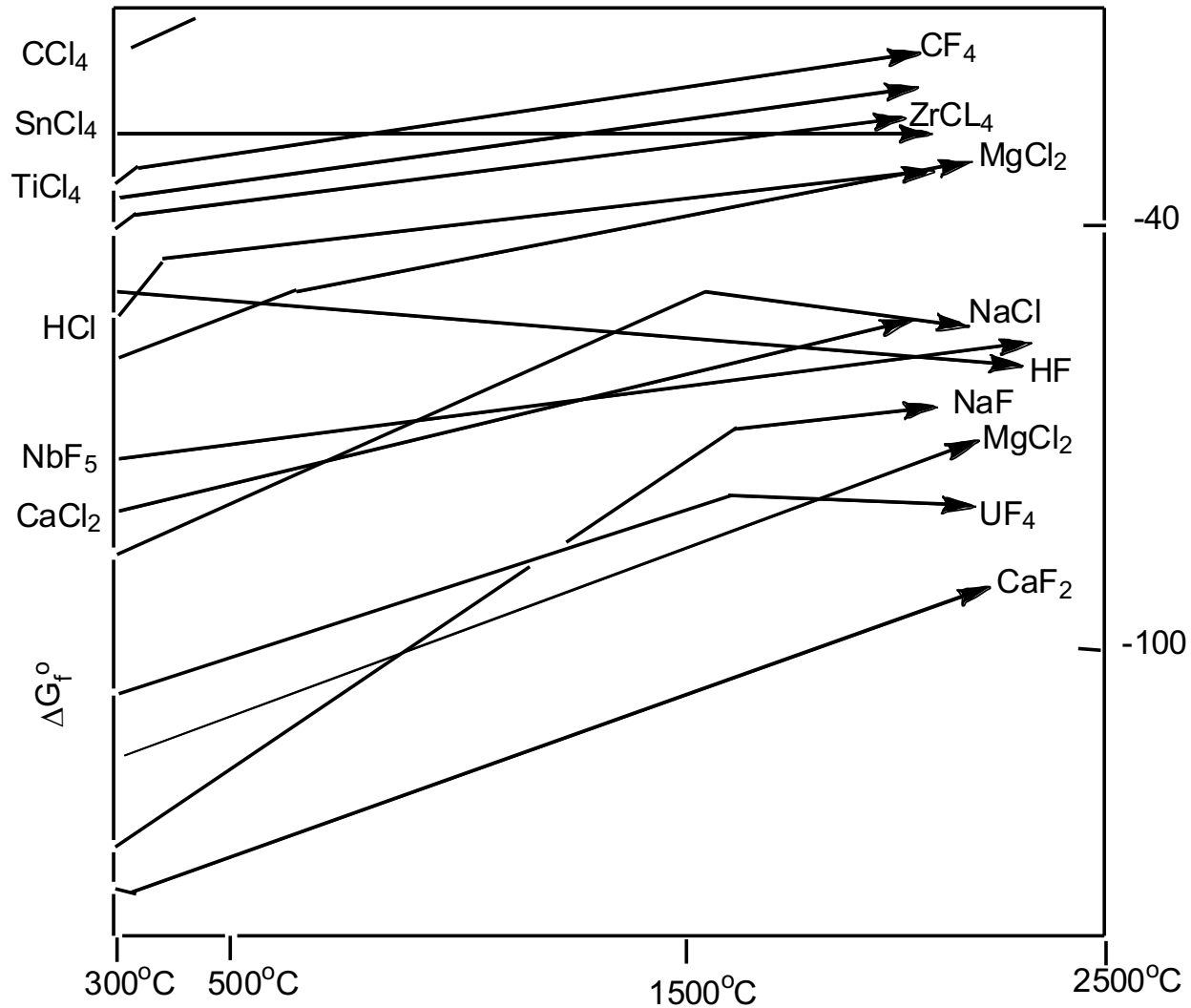


H_2 is also a poor reducing agent for metal sulfides.

Ellingham Diagram - Metal Sulfides



Ellingham Diagram - Metal Halides



Purification of Elements

Special attention to metals

1. Fusion, distillation, crystallization.

- Fusion removed adsorbed gases (SO_2 , O_2 , etc.)
- Distillation of volatile metals to remove impurities
- Fractional distillation of OsO_4 and RuO_4 from other Pt-metals in the presence of oxidising agents.
- Fractional Crystallization of Pt/Ir as $(\text{NH}_4)_2\text{MCl}_6$

2. Oxidative refining

- When impurities have more affinity to oxygen than the metal.
- Pig iron contains C, Si, P, and Mn, which can be purified by blowing air through the molten metal in Bessimer Convertor.
- CO , SiO_2 , P_4O_{10} , MnO formed combine with added CaO to give slag
- $\text{Ca}_3(\text{PO}_4)_2$, MnSiO_3

3. Thermal Decomposition

- Carbonyl (Mond process) for purification of Fe, Ni, etc.
- Van Arkel de Boer's filament growth method (ZrI_4 , BI_3 , etc.)
- Decomposition of Hydrides (AsH_3 , SbH_3 etc.)

Purification of Elements

Special attention to metals

- 4. Electrolytic refining**
- 5. Zone refining**
- 6. Chromatographic methods**
- 7. Solvent Extractions**
- 8. Ion-Exchange Methods**