Topic II
Basic principles of extraction of metals from ores & purification

Extraction of Metals

-the chemistry within

(An approach through Ellingham principles)

Elemental Composition of earth's crust

Oxygen	46.71
Silicon	27.69
Aluminum	8.07
Iron	5.05
Calcium	3.65
Sodium	2.75
Potassium	2.58
Magnesium	2.08
Titanium	0.62
Hydrogen	0.14
Phosphorus	0.13
Carbon	0.094
Manganese	0.09
Sulfur	0.052
Barium	0.05
Chlorine	0.045
Chromium	0.035
Fluorine	0.029
Zirconium	0.025
Nickel	0.019

92 %

99.5 %

99.97 %

All other elements = 0.03 %

These are mostly present in the form of compounds - ores

Need for efficient separation techniques

Methods of Separation / Extraction

(Not an exhaustive list)

1. Mechanical separation
2. Magnetic separation
3. Thermal decomposition
4. Displacement
5. High temperature chemical reduction
6. Electrolytic reduction

And so on ……

Thermal decomposition

Unstable compounds $\xrightarrow{\Delta}$ Constituent elements

$Ag_2O \rightarrow 2Ag + \frac{1}{2}O_2$

Marsh test: As, Sb salt + $Zn/H_2SO_4 \rightarrow$ $As/SbH_3 \rightarrow$ Silver mirror of the

Decomposition of nitrates, nitrites and ammonium compounds

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

Ammonium nitrate on strong heating yields dinitrogen oxide ("laughing gas") and water.

Ammonium nitrite on heating yields nitrogen gas and water.

Barium azide on heating yields barium metal and nitrogen gas.

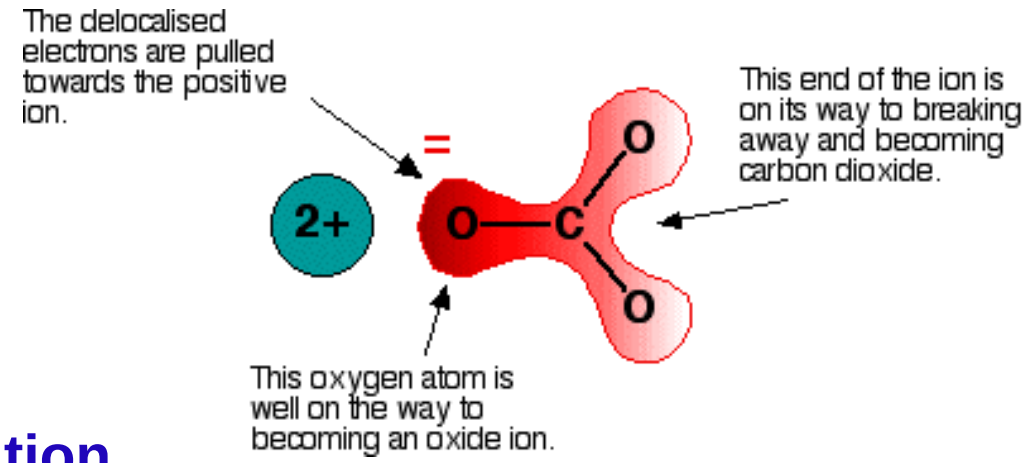
Sodium nitrate on heating yields sodium nitrite and oxygen gas.

Thermal decomposition: Carbonate & azide

Carbonates decompose to give metal oxide and carbondioxide

$CuCO_3 \rightarrow CuO + CO_2$

$CaCO_3 \rightarrow CaO + CO_2$



The mechanism of decomposition seems to involve excited azide ions (through internal conversion) and excitations. The activation energy of 14 kcal mol^{-1} appears to be associated with the promotion of electron in the presence of sodium metal.

$2NaN3 + 1/2O_2 \rightarrow Na_2O + 3N_2$

$NaN_3 \rightarrow Na + 3/2N_2$

Airbag formulations contained mixtures of oxidizers and sodium azide and other agents including ignitors and accelerants. An electronic controller detonates this mixture during an automobile crash:

Lead azide ($Pb(N_3)_2$) is explosive. It is used in detonators to initiate secondary explosives.

Barium azide $Ba(N_3)_2$ is explosive, but less sensitive to mechanical shock than lead azide. $Ba(N_3)_2 \rightarrow Ba + 3\ N_2$

Thermal decomposition

Monds Process: (Reduction followed by thermal)

Volatile nickel tetracarbonyl formation from the reaction of NiO with water gas (H_2 + CO) (50 ^oC)

Subsequent decomposition of $Ni(CO)_4$ at (230 ^oC)

Kroll Process: (Reductive separation): Reduction of titanium tetrachloride by magnesium or sodium (~950-1150^oC). Kroll produced Ti by reducing $TiCl_4$ with Ca.

van Arkel-deBoer process: Crude Ti (525 K) or Zr (878 K) is heated with I_2 to get vapours of MI_4. The vapours are then decomposed on a tungsten filament kept at high temp (1675 K for Ti & 2075 K for Zr) on which the pure metal gets deposited and is then peeled off after cooling.

Displacement of one element by other

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

$Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu$

$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$

$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$

Table 6.10 Standard electrode potentials (volts at 25 °C)

Li^+	Li	−3.05
K^+	K	−2.93
Ca^{2+}	Ca	−2.84
Al^{3+}	Al	−1.66
Mn^{2+}	Mn	−1.08
Zn^{2+}	Zn	−0.76
Fe^{2+}	Fe	−0.44
Cd^{2+}	Cd	−0.40
Co^{2+}	Co	−0.27
Ni^{2+}	Ni	−0.23
Sn^{2+}	Sn	−0.14
Pb^{2+}	Pb	−0.13
H^+	H_2	0.00
Cu^{2+}	Cu	+0.35
Ag^+	Ag	+0.80
Au^{3+}	Au	+1.38

O_2	OH^-	+0.40
I_2	I^-	+0.57
Br_2	Br^-	+1.07
Cl_2	Cl^-	+1.36
F_2	F^-	+2.85

Electrochemical Series

Increasing oxidising strength

Increasing reducing strength

strongest oxidant	$Au^+(aq)$	+	e^-	→	$Au(s)$		weakest reductant
	$O_2(g) + 4H^+(aq)$	+	$4e^-$	→	$2H_2O(l)$		
	$Ag^+(aq)$	+	e^-	→	$Ag(s)$		
	$Fe^{3+}(aq)$	+	e^-	→	$Fe^{2+}(aq)$		
	$O_2(g) + 2H_2O(l)$	+	$4e^-$	→	$4OH^-(aq)$		
	$Cu^{2+}(aq)$	+	$2e^-$	→	$Cu(s)$		
	$Sn^{4+}(aq)$	+	$2e^-$	→	$Sn^{2+}(aq)$		
	$2H^+(aq)$	+	$2e^-$	→	$H_2(g)$		
	$Pb^{2+}(aq)$	+	$2e^-$	→	$Pb(s)$		
	$Sn^{2+}(aq)$	+	$2e^-$	→	$Sn(s)$		
	$Ni^{2+}(aq)$	+	$2e^-$	→	$Ni(s)$		
	$Co^{2+}(aq)$	+	$2e^-$	→	$Co(s)$		
	$Fe^{2+}(aq)$	+	$2e^-$	→	$Fe(s)$		
	$Cr^{3+}(aq)$	+	$3e^-$	→	$Cr(s)$		
	$Zn^{2+}(aq)$	+	$2e^-$	→	$Zn(s)$		
	$2H_2O(l)$	+	$2e^-$	→	$H_2(g) + 2OH^-(aq)$		
	$Al^{3+}(aq)$	+	$3e^-$	→	$Al(s)$		
	$Mg^{2+}(aq)$	+	$2e^-$	→	$Mg(s)$		
	$Na^+(aq)$	+	e^-	→	$Na(s)$		
	$Ca^{2+}(aq)$	+	$2e^-$	→	$Ca(s)$		
weakest oxidant	$K^+(aq)$	+	e^-	→	$K(s)$		strongest reductant
	$Li^+(aq)$	+	e^-	→	$Li(s)$		

stronger oxidizing agent

stronger reducing agent

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

More Electropositive

K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, Fe^{2+}, Sn^{2+}, Pb^{2+}, H^+, Cu^{2+}, Ag^+

More Electronegative

F^-, SO_4^{2-}, NO_3^-, Cl^-, Br^-, I^-, OH^-

Electrolytic reduction

Electron – Strongest known reducing agent

Electrolysis is the passing of a direct electric current through an ionic substance that is either molten or dissolved in a suitable solvent, causing chemical reactions at the electrodes & separation of materials.

An electrolyte: a substance, frequently an ion-conducting polymer that contains free ions, which carry electric current in the electrolyte. If the ions are not mobile, as in a solid salt then electrolysis cannot occur.

A direct current (DC) electrical supply: provides the energy necessary to create or discharge the ions in the electrolyte. Electric current is carried by electrons in the external circuit.

Two electrodes: electrical conductors that provide the physical interface between the electrolyte and the electrical circuit that provides the energy. Choice of suitable electrode depends on chemical reactivity between the electrode and electrolyte.

Electrolytic reduction

1. Highly electropositive metals, e.g. alkaline earth metals are produced this way (Electrolytic reduction of their fused halides)

2. Less electropositive elements, viz., Cr, Cu & Zn can be made by electrolysis even from aqueous solution

3. Ionic materials (salts) are electrolyzed – reduction at cathode.

4. Some eg., Al, Ca, Cl_2, Cu, Fl2, H2, Li, Mg, K, Na, NaOH, Zn, etc.

5. Excellent method, gives pure metal, but very expensive

High temperature chemical reduction

1. Many metals are found as their oxides. Some are found as sulfides and halides.

2. Oxide Ores: Directly reduced (smelted) to the metal. General reducing agents: C , Al, Si, H_2. 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

High-T chemical reduction
Thermodynamic considerations ….

1. Used to identify which reactions are spontaneous under the prevailing conditions
2. Kinetic equilibrium is reached easily at such high temperatures
3. To choose most economical reducing agent and reaction condition

Criterion for spontaneity

$\Delta G^o = - RT \ln K$

•Negative ΔG^o corresponds to $K > 1$; favorable reaction

•Kinetics is not important as reductions are done at high temperature & are fast

High-T chemical reduction
Thermodynamic considerations ….

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

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^o) 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^O (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

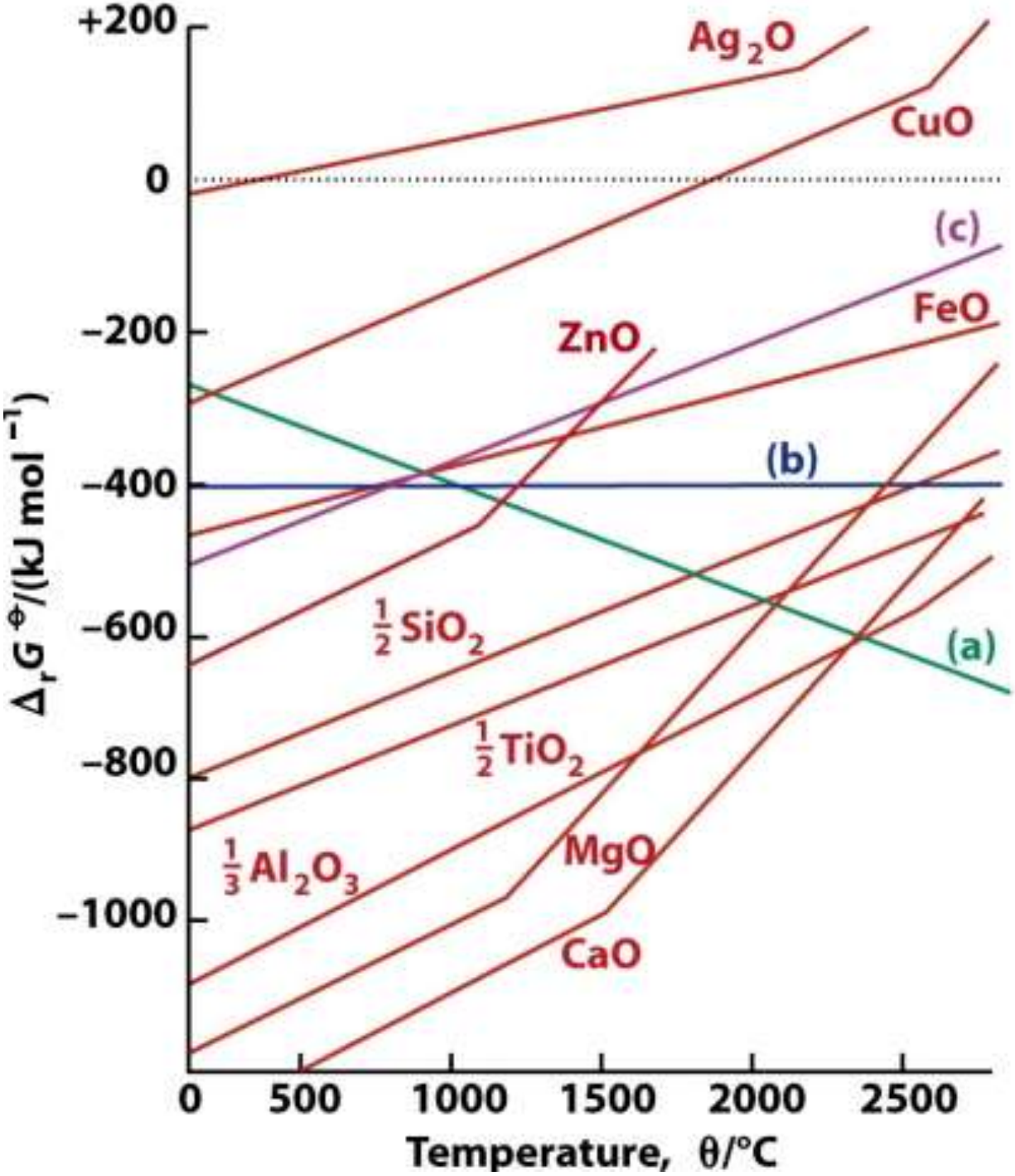
$$\frac{2X}{Y} M \text{ (Solid or molten metal)} + O_2(g) \rightarrow M_xO_y \text{ (Solid or molten oxide)}$$

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

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

This is called Ellingham Diagram

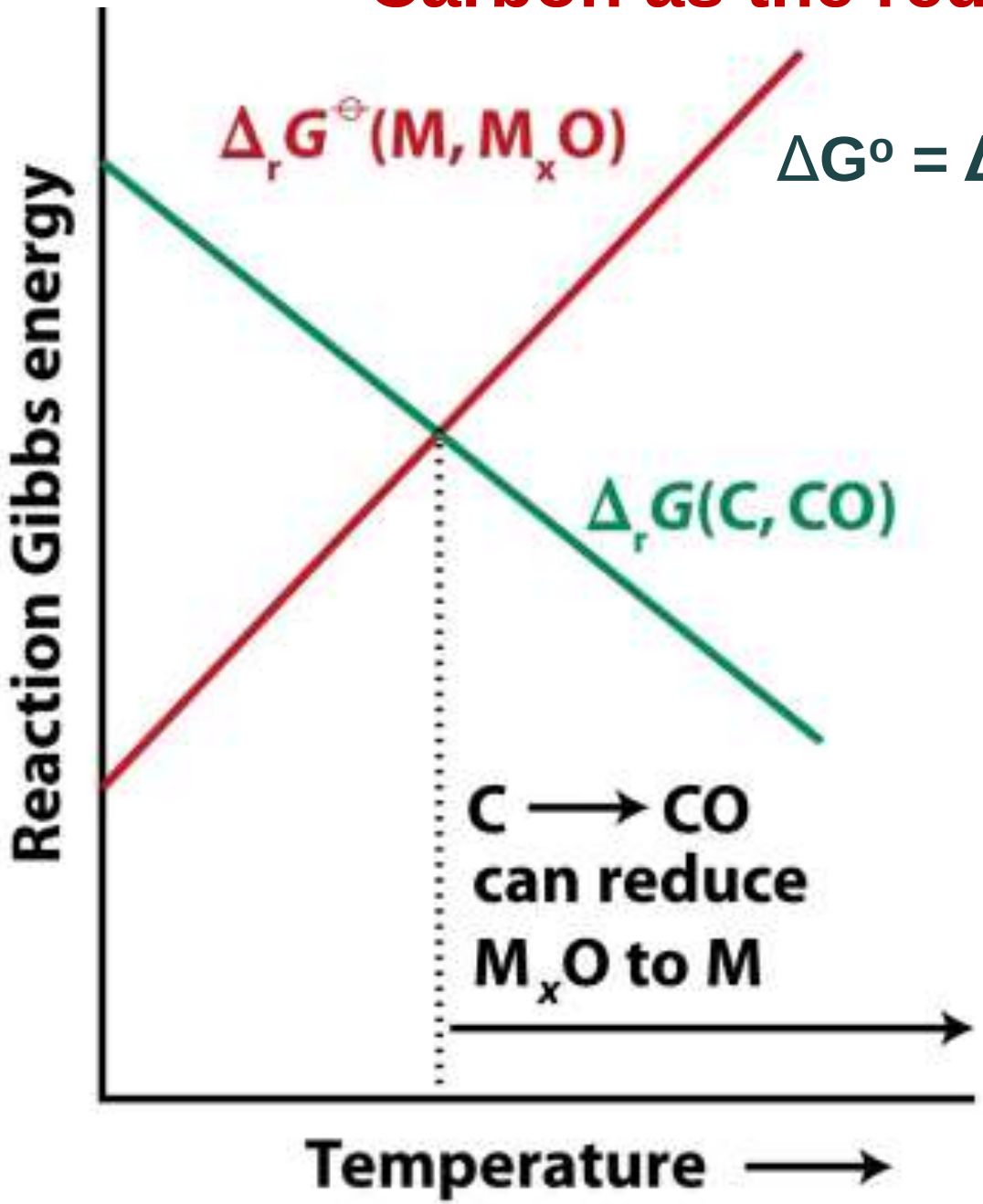
The intercept & slope gives ΔH^o & $-\Delta S$ respectively



Properties of Ellingham diagram

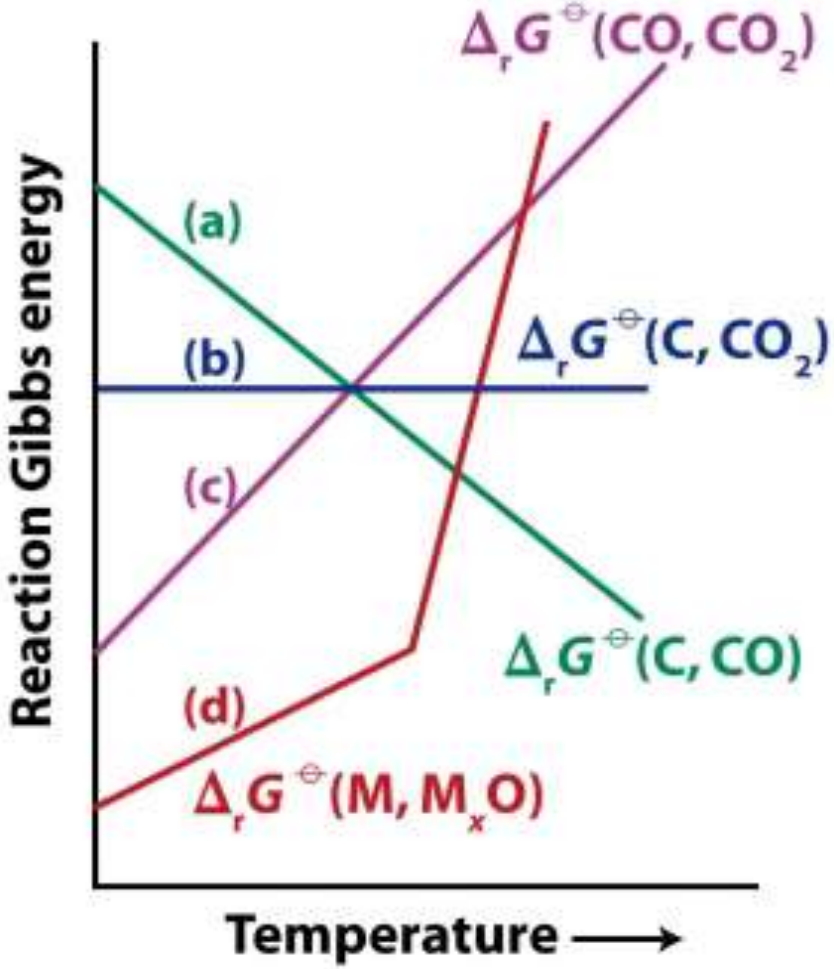
- All metal oxide curves slope upwards
- If materials melt / vaporize, the slope changes
- When the curve crosses $\Delta G^o = 0$, decomposition of oxide begins (Ag, Au, Hg)
- Electropositive metal curves are at the bottom of the diagram
- Any metal will reduce the oxide of other metal which is above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

Carbon as the reducing agent



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

Carbon as the reducing agent



$CO(g) + ½O_2(g) \rightarrow CO_2(g)$
(ΔS –ve)

$C + O_2(g) \rightarrow CO_2(g)$
(ΔS constant)

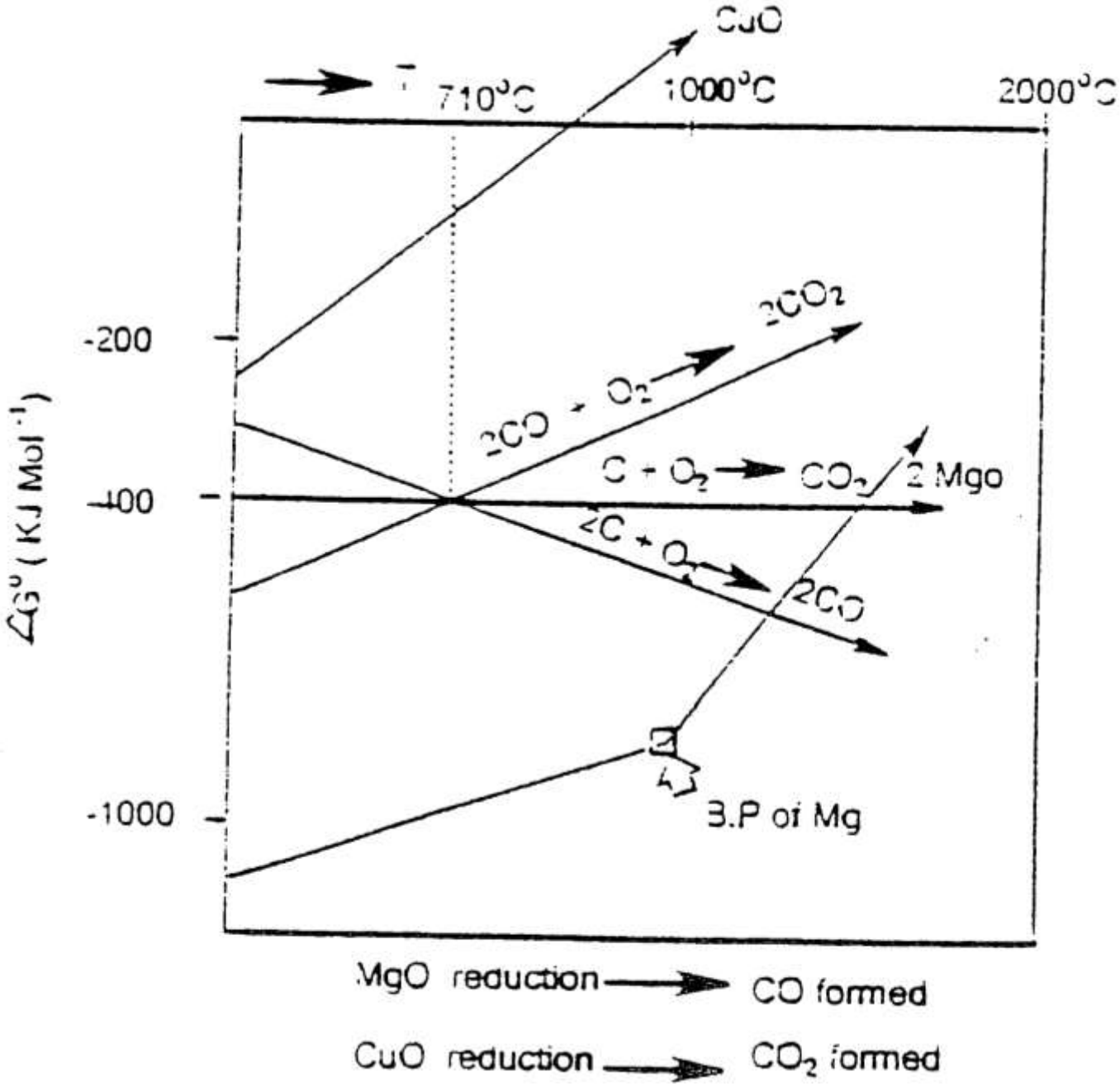
$C + ½O2(g) \rightarrow CO(g)$
(ΔS +ve)

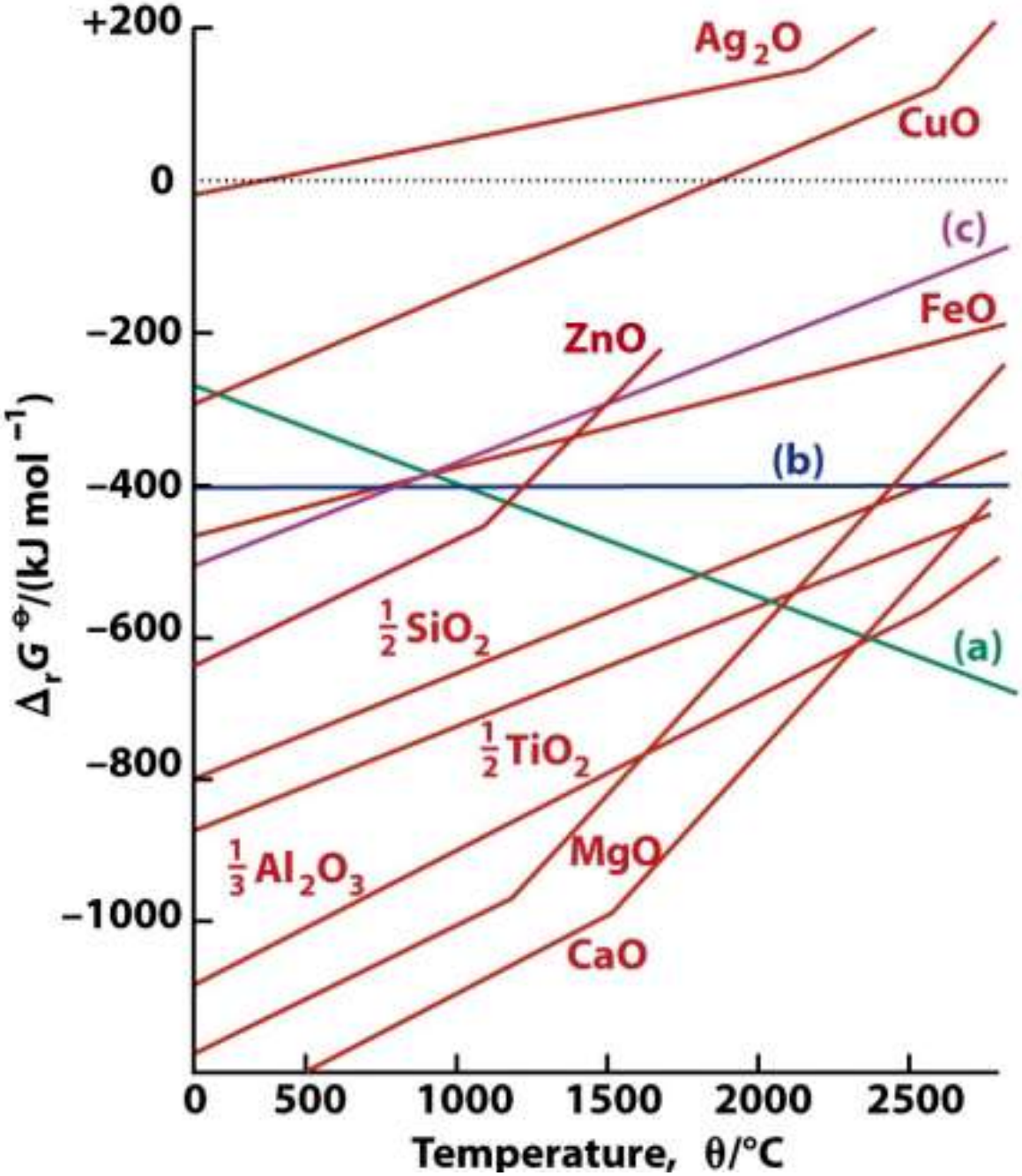
When C → CO line is below M→MO line, C reduces MO and produces CO.

When C → CO_2 line is below M →MO line, C reduces the MO and produces CO_2.

When CO → CO_2 line is below M → MO line, CO reduces the MO and produces CO_2.

The three curves intersect at 710 ^oC. <710 ^oC, CO is better reducing & >710 ^oC, Carbon is better reducing.

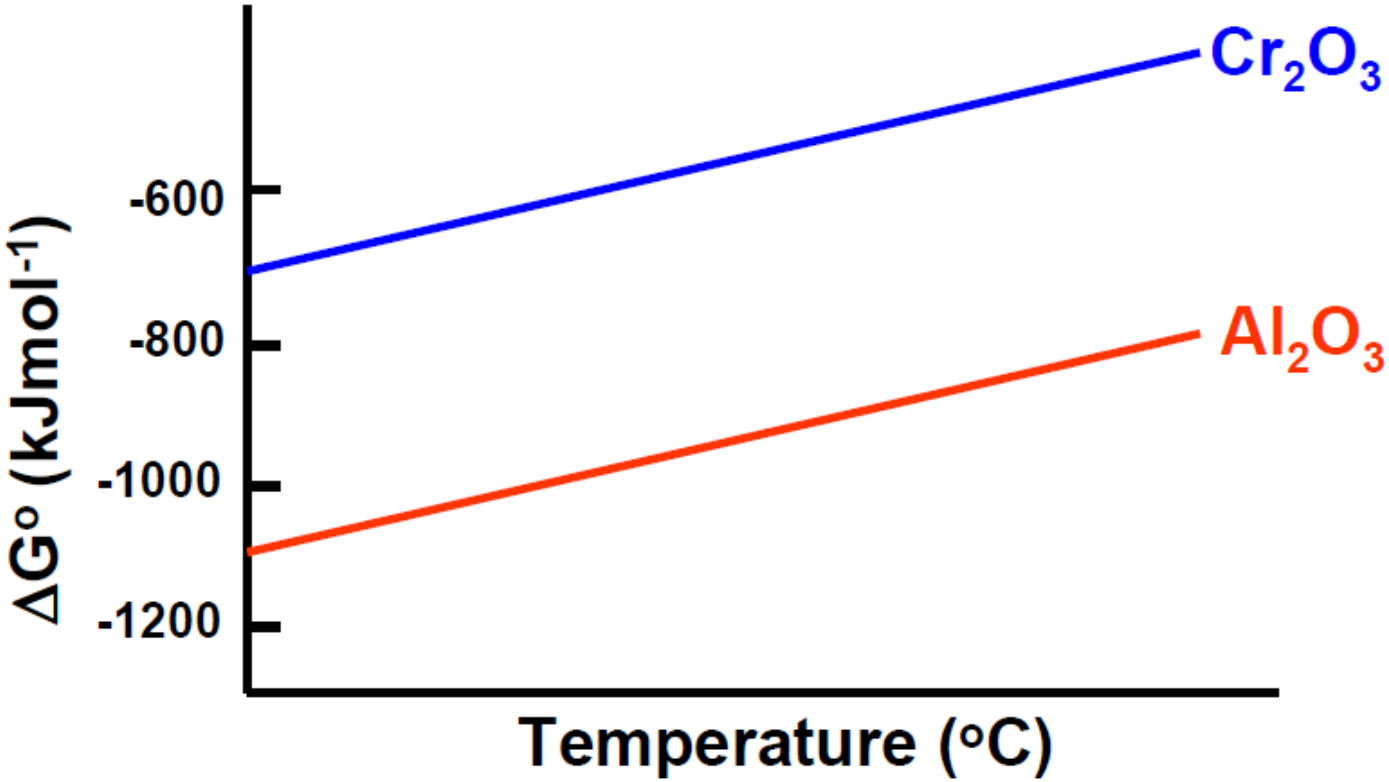

CuO
T
710°C
1000°C
2000°C
-200
-400
-1000
ΔG° (KJ Mol⁻¹)
2CO₂
2CO + O₂
C + O₂ → CO₂
2 Mgo
2C + O₂
2CO
B.P of Mg
MgO reduction → CO formed
CuO reduction → CO₂ formed



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



$4/3\ Al + O_2 \rightarrow 2/3\ Al_2O_3$ $\Delta H = -266$ Kcal/mol

$4/3\ Cr + O_2 \rightarrow 2/3\ Cr_2O_3$ $\Delta H = -180$ Kcal/mol

$4/3\ Al + 2/3\ Cr_2O_3 \rightarrow 4/3\ Cr + 2/3\ Al_2O_3$ $\Delta H = -86$ Kcal/mol

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

Thermit Process – Why is it not spontaneous

$4/3\ Al + 2/3\ Cr_2O_3 \rightarrow 4/3\ Cr + 2/3\ Al_2O_3 \quad \Delta H = -86\ Kcal/mol$

ΔG is negative at all temperatures.

ΔS is very small since there are no gaseous products

Hence, ΔG is approximately same at different Temps

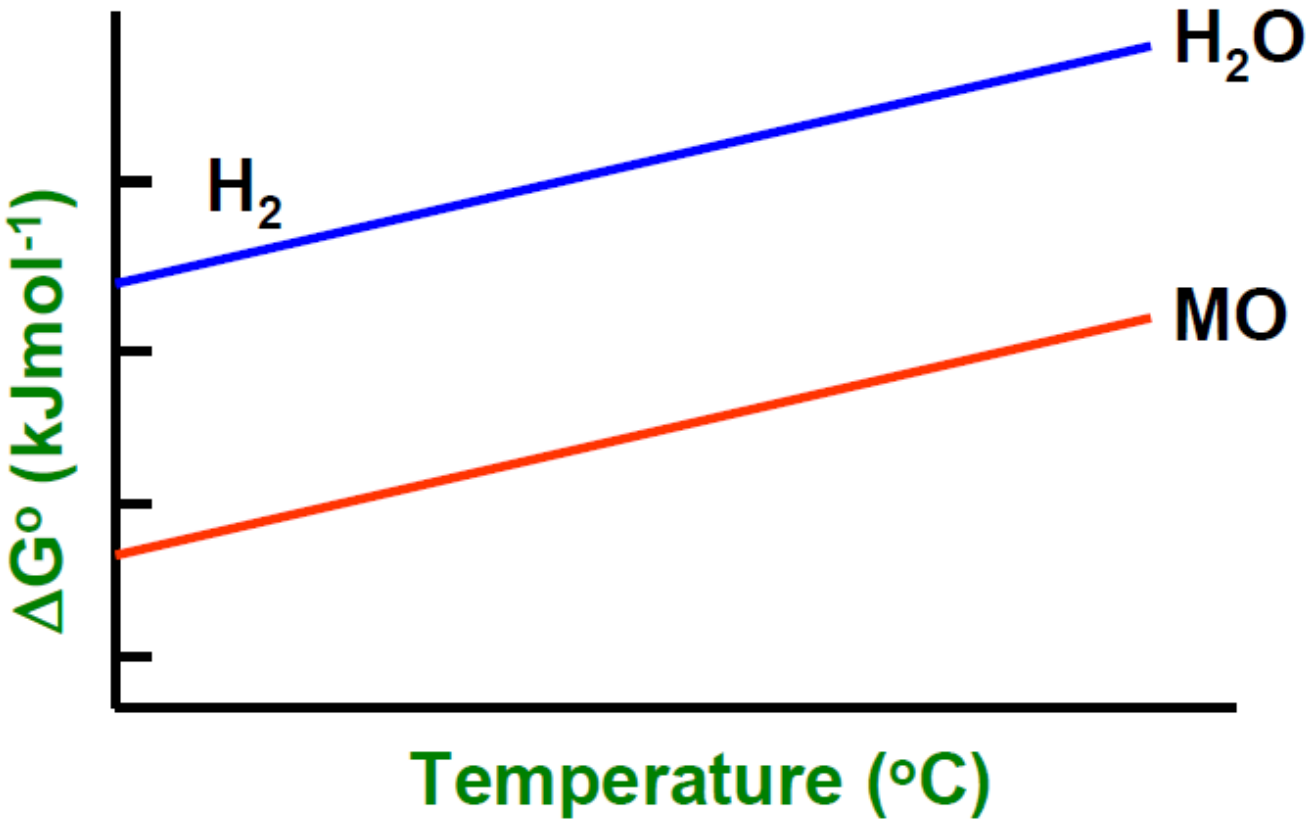
However Al reduction requires higher temperature to trigger off. Kinetic factor: Activation energy

Priming the reaction with Mg-ribbon and barium peroxide / KNO_3+S+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.

H_2 -Poor reducing agent



- $2H_2(g) + O_2(g) \rightarrow 2H_2O$; 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 → CS_2 has no slope in ED.

First roasted to MO and then reduced to metal

$2MS + 3O_2 \rightarrow 2MO + 2SO_2$

↓ C

Self reduction:

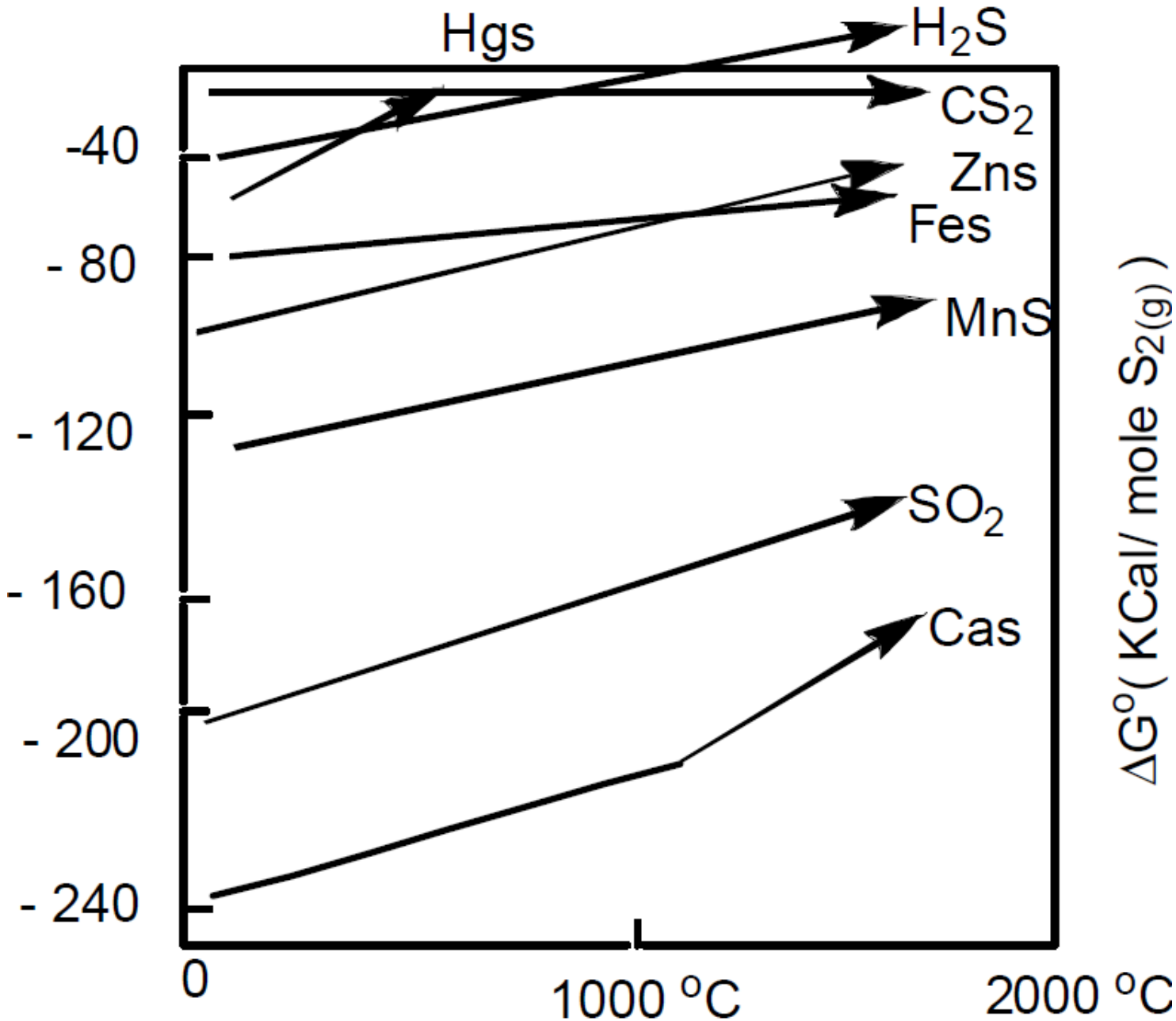
CuS [CuS + CuO] -→ Cu + SO_2

$$2\,PbS_{(s)} + 3/2\,O_{2(g)} = PbO_{(s)} + PbS_{(s)} + SO_{2(g)}$$

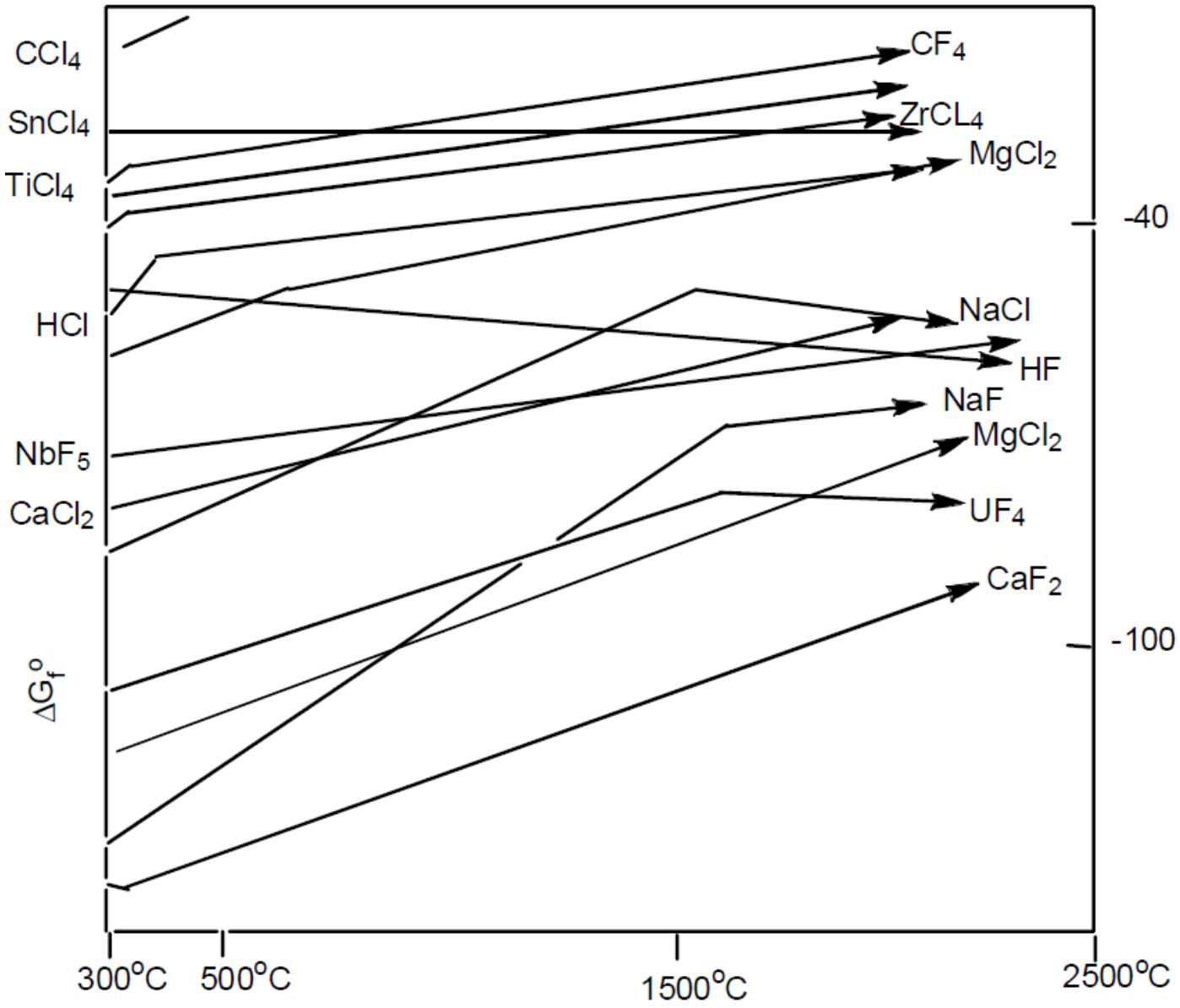
$$PbS_{(s)} + 2PbO_{(s)} \rightarrow 3Pb_{(s)} + SO_{2(g)}$$

H_2 is also a poor reducing agent for metal sulfides.

Ellingham diagram – Metal Sulfides



Ellingham diagram – Metal Halides



Purification of Elements

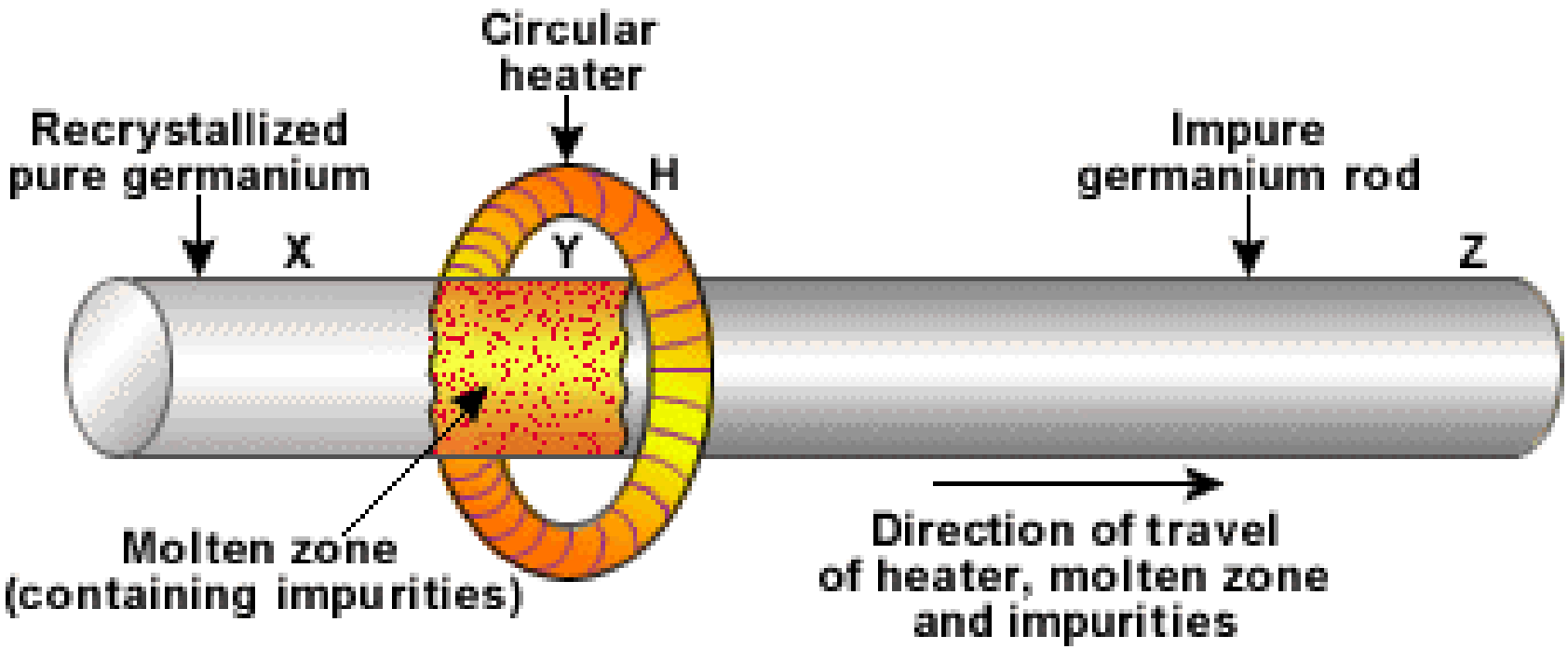
1. Thermal Decomposition
   - Carbonyl (Mond process) for purification of Fe, Ni
   - Van Arkel de Boer's filament growth method (ZrI_4, BI_3)
   - Decomposition of Hydrides (AsH_3, SbH_3 etc.)

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 will combine with the added CaO to give slag - $Ca_3(PO_4)_2$, $MnSiO_3$

Purification of Elements

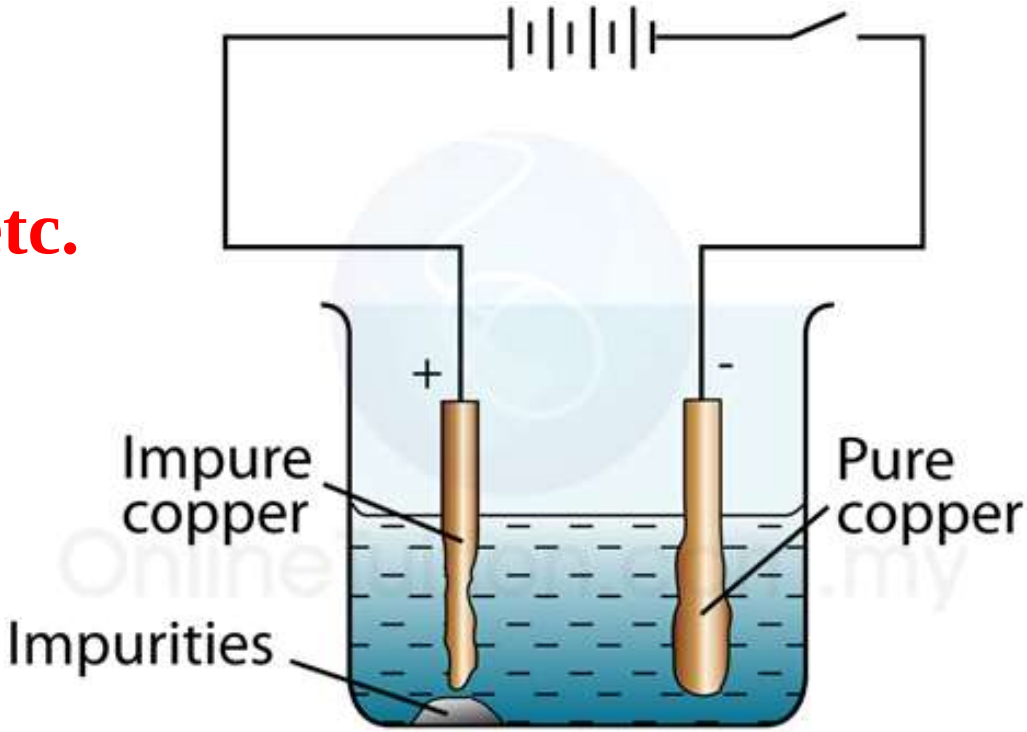
3. Zone refining (refinement of pure silicon to ultrapure silicon)

- impurities are more soluble in the liquid phase as compared to the solid phase



Zone refining of germanium metal.

Purification of Elements

4. Electrolytic refining: The pure metal is deposited at the cathode and the impurities from the anode fall as mud. The impurities in this anode mud are either more reactive or less reactive than the metal to be refined. More reactive impurities dissolve into the electrolytic solution & less reactive impurities deposit into anode.

This method is used for refining Au, Ag, Cu, Ni, etc.