

Extraction of Metals

and the Chemistry Involved in it

Elemental Composition of earth's crust		
Oxygen	46.71	92 %
Silicon	27.69	
Aluminum	8.07	
Iron	5.05	
Calcium	3.65	
Sodium	2.75	99.5 %
Potassium	2.58	
Magnesium	2.08	
Titanium	0.62	
Hydrogen	0.14	
Phosphorus	0.13	99.97 %
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	

All other elements = 0.03 %

These are mostly 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**

Mechanical separation

- Free elemental form – unreactive elements
- Coinage & Pt metals Gold; 19.3 g/cm³,
- separated by *panning*
- Based on the density variation
- By sieving method

Magnetic separation

Removal of ferrous impurities/materials

Thermal decomposition

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



Marsh test: As, Sb salt + Zn/H₂SO₄ →

As/SbH₃ → Silver mirror of the metal

Decomposition of NaN₃ to Na and N₂

Mond process; production of nickel

van Arkel process

Displacement of one element by other

In principle, any element may be displaced by another element which has more negative E_0 in electrochemical series.



Table 6.11 Standard electrode potentials (V)

$\text{O}_2 \mid \text{OH}^-$	+0.40
$\text{I}_2 \mid \text{I}^-$	+0.57
$\text{Br}_2 \mid \text{Br}^-$	+1.07
$\text{Cl}_2 \mid \text{Cl}^-$	+1.36
$\text{F}_2 \mid \text{F}^-$	+2.85

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

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, 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

Electrolytic reduction

- 1. Electron – Strongest known reducing agent**
- 2. Highly electropositive metals, e.g. alkaline earth metals are produced this way (Electrolytic reduction of their fused halides)**
- 3. Less electropositive elements, viz., Cr, Cu & Zn can be made by electrolysis even from aqueous solution**
- 4. Ionic materials (salts) are electrolyzed – reduction at cathode**
- 5. Excellent method, gives pure metal, but very expensive**

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

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

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

What is an Ellingham Diagram?

The choice of a reducing agent and the conditions for a particular extraction process can be assessed by using an Ellingham diagram.

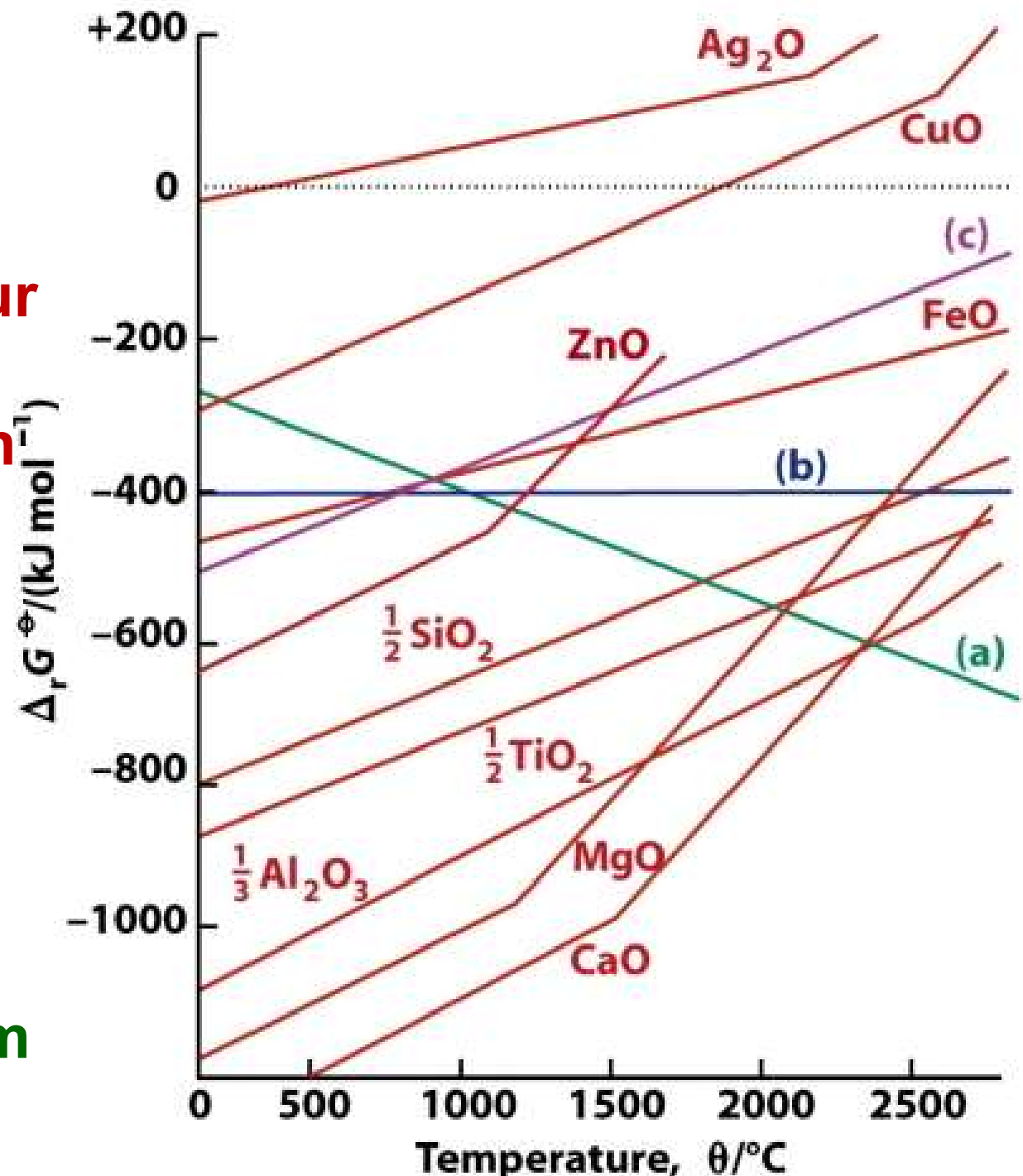
This illustrates how $\Delta_f G^\circ$ for a range of metal oxides and CO varies with temperature. In order that values are mutually comparable, $\Delta_f G^\circ$ refers to the Gibbs energy of formation per half-mole of O_2 .

Thus for SrO , $\Delta_f G^\circ$ refers to: $Sr + 1/2O_2 \rightarrow SrO$
and for Al_2O_3 : $2/3Al + 1/2O_2 \rightarrow 1/3Al_2O_3$

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

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

This graph is called
Ellingham Diagram



- As the temperature increases, each metal oxide becomes less thermodynamically stable (less negative $\Delta_f G^\circ$)
- CO becomes more thermodynamically stable at higher temperatures (more negative $\Delta_f G^\circ$); the relative stabilities of the oxides at any given temperature can be seen directly from an Ellingham diagram.

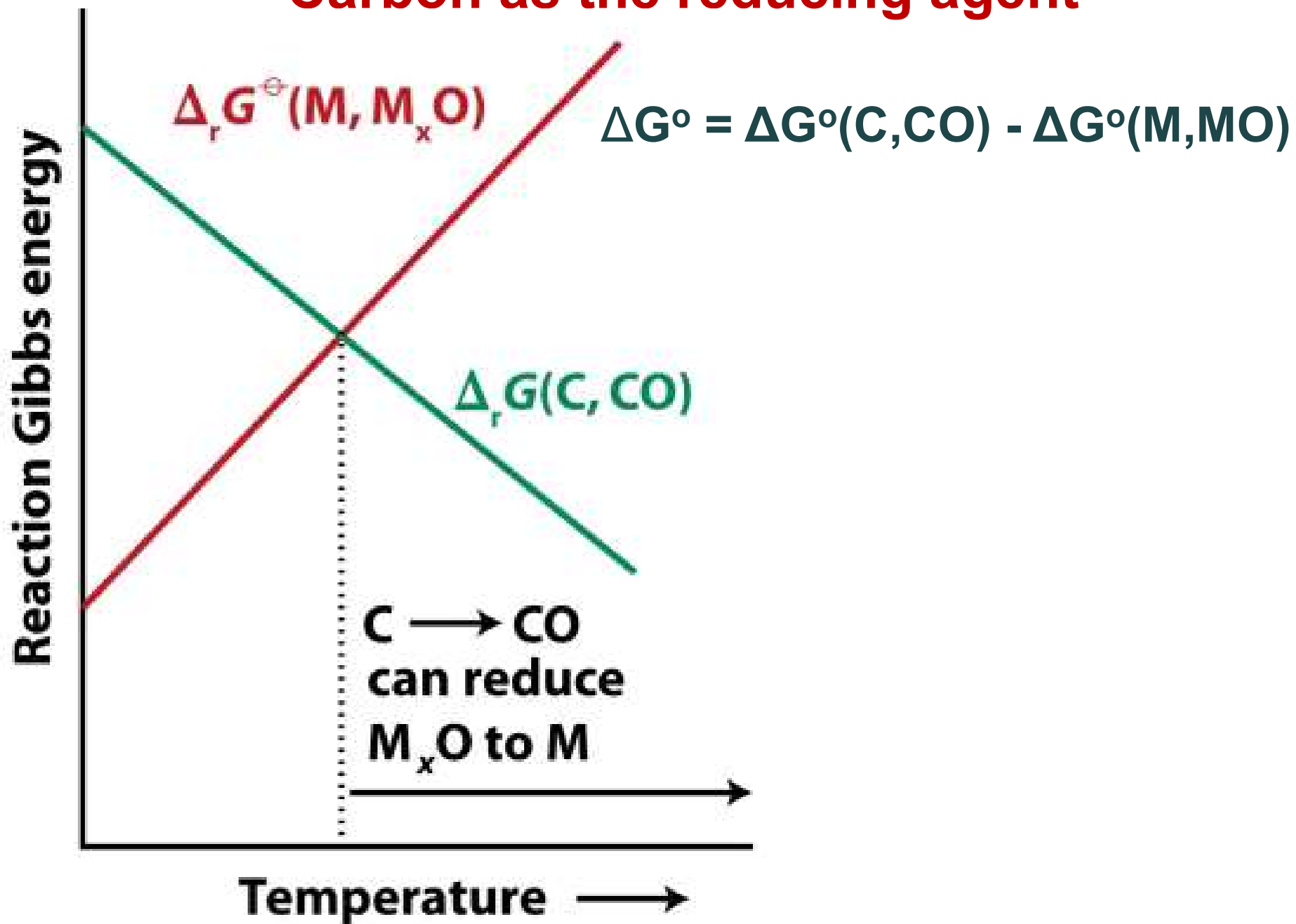
The third point indicates how an Ellingham diagram can be applied. For example, at 1000 K, CO is more thermodynamically stable than SnO_2 , and carbon can be used at 1000K to reduce SnO_2 . On the other hand, reduction of FeO by carbon occurs at $T > 1000 \text{ K}$.



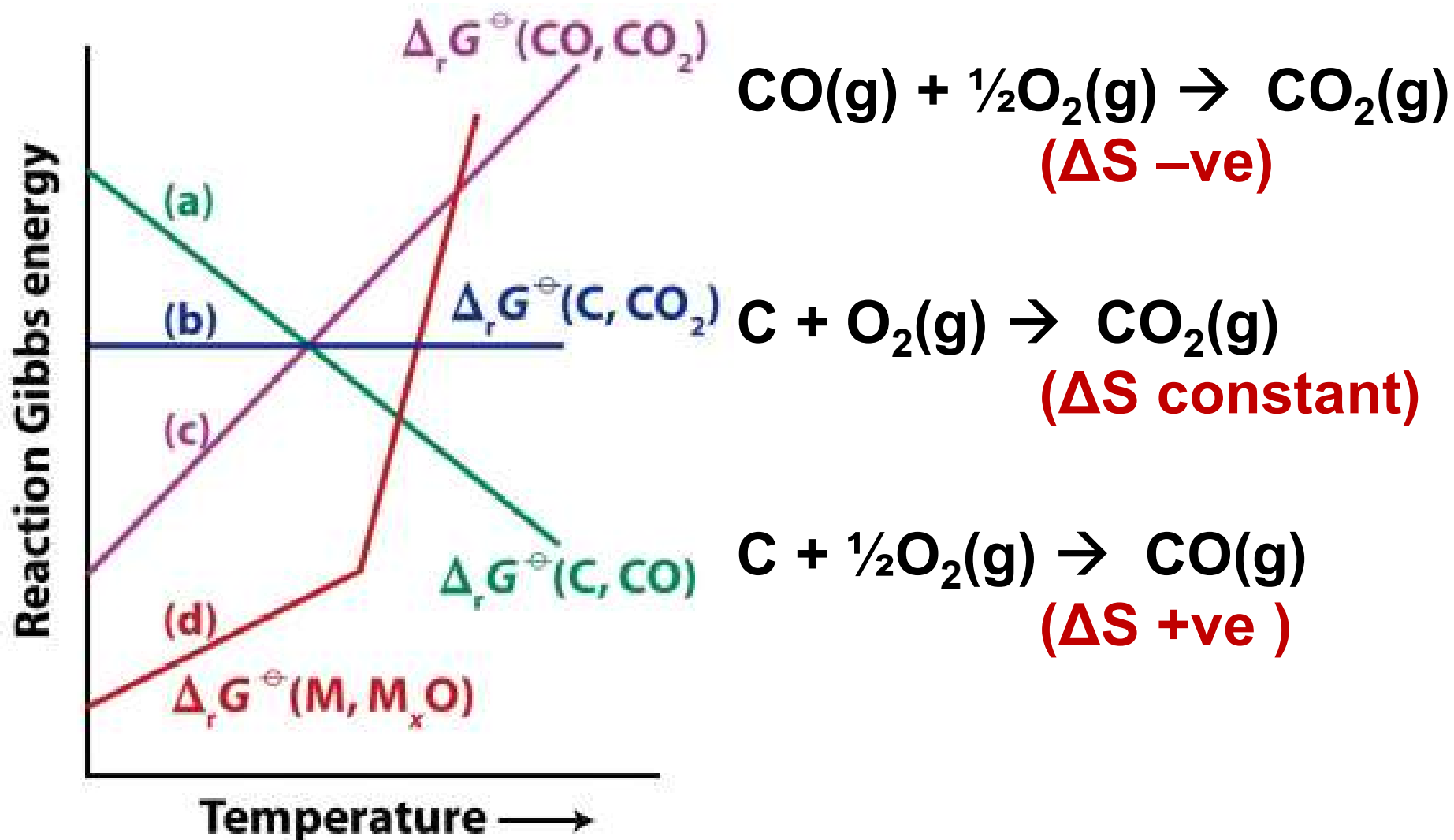
Properties of Ellingham diagram

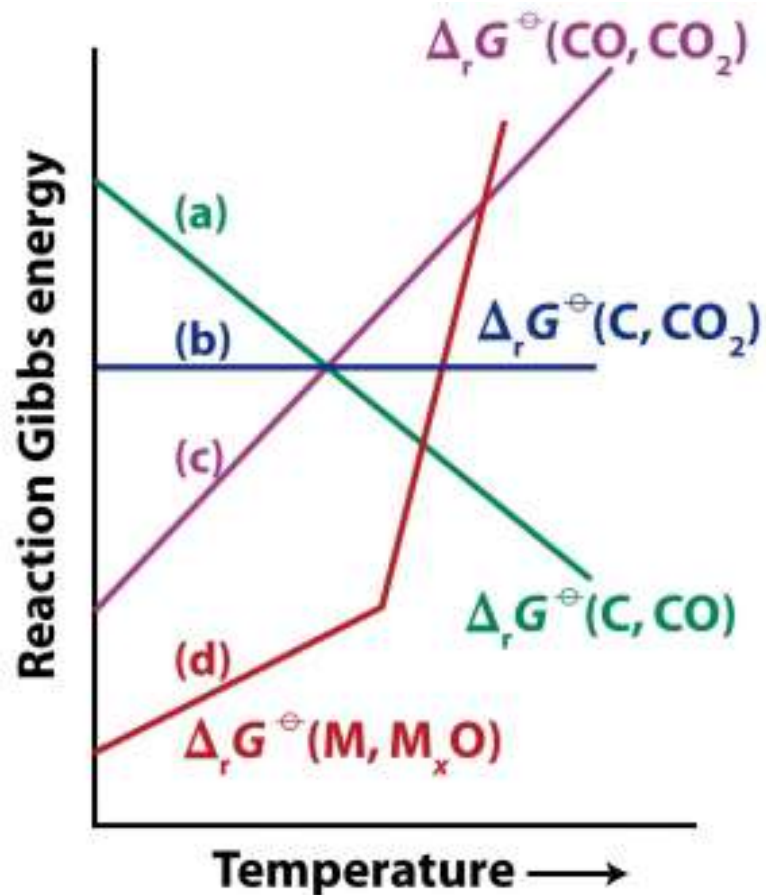
- All metal oxide curves slope upwards
- If materials melt / vaporize, the slope changes
- When the curve crosses $\Delta G^\circ = 0$, decomposition of oxide begins (Ag, Au, Hg)
- Electropositive metal curves are at the bottom of the diagram
- Any metal will reduce the oxide of other metal which is 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



Carbon as the reducing agent





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

When $C \rightarrow CO_2$ line is below $M \rightarrow MO$ line, C reduces the MO and produces CO_2 .

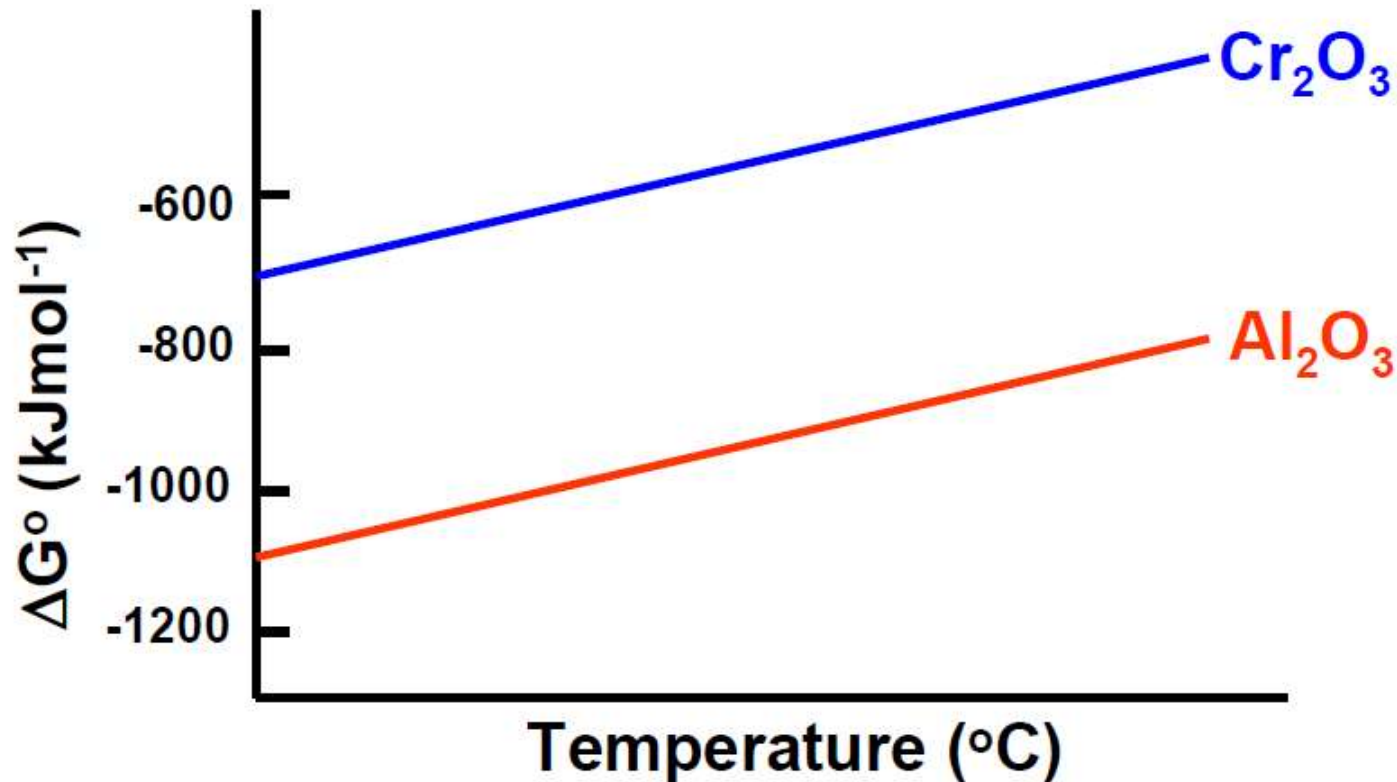
When $CO \rightarrow CO_2$ line is below $M \rightarrow MO$ line, CO reduces the MO and produces CO_2 .

The three curves intersect at 710 °C

Below 710 °C, CO is better reducing agent.

Above 710 °C, carbon is better reducing agent.

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

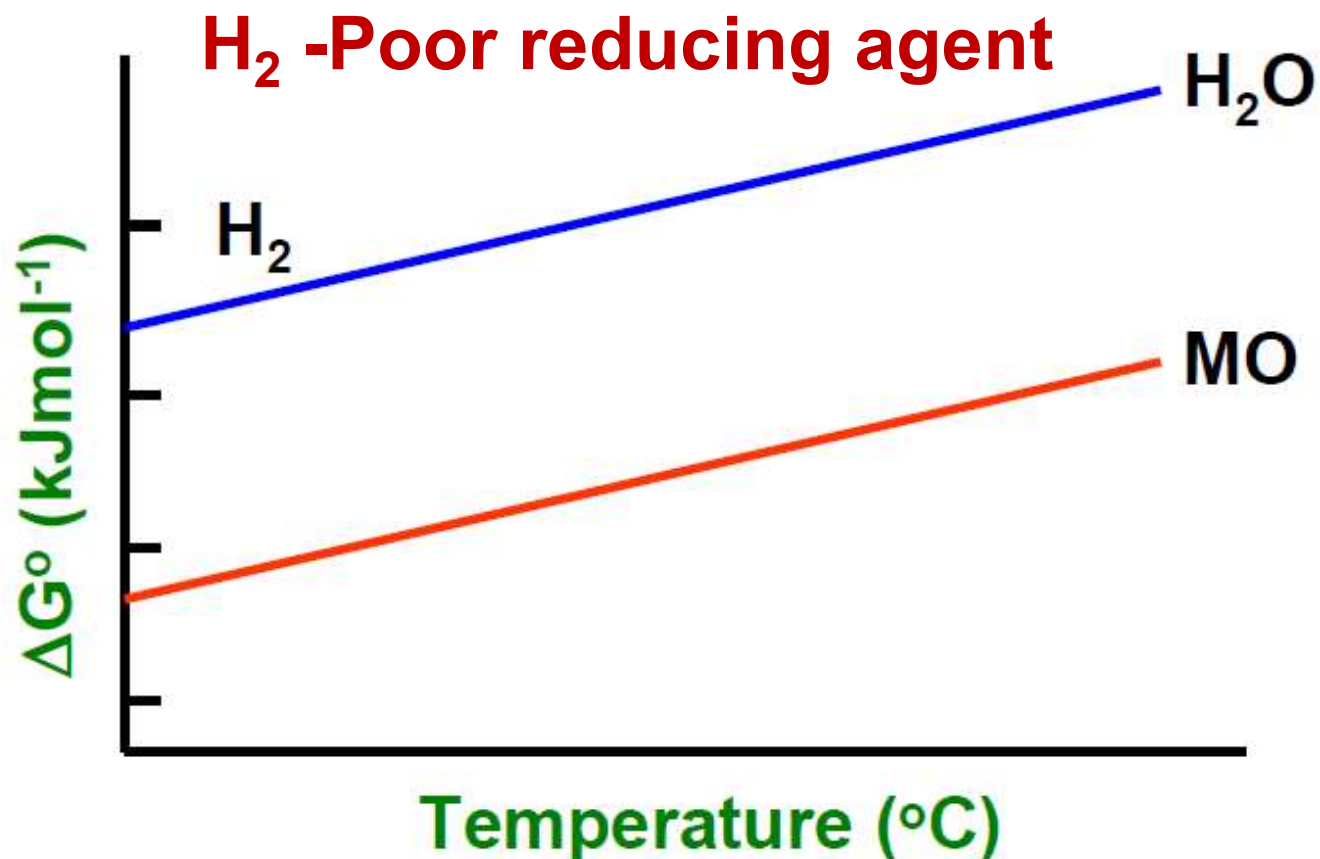
Hence, ΔG is approximately same at different temps

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

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




- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}$; 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
 $2MS + 3O_2 \rightarrow 2MO + 2SO_2$
C

Self reduction:
 $CuS \quad [CuS + CuO] \rightarrow$
 $Cu + SO_2$

H_2 is also a poor reducing agent for metal sulfides.

Ellingham diagram – Metal Sulfides

