Lecture 7

Elligham Diagram

Ellingham Diagram

When metal oxides get reduced by carbon,
one of the following process occur

$$MO + C \leftrightarrows M + CO$$

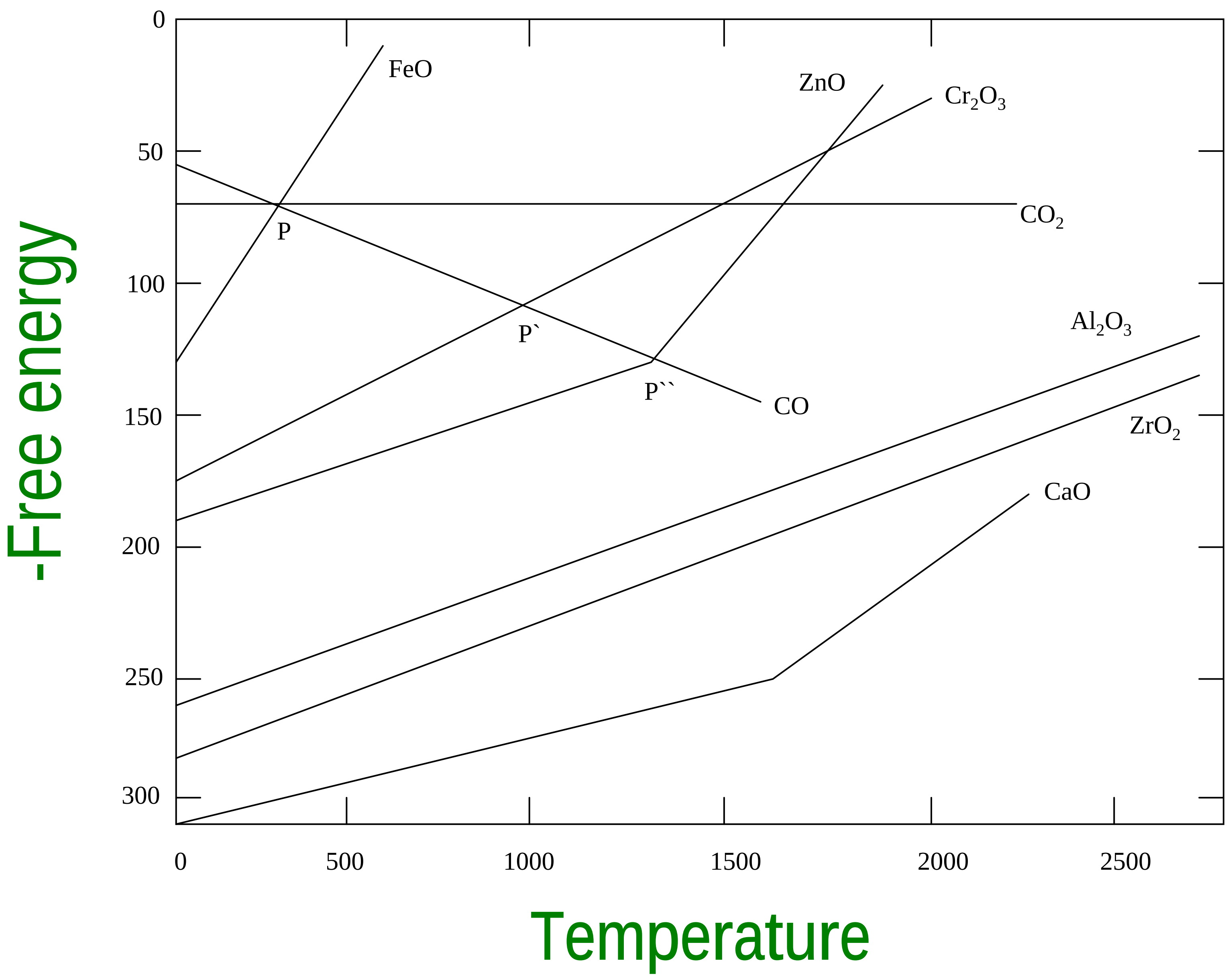
$$MO + \frac{1}{2} C \leftrightarrows M + \frac{1}{2} CO_2$$

These equilibria can be discussed in terms of the thermodynamic function of the reactions,

1. $M + \frac{1}{2} O_2 \leftrightarrows MO$
2. $\frac{1}{2} C + \frac{1}{2} O_2 \rightarrow \frac{1}{2} CO_2$
3. $C + \frac{1}{2} O_2 \leftrightarrows CO$
4. $CO + \frac{1}{2} O_2 \leftrightarrows CO_2$

Temperature dependence of these reactions depend on the entropy change,

$(d\Delta G/dT)_P = -\Delta S$ ΔS° of reaction 3 is higher than that of 2, since there is an increase in number of moles.
In entropy units, the former is only 0.1 and the later is 8.5.
Thus, ΔG decreases sharply with temperature for 3.



-Free energy
0
50
100
150
200
250
300
FeO
ZnO
Cr_2O_3
CO_2
P
P`
P``
CO
Al_2O_3
ZrO_2
CaO
0
500
1000
1500
2000
2500
Temperature

The Gibbs function for reaction 1 represents the metal's affinity for oxygen. At room temperature $\Delta H°$ dominates $\Delta G°$. The entropy of r^n is about the same for different metals because of similar volume change.
Thus ΔG has similar temperature dependence for different metals. Look at the graphs.

The kinks correspond to evaporation of the metals.
Reduction of oxide by carbon depends on the affinity of metal to oxygen in comparison to carbon. Gibbs function for the relevant processes can be expressed in terms of the Gibbs functions for the oxidation r^{ns}. Inverting 1 and adding to 3

$$MO + C \leftrightarrows M + CO \qquad \Delta G° = \Delta G°(3) - \Delta G°(1)$$
$$MO + \tfrac{1}{2} C \leftrightarrows M + \tfrac{1}{2} CO_2 \qquad \Delta G° = \Delta G^o(2) - \Delta G°(1)$$
$$MO + CO \leftrightarrows M + CO_2 \qquad \Delta G° = \Delta G^o(4) - \Delta G^o(1)$$

Equilibrium lies to the right if $\Delta G° < 0$.

This will happen if $\Delta G°$ (1) lies below the carbon r^{ns} 2 – 4.

At any temperature the feasibility of the r^n can be predicted examining the diagram. CuO can be reduced to copper any temperature above room temperature. Ag_2O can be decomposed above 200°C simply by heating. Above 200°C the decomposition is spontaneous. Al_2O_3 can be decomposed only above 2000°C.

It cannot be reduced to metal by CO even up to 3000°C.

Position of equilibrium at any temperature can be obtained by measuring the vertical separation between the lines.

Similar curves can be drawn for sulphides, nitrides, phosphates, halides, etc.

Drawbacks of Ellingham diagram

1. Determination of minor energy differences becomes difficult if the lines lie closely.
2. $\Delta G°$ values do not take into account of activities which may be different form unity.
3. No account of the kinetics of the reaction is taken in measurements of thermodynamic quantities.

Any oxide having a $\Delta G°$ value more negative than the given oxide can be used to reduce the oxide.