

METALLURGY

4th SEMESTER

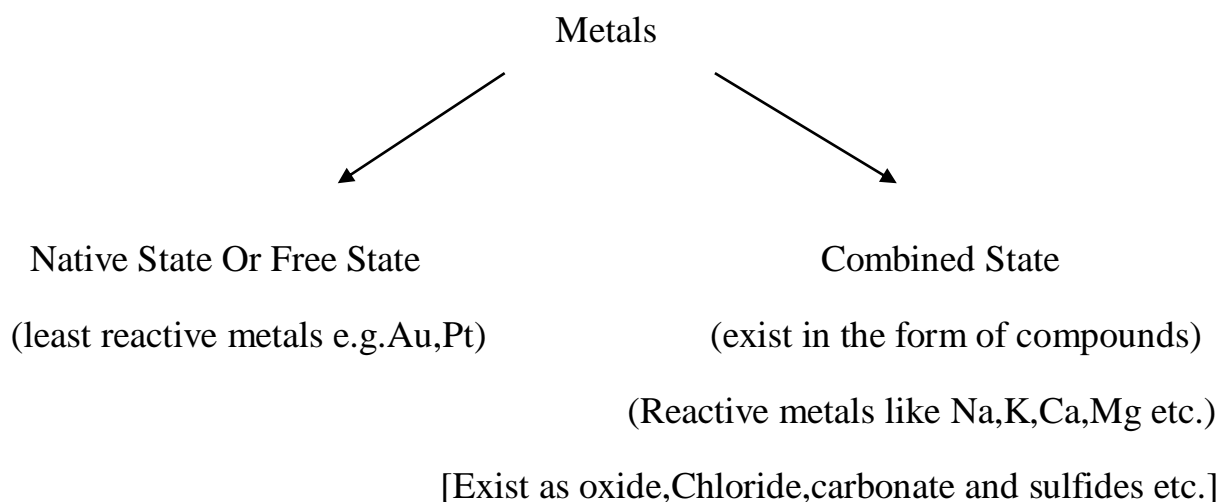
Dr Sukla Chakladar,

Associate Professor,RNLKWC(A),Midnapore

General Principles of metallurgy

1. Chief modes of occurrence of metals based on standard electrode potentials:

The metals are very useful to us. Earth crust is the major source of metals. Sea water is also a source where the metals salts remain in dissolved form. Al is the most abundant metal in the earth crust and the second abundant metal is Fe. Metals exist in the earth crust in two forms.



*Combined as well as native state: Cu, Ag

Reactivity series of metals are arranged on the basis of standard reduction potentials of metals. Standard reduction potential of metals at 25⁰ C are shown in the table. The table shows that from Li downwards Std Electrode potentials get increased accordingly, which indicates the tendency of being reduced gets increased down the series. Thus below the position of the metal in the reactivity series, greater is the probability of the metal to exist as in the free or native state. Thus the metals lying top in the series are most reactive and do not exist in the free

state at all and exist in the combined form. As we go down the series, probability of finding the metal in earth crust gets increased.

Table:Standard Electrode Potentials in Aqueous Solution at 25°C

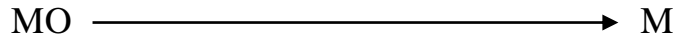
Cathode (Reduction) Half-Reaction	Standard Potential E° (volts)
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.92
$\text{Rb}^+(\text{aq}) + \text{e}^- \rightarrow \text{Rb}(\text{s})$	-2.925
$\text{Cs}^+(\text{aq}) + \text{e}^- \rightarrow \text{Cs}(\text{s})$	-2.923
$\text{Ba}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ba}(\text{s})$	-2.90
$\text{Sr}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sr}(\text{s})$	-2.89
$\text{Ca}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.76
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.38
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Cr}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.74
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.41
$\text{Cd}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40
$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.23
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Fe}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.04
$2\text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	0.15
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu}^+(\text{aq})$	0.16
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34
$\text{Cu}^+(\text{aq}) + \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.52
$\text{Hg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Hg}(\text{s})$	0.789
$\text{Hg}_2^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow 2\text{Hg}(\text{s})$	0.789
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.80
$\text{Pd}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{Pd}(\text{s})$	0.987
$\text{Pt}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Pt}(\text{s})$	1.200
$\text{Au}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Au}(\text{s})$	1.500
$\text{Au}^+(\text{aq}) + \text{e}^- \rightarrow \text{Au}(\text{s})$	1.68

2. Ellingham diagrams for reduction of metal oxides using carbon and carbon monoxide as reducing agent

Principle of Metallurgy: Extraction of METAL from METAL OXIDE

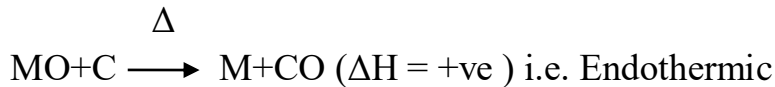
⇒ Reduction Of metal oxide to metal ⇒ Smelting

Reducing agent (C or CO)



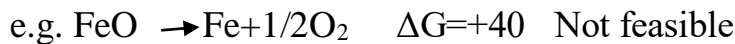
Ellingham diagram will tell us which one will be perfect idea of reducing agent (C or CO) to reduce a particular metal oxide.

- Some metal oxides get reduced easily while others are very difficult to reduce.
- In any case heating is required.



- Study of variation in temperature during thermal reduction is called **Pyrometallurgy**.
- Gibbs Free Energy ($\Delta G = \Delta H - T\Delta S$): The energy associated with a chemical reaction that can be used to do work. For spontaneous reaction, $\Delta G = -ve$
So, $T\Delta S > \Delta H$, for a reaction to be spontaneous.

Role of reducing agent is to make ΔG negative.



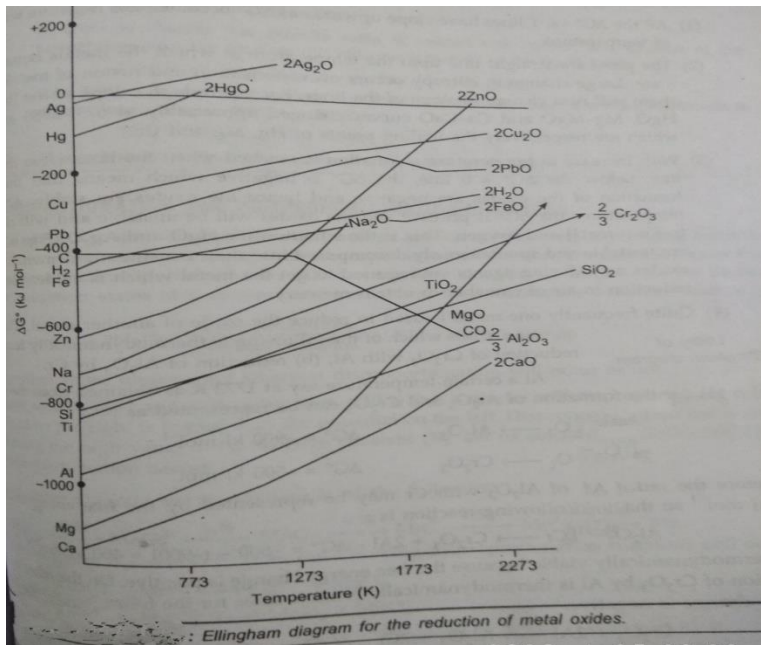
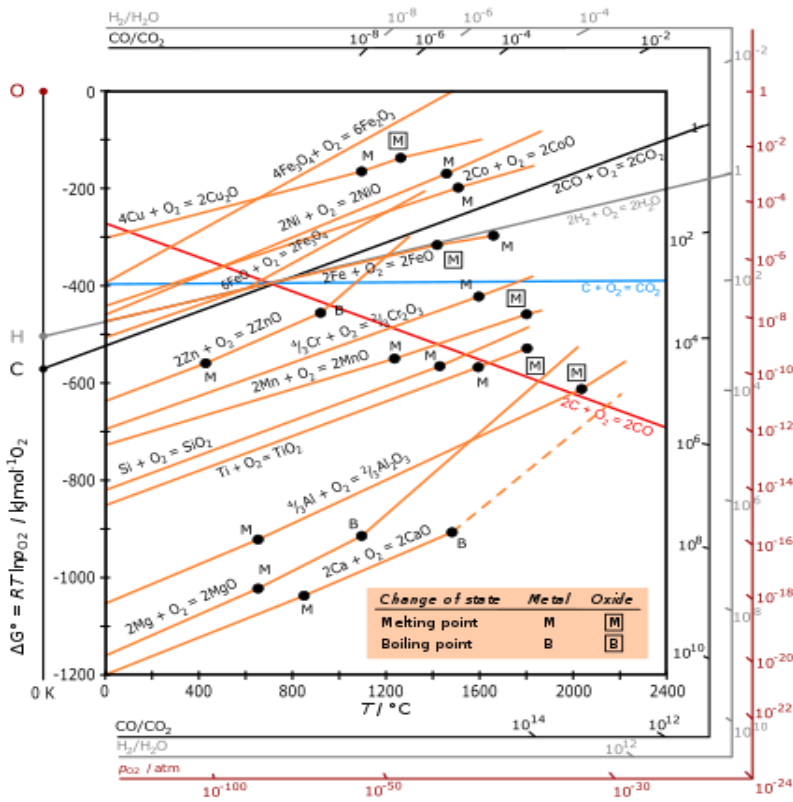
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Some features of Ellingham diagram

An Ellingham diagram shows the relation between temperature and the stability of a compound. It is basically a graphical representation of Gibbs Energy Flow. In metallurgy, we make use of the Ellingham diagram to plot the reduction process

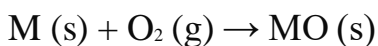
equations. This helps us to find the most suitable reducing agent when we reduce oxides to give us pure metals.



Let us take a look at some important properties of the Ellingham Diagram

1. It is a plot of ΔG^0 (KJ/Mole) of O_2 vs. temperature of formation of oxide. The slope of the curve is the entropy and the intercept represents the enthalpy.
2. Each line of converting metals to metal oxide slope upwards because ΔG becomes less -ve at higher temperature. (that means metal oxide formation from metals is less easy at higher temperatures)
3. Each plot is straight line, except some change in phase (s \rightarrow liq or liq \rightarrow g) The pt of inflection in that respective line is m.p/b.p of the metal. The plots are straight line upto the temperature at which the metals remain in solid state. Large change in entropy occurs on vaporization and fusion of metals and thus there will be a change in slope of the lines. For example the slope of the lines of Hg-HgO, Mg-MgO and Ca-CaO curves changed appreciably at 629, 1380 and 1713 K which are respectively the boiling points of Hg, Mg and Ca.
4. With increase in temperature a situation is reached when the lines cross the $\Delta G = 0$ line. Below the $\Delta G = 0$ line, the ΔG is negative which means that the heats of formation of the oxides are stable. Above these temperatures the ΔG is positive and the oxides will be unstable and will decompose to form M and oxygen. This is the situation for HgO and Ag_2O which are unstable and spontaneously decomposed into their constituent elements. For these oxides no reducing agents are required to get the metal which is evident for the self reduction in air of cinnabar to obtain mercury.

The reaction of metal with air can be generally represented as



Now when reducing metal oxides the ΔH is almost always negative (exothermic) reaction. Also since in the reaction (as seen above), we are going from the gaseous state to the solid state ΔS is also negative. Hence as the temperature increases, the value of $T\Delta S$ will also increase, and the slope of the reaction goes upwards. (**For your understanding:** ΔS becomes negative; T becomes more positive; so $-T\Delta S$ becomes more positive. In this way ΔG becomes more and more positive i.e. less negative with the rise of temperature. It indicates metal oxide formation from metal becomes nonspontaneous with increase of temperature. That means reverse process i.e. reduction of metal from metal oxide becomes easier at very high temperature. But due to large expense of thermal energy to extract metal from metal oxide, it is essential to

find out a suitable reducing agent so that at comparatively low temperature i.e at low expense of thermal energy we can extract the desired metal. Industry find out the procedure at which low cost but more production. Ellingham diagram will tell us which reducing agent at which temperature is more suitable for reduction of any metal oxide.)

- Metals that have curves at the bottom of the diagram reduce the metals found more towards the top. (**For your understanding:** That is any metal lying at the bottom in the diagram is better reducing agent than a metal lying at the top. As the M lying at the bottom has more negative ΔG value (more spontaneous) for its oxide formation reaction than that M lying at the top. So bottom M will form MO easily by reducing the top MO (since its oxide formation has less negative ΔG value i.e. less spontaneous).)
- There are cases when the entropy is not negative, and the slope will not be upwards. Let us take a look at few such examples

$C(s) + O_2(g) \rightarrow CO_2(g)$: Entropy of solids is negligible. So here one molecule of gas is resulting in one molecule of gas. Hence there is almost no net entropy. So there will be no slope, it is completely horizontal.

$2C(s) + O_2(g) \rightarrow 2CO(g)$: Here one mole of gas is giving you two moles of gas as products. So here the entropy will be positive. And as a result, this curve will go downwards.

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$: Here three mole of gas is giving you two moles of gas as products. So here the entropy will be negative. And as a result, this curve will go upwards

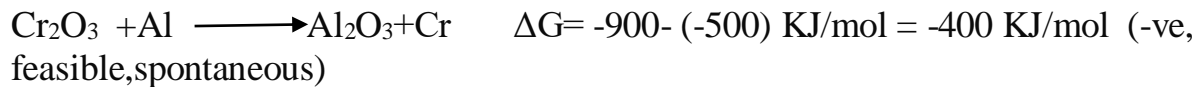
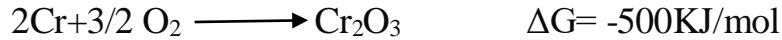
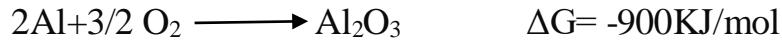
Uses of Ellingham Diagram

1) Aluminothermite Process

The line of Al on the graph actually lies lower than most of the other metals such as iron. This essentially means Aluminium can be used as a reducing agent for oxides of all the metals that lie above it in the graph. Since aluminium oxide is more stable it is used in the extraction of chromium by a thermite process.

Q. Which one is thermodynamically feasible - a) Reduction of Cr_2O_3 by Al or b) reduction of Al_2O_3 by Cr.

At a certain temperature say at 1773 K (Diagram) ,

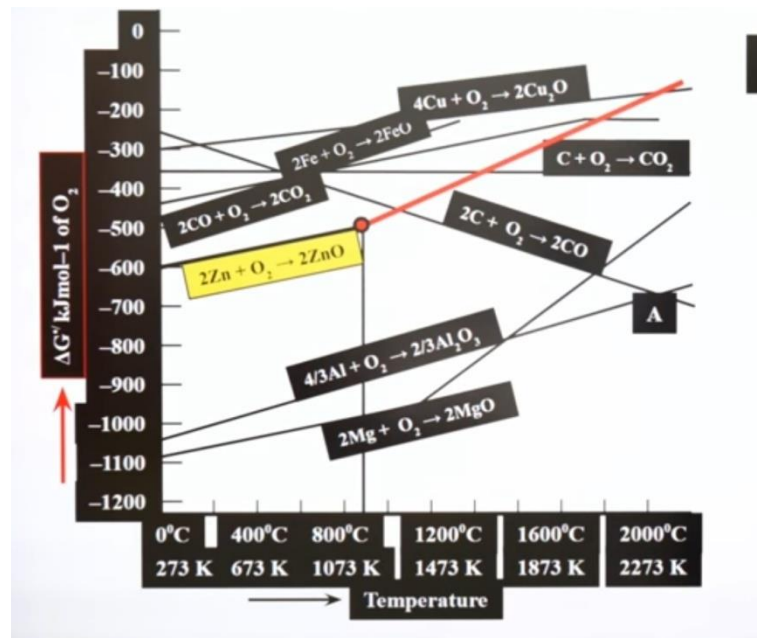


2. Carbon reduction process:

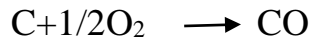
Q1. Out of C and CO, which is a better reducing agent for the reduction of ZnO?

C is the better reducing agent for ZnO compared to CO. Reduction of ZnO to Zn is carried out at a temperature of 1673 K. However, it has been observed that above 1273 K, ΔG of formation of ZnO. Therefore, C can easily reduce ZnO to Zn under these conditions. Also, ΔG of formation of CO_2 from CO is always more than ΔG of formation of ZnO. Therefore, CO cannot be used to reduce ZnO.

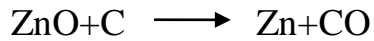
Q2. Can C reduce ZnO to Zn a) 1000K b) 1500K?



Answer it from the ΔG values obtained from the Ellingham diagram at the both the temperatures for the following two reactions line

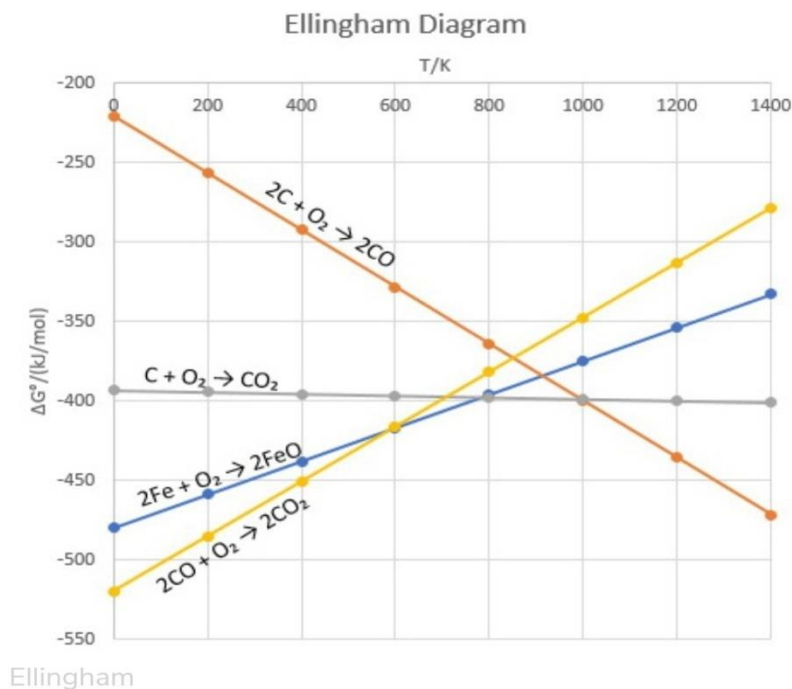


and from that calculate the overall ΔG for the reaction,



Find that whether overall ΔG at the respective temperatures negative or positive and then predict your answer.

Q3. From the following graph predict the temperature above which say carbon or carbon monoxide will reduce FeO.



Below 600K, Only CO reduces FeO.

Above 800K, reduction by conversion of coke to carbon dioxide is spontaneous.

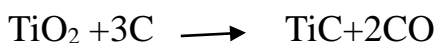
Above 900 K, reduction by conversion of coke to CO is spontaneous.

Thus, for the reduction of FeO, CO is the better reducing agent below 600K, but C is the better reducing agent above 800K.

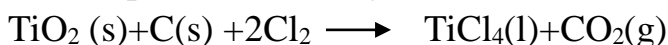
[a key point in the graph is the point where two reaction lines cross. At this point, ΔG is the same for each reaction. On either side of the crossover point, the reaction represented by the lower line (the one with the more negative value of ΔG) will be spontaneous in the forward direction, while that represented by the upper line will be spontaneous in the reverse direction.]

Q. Applying Ellingham diagram predict whether rutile(TiO_2) will be reduced by carbon?

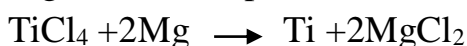
Ans. In the Ellingham diagram the curve of carbon is below the curve of titanium at about 1900K. At this high temperature of course TiO_2 is reduced but instead of titanium metal, titanium carbide will be formed.



In order to obviate this difficulty rutile is treated with carbon and chlorine at this temperature whereby titanium(IV) chloride is formed in the liquid state.



Now TiCl_4 is purified by fractional distillation and then reduced by molten Mg in Ar atmosphere at 1000-1150°C.



This is known as Kroll process for the extraction of titanium.

Limitations of Ellingham Diagram

- It does not consider the kinetics of the reactions.
- Also, it does not provide complete information about the oxides and their formations. Say for example more than one oxide is possible. The diagram gives us no representation of this scenario