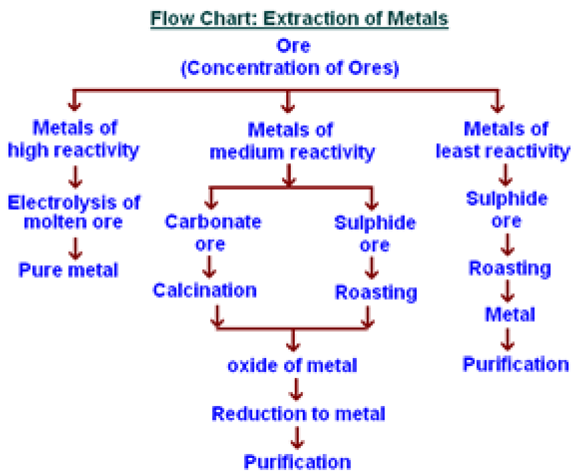
***Steps of Extraction of Metals :***




**Roasting:** Heating of sulphide ores in the presence of excess air to convert them into oxides is known as ROASTING.

**Calcination:** Heating of carbonate ores in the limited supply of air to convert them into oxides is known as CALCINATION.

**Reduction:** Heating of oxides of metals to turn them into metal is known as REDUCTION.

**Purification:** Metal; so obtained is refined using various methods.

## Hydrometallurgy

The most selective methods for separating metals from their ores are based on the formation of metal complexes. For example, gold is often found as tiny flakes of the metal, usually in association with quartz or pyrite deposits. In those circumstances, gold is typically extracted by using *cyanide leaching*, which forms a stable gold–cyanide complex—$[Au(CN)_2]^-$:

$$4Au(s) + 8NaCN(aq) + O_2(g) + 2H_2O(l) \rightarrow 4Na[Au(CN)_2](aq) + 4NaOH(aq)$$

Virtually pure gold can be obtained by adding powdered zinc to the solution:

$$Zn(s) + 2[Au(CN)_2]^-(aq) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s)$$

A related method, which is used to separate $Co^{3+}$, $Ni^{2+}$, and $Cu^{+}$ from Fe, Mn, and Ti, is based on the formation of stable, soluble ammonia complexes of ions of the late transition metals.

## Thermodynamics

There is an overlap between the study of physics and chemistry, known as Physical Chemistry. And here is where the concept of thermodynamics exits. Thermodynamics is the branch of science that deals with a relationship between thermal energy i.e. heat and other forms of energy.

Thermodynamics is the study of the energy transfer that occurs during chemical as well as physical changes. It also allows us to predict and measure these changes.

## Thermodynamics in Metallurgy

The main thermodynamic concept we must concern ourselves with when it comes to metallurgy is Gibbs Free Energy. In thermodynamics, whether a process will happen spontaneously or not will be determined by Gibbs Free Energy. The symbol ΔG. If this value of ΔG is negative then the reaction will occur spontaneously. We will now look at two equations to arrive at ΔG

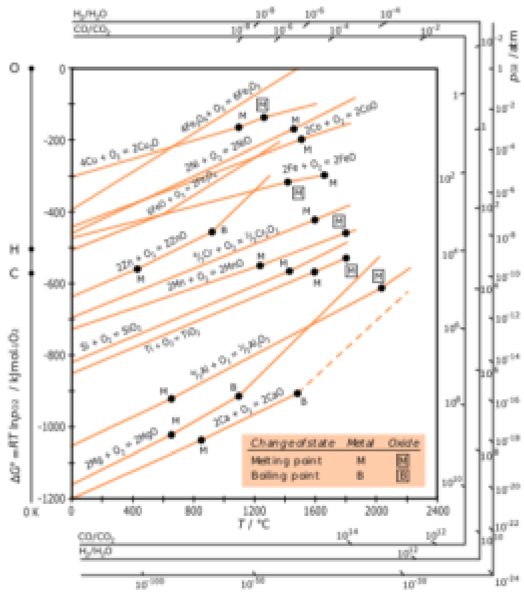
$$\Delta G = \Delta H - T\Delta S$$

ΔH is the change in enthalpy. Here a positive value will depict an endothermic reaction, while a negative value will be an exothermic reaction. So when the reaction is exothermic, it makes ΔG negative. ΔS is the Entropy or the randomness of molecules. This changes very sharply when the state of the matter changes. Another equation which relates the Gibbs Free Energy to the equilibrium constant is

$$\Delta G^\circ = RT\ln K_{eq}$$

$K_{eq}$ is the equilibrium constant. It is calculated by dividing the active mass of products by the active mass of reactants. R is the universal gas component. Now to attain a negative value of ΔG (which is desirable) the value of the equilibrium must be kept positive.

## 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

- Here ΔG is plotted in relation to the temperature. The slope of the curve is the entropy and the intercept represents the enthalpy.
- As you know the ΔH (enthalpy) is not affected by the temperature
- Even ΔS that is the entropy is unaffected by the temperature. However, there is a condition here, that a phase change should not occur.
- We will plot the temperature on the Y-axis and the ΔG on the X axis
- Metals that have curves at the bottom of the diagram reduce the metals found more towards the top

The reaction of metal with air can be generally represented as

$$M (s) + O_2 (g) \rightarrow MO (s)$$

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 TΔS will also increase, and the slope of the reaction goes upwards

## Exceptions to Ellingham Diagram

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) + O2 (g) → CO2 (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)+ O2 (g) → 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.

## 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

## Uses of Ellingham Diagram

1) Alumino Thermic Process

The Ellingham curve 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.

2) Extraction of Iron

Extraction of iron from its oxide is done in a blast furnace. Here the ore mixes with coke and limestone in the furnace. Actually, the reduction of the iron oxides happens at different temperatures. The lower part of the furnace is kept at a much higher temperature than the top. This process was developed after understanding the reactions with the help of thermodynamics. These reactions are as follows

*At temperatures of 500-800 K*

$3Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2$

$Fe_3O_4 + 4CO \rightarrow 3Fe + 4\ CO_2$

$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$

*At temperatures of 900-1500 K*

$C + CO2 \rightarrow 2CO$

$FeO + CO \rightarrow Fe + CO_2$

## Solved Question for You

Question: In which of the following pair of metals, both are commercially extracted from their respective ores by carbon reduction method?

a. Zn, Cu

b. Fe, Cu

c. Sn, Zn

d. Fe, Zn

Answer: The correct option is "C". The oxide ores of Tin and Zinc are reduced with carbon to form metals. And so Tin and Zinc are commercially extracted from their respective ores by carbon reduction.