

## **General methods for extraction (isolation) of metals (elements)**

The concentrated ore often requires conversion into a compound suitable for conversion into the element. For production of crude metals, pyrometallurgical processes are employed. In pyrometallurgy thermodynamic factors are of chief importance. Since chemical equilibrium is rapidly reached at the high temperature employed in these methods, kinetic factors need not be considered.

Oxide ores are directly reduced (smelted) to the metal. A variety of reducing agents are used, carbon being the one most widely employed. Al, Si and hydrogen are other reducing agents used. These are preferred to carbon, wherever the metal to be isolated forms a carbide. The bulk of the impurities is removed by use of suitable fluxes to form a slag.

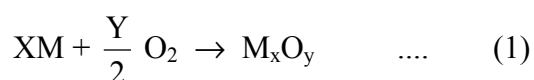
Sulphide ores are invariably roasted to convert them to oxide and then reduced to the metal. The roasting process also removes volatile impurities such as arsenic. For thermodynamic reasons, an oxide rather than a sulphide is used for reduction. Sometimes, the sulphides are oxidized to sulphate or some other soluble salt and the metal obtained from it by chemical or electrolytic reduction.

The highly electropositive metals, such as the alkali and alkaline earth metals are isolated by electrolytic reduction of their fused halides, since no suitable chemical reducing agent is available and aqueous solutions could not be used due to reactive nature of these metals. Less electropositive metals like Cr, Cu and Zn can be prepared by electrolysis of concentrated aqueous solutions of their salts. An advantage of the electrolytic over oxide reduction method for extraction is high purity of the electrolytically isolated metal.

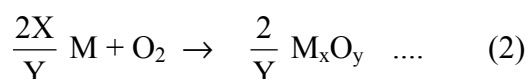
When neither oxide reduction nor electrolysis is suitable for chemical reasons, reduction of a metal halide by reactive metals such as Mg, Na and Ca is resorted to e.g. reduction of  $\text{TiCl}_4$  by Mg in an inert atmosphere.

## **Physico-chemical principles underlying the extraction of metals. Free energy of formation of oxides :**

Free energy considerations play an important role in the understanding of many pyrometallurgical processes. The free energy of formation  $G_f$  of an oxide may be considered as the standard free energy of the reaction :



In a similar manner, one can talk of free energy of formation of an oxide per mole of  $O_2$  as free energy of the reaction.



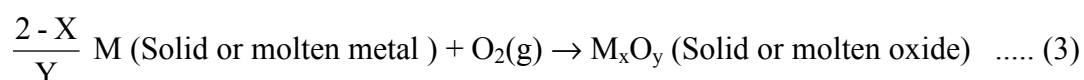
If  $\Delta G_f$  (standard free energy of formation) has a minus sign at a given temperature then the oxide can be expected to form spontaneously from the metal and oxygen. If  $\Delta G_f$  has a positive sign, the oxide will be expected to decompose spontaneously into its elements.

The heats of formation of a number of oxides, expressed per mole of  $O_2$  are listed in Table-1.

Table-1 : Heats of formation of some metal oxides

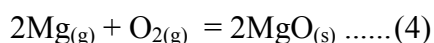
Oxide	$\Delta H_f$ (per mole of $O_2$ (g))	$E^0$ ( $M_{aq} / M$ )
$MgO$	-288 Kcal	-2.37 volts
$Al_2O_3$	-266 Kcal	-1.66 volts
$ZnO$	-166 Kcal	-0.76 volts
$NiO$	-177 Kcal	-0.25 volts
$CuO$	-74 Kcal	+0.34 volts
$Ag_2O$	-15 Kcal	+0.78 volts

In the formation of a metallic oxide according to eqn. (3), the entropy change is essentially that which occurs when one mole of gaseous phase,  $O_2(g)$  is removed from the system, provided both the metal and the oxide are in solid/liquid state and are not vaporized.



There may be small changes in disorder, hence, entropy associated with the change from the metal phase to the oxide phase but the main factor influencing  $\Delta S_f$  is the using up of the highly disordered gaseous phase. Hence,  $\Delta S_f$  will be negative and entropy change is roughly same for all metal systems, provided the boiling point of neither metal nor oxide is exceeded. This change in entropy is approximately 50 cal. mole<sup>-1</sup> deg.<sup>-1</sup>.

Fig. 1 is a plot of  $\Delta G_f$  in kJ/mole  $O_2$  against temperature for various metallic oxides. Below the boiling point of various metals, slopes of all the graphs are same, since in  $\Delta G_f = \Delta H_f - T \Delta S_f$ ,  $T \Delta S_f$  factor is the same whatever the metal may be, if slight changes of  $\Delta H_f$  with temperature are disregarded. When boiling point of the metal is exceeded, slope will increase since the reaction now involves a larger entropy change. For instance, above 1100 °C, three moles of gas phase are converted into solid phase in the reaction.



Above a certain temperature,  $\Delta G_f$  becomes positive for some of the oxides. This explains why mercury(II) oxide, for instance, decomposes spontaneously into its elements when heated. The diagram predicts decomposition of tin (IV) oxide and zinc oxide on strong heating, but it does not give much hope for obtaining, say, pure

magnesium by straight forward heating of the oxide to a high temperature. Thus, heat alone is not sufficient to decompose oxides of most metals.

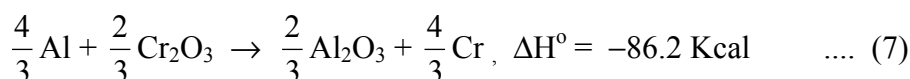
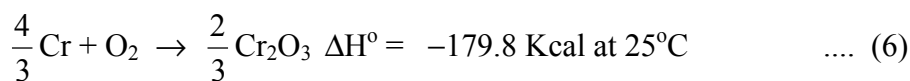
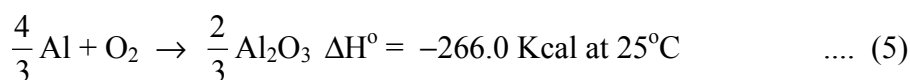
A comparison of Fig. 1 with the data given in Table-1 clearly indicates that those metal oxides with least negative heat of formation have lowest stability towards heat. Also stability order of the oxides of metals parallels roughly, but not exactly the order in the redox series.

### Reduction of metallic oxides :

Since many metallic oxides cannot be reduced by the action of heat alone, it is necessary to employ a reducing agent for their reduction. Aluminium, carbon and hydrogen are quite useful for such purposes. The ensuing discussion throws light on how to find whether a given substance will reduce the oxide of a given metal or not.

### Thermit process :

This method employs aluminium metal as reducing agent. Let us consider the reaction between chromium(III) oxide and aluminium.

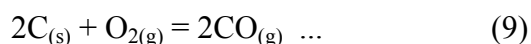
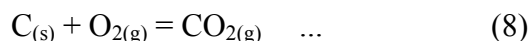


It may be seen that the reaction will be accompanied by evolution of heat. Similarly, from a knowledge of  $\Delta G_f$  values for the two oxides,  $\Delta G_f$  for the reaction can be shown to be negative. Fig. 1 shows the two curves obtained by plotting  $\Delta G_f$  for the two oxide against temperature.

At all accessible temperatures,  $\Delta G_f$  is markedly negative and we would expect the reaction to proceed. In fact, the entropy change,  $\Delta S^\circ$ , of this reaction will be quite small, since no gaseous products or reactants are involved and the effect due to different structures of various phases will be very small. Hence,  $\Delta G^\circ$  will be approximately same at room temperature, as well as at higher temperatures, but the reactions need to be raised to a higher temperature to ‘trigger it off’. This can be done by priming it with magnesium ribbon and barium peroxide. Once started, the reaction is highly exothermic and very high temperatures will be reached. The reduction of oxides with aluminum is called “**thermit**” process or “**Goldschmidt**” process. Even though this process could be applied in principle, to all but most electropositive metals, it actually finds very little application on an industrial scale as other reducing agents (e.g. carbon) cheaper than aluminum are available. However, some manganese and chromium are produced in this way.

### Carbon as Reducing agent :

Since carbon is the only reducing element, which occurs native in large quantities, it has been used on a large scale for reduction of metal oxides in the extraction of metals. Carbon burns in oxygen at temperatures below 710°C to form carbon dioxide but at higher temperatures it gives carbon monoxide as the product.



The formation of  $\text{CO}_2$  (by equation 8) is accompanied with little entropy change as one mole of gaseous  $\text{O}_2$  forms one mole of gaseous  $\text{CO}_2$ . The disappearance of well ordered solid phase lattice of carbon has little effect on the entropy change,  $\Delta S^\circ$ . For this reaction, we have  $\Delta G^\circ = -94.1 \text{ Kcal}$  at  $25^\circ \text{C}$ , and  $\Delta S^\circ = +0.7 \text{ cal. deg.}^{-1}$ .

Carbon can also react with  $\text{CO}_2$  to form  $\text{CO}$ , which is favoured at high temperatures since it involves an increase in the disorder,  $\Delta S$  is positive because two moles of  $\text{CO}$  are formed from only one mole of  $\text{CO}_{2(g)}$ .



For this reaction (eqn. 10) we have,  $\Delta H^\circ = +41.8 \text{ Kcal}$  at  $25^\circ \text{C}$ ,  $\Delta S^\circ = +42.1 \text{ Kcal deg.}^{-1}$

Adding equations (8) and (10), we see that carbon reacts with oxygen to form carbon monoxide (by equation 9). For this reaction we have  $\Delta H^\circ = -52.8 \text{ Kcal}$ ,  $\Delta S^\circ = +42.8 \text{ Kcal. deg.}^{-1}$ .

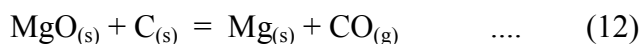
Equation (9) also has a favourable entropy change, which will make the entropy term  $T\Delta S$  more significant at higher temperatures :

Fig. 1 shows that of the two possible reactions between carbon and oxygen, the one which actually occurs at a given temperature is the one which has more negative  $\Delta G^\circ$ . The bold line in the free energy graph indicates this. It is the  $+\Delta S^\circ$  for equation (9) which causes free energy plot to slope downwards above about  $710^\circ \text{C}$ . It may also be seen from Fig. 1 that carbon monoxide could be an effective reducing agent only at temperature below  $710^\circ \text{C}$  according to the reaction :



In the region around  $710^\circ \text{C}$ , where the two reactions (8) and (9) have approximately equal  $\Delta G^\circ$  values (the two lines actually cross), the products of combustion will be a mixture of  $1\text{CO}_{(g)} + \text{CO}_{2(g)}$ . The downward slope of carbon-oxygen graph shows that carbon can reduce oxides of most metals provided the temperature is high enough.

Consider the possible reaction:



for which  $\Delta H^\circ = +117.4 \text{ Kcal at } 25^\circ\text{C}$ . Free energy change of the reaction can be derived by considering separate  $\Delta G^\circ$  values for the two reactions.

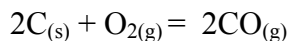
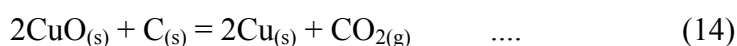


Fig. 1 shows that this reaction will have a value of  $\Delta G^\circ = 0$  at a point where the two lines representing (9) and (12) cross each other. The equilibrium constant equals unity at  $\sim 1900^\circ\text{C}$  (from the graphs). Above this temperature,  $\Delta G_f$  for the reaction becomes negative and the reaction is favored. It is to be noted that the formation of magnesium vapor steepens the MgO curve and makes the temperature for reduction lower than it would otherwise be.

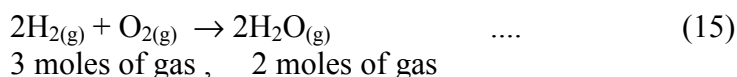
The same conclusion can be arrived at in a qualitative manner in other ways also. Reaction (11) is endothermic. Hence equilibrium will be according to the Le Chatelier principle, shifted towards the r.h.s.. Formation of metal is thus favored at high temperatures. Furthermore, when magnesium vapor is formed as a result of the reduction of MgO by carbon,  $\Delta S$  for the reaction is strongly positive and if  $T$  becomes high enough for  $-T \Delta S$  term to off-set the adverse positive value of  $\Delta H$  the forward reaction will become predominant.

Fig. 1 shows a complete diagram of the free energies of some metal oxide systems, together with carbon and also hydrogen. The temperature at which the 'carbon' curve intersects the 'metal' curve is the temperature at which the equilibrium constant for the reduction becomes unity. The diagram shows for instance, that  $\text{TiO}_2$  requires about  $1800^\circ\text{C}$  for reduction to titanium and  $\text{ZnO}$  only  $1000^\circ\text{C}$ . In the case of reduction of copper(II) oxide, the diagram predicts that carbon dioxide rather than monoxide will be the main product of the reaction.



Hydrogen as a reducing agent :

Hydrogen is not a very effective reducing agent for obtaining metals from their oxides, as shown by Fig. 1. The reason is that  $S^\circ$  for the reaction

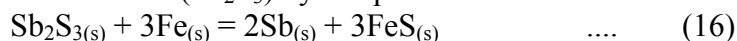


is negative as r.h.s. is less disordered. Hence, the plot of  $\Delta G^\circ$  against  $T$  rises with temperature, indicating that not many metal oxide plots are intercepted by  $\text{H}_2$  curve. Thus, hydrogen reduces oxides such as those of copper(I) and copper(II), but not the oxide of aluminium magnesium and calcium. Oxides of iron are reduced only with difficulty. In case of magnetic oxide of iron,  $\text{Fe}_3\text{O}_4$  an equilibrium is readily established.

## Reduction of sulfides and chlorides of metals :

Although carbon reduces oxides quite effectively, it is not so effective when used directly on sulfides or chlorides of metals. In the case of chlorides, reaction is prevented by the fact that entropy of the reaction is not favorable. (Fig. 2). This carbon cannot be used as reducing agent in the case of chlorides and hydrogen has only a few applications e.g. in reduction of  $\text{SiCl}_4$ . Hence, recourse is made to reactive electropositive metals, such as Mg or Na as in production of zirconium and titanium, from their tetrachlorides.

Similar case occurs with sulfides, carbon forms only one stable sulfide,  $\text{CS}_2$  (b.p.  $46^\circ$ ). The situation is analogous to the case which would occur if carbon is incapable of forming CO. The downward sloping part of the curve in Fig. 1 does not exist in Fig. 3. Hence carbon will reduce sulfides directly, but also with considerable difficulty. As may be seen from Fig. 3, free energies of formation of most of metal sulfides are greater than those for  $\text{CS}_2$  and  $\text{H}_2\text{S}$ , the former is in fact an endothermic compound. Thus, neither  $\text{H}_2$  nor C is a suitable reagent for reduction of metal sulfides. This difficulty can be overcome by using a more powerful reducing agent in a few exceptional cases e.g. reduction of stibnite ( $\text{Sb}_2\text{S}_3$ ) by scrap iron.

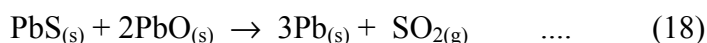


in reverberatory furnace when a fused ferrous sulfide is formed. Similar method is applicable to bismuth.

In actual practice, sulfide ores are roasted by heating them in a stream of air. This reaction converts the ore into oxide, with the formation of  $\text{SO}_{2(g)}$ , e.g. galena ( $\text{PbS}$ ).

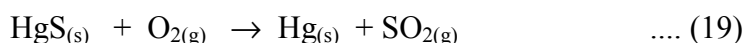


Metallic lead may then be obtained by incomplete roasting to produce a mixture of  $\text{PbS}$  and  $\text{PbO}$ , followed by heating in absence of air. This kind of reduction involving partial oxidation followed by heating in absence of air is called autoredox (or air reduction).



Such a method is possible for lead since the formation of  $\text{PbO}$  is not very exothermic. It would not be possible for metals where  $\Delta H$  of the oxide is strongly negative. In such cases, a reducing agent such as carbon must be used.

Mercury(II) oxide, which occurs as "Cinnabar" is converted directly to the metal when roasted,



This happens unlike the reaction observed for lead above because at the roasting temperature, the free energy of formation of  $\text{HgO}$  is positive. Thus,  $\text{HgO}$  decomposes into Hg and  $\text{O}_2$ .

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DEPARTMENT OF CHEMISTRY

CH-102 (INORGANIC) : TUTORIAL NO. 2

- 1] Why are the metals Al and Ti not produced by pyro-metallurgical extraction of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ?
- 2] Using the Ellingham diagram of oxides, determine whether Aluminum can be used to reduce  $\text{MgO}$ .
- 3] Ellingham diagram predicts a negative  $\Delta G^\circ$  value for the reduction of  $\text{Cr}_2\text{O}_3$  with Al at room temperature. In fact the reduction is carried out at a much higher temperature. Suggest an explanation.
- 4] What is the reducing species in the self-reduction of  $\text{CuS}$  ore?
- 5] Can carbon be used as a reducing agent for the reduction of the metal sulphide ores ?
- 6] Is there any correlation between the heats of formation of the metal oxides and their position in the electrochemical series? Comment.
- 7] Aluminum and ammonium perchlorate are used as solid propellant in booster rockets? Comment.
- 8] Account for the fact that the roasting of  $\text{PbS}$  in air gives  $\text{PbO}$  whereas that of  $\text{HgS}$  gives  $\text{Hg}$ .
- 9] Sodium metal is produced commercially by the electrolysis of a mixture of 40%  $\text{NaCl}$  and 60%  $\text{CaCl}_2$ . What is the role of  $\text{CaCl}_2$  in this process? Will Ca also be produced along with Na?
- 10] How is very pure Silicon obtained for Semiconductor application?

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