




TECHNICAL ARTICLE

# Constitutive Topics in Physical Chemistry of High-Temperature Nonferrous Metallurgy: A Review—Part 2. Reduction and Refining

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In this Part 2 of the review, we demonstrate the roles of phase rule, free energy and activity in the reduction and refining of different nonferrous metals categorized as common, reactive, rare and refractory. Based on the discussions in the following sections, the reader will appreciate the contributions of phase rule, activity and free energy in the selection of particular steps in the extraction of different types of metals. It also demonstrates how difficult reactions like the removal of nickel from blister copper can be made feasible by generating conditions according to the van't Hoff isotherm.

## INTRODUCTION

In Part 1 of this review,<sup>1</sup> we discussed the physical chemistry of high-temperature processing of sulfide minerals. In this Part 2, we will focus on reduction and refining methods for the production of nonferrous metals. To develop new extraction methods or improve existing processes, it is essential to apply physicochemical principles at various steps of reduction and refining in the extraction/production of nonferrous metals. This review will demonstrate how the knowledge of physicochemical principles is critical in the development of different processes for the recovery of metal values and chemicals from concentrates, lean ores and minerals, and waste residues.

## REDUCTION OF OXIDES

A number of metals such as iron, lead, zinc, chromium, uranium, thorium, beryllium and zirconium are produced by the reduction of their oxides obtained by either the concentration of ores or the roasting of sulfide concentrates. The selection of the reducing agent depends on physical characteristics such as melting and boiling points and vapor pressure of the metal and the relative stability of its oxide compared with the oxides of impurity metals and gangue minerals. Carbon, carbon monoxide and hydrogen are the reducing agents of

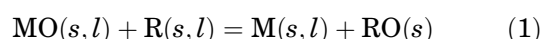
great importance in the extraction of common metals such as iron, lead and zinc, whereas metals like magnesium, calcium and sodium having higher affinity for oxygen and halides are used in the production of very reactive metals such as uranium, thorium and beryllium.

## Thermodynamics of Reduction of Oxides

The physicochemical principles involved in metallothermic reduction and the role of CO/CO<sub>2</sub> and H<sub>2</sub>/H<sub>2</sub>O ratios in the gaseous reduction of oxides<sup>2,3</sup> presented in this section will be useful in understanding various extraction and refining processes.

### *Metallothermic Reduction of Oxide*

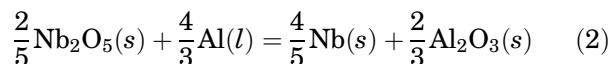
A metal R can be used as a reducing agent in reduction of the metal oxide MO if R has greater affinity for oxygen compared with the metal M, that is, RO is more stable than MO. Under these conditions the free energy change of the desired reaction



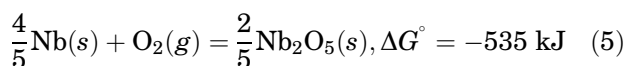
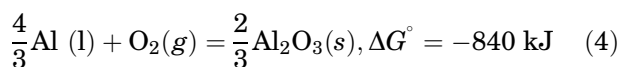
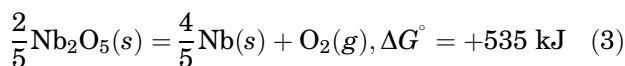
is negative. For example, the high negative value of  $\Delta G^\circ$  for the reduction of Fe<sub>2</sub>O<sub>3</sub> by aluminum [Fe<sub>2</sub>O<sub>3</sub>(s) + Al(l) = 2 Fe(l) + Al<sub>2</sub>O<sub>3</sub>(s)] at 1200°C produces Fe and Al<sub>2</sub>O<sub>3</sub>. This forms the basis of the aluminothermic reduction of hematite ore, which has been used extensively for the repair of railway

tracks. The reaction is initiated by igniting a magnesium ribbon embedded in the preheated charge of hematite and aluminum contained in a steel-capped vessel. Since the reaction is highly exothermic the heat generated is sufficient to produce molten iron. The technique popularly known as the thermite or aluminothermic process has been extensively used to produce manganese, chromium and ferroalloys such as ferroniobium and ferrovanadium.

The Ellingham diagram<sup>3,4</sup> that presents graphically the variation with temperature of the standard free energy of formation of different oxides is quite helpful in the selection of the appropriate metal for reduction. For simplicity, such diagrams are constructed assuming unit activities of the metal and its oxides. The concept of depicting  $\Delta G^\circ$  vs  $T$  using one mole of  $O_2$  gas gives an easy way of estimating the free energy change for the reduction of the oxide represented by the upper of the two curves by the metal whose oxide formation is represented by the lower curve at the chosen temperature. To demonstrate the usefulness of the Ellingham diagram, let us consider the reduction of  $Nb_2O_5$  with Al at 1200 K, according to the reaction:



The free energy change of the above reaction at 1200 K can be calculated from the  $\Delta G^\circ$  values of the following reactions given in the diagram<sup>3</sup>:



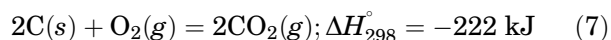
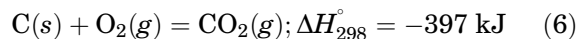
From the first law of thermodynamics we find that  $\Delta G^\circ$  for reaction (2) can be obtained by either the difference between  $\Delta G^\circ$  for reactions (4) and (5) or summing up reactions (3) and (4).

Thus,  $\Delta G^\circ$  for reaction (2) at 1200°C works out to be  $-305$  kJ. The calculated equilibrium constant of  $1.8910^{13}$  indicates large niobium content in the resulting product. A similar consideration indicates why lead cannot be used to obtain niobium from niobium oxide according to the reaction  $[2/5 Nb_2O_5(s) + 2Pb(l) = 4/5 Nb(s) + 2 PbO(s)]$  because the free energy change of the reaction is positive.

The slope of the  $\Delta G^\circ$  vs  $T$  curve  $[\frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ]$  is the standard entropy change of the corresponding reaction. In the Ellingham diagram,<sup>3</sup>  $\Delta G^\circ$  vs  $T$  plots are virtually straight lines as long as the reactants and products remain in the same physical state. Consumption of one mole of  $O_2$  in the formation of the oxide makes the system more

ordered; hence, the entropy ( $\Delta S^\circ$ ) of the system decreases and the lines have positive slopes. Since liquids and vapors are less ordered than the solids, the slope of the line,  $-\Delta S^\circ$ , becomes more positive, i.e.,  $\Delta S^\circ$  becomes more negative, at the melting and boiling points of the reactant metal.

Contrary to the above, the two lines corresponding to the formation of  $CO_2$  and  $CO$  from carbon have negative slopes.



The line corresponding to reaction (6) is almost horizontal because there is only a small change in entropy ( $\Delta S^\circ = 0.8 \text{ JK}^{-1}$ ) for reaction (6) since the number of moles of the gas is not changed by the reaction. However, the line representing reaction (7) has a pronounced negative slope ( $\Delta S^\circ > 0$ ) because of the increase in the number of gas molecules and hence a large increase in entropy ( $\Delta S^\circ \sim +170 \text{ JK}^{-1}$ ). The two lines related to the formation of  $CO_2$  and  $CO$  with appreciable difference in the slope are of great significance in metal production. Their intersection at 720°C indicates that  $CO$  is not only more stable than  $CO_2$  above this temperature but also becomes increasingly stable compared with metal oxides with increasing temperature. The points of intersection of the  $CO$  line and the stable oxides, namely  $Al_2O_3$ ,  $MgO$  and  $TiO_2$  in the diagram, indicate that these oxides can be reduced with carbon at above 2000°C, 1840°C and 1730°C, respectively. But this does not allow the production of pure metals due to formation of stable carbides and oxygen pickup from refractory oxides. Furthermore, smelting operations at such high temperatures would be highly expensive because of fuel requirements and the difficulty of procuring refractory containers serving for sufficiently longer time. These problems have forced metallurgists to develop alternative routes for producing aluminum by the electrolysis of  $Al_2O_3$  dissolved in fused cryolite, magnesium by the electrolysis of  $MgCl_2$  dissolved in fused chlorides and titanium by the reduction of  $TiCl_4$  vapors by liquid magnesium.

Since the Ellingham diagram is constructed for reactions taking place under standard conditions, that is, unit activities of reactants and products, it must be used with due care and proper understanding. It is important to note that the van't Hoff isotherm is more useful in judging the thermodynamic feasibility of reactions whenever the activities of reactants and products differ significantly from unity. The silicothermic reduction of  $MgO$  (the Pidgeon process) sets a good example for understanding the problem of deviation from unit activity. Since the free energy change for the following reaction under standard conditions is positive

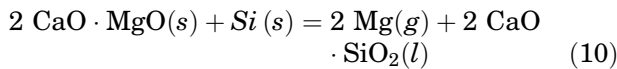
( $\Delta G^\circ = +280$  kJ at  $1200^\circ\text{C}$ ), the reaction will not proceed in the forward direction.



Making use of the van't Hoff isotherm the actual free energy change for reaction (8) is given by

$$\Delta G = \Delta G^\circ + RT \ln K = \Delta G^\circ + RT \ln \left( \frac{p_{\text{Mg}}^2 a_{\text{SiO}_2}}{a_{\text{MgO}}^2 a_{\text{Si}}} \right) \quad (9)$$

$\Delta G$  becomes negative, even if  $\Delta G^\circ$  is positive, at reduced pressure of magnesium and at lower activity of  $\text{SiO}_2$ . The Pidgeon process thus operates at a reduced pressure and the activity of silica is brought down to  $< 0.0001$  by using calcined dolomite ( $\text{CaO} \cdot \text{MgO}$ ) instead of  $\text{MgO}$ . Thus, calcined dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ) is reduced with silicon  $1200^\circ\text{C}$  in a retort at a reduced pressure of about  $10^{-4}$  atm according to the reaction:



The Pidgeon process is much simpler than the reduction of  $\text{MgO}$  with carbon at  $1900^\circ\text{C}$  ( $\text{MgO} + \text{C} = \text{Mg} + \text{CO}$ ). In the carbothermic reduction process magnesium vapor is reoxidized by  $\text{CO}$  on cooling. To prevent the formation of finely divided pyrophoric magnesium powder, the magnesium vapor needs to be quenched in cold hydrogen.

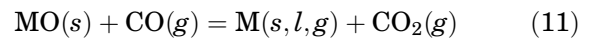
#### *Metallothermic Reduction Through Halide Intermediates*

The most commonly used reducing agent carbon has not been successfully employed in reduction of refractory oxides of rare and reactive metals, namely, beryllium, calcium, magnesium, niobium, sodium, tantalum, thorium, titanium, uranium, vanadium and zirconium. The reduction of these oxides is feasible only at high temperatures and invariably gives rise to the formation of carbides; the resulting metals often dissolve large amounts of oxygen, even in solid state. The decomposition of carbides and the removal of oxygen are extremely difficult and expensive. Hence, these refractory oxides are reduced with a metal such as calcium that has a very high affinity for oxygen. However, in the calciothermic reduction the separation of the deoxidation product (solid  $\text{CaO}$ ) presents a difficult problem. To overcome these problems, the refractory oxides are converted into chlorides or fluorides and reduced with calcium or magnesium. In such reduction reactions slag and metal can be easily separated by producing either molten slag or molten metal. For example, molten magnesium chloride slag is produced during the reduction of gaseous titanium tetrachloride<sup>5</sup> or zirconium tetrachloride with magnesium whereas liquid uranium<sup>6</sup> is

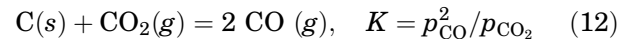
obtained by the reduction of uranium tetrafluoride with calcium. Since the occurrence of minerals as halides is rare, the stable oxides of rare and reactive metals need to be converted into suitable halides to adopt the alternative route for metal extraction. The halides of reactive metals can be easily reduced with metals such as magnesium or calcium because they are less stable than their oxides. From the economic viewpoint, chlorides and fluorides are preferred over bromides and iodides, whereas fluorides are preferred over chlorides because of their non-hygroscopic nature.  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{MgO}$  are chlorinated in the presence of carbon, whereas  $\text{UO}_2$  and  $\text{ThO}_2$  are converted into fluorides by hydro-fluorination

#### *Reduction with Carbon Monoxide in the Presence or Absence of Carbon*

Consider the reduction of metal oxide ( $\text{MO}$ ) with carbon monoxide according to the reaction.



The equilibrium constant  $K$  for the above reaction is given by  $K = p_{\text{CO}_2}/p_{\text{CO}}$  provided  $\text{M}$  and  $\text{MO}$  exist in pure state (i.e.,  $a_{\text{M}} = a_{\text{MO}} = 1$ ). The ratio varies from about  $10^5$  for the reduction of  $\text{Cu}_2\text{O}$  to  $\text{Cu}$  and  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$  to  $10^{-4}$  or less for the reduction of  $\text{MnO}$  and  $\text{SiO}_2$ <sup>7</sup> and even lower for the reduction of  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ . However, in the presence of carbon, the following reaction, known as the Boudouard reaction, needs to be considered.

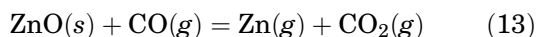


The increase in the number of gaseous molecules in reaction (12) complicates the equilibria. Thus, in a system where there are simultaneous reductions with  $\text{C}$  as well as  $\text{CO}$  gas, the ratio ( $\frac{p_{\text{CO}_2}}{p_{\text{CO}}} = \frac{p_{\text{CO}}}{K}$ ) is a function of  $p_{\text{CO}}$  and of the total pressure ( $p_{\text{CO}_2} + p_{\text{CO}}$ ). In the absence of solid carbon, reaction (12) may be overlooked. In such a case, the reduction will proceed at the lower ratio of  $\frac{p_{\text{CO}_2}}{p_{\text{CO}}}$  in the gaseous mixture than the equilibrium value for the concerned metal-metal oxide. As recorded by Rosenqvist,<sup>7</sup> a very small concentration of  $\text{CO}$  in the gaseous mixture (i.e., a ratio between  $10^5$  and  $10^2$ ) will reduce  $\text{Cu}_2\text{O}$ ,  $\text{PbO}$  and  $\text{NiO}$ , suggesting thereby that if reduction is initiated with pure  $\text{CO}$ , the entire amount of  $\text{CO}$  will be converted into  $\text{CO}_2$ . Contrary to this, the reduction of  $\text{Cr}_2\text{O}_3$ ,  $\text{MnO}$  and  $\text{SnO}_2$  will stop as soon as traces of  $\text{CO}_2$  (i.e., at a very low ratio of  $\frac{p_{\text{CO}_2}}{p_{\text{CO}}} = 10^{-5}$ ) are formed in the pure  $\text{CO}$  used initially. This leads one to believe that the reduction of these oxides with  $\text{CO}$  is practically impossible.

The reduction of  $\text{ZnO}$  presents an exceptional case because of the formation of liquid as well as gaseous zinc depending on temperatures. When liquid zinc is formed, the gas ratio is a function only of temperature. The equilibrium is disturbed on the formation

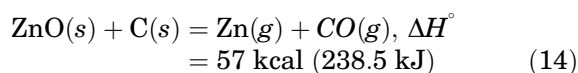


of zinc vapor at a higher temperature according to the following reaction:



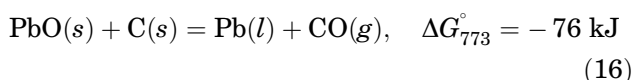
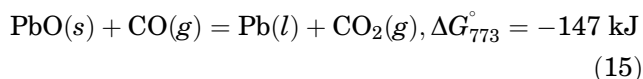
The gas ratio for the above reaction is given by  $\frac{p_{\text{CO}_2}}{p_{\text{CO}}} = \frac{K}{p_{\text{Zn}}}$ . Reactions (12) and (13) are reversible; hence on cooling, the resultant gas mixture containing Zn, CO and CO<sub>2</sub> may form ZnO. During cooling, the presence of even as little as 1% CO<sub>2</sub> in the gas mixture containing 50% each of Zn and CO will reoxidize nearly 2% of zinc. However, on lowering the CO<sub>2</sub> concentration to 0.1% in the presence of excess carbon at high temperatures, only 0.2% of zinc gets reoxidized. The thin layers of ZnO formed over zinc droplets prevent further coalescence.

The highly endothermic simultaneous reduction<sup>3,7</sup> of zinc oxide with carbon according to the reaction



presents a serious problem in providing the large amount of heat to the reaction mixture. In the retort process the required heat generated in an outer combustion chamber is transferred by conduction through the retort wall into the charge. This arrangement not only puts a limit on the rate of production but also poses additional problems during cooling and condensation of the flue gases in the condenser by the release of large quantities of heat, approximately 400 kcal (1674 kJ) per kilogram of zinc. The problem of condensing without oxidation of the zinc vapor was resolved by the Imperial Smelting Corporation by developing specially designed lead splash condensers and blast furnaces capable of smelting mixed ZnO-PbO sinters.

In the blast furnace smelting of mixed ZnO-PbO sinters, obtained by blast roasting of galena and sphalerite concentrates, the following reduction reactions of PbO with CO and C need to be analyzed in addition to reactions (12, 13 and 14).



The above reactions together with values of free energy changes demonstrate that the reduction of PbO with CO at 500°C not only provides a greater driving force than reduction with coke, but also indicates that reaction (15), being a solid-gas reaction, will be kinetically faster than a solid-solid reaction (16). In addition, we should note that (1) reaction (14) between ZnO and coke at 1000°C produces zinc vapor with a free energy change of -29 kJ and (2) reaction (13) between ZnO and CO

with a positive standard free energy change of +76 kJ at 1000°C will proceed only if the partial pressure of CO is high. According to Rosenqvist,<sup>7</sup> ZnO can only be reduced at 1000°C with a gas mixture having a  $p_{\text{CO}_2}/p_{\text{CO}}$  ratio < 0.02. The gaseous zinc produced by reaction (13) will get reoxidized during cooling when the temperature goes below 950°C because of higher stability of ZnO than CO<sub>2</sub> at 950°C.

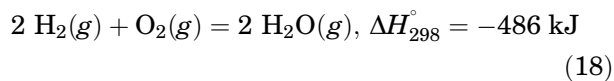
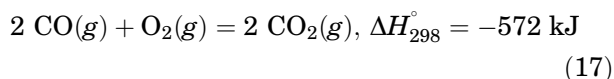
The presence of FeO (gangue in the concentrate) in ZnO-PbO sinters further complicates the reduction reactions in the Imperial Smelting process that produces molten lead bullion and gaseous zinc. The bullion is collected in the hearth of the blast furnace, and zinc vapor is rapidly shock cooled in a condenser on passing through the top of the furnace. Since zinc metal is produced as a vapor and lead as a liquid and unreduced FeO has to be transferred into the slag, the requirements of the Imperial blast furnace differ from those of lead and iron blast furnaces. Because of the simultaneous production of lead and zinc, the operational conditions in the Imperial furnace have some similarity to those of the lead blast furnace. As ZnO is more stable than PbO, the reduction of the former requires stronger reducing conditions than the latter. In the Imperial Smelting process gases generated in the furnace by the combustion of coke for reduction of ZnO are so reducing that lead oxide is reduced without any significant reduction of iron oxide. Therefore, one has to set conditions for the simultaneous reduction of PbO and ZnO without reducing FeO because the CO<sub>2</sub>/CO ratio is of a similar order in zinc and in iron blast furnaces. Morgan and Lumsden<sup>8</sup> reported that the gas leaving the Imperial blast furnace with a CO<sub>2</sub>/CO ratio of 0.57 would not reduce iron oxide from the slag or present in the burden because at 1250°C the equilibrium ratio for the reduction of wustite to iron is 0.31. The reduction of iron oxides has to be prevented because solid iron will badly affect the gas flow and affect the reduction equilibria.

The re-oxidation of zinc vapors to ZnO [ $\text{Zn}(g) + \text{CO}_2(g) = \text{ZnO}(s) + \text{CO}(g)$ ] by CO<sub>2</sub> is prevented by maintaining a temperature > 1000°C in the stack of the blast furnace by burning CO in preheated air, injected at a controlled rate at the top of the stack. Since the combustion of CO to CO<sub>2</sub> is highly exothermic, a temperature > 1000°C is easily attained in the stack. The Imperial Smelting process employs a specially designed lead splash condenser to prevent the reversion of zinc to ZnO by “shock cooling” of the zinc vapor present in the flue gas with a relatively high CO<sub>2</sub> concentration. The condenser is divided into four sections, each section containing two four-baffled rotors immersed in molten lead. Liquid lead is splashed as tiny droplets in the condenser by the rotating blades. This action compels the flue gas containing zinc vapor from the blast furnace to follow a zigzag path through the splashed droplets. In this way, the gas is thoroughly

scrubbed and shock cooled to  $< 500^{\circ}\text{C}$  at the exit from a temperature of  $1000^{\circ}\text{C}$  at entrance. This procedure causes condensation and dissolution of  $> 95\%$  of the zinc vapor in lead droplets. Lead containing 2.65% zinc pumped at  $550^{\circ}\text{C}$  into a jacketed launder is cooled to  $450^{\circ}\text{C}$ . As only 2.2% zinc is soluble in molten lead at  $450^{\circ}\text{C}$ , the excess liquid zinc floating above the dense liquid lead is separated. The lead containing 2.2% zinc is recirculated to the condenser for further operation. One of the most important features of the Imperial process includes the high efficiency of the lead splash condenser despite the high  $\text{CO}_2/\text{CO}$  ratio in the flue gas (14%  $\text{CO}_2$  and 10–12%  $\text{CO}$ ). Satisfactory zinc elimination and condensation have been achieved without any deposition of  $\text{ZnO}$  on the wall of the condenser. This permits a reasonably low fuel-to-zinc ratio (1.1 ton of zinc produced per ton of carbon consumed). The high efficiency of the Imperial lead splash condenser is related to the use of liquid lead for shock cooling of zinc vapors because lead can be more effectively splashed as tiny droplets because of its lower vapor pressure than zinc at the working temperature.

#### Reduction with Hydrogen

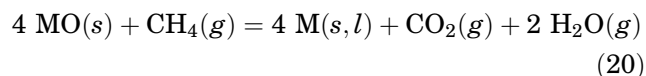
Hydrogen is expensive and hence is used under special conditions. However, the main reason for its limited application is the low exothermicity of reactions when oxides are reduced with hydrogen. This can be judged by comparing the heat evolved in oxidation of  $\text{CO}$  and  $\text{H}_2$ .



The above heat changes indicate that the reduction of  $\text{MO}$  with  $\text{H}_2$  will be less exothermic than the reduction by  $\text{CO}$ . In case a mixture of  $\text{CO}$  and  $\text{H}_2$  is used as the reductant, the reactions will have to satisfy the water gas equilibrium according to the following:



Natural gas consisting mainly of methane can be used in the reduction of oxides.

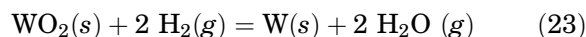
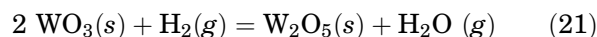


Although methane is a reducing agent of considerable significance, its decomposition to soot and hydrogen above  $500^{\circ}\text{C}$  makes its direct use problematic.

The relative positions of the lines concerning reactions (6), (7) and (18) in the Ellingham diagram<sup>3</sup> suggest that hydrogen is a better reducing agent

than carbon and carbon monoxide, respectively, at temperatures  $< 650^{\circ}\text{C}$  and  $> 800^{\circ}\text{C}$ . However, for the reduction of iron oxide, hydrogen presents better reduction kinetics in the temperature range of  $1150\text{--}1350^{\circ}\text{C}$ .<sup>9,10</sup> In certain cases, a mixture of the two gases is used.

On the industrial scale,<sup>5,11</sup> tungsten and molybdenum are produced by the reduction of tungstic oxide ( $\text{WO}_3$ ) and molybdic oxide ( $\text{MoO}_3$ ) with hydrogen. In the extraction of tungsten from sheelite ( $\text{CaWO}_4$ ) and wolframite [ $(\text{Fe}(\text{Mn})\text{WO}_4)$  concentrates,<sup>11</sup> first yellow tungstic oxide ( $\text{WO}_3$ ) is obtained by the decomposition of the intermediate product ammonium paratungstate [ $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 11\text{H}_2\text{O}$ ]. Its reduction takes place in the following stages:



A higher temperature and higher hydrogen concentration in the gas are required in every later stage of reduction. During operation, the nickel boats loaded with tungstic oxide moves counter-currently to the flow of purified hydrogen gas in a steel tube of 50–100 mm diameter, kept in the electrically heated tube furnace. It is allowed to pass gradually through the zone of increasing temperature (maximum  $850\text{--}860^{\circ}\text{C}$ ) and to expose it gradually with drier hydrogen until its arrival at the water-cooled discharge end. The reduction is facilitated by the catalytic adsorption of dissociated hydrogen molecules on the surface of tungsten metal. However, the catalytic effect is extensively retarded by the presence of moisture.

The moisture content of the gas, which is affected by temperature, plays an important role in controlling the particle size of the reduced powder. Finer powder is obtained by maintaining a high rate of hydrogen flow, which is useful in removing water vapor generated during reduction.

To produce anhydrous molybdic oxide ( $\text{MoO}_3$ ), a rich molybdenite concentrate is first roasted at a temperature  $< 650^{\circ}\text{C}$ . The calcine is digested in an ammonia solution, and molybdic acid ( $\text{H}_2\text{MoO}_4$ ) is precipitated from the purified leach liquor after removal of copper and iron from the solution. Finally, the molybdic acid is calcined at  $400\text{--}450^{\circ}\text{C}$  in a muffle furnace to obtain anhydrous molybdic oxide ( $\text{MoO}_3$ ).

The mechanism of reduction of molybdenum trioxide to molybdenum metal with hydrogen gas follows a path similar to the three-stage reduction of tungstic oxide. The first step is carried out at  $450^{\circ}\text{C}$  to prevent the melting of the partially reduced  $\text{MoO}_3$  at about  $550^{\circ}\text{C}$ . The second step at  $1100^{\circ}\text{C}$  and the last step require higher temperatures and lower water vapor contents in the gaseous mixture.

### Kinetics of Reduction of Oxides

In a gas–solid reaction of the type  $MO(s) + A(g) = M(s) + AO(g)$ , the reduction takes place in a number of steps:

- (1) Transfer of A from the bulk gaseous phase to the outer surface of the solid,
- (2) Diffusion of A to the reaction interface,
- (3) Chemical reaction at the interface (adsorption of reaction species, chemical reaction and desorption of reaction product species) and
- (4) Diffusion of AO away from the interface into the bulk of the gas phase.

The overall rate of reaction depends on whether the product M forms a porous layer and the relative kinetics of the chemical reaction at the MO/M interface and of the diffusion through the product layer. Szekely et al.<sup>12</sup> have discussed these cases in detail.

The rate of reaction can be expressed in terms of the fraction of solid reacted ( $f$ ), which is defined, using a spherical solid without change in the overall size as an example, as

$$f = \frac{\omega_0 - \omega}{\omega_0 - \omega_f} = \frac{4/3\pi r_0^3 - 4/3\pi r^3}{4/3\pi r_0^3} = 1 - \frac{r^3}{r_0^3} \quad (24)$$

where  $\omega_0$ ,  $\omega_f$  and  $\omega$  represent, respectively, the original weight, final weight and weight of the solid at any time  $t$ , and  $r_0$  and  $r$  are, respectively, the initial radius and radius of the unreacted solid at any time  $t$ . If  $k$  and  $c$  are, respectively, the rate constant based on the consumption rate of the gaseous reactant and the molar concentration of reactant gas, the conversion versus time for a system with a first-order reaction in which the diffusion through the product layer is much faster than the interfacial reaction is given by

$$1 - (1 - f)^{1/3} = \frac{bkc}{r_0\rho} t \quad (25)$$

where  $b$  is the number of moles of the solid reactant reacted by one mole of the gaseous reactant.

When the diffusion through the solid product layer controls the overall rate, the conversion versus time is described by<sup>12</sup>

$$\frac{6bD_e(c - c^{eq})}{\rho r_0^2} t = 1 + 2(1 - f) - 3(1 - f)^{2/3} \quad (26)$$

where  $D_e$  stands for effective diffusivity through the product solid layer.

When the reactant solid contains porosity, the expression of the overall rate is more complex, and the reader is referred to a monograph on the subject by Szekely et al.<sup>12</sup>

### REFINING

The production of every metal is initiated with the objective of obtaining a pure metal, but a few impurities are picked up during the processing of

the ores and residues in the presence of fluxes and fuels. Hence, refining to remove these impurities and produce the metal as purely as possible constitutes a major step in the process flow sheet because many physical, chemical and mechanical properties of metals are affected by them. In addition to bringing the metal into effective usage, refining is often necessary to recover precious metals, such as gold and silver, as by-products. On the other hand, the refining of hot metal (pig iron) produces steel with controlled amounts of impurities. The presence one impurity may not affect the particular property, but another may be affected to a great extent by the same. For example, traces of oxygen do not alter the density of copper, but the electrical conductivity is significantly decreased by the dissolved oxygen. Zirconium, having a low neutron absorption cross-section of 0.15 barn per atom, is a valuable material for fuel cans, but it becomes worthless for nuclear reactors in the presence of a small amount of hafnium (over 200 ppm) because of its very high neutron absorption cross section of 115 barn per atom.

The different techniques of refining common metals such as copper, lead, zinc, nickel and tin exploit the differences in the physical and chemical characteristics of the metal and impurities. While processing reactive metals such as uranium, thorium, titanium and zirconium, the impurities associated with the ore are eliminated right at the beginning, for example, the leach liquor is often purified by chemical separation techniques, namely, chemical precipitation, ion exchange and solvent extraction.

### Principles

The pure phase, being thermodynamically unstable, easily absorbs impurities by lowering its free energy. Since the purer phase has an inherent tendency to pick up impurities, purification becomes increasingly difficult while approaching the pure state, that is, the state where impurities are held at low chemical potential. Hence, it is advisable to bring the impure metal in contact with slag or expose it to a vacuum that can pick impurities at lower chemical potential. However, it is difficult to attain 100% purity because the chemical potential of an impurity decreases with decreasing concentration. In all the refining techniques, favorable conditions can be optimized making use of the physicochemical principles, which requires knowledge about the activities of the metal and impurities. A system consisting of a metal with several impurities has to be thermodynamically treated as a multi-component solution, which would require adequate knowledge of interaction coefficients<sup>13</sup> accounting for various possible interactions in the system.

In most refining processes, advantage is taken of differences in the physical and chemical



characteristics of the metal and impurities. In this review we limit our discussion to the two main groups of refining processes based on metal–slag and metal–gas reactions.

### Metal–Slag Processes

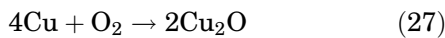
In these processes the impurities having more affinity for oxygen, sulfur and chlorine are oxidized to a respective slag or gas and removed. This method of refining has been popularized as fire refining. The conversion of pig iron to steel by blowing air or oxygen into hot metal for the removal of carbon, silicon, manganese and phosphorus is the best example of this technique. Crude lead, bismuth and tin are treated with sulfur to remove copper. Similarly, zinc from lead; zinc, copper and lead from bismuth; lead from tin and silver; and copper and zinc from gold can be removed by chlorination. Oxidation is facilitated by the addition of some oxide of the metal to be refined.

To generate optimum conditions for adequate refining, knowledge of the activities of elements dissolved in the metallic phase and of oxides dissolved in the slag is essential.

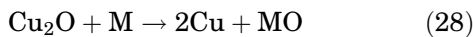
### Fire Refining of Copper

Sulfur and oxygen contents of copper obtained from single-step smelting or continuous converting<sup>14</sup> processes vary, respectively, from 0.7 wt.% to 1 wt.% and 0.2wt.% to 0.4 wt.%, whereas the Peirce-Smith converter produces a blister containing 0.01–0.05 wt.% S and 0.2–0.5 wt.% O. During solidification of copper, sulfur dioxide bubbles evolve because of the reaction between the dissolved sulfur and oxygen. It is estimated that 0.01 wt.% S and 0.01 wt.% O dissolved in copper would give rise to the formation of 2 cm<sup>3</sup> of SO<sub>2</sub> at 1083°C per cm<sup>3</sup> of solidified copper. Thus, the blister needs to be fire refined for commercial usage. For a high-quality product, fire refined copper is further subjected to electrolytic refining.

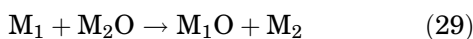
During fire refining air is blown through pipes inserted in molten blister copper charged in a rotary furnace, maintained at 1150–1200°C. Owing to the larger mass, copper first gets oxidized to form cuprous oxide, which is distributed all over in the melt.



Cu<sub>2</sub>O oxidizes the impurities (*M*) having higher affinity for oxygen than copper:



In addition to Cu<sub>2</sub>O, oxide(s) of impurity metal(s) may take part in the oxidation of some impurities depending upon their affinity for oxygen. For example, *M*<sub>1</sub>, having more affinity for oxygen than *M*<sub>2</sub>, gets oxidized and removed as *M*<sub>1</sub>O:



The removal of the slag, floating on the bath, formed collectively by oxides of impurity metals, facilitates further refining because of the decreased chemical potential of impurity oxides in it. Depending on the extent of affinity for oxygen in decreasing order, the sequence of removal from molten copper is as follows: Al, Si, Mn, Zn, Sn, Fe, Ni, As, Sb, Pb and Bi.

Nickel, having lower affinity for oxygen than copper, can be removed from the blister at 1250°C by generating conditions to get a negative free energy change for the reaction (Cu<sub>2</sub>O + Ni → NiO + 2Cu). Since the standard free energy of the formation of Cu<sub>2</sub>O is less than that of NiO, copper will get preferentially oxidized and lost in the slag. According to the van't Hoff isotherm the free energy change under non-standard conditions is given by

$$\Delta G = \Delta G^\circ + RT \ln \left( \frac{a_{\text{NiO}}}{a_{\text{Cu}_2\text{O}} \cdot a_{\text{Ni}}} \right) \quad (30)$$

Hence, Δ*G* can be made negative by lowering the value of *a*<sub>NiO</sub> by adjusting the slag composition. Silver and gold cannot be eliminated by fire refining because of their very weak affinity for oxygen.

Since fire refining is done by air blowing, which reduces sulfur to approximately 0.002% at the expense of dissolving an appreciable quantity of oxygen in copper. The [S]-[O] dissolution equilibria can be expressed as<sup>14</sup>

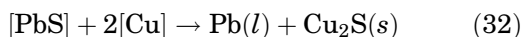
$$[\text{S}] + 2[\text{O}] = \text{SO}_2(\text{g})K = \frac{p_{\text{SO}_2}}{[\% \text{S}] \cdot [\% \text{O}]^2} = 10^6 \text{ at } 1200^\circ\text{C} \quad (31)$$

From the high value of the equilibrium constant it is evident that sulfur elimination continues along with oxygen dissolution in copper even when [S] is reduced to 0.002% at *p*<sub>O<sub>2</sub></sub> ~ 0.2 atm and *p*<sub>SO<sub>2</sub></sub> > 1 atm. Finally, at the end of refining the residual sulfur in the copper melt reduces to about 0.001 wt.%, but [O] increases to about 0.6 wt.%. During solidification the decreasing solubility of oxygen in solid copper causes precipitation of the entire oxygen as solid Cu<sub>2</sub>O to generate about 6 wt.% of oxide inclusion. Since the electrical and mechanical properties of copper get significantly deteriorated in the presence of oxygen, molten copper is deoxidized by introducing a reducing gas or hydrocarbon after skimming off the slag. Most of the oxygen from the molten copper is removed by hydrocarbon according to the reactions C(s) + [O] = CO(g), CO(g) + [O] = CO<sub>2</sub>(g) and H<sub>2</sub>(g) + [O] = H<sub>2</sub>O(g). The hydrocarbon blow is stopped when the oxygen content of the bath attains a value of 0.15%. In this way copper oxide precipitation is minimized but hydrogen generated from the hydrocarbon dissolves in copper to a limited extent. The fire refined copper containing ~ 0.002wt% S, 0.15 wt.% O and 2 × 10<sup>-5</sup> wt.% H is cast into anodes to be refined to 99.99% purity by

electrolytic refining, during which silver and gold are recovered

### Refining of Lead Bullion

The refining of lead bullion is carried out in a number of steps to recover silver and gold and to remove impurities such as copper, zinc, arsenic, antimony, tin, bismuth and sulfur, each present in the range varying from 0.1 wt.% to 1.5 wt.%. Copper is removed by stirring the bullion with sulfur at 330–350°C in a kettle. PbS first formed gets dissolved in molten lead. However, a higher affinity of sulfur for copper than lead favors the formation of Cu<sub>2</sub>S at equilibrium.



The higher the level of sulfur dissolved in the molten lead (as PbS), the lower will be the residual copper in lead.

$$[\% \text{Cu}] = \frac{1}{\sqrt{K[\% \text{S}]}} \quad (33)$$

As Cu<sub>2</sub>S is lighter and insoluble in lead, it rises to the surface of the bath as a dross, consisting of Cu<sub>2</sub>S, and mechanically entrapped lead with a little PbS. The loss of lead can be reduced by raising the bath temperature to 370°C before skimming. The sulfide dross containing 95% Pb and 3% Cu is recycled.

In the next step of fire refining, zinc, arsenic, antimony and tin, having a stronger affinity for oxygen than lead, are removed by oxidation of the bullion with air and litharge (PbO) in a reverberatory furnace at 350°C. The resulting oxides, ZnO, As<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub>, being amphoteric and insoluble in lead, respectively, form zincates (PbO·ZnO), arsenates (3PbO·As<sub>2</sub>O<sub>3</sub>), antimonates (PbO·Sb<sub>2</sub>O<sub>3</sub>) and stannate (PbO·SnO<sub>2</sub>) with PbO. The floating compound mixture on the surface of molten lead is skimmed off. Oxidation can be sped up by blowing air through the molten bullion. Since lead becomes more ductile after the removal of zinc, arsenic, antimony and tin, the process is given the name “softening.” Although silver and gold do not get oxidized, they join the dross with some molten lead droplets containing dissolved Ag and Au. This is the most serious drawback of fire refining of lead.

To recover silver and gold, the partially refined lead is treated with zinc at 450°C (Parkes Process). Excess zinc dissolved in lead is removed by chlorination at 390°C (Betterton Process). Bismuth is removed as solid intermetallics by the addition of Ca-Mg alloy.

### Metal-Gas Processes

Under this category, distillation, vacuum treatment, carbonyl decomposition, disproportionation reaction and iodide decomposition form important examples. Disproportionation reaction and iodide decomposition techniques play an important role in the preparation of ultra-pure reactive metals.

### Distillation

The distillation technique simply makes use of the difference in the boiling points of the impurity metals (*i*) and the base metal (*M*) in separation and refining. The technique is also useful in the separation/refining of salts, for example, the preparation of high-purity TiCl<sub>4</sub> (99.98%) from the gaseous product obtained after the chlorination of rutile. However, operating problems restrict this method to refining metals having a boiling point < 1000°C. For example, mercury, cadmium, sodium and zinc with their respective boiling points of 357°C, 765°C, 892°C and 907°C can be refined by the distillation technique under normal atmospheric pressure. A few more metals such as tellurium (boiling point 990°C), magnesium (1105°C), calcium (1487°C), antimony (1635°C) and lead (1740°C) exerting a vapor pressure of 10<sup>-3</sup> atm at 509°C, 608°C, 803°C, 877°C, and 953°C, respectively, can be distilled at 1000°C under a vacuum of the order of 10<sup>-3</sup> atm. However, this technique offers only a limited degree of separation because of simultaneous interactions between impurity metals and the base metal and impurities present in small quantities. Often, two or more metals having vapor pressures of the same order at the operating temperature may evaporate simultaneously. In such cases, separation may be facilitated by selective condensation where arrangement is made for condensation of the more volatile element in the cooler part of the condenser and that of the less volatile element in the hottest part.

Langmuir has derived the following expression for the rate of evaporation of a species *i* from the surface of the molten metal under equilibrium conditions.

$$\text{Rate of evaporation, } r_i = p_i \left( \frac{M_i}{2\pi RT} \right)^{1/2} \quad (34)$$

where *R* is the gas constant, and *M<sub>i</sub>* and *p<sub>i</sub>* stand, respectively, for the molecular weight and the vapor pressure of the species *i* in the melt. The maximum rate of evaporation is achieved when the numbers of molecules leaving the melt surface are in equilibrium with those condensing on the surface. To account for deviation from ideal behavior, the above equation is modified by introducing *a<sub>i</sub>*, the activity of the species *i* in the melt.

$$r_i = p_i^\circ \cdot a_i \left( \frac{M_i}{2\pi RT} \right)^{1/2} \quad (35)$$

where *p<sub>i</sub><sup>o</sup>* is the vapor pressure of the species *i* over pure liquid. Since Eq. 35 also denotes the rate of transfer of atoms/molecules from the melt to the gaseous phase, the ratio of rates of evaporation of the species *i* as solute and of the base metal *M* as solvent at a particular temperature is given by

$$\frac{r_i}{r_M} = \frac{p_i^\circ a_i}{p_M^\circ a_M} \left( \frac{M_i}{M_M} \right)^{1/2} \quad (36)$$

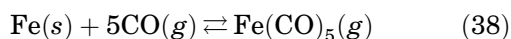
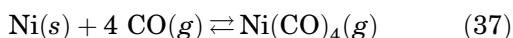


where  $r_M, p_M^\circ$  and  $a_M$  represent, respectively, the rate of evaporation, vapor pressure over pure metal M and activity of the metal M at the chosen temperature. Equation (36) provides a basis for refining by distillation (fractional distillation) because the ratio  $\frac{r_i}{r_M}$  increases with increased vaporization (i.e., removal) of the solute  $i$ . Thus, the relatively high volatile impurities can easily be removed while retaining most of the solvent metal by selecting the appropriate distillation temperature. Contrary to this procedure the entire melt may be evaporated and the components from the gaseous phase can be separated by fractional condensation at appropriate temperatures. This procedure has been most successfully employed for the separation of  $\text{TiCl}_4$  and  $\text{ZrCl}_4$  from the resultant mass obtained by the chlorination of rutile and zircon, respectively.

Based on the above discussions it is concluded that the metal-impurity systems with a larger difference in vapor pressures can be separated by single-stage distillation, whereas a special technique known as rectification is needed for systems with small differences in vapor pressures. For example, the crude zinc (boiling point  $907^\circ\text{C}$ ) obtained from the blast furnace containing 2–3 wt.% Pb (boiling point  $1740^\circ\text{C}$ ) and 0.3–0.5 wt.% Cd (boiling point  $765^\circ\text{C}$ ) is refined in a multistage rectification column consisting of 30–40 trays, operated in the temperature range  $800$ – $1200^\circ\text{C}$ . Since the vapor pressures of cadmium and lead are, respectively, much higher and much lower than that of zinc, both zinc and cadmium are distilled away, leaving lead in molten state, which can be drained off. The zinc vapor is condensed while cadmium is retained in the gaseous state. To obtain a higher purity product, distillation has to be repeated several times, but at the cost of yield.

### Carbonyl Process

The Mond carbonyl process has been successfully employed to produce pure nickel. In the extraction of nickel, a sulfide ore [pentlandite ( $\text{NiFe}_9\text{S}_8$ )] containing about 1–3% Ni and some Co, Cu and Fe is processed to obtain nickel sulfide by multi-step operation.<sup>1</sup>  $\text{Ni}_3\text{S}_2$  is dead roasted to nickel oxide, which is reduced with carbon or hydrogen at  $400^\circ\text{C}$  to produce crude nickel. The impure nickel containing 15–20% iron and some cobalt and copper is treated with CO gas in the volatizer (carbonyl chamber) to form  $\text{Ni}(\text{CO})_4$  vapor at  $50^\circ\text{C}$  and 1 atm pressure or produce liquid carbonyl at  $50^\circ\text{C}$  and 20 atm. In both the cases some  $\text{Fe}(\text{CO})_5$  is also formed. Very little cobalt carbonyl,  $\text{Co}_2(\text{CO})_8$ , may be present in the gas phase, but copper and precious metals present in the crude do not form any carbonyl under these operating conditions.

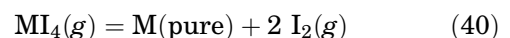
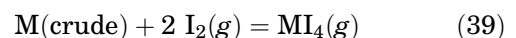


Since  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$ , respectively, boil at  $43^\circ\text{C}$  and  $105^\circ\text{C}$ , most of nickel and only a small fraction of iron will volatilize as  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$  leaving the impurities as solid residues on passing dry CO over the crude nickel placed in a chamber at  $80^\circ\text{C}$ . Reaction (37) proceeds with a very large decrease of entropy due to the tremendous decrease in volume by consuming 4 mol of CO to form 1 mol of  $\text{Ni}(\text{CO})_4$ . Hence, the free energy change of the reaction (37) will be dictated by the entropy change, and, being only slightly exothermic, it will proceed in the reverse direction at temperatures  $> 100^\circ\text{C}$ . Thus, when the resulting gas containing  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$  is directed in another chamber (decomposer) maintained at  $160$ – $180^\circ\text{C}$ , the former decomposes to pure nickel and CO, whereas  $\text{Fe}(\text{CO})_5$  requiring a still higher temperature for decomposition remains in the gaseous phase. The decomposition of  $\text{Ni}(\text{CO})_4$  is facilitated by the presence of finely divided nickel powder in the decomposer, acting as seed; 99.99% pure Ni shots of about 6 mm diameter are grown by continued deposition. The gaseous phase consisting of mainly CO is recirculated into the volatizer over the crude nickel after liquefying  $\text{Fe}(\text{CO})_5$ .

Since the rate of the carbonyl formation reactions increases with temperature  $> 50^\circ\text{C}$ , there is a greater chance of contamination of the gaseous carbonyls formed at higher temperatures. According to Le Chatelier's principle, reactions (37) and (38) will proceed in the forward direction with an increase in pressure, but the decomposition temperatures of both carbonyls will also increase.  $\text{Fe}(\text{CO})_5$  decomposes at a higher temperature than  $\text{Ni}(\text{CO})_4$  because the former consumes 5 mol of CO gas in its formation, whereas fewer molecules (4) are consumed in the formation of the latter. On an industrial scale, liquid  $\text{Ni}(\text{CO})_4$  is produced by passing CO gas over the crude nickel at  $50^\circ\text{C}$  and 20 atm. The nickel carbonyl contaminated with iron carbonyl is thermally decomposed at  $205^\circ$ – $250^\circ\text{C}$  to obtain pure nickel, and almost all  $\text{Fe}(\text{CO})_5$  is retained in the gaseous phase.

### Iodide Decomposition

Van Arkel and de Boer<sup>15</sup> introduced the iodide decomposition technique, which is based on the reversibility of the reaction between a metal and iodine:



The method forms a typical example of purification by chemical vapor deposition and is now extensively employed for the production of high-purity rare metals. The metal iodide formed at a lower temperature (i.e., the bulb temperature) decomposes at a much higher temperature (filament temperature). The iodine regenerated by

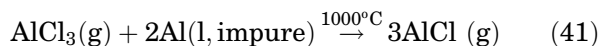
decomposition is reused for additional iodide formation. According to Le Chatelier's principle, the iodide formation (reaction 39) and the decomposition (reaction 40) are, respectively, favored at a high and a reduced pressure. Despite the decomposition reaction leading to the production of metal being favored at low pressure, the pressure cannot be reduced below a certain level. This level corresponds to the pressure at which the rate of evaporation of the metal at the filament temperature becomes equal to the rate of deposition after decomposition. In practice, a pressure of the order of  $10^{-3}$  to  $10^{-4}$  atm has been found adequate. Based on their thermodynamic and kinetic studies on the van Arkel iodide process, Shelton<sup>16,17</sup> concluded that the rate of deposition of zirconium was controlled by the vapor transport process (i.e., diffusion of iodine from the filament) at ambient and filament temperatures. According to him, the chemical reactivity of the feed material and the geometry of the reactor play important roles in controlling the rate.

Generally, a batch type reactor (bulb) made of glass or silica, fitted with an incandescent filament together with the facility of electric heating, is employed in the iodide process. However, high-purity titanium and zirconium are produced on a large scale using a reactor made of Inconel.<sup>18</sup> The metal released by decomposition of the metal iodide is deposited on a tungsten or molybdenum filament of about 2.5 micron diameter. In the first step, the metal iodide is formed by the reaction between the impure metal and iodine vapor. The metal iodide is decomposed upon reaching the hot filament. The liberated iodine reacts with the crude metal again to form additional iodide vapor. In the preparation of high-purity titanium, zirconium, hafnium and thorium, the bulb and filament are, respectively, maintained in temperature ranges of 200–525°C and 1100–1600°C.

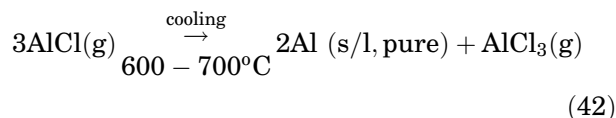
The yield per cycle is about 20% of the crude loaded in the reactor. The impurities can be reduced from 5000 ppm to 1000 ppm in one cycle and to below 200 ppm by repeated treatments. However, the iodide process suffers from the problem of contamination of the metal by the residual gases in the vessel and transfer of metallic impurities from the vessel to the filament by iodine vapors.

#### Disproportionation Process

The formation and decomposition of halides of the same metal at different temperatures making use of the different valences are called “disproportionation reaction.” The disproportionation reaction process has been successfully used in preparation of high-purity aluminum, beryllium, titanium, zirconium and niobium. For example, aluminum monochloride can be vaporized by passing aluminum trichloride gas into the molten bath of impure aluminum at 1000°C according to the reaction:

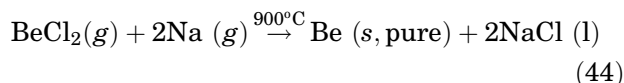
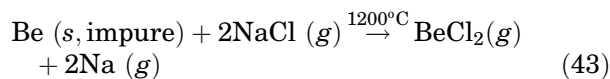


The above reaction can be reversed to recover solid or liquid aluminum at a lower temperature:

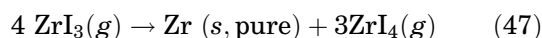
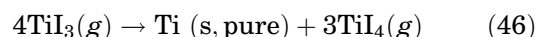
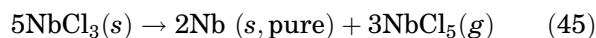


The regenerated  $\text{AlCl}_3$  gas is recycled for further reaction with impure aluminum. However, only crude aluminum having low concentrations of Ca, Ti, Mn, Mg, Zn and Cu can only be purified by this process to produce aluminum metal of 99.999% purity.

In the preparation of ultra-pure beryllium, impure beryllium is allowed to react with sodium chloride vapor at about 1200°C to obtain beryllium chloride gas and sodium vapor in the first step (reaction 43). In the second step, the resultant product is cooled to about 900°C to produce pure beryllium (reaction 44).



Some other relevant examples are<sup>3</sup>



## CONCLUDING REMARKS

This review highlights the importance of physical chemistry in the development and improvement of processes for extraction and refining of non-ferrous metals. The knowledge of the free energy, activity, van't Hoff isotherm and Le Chatelier's principle has been extremely useful in refining various types of metals by different methods. Special mention can be made about the production of magnesium by the silicothermic reduction of calcined dolomite, development of the Imperial Smelting process, and iodide decomposition and disproportionation processes for ultra-high purification.

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