Among the various, possible applications of thermodynamics to extractive metallurgical processes, the availability of chemical potential diagrams and calculation methods combining stoichiometric relations with equilibrium constants are emphasized. In hydro-metallurgical processes, the value of potential-pH diagrams has been well recognized and the application of similar techniques to rather complex systems containing ligands such as the cyanidation process is very interesting. In the roasting of sulfide ores, various information is derived from sulfur-oxygen potential (log $\rho_{S_2}$ - log $\rho_{O_2}$) diagrams. Especially convenient for sulfation roasting are the $SO_3$-$O_2$ potential diagrams. Various smelting processes including the direct production of metal from sulfide ore are discussed with the use of chemical potential diagrams. Based upon the prediction derived from sulfur-oxygen potential diagram, the recovery of elemental sulfur from oxidation of FeS is evaluated by stoichiometric calculations. Volatilization behavior of elements such as zinc, cadmium, and mercury are also explained by similar diagrams and the possibility of the direct distillation of zinc sulfide is predicted by stoichiometric calculations. Analogous calculations are used to clarify the reasons why the segregation process is amenable to copper oxide ore but not to nickel ore.

Thermodynamics has wide applicability in the field of extractive metallurgy. However, this discipline has not been accepted by industrial engineers as widely as might have been hoped. Recently, a considerable number of researchers has directed their efforts to bridge this gap between fundamental theories and practical processes.

Various thermodynamic techniques have been developed to evaluate practical problems and to estimate optimum conditions. In this paper, the effectiveness of chemical potential diagrams and stoichiometric calculations incorporating equilibrium constants are emphasized. Both methods are not new but very useful especially for evaluating optimum conditions in complex operations and for predicting the possibility of new processes.
An excellent general description of chemical potential diagrams is given by Masuko.¹ The chemical potential of a given component is generally expressed as:

\[ \mu_i = \mu_i^0 + RT \ln a_i \]  

thus, \( \log a_i \) corresponds to a chemical potential at a definite temperature. For the reaction in the metal-oxygen system,

\[ 2 M(s) + O_2 = 2 MO(s) \]  

when the condensed phase activities are unity,

\[ \Delta G^o = A + BT = RT \ln p_{O_2} \]  

The right side of Eq. [3], \( RT \ln p_{O_2} \), is termed the oxygen potential and is proportional to \( \log p_{O_2} \) at a given temperature. It is well understood from Eq. [3] that \( \log p_{O_2} \) vs \( 1/T \) diagrams and even the Ellingham diagram are renditions of chemical potential diagrams. The applicability of such simple diagrams is well recognized. Thus, only the more complex systems will be treated in this paper with the occasional use of stoichiometric calculations.

HYDROMETALLURGY

A well known example of chemical potential is pH or \( -\log a_{H^+} \) which defines the hydrogen ion potential in an aqueous solution. To choose a simple example, the hydrolysis equilibria,

\[ M^{2+} + 2 H_2O = MOH_2 + 2 H^+ \]  

\[ \log K_4 = 2 \log a_{H^+} - \log a_{M^{2+}} = -2 \log a_{H^+} - 2 \log a_{M^{2+}} \]  

is calculated based upon the data compiled by this author,² and is illustrated by plotting \( \log a_{M^{2+}} \) vs pH to construct the chemical potential diagram, as shown in Fig. 1. This figure can be applied to explain leaching, purification, or waste water treatment.

As indicated in Fig. 1, a shift to the left of up to 3 pH units occurs in the hydrolysis lines when the temperature is increased from 25 to 200°C. An even larger shift in pH value occurs in the dehydration of the hydroxide into oxide. In the solution purification process at ordinary temperatures, it is well known that ferric ions but not ferrous ions are separable from nonferrous ions by precipitation at pH 2 to 4. At 200°C, precipitation of the ferric ion is accomplished even in more strongly acidic solutions. In considering the reverse reaction of the leaching of oxides, the selective separation of the nonferrous species from iron oxide can easily be realized at 200°C by the use of strong acids. However, it may be difficult to carry out the same leaching process at room temperature because weak acids in the pH 2 to 4 range must be used. These principles are widely accepted in various metallurgical processes and can easily be illustrated by referring to \( \log a_{M^{2+}} \) vs pH, chemical potential diagrams.

The simplified, basic reactions of the Bayer Process are as follows:

for Gibbsite: \( Al(OH)_3 + OH^- = AlO_2^- + 2 H_2O \)  

for Boehmite: \( AlOOH + OH^- = AlO_2^- + H_2O \)  

These equilibria are represented in Fig. 1(b) according to the data given by Russell et al.³ The horizontal axis, pH, varies with temperature according to Eq. [8],

\[ pH_{200} = pH_{25} \cdot Kw_{25}/Kw_{200} = 0.805 pH_{25} \]  

where \( Kw \) is the dissociation constant of water.

Accounting for this effect, caustic leaching is still easily achieved at high temperature. Moreover, as shown in Fig. 1(b), it is easier to leach gibbsite than boehmite at 200°C, while at 25°C no significant difference exists. Undoubtedly, the application of increased temperatures in the Bayer Process is primarily based on kinetic aspects. However, invaluable contributions are derived from a thermodynamic examination.⁴

The Eh-pH diagram for aqueous solution systems is well understood and can be established also at elevated temperatures in connection with the above discussion. In this case, “potential” refers to the potential of electrons and suggests the degree of oxidation or reduction. The application of Eh-pH diagrams to evaluate sulfide leaching processes is excellently summarized by Peters.⁵ Following his description, results based upon the data compiled by Sillen⁶ and Latimer⁷ are illustrated in Fig. 2 in order to explain the cyanidation process. Based upon the following data,

\[ Au^+ + e^- = Au \quad E = 1.68 + 0.0591 \log a_{Au^+} \]  

\[ Ag^+ + e^- = Ag \quad E = 0.80 + 0.0591 \log a_{Ag^+} \]  

both gold and silver are very stable. However, if the activities of Au⁺ and Ag⁺ can be reduced to extremely low levels, the potential, \( E \), may decrease to a level where the metals can be placed into solution.

In the cyanide solution, the complexing reactions,