# Application of Physico-chemical Principles in Extraction Metallurgy

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*Physical chemistry has two important tools namely, thermodynamics which indicates the possibility of a reaction, and kinetics giving the rate at which a reaction proceeds. This paper indicates how these tools can profitably be utilized for the extraction of metals. The authors illustrate as to how physical chemistry has been helpful in the clear understanding of the high-temperature reactions and in searching out new methods for metal-winning. A few instances where thermo-dynamic data have been applied for developing scientific extraction methods are pointed out and their limitations indicated. The instances cited include the separation of nickel and zinc from a mixture of their oxides, the preparation of titanium tetraiodide and the development of Pidgeons process for the production of magnesium.*

P HYSICAL chemistry is interested in establishing energy relations obtained in physical and chemical changes in order to assess the feasibility, extent and the rate at which they occur, and finally to determine the controlling factors. The object of this paper is to show how these relations can act as a guide in deciding the feasibility of a process and help in materialising the same. Mention has also been made about a few of the processes so developed at the National Metallurgical Laboratory. For detailed information about the various principles[1, 2] and their applications[3] various literature on the subject may be referred to.

In a reaction, the change in heat content $\triangle$ H is not fully convertible into work of chemical information. The energy available for such change is called Free Energy and is expressed by the equation

$$\triangle F = \triangle H - T \triangle S \quad \ldots\ldots(1)$$

where S is the entropy, $T \triangle S$ represents a change in the bound energy which is not available to do any useful work.

Again in a reaction tending to equilibrium $\triangle$ F is given by the relation

$$\triangle F = -RT \text{ in } K + RT \ln (\pi a \text{ product}/\pi a \text{ reactant})$$
$$\text{non equilibrium} \quad \ldots\ldots(2)$$

where K stands for the product of the active concentrations of the products (i.e. resultants) divided by that of the reactants when equilibrium has been established and is called the equilibrium constant, while the term in brackets stands for the activity product ratio of the same nature as K but pertaining to the actual condition.

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From $Eq^n$ (2), we have

$$\triangle F = \triangle F^o + RT \ln (\pi a \text{ product}/\pi a \text{ reactant})$$
$$\text{non-equilibrium} \ldots (3)$$

where $F^o$ stands for $-$ RT log K and is called the standard free energy. It is related to temperature by the equation[4].

$$\triangle F^o = \triangle H_o - \triangle \mathcal{L}T \log {}_eT - \tfrac{1}{2} \triangle \beta T^2 - 1/6 \triangle \gamma T^3 + 1T \ldots (4)$$

where $\triangle H_o, \triangle \mathcal{L}, \triangle \beta, \triangle \gamma$ and I constants, I, being equal to KR.

In equation (2), if the activity ratio in bracket is smaller than K or the activities of the reactants are more predominant than the ratio indicated by K, then F is negative and the reaction tends to occur in the direction implied by the chemical equation. If the converse is true, F is positive to the reaction as written but negative for the reverse reaction then the reaction occurs in the opposite direction.

## GRAPHICAL REPRESENTATION AND COMPILATION

### OF STANDARD FREE ENERGY CHANGES

The standard free energy change for any reactions assesses the possibility of such a reaction and these data for various temperatures and pressures are of great advantage in determining the optimum conditions of working. The greater the free energy change, the greater are the chances for the reaction to occur. The standard free energy change with respect to temperature have been plotted by Ellingham[5] and Richardson & Jeffes[6] for oxides, and by Kellogg[7] for chlorides, while Kelley and his co-workers[8] calculated data for carbonates, sulphides, sulphates, carbides and nitrides etc. The free energy diagrams for oxide, sulphide and chloride
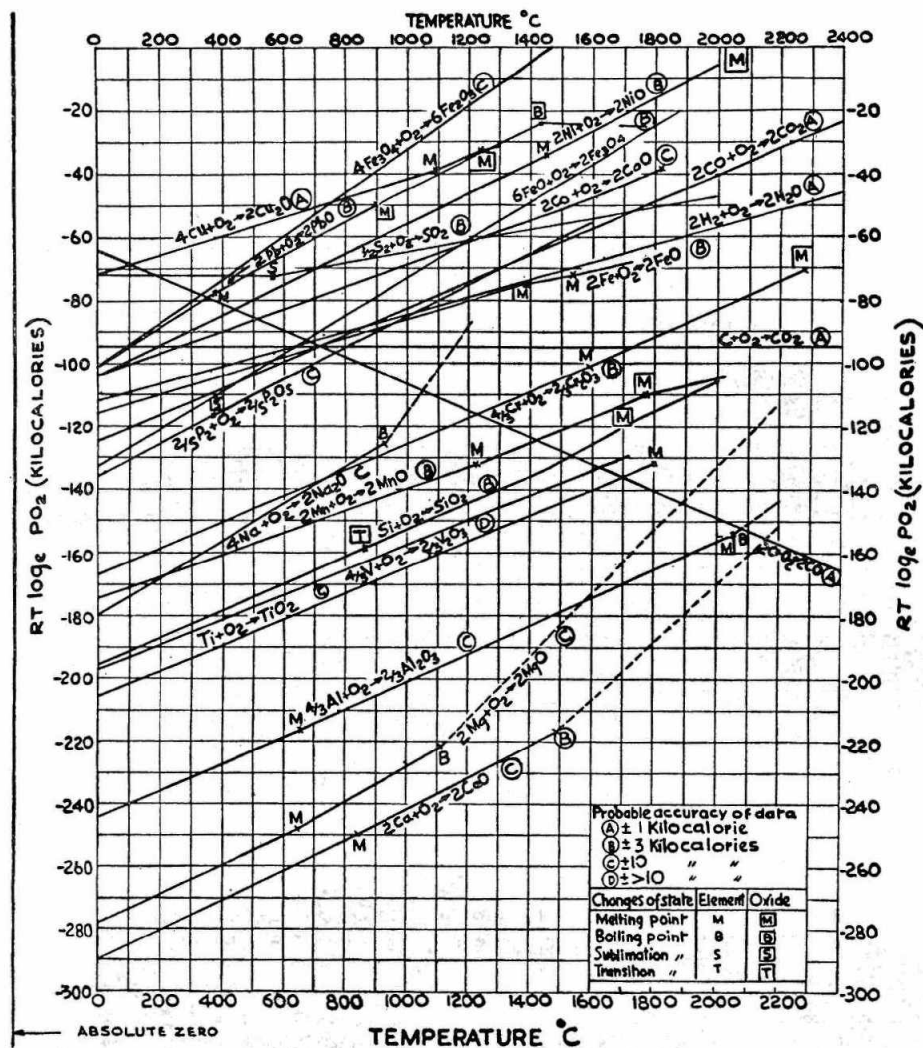
FIG. 1—*Standard free energies of formation as a function of temperature of oxides involving one gram-mole oxygen.*
[Richardson & Jeffes[6]]

are given in Figs. 1-3. The standard free energy change in these diagrams is associatd with one gram molecule of the combining gas with the corresponding stoichiometric amounts of the metal.

The $\triangle F^\circ$—T plots are linear and show a break or a change in gradient at points where a change in entropy takes place followed by fusion or melting etc. A pressure correction chart is also incorporated and the free energy data may be extrapolated for the gaseous participants at an atmospheric pressure.

### APPLICATIONS

The free energy diagrams are very useful in studying the possibilities of new reaction and show immediately as to which metal forms more stable compounds than others. The lower the metals in the diagram the stabler the compound it forms and the vertical distance at any temperature between two compounds indicates the tendency of the metal to reduce the compound higher in the diagram forming stabler compounds. From the oxides chart, it is observed that aluminium forms a stabler

oxide than silicon and thus on reacting aluminium with silica, the oxygen of the latter should be transferred to the former producing silicon metal. This reaction has been studied by Nijhawan and coworkers[9], and aluminium silicon alloy produced. Applying similar consideration of free energy changes it is observed that aluminium could also be used to reduce titanium dioxide and in fact an alloy containing 60 percent titanium has been produced at the National Metallurgical Laboratory[10].

These diagrams could also be used for studying the reducibility or the oxidisability of the compounds, this being one of the most important factors in pyrometallurgical operation. It is indicated from the diagrams that in the reduction of manganese ore high in phosphorus and iron, iron and phosphorus would be preferentially reduced leaving a manganese-rich slag.

As a part of a scheme worked out at National Metallurgical Laboratory for recovering the nickel and zinc separately from the waste liquor from the silver hefinery, under construction in Calcutta,

Bhatnagar & Banerjee[11] separated the two metals by first precipitating them as hydroxides and then chlorinating the oxides mixture with hydrochloride acid gas.

The reaction of a metallic oxide with hydrochloride acid may be presented as:—

$$MO + 2HCl = MCl_2 + H_2O \text{ (g)} \quad \ldots\ldots(5)$$
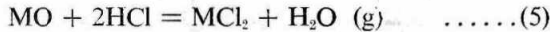
The possibility of separation of nickel and zinc oxides from this mixture is conceived from thermodynamic considerations of the reactions:—

$$NiO + 2HCl = NiCl_2 + H_2O \text{ (g)} \quad \ldots\ldots(6)$$
$$ZnO + 2HCl = ZnCl_2 + H_2O \text{ (g)} \quad \ldots\ldots(7)$$
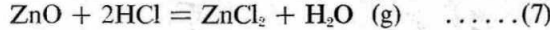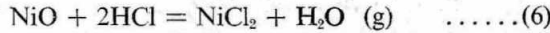
The standard free energy change for the reactions (6) and (7) have been calculated at 1000°K (727°C), 1500°K (1227°C) and 2000°K (1727°C) to supplement the data of Kellogg[7] at 737°K (500°C) and 1273°K (1000°C) and reported in Table I.

TABLE I—STANDARD FREE ENERGY CHANGES AT DIFFERENT TEMPERATURES FOR THE REACTIONS OF HCl WITH NiO AND ZnO

| Reaction | Standard Free Energy Change at °K in K. Cals. | | | | |
|---|---|---|---|---|---|
| | 773 K* | 1000°K | 1273°K* | 1500°K | 2000°K |
| NiO–2HCl = NiCl_2–H_2O | – 10.8 | – 5.25 | + 0.20 | – 2.47 | – 9.78 |
| ZnO–2HCl = ZnCl_2–H_2O | – 10.5 | – 7.65 | – 11.0 | – 15.7 | |

* Values taken from Kellogg's[7] data

$\triangle F^\circ$ for nickel chloride, zinc chloride and HCl have been taken from Kellogg's data[7]; the $\triangle F^\circ$ for NiO and $H_2O$ from paper by Richardson[6] and $\triangle F^\circ$ for ZnO from data by Kelly[8].

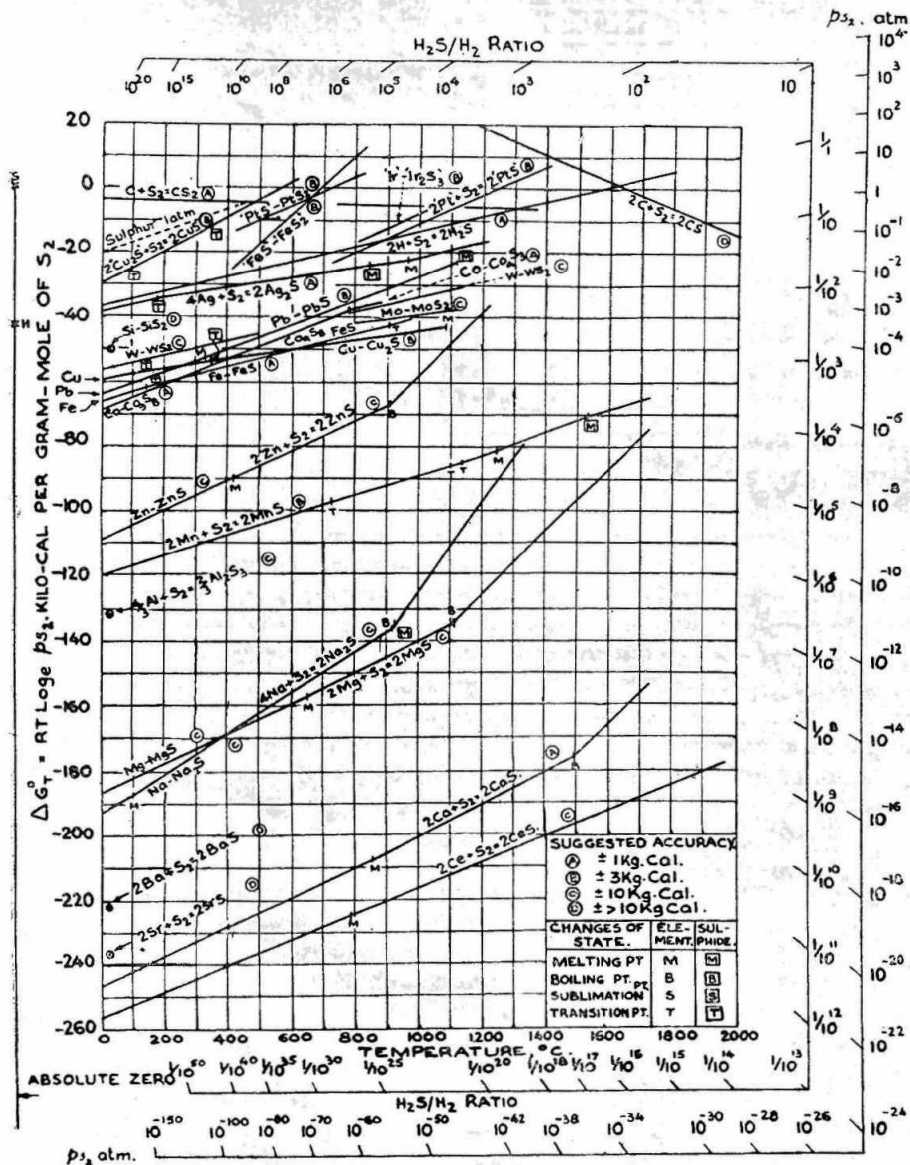The trend of the free energy change for reaction (6) and (7) has been shown in Fig. 4. It is noticed

FIG. 2—*Standard free energy of formation as a function of temperature of sulphide for reactions involving one gram-mole of $S_2$ gas.*
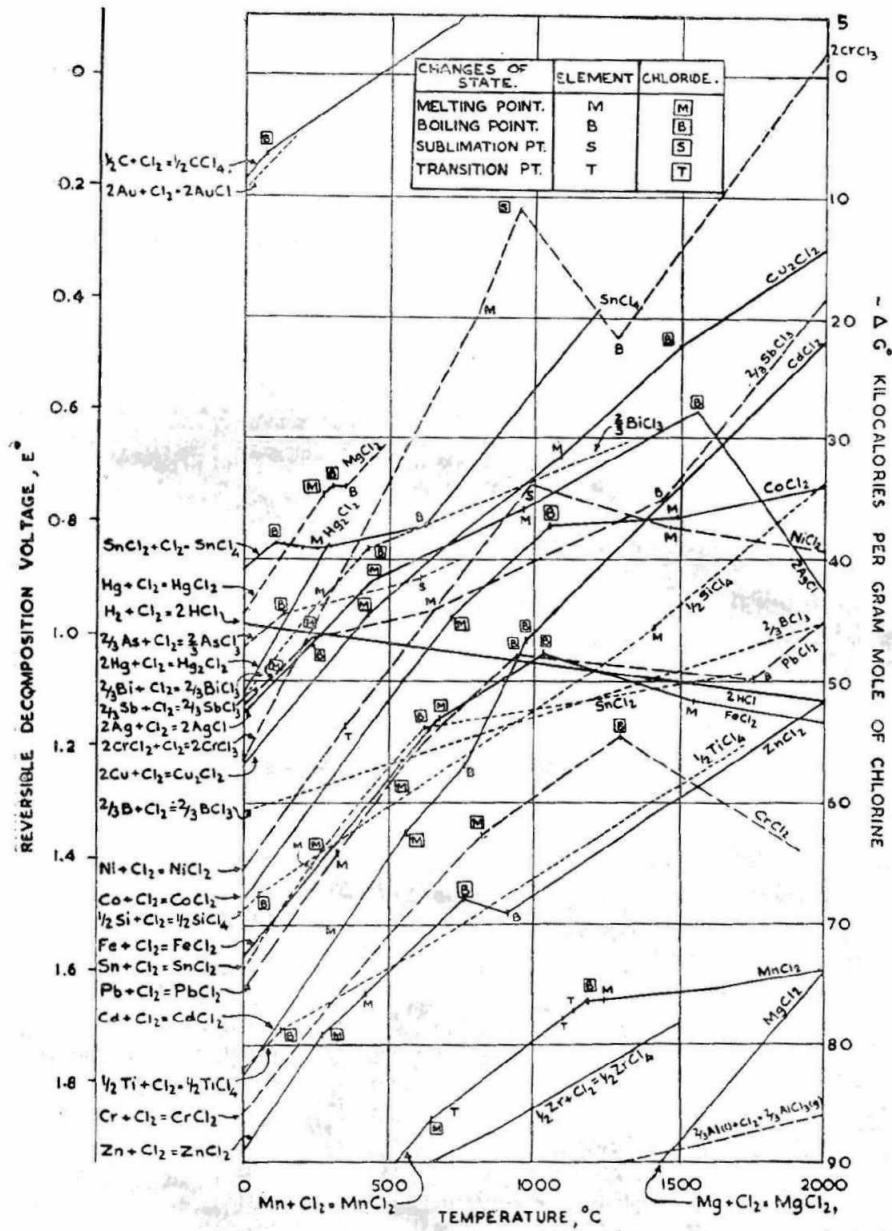
[Richardson & Jeffes[6]]

FIG. 3(a)—*Standard free energies of formation/ temperature of chlorides involving one gram-mole of chlorine gas between 0 and −90 K. Cal.* [Kellog[7]]

from the free energy diagram for both the reactions that separation should be most effective at about 1000°C, and nickel oxide should not react with the HCl at that temperature due to a positive free energy change. These ideas, of course, presume unit activity for the reactants and resultants.
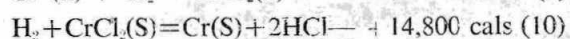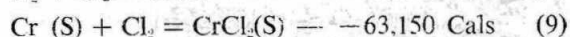
The experiments carried out by the authors indicated that though zinc oxide was preferentially removed, a part of nickel oxide was also removed at 1000°C and a residue containing 95-97 percent nickel oxide was obtained, from a 50:50 mixture, The removal of part of nickel oxide has been explained due to various factors e.g. removal of one of the reaction products i.e NiCl₂ from that zone of reactions, the formation of a cake-like residue where

the surface has become very much depleted of zinc oxide with consequent increase of nickel oxide activity.

The investigation was then directed to a 95 per cent nickel oxide and 5 per cent zinc oxide mixture obtained by Dutta & Banerjee[12] by the addition of caustic soda and sodium hypochlorite in the neutralised spent liquor. After 1 minute of chlorination more than 99.9 per cent of zinc oxide was removed while the amount of nickel oxide removed was only 1.25 per cent.

It is, however, not always necessary that the free energy curve for the reducing agent should be below the curve of the metal to be reduced and the

free energy change justify the reaction : the use of such conditions whereby the activity of the reducing agent may be increased does initiate the reaction. This is particularly true where the gaseous phases are concerned as the activity or fugacity may be effectively controlled. The reduction of $CrCl_2$ with hydrogen as developed by Maier[18] clearly indicates the feasibility of such reaction. The process is operated at 800°C and the free energy changes for the reactions involved are :—

$$\triangle F° \text{ at } 800°C$$

$$H_2 + Cl_2 = 2HCl \quad\text{———}\quad -48,350 \text{ cals} \quad (8)$$
$$Cr (S) + Cl_2 = CrCl_2(S) \text{——} -63,150 \text{ Cals} \quad (9)$$
$$H_2 + CrCl_2(S) = Cr(S) + 2HCl \text{——} + 14,800 \text{ cals} \quad (10)$$

and thus apparently the reduction of $CrCl_2$ with hydrogen should not be possible. The limiting case where the reaction may be possible from left to right is when :

$$Rt \ln \frac{P^2 HCl}{P_{H_2}} = -14,800 \text{ at } 800°C \text{ this assumes}$$

unit activity of Cr and $CrCl_2$ and thus

$$\log \frac{P^2 HCl}{P_{H_2}} = -3.017 \quad\quad (11)$$

For one atmospheric pressure when the partial pressure of HCl and hydrogen will be 0.031 and 0.969 atmosphere respectively, the reaction is possible. Thus if the amount of HCl in the reducing gas is kept below 3.1 percent by supplying fresh
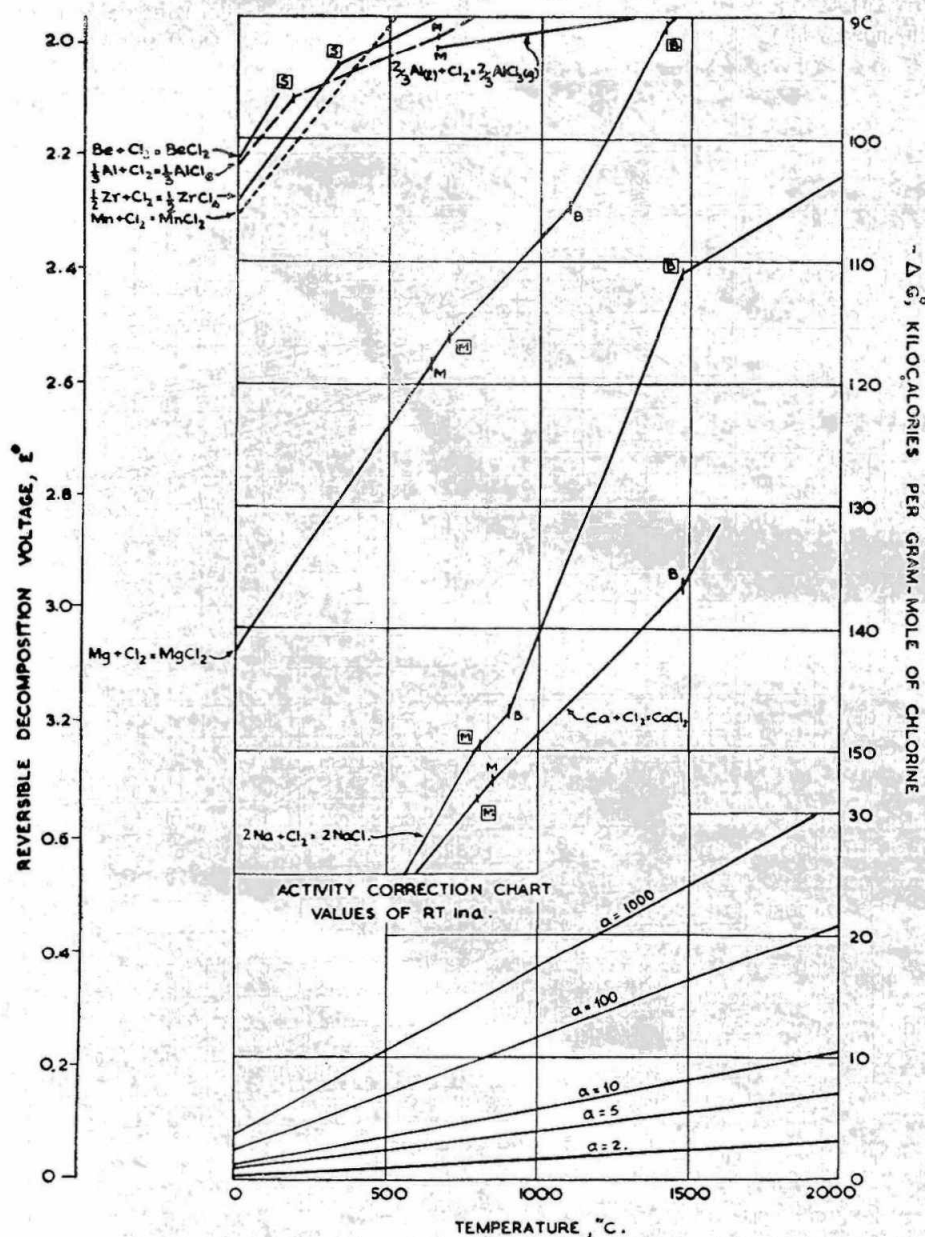


FIG. 3(b)—*Standard free energies of formation/ temperature of chlorides involving one gram-mole of chlorine gas between −90 and −150 K. Cal.* [Kellog[7]]
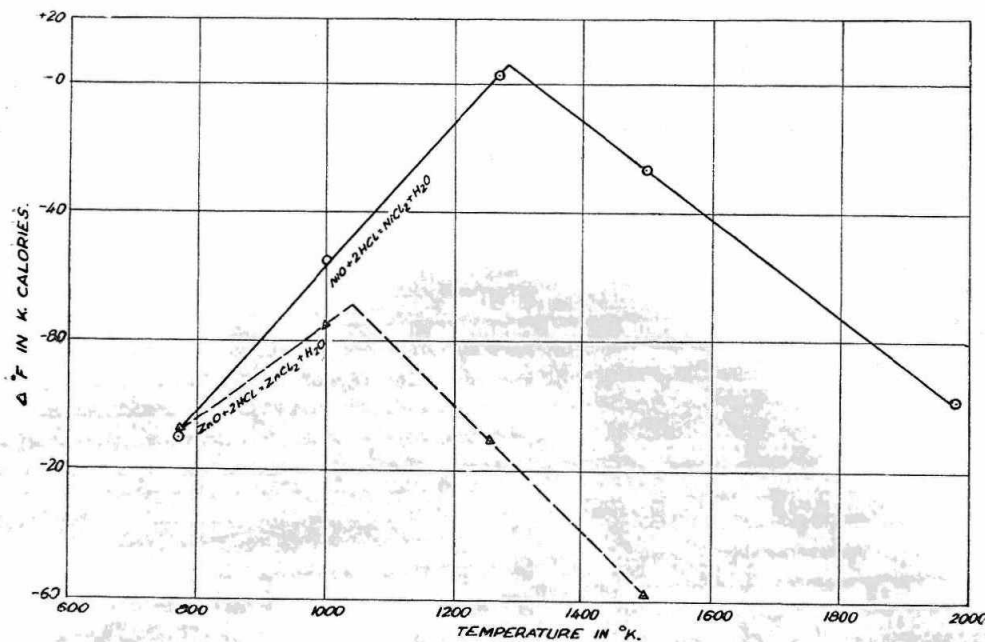
FIG. 4—*Free energy change at different temperatures for the chlorination of nickel and zinc oxides.*

dry hydrogen and continuously removing the HCl formed, the $\triangle F°$ will be negative and the reduction reaction will proceed.

In many cases limitations to the completion of a reaction are set up by the conditions of equilibrium when the value of constant K is so small that only an insignificant amount of products are formed. Such reaction, however, are very important for metal winning and in fact offer the only convenient method. The adjustment of factors which control the equilibrium can, however, be used to complete the reaction.

The measures adopted for the completion of the reaction without change of temperature are the pressure over the system, removal of one of the reaction products and/or a combination of the reaction product to form a stable compound. These principles are liberally adopted in vacuum metallurgy. The principles of vacuum metallurgy have already been discussed in detail by the authors[14]. Two typical examples will however be discussed to show how physico-chemical principles can help in determining the line of work to be adopted for such processes.

#### REDUCTION OF ZnS WITH Fe

Kelly[15] studied the direct reduction of zinc sulphide with iron, the vapour phase at 1 atmosphere being mostly zinc but a very high temperature was required for displacing the equilibrium (in the liquid phase).

Iron sulphide is formed during the reaction and at 1188°C, a eutectic of ZnS—FeS is formed.

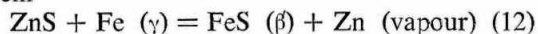If the temperature is kept below 1188°C, the system

$$ZnS + Fe \ (\gamma) = FeS \ (\beta) + Zn \ (vapour) \ (12)$$

### TABLE II

| T°C | $P_{Zn}$ mm Hg | $P_{ZnS}$ mm Hg |
|---|---|---|
| 880 | 1 | $1.4 \times 10^{-3}$ |
| 1000 | 10 | $2.0 \times 10^{-3}$ |
| 1170 | 100 | $4.5 \times 10^{-1}$ |
| 1170 | 100 | $4.5 \times 10^{-1}$ |

become monovariant and the vapour pressure of the system was found to change with temperature, as will be evident from the Table II.

Experiments were performed with an ore concentrate containing 79.5% ZnS and a commercial (synthetic) product containing 97.7% of zinc sulphide using a vacuum induction furnace with 0.1 mm residual pressure. Practically same rate of conversion was observed in both the cases.

In one series of run, the following results were obtained :

### TABLE III

| T° | Time | Zinc Distilled |
|---|---|---|
| 940° | 0 hrs. (after heating | 33.0% |
| | 2 hrs | 83.5% |
| | 3 hrs | 97.3% |
| 1000°C | 45-60 min. | complete |

A typical analysis of zinc distillate obtained from the ore concentrate was as follows :

Pb—0.11%, Cd—0.11% and rest zinc.

Contamination of the distillate with zinc sulphide was prevented by controlling the condensation temperature so that rate of evaporation could never exceed the rate of reaction and by filtering the vapour through iron.

The reaction offers interesting possibilities as stages of roasting and carbon reduction are avoided and the metal is produced in one stage. Any noble metals present would be left in the residue. Possibilities of experiments on simlar line with zinc concentrate from Zawar Mines under reduced pressures have already drawn the attention of the authors.

## DEVELOPMENT OF PIDGEON PROCESS

The principles of increasing the partial vapour pressure of the desired component by converting the other component into a material of lower vapour pressure is exemplified in the Pidgeon process for the production of metallic magnesium.

The basic methods exploited for the production of magnesium metal by thermal reduction are (1) reduction of MgO by carbon and (2) reduction by a metal or metalloid, the oxide of which is non-volatile at the temperature of reaction.

For the reduction of MgO by carbon according to equation $MgO + C \rightleftharpoons CO + Mg$ (g), a high temperature of 1900°C has to be applied to make the reaction proceed to the right, as at lower temperatures CO and Mg combine to reform MgO[17]. This difficulty of reverse reaction was, however, overcome by Hansgirg[18] through shock cooling the equilibrium mixture at high temperature, by blasting with large excess of cold hydrogen. The product so obtained was, due to interference of carbon monoxide, in the form of a fine powder of submicroscopic particle size and of pyrophoric nature, the melting of which was risky. It required to be distilled either in vacuum or in presence of an inert gas, thus sacrificing the simplicity of the process.

A second system for reduction was, therefore, searched for where magnesium metal will be the only gaseous product and the product is not obtained in fine pyrophoric powder. Free energy considerations, keeping the above mentioned conditions in view, advocated the use of silicon and aluminium for commercial production, though ferro-sililon is the mostly used material. The action is represented as

$$2MgO + Si = 2 Mg (g) + SiO_2$$
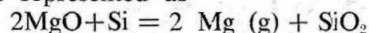
According to Doerner[19] $P_{Mg}$ was 0.19 mm Hg and 0.38 at 1200°C and 1300°C respectively. According to Schneider and Hess[20] it was however, 1.9 mm at 1200°C but they stated that magnesium existed as orthosilicate (forsterite). Forcing the reaction to the right by continuous removal of magnesium was therefore not found to be commercially feasible.

In an attempt to increase the vapour of magnesium by keeping the activity of the other product silicon dioxide extremely low, the well-known Pidgeon process came into existance, wherein dolomite was used and stable calcium silicate was formed at moderately high temperature (1100—

1300°C) by reaction with lime according to the following equation :

$$2MgO + 2CaO + Si(Fe)$$
$$= 2 CaO, SiO_2 + 2Mg(g) + (Fe) \quad \ldots (14)$$
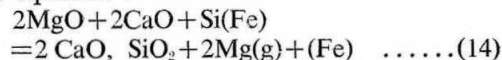
The rapid distillation rate in the Pidgeon process was later found by L. M. Pidgeon and J. A. King[21] to be due to high vapour presure of magnesium under the stated conditions being 10-1—30.2 mm Hg within the temperature range of 1100—1190°C.

It is thus seen that thermodynamic data help in understanding the reaction mechanism and in developing new methods for metal extraction. Even in cases where the available thermodynamic data cannot be directly applied, it gives informaton about the adjustment of factors like pressure, removal of the reaction products etc. which can be profitably used to take a reaction to completion.

## REFERENCES

1. GOODEVE, C. F. A general discussion on the physical chemistry of process metallurgy. Faraday Society. 1948, pp. 9-23.
2. Lecture on physical chemistry of steel making (Institute of Metals, India, 9th Annual Meeting), Lecture No. 1, physico-chemical principles by T. Banerjee.
3. A general discussion on the physical chemistry of process metallurgy, Faraday Society, 1948.
4. WELCH, A. J. E. Principles of extraction and refining of metals, (Instt. of Metallurgists), March 1951. Refresher course Lecture 1950.
5. ELLINGHAM. H. J. T. J. Soc. Chem. Ind. 63 (1944) 125.
6. RICHARDSON, F. D., and JEFFES, J. H. E. J. Iron & Steel Inst. 160 (1948) 261.
7. KELLOGG. H. H. J. of Metals, 188 (1950) 862.
8. KELLEY, K. K. U. S. Bur. of Mines Bull. 384 (1935), 406, (1937) 407 (1937).
9. KRISHNAN, R. M., CHATTERJEE, A. B., KHANAN and NIJHAWAN, B. R. N. M. L. RR/37/54, March 1954, paper contributed to the Symposium on 'Non-Ferrous Metal Industry in India'.
10. SHARMA, R. A., KAPOOR, A. N., and CHATTERJEE, A. B. N. M. L. RR/75/56, July 1956.
11. SHARMA, R. A., BHATNAGAR, P. P. and BANERJEE, T. J. Sci. I. Res. 15B (1956) 378-382.
12. DUTTA, R. K. and BANERJEE. T. Ibid 11B (1952) 54.
13. MAIER, C. G. U. S. Bur. of Mines Bull. 436 (1942).
14. BHATNAGAR, P. P. and BANERJEE, T. Vacuum—a new tool in extractive metallurgy, N. M. L. LR 25/54, paper contributed to the Symposium on 'Non-ferrous Metal Industry in India'.
15. KELLY, K. K. U. S. Bur. Mines. Bull., 406 (1937).
16. GROSS, P and WARINGTON, M. The physical chemistry of process metallurgy. Faraday Society, 1948, 216.
17. SLADE, J. Chem. 93, (1907) 327.
18. HANSGIRG. German Pat. 529, 120, 1029.
19. DOERNER. U. S. Bur. Mines Bull. P. July 1937.
20. SCHNEIDER, and HASSE. Z. Electrochem, 46 (1940) 24.
21. PIDGEON, L. M. and KING, J. A. Transactions of Faraday Soc. Symposium on the physical chemistry of process metallurgy, 1948. p. 197-206.