

THERMODYNAMIC ASPECTS OF CHEMICAL REACTIONS, AS APPLIED TO THE SMELTING AND REFINING OF LEAD

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Abstract

With a reference to the formulae employed in chemical thermodynamics, available data on thermodynamics of chemical reactions involved in the extraction and refining of lead are brought together. Equilibrium constants of the reactions have been calculated from the standard free energy data to explain the desideratum of optimum working conditions required during roasting, smelting and refining of lead. Graphs showing the changes with temperature of standard free energies of formation of oxides, sulphides, chlorides, fluorides, sulphates, carbonates and silicates have been incorporated for ready reference.

Introduction

APPPLICATION of the laws of thermodynamics permits the study of chemical reactions involved in different metallurgical processes. Thermodynamics thus provides a useful method of predetermining the possibility of a chemical reaction to occur under given conditions of temperature, pressure and composition. Review of thermodynamical factors of chemical reactions involved in the smelting and refining of lead has been dealt with based on the conventional processes in use thereof. In doing so it has not been possible to include physico-chemical studies of all aspects of lead metallurgy.

Free Energy of Reaction

Available portion of the total energy of a system is known as free energy (G) (F by some American authors) and is defined by the relation

$$G = H - TS \dots \dots \dots (1)$$

where H is the heat content and S is the

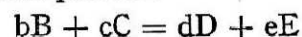
entropy of the system. All systems tend to reach maximum stability. The free energy of any system, therefore, tends to attain a minimum value under conditions of constant pressure and temperature. Hence, the change in free energy ΔG is indicative of the direction and extent to which a chemical reaction, phase transformation and change of state can proceed. It is the driving force of any chemical reaction. The standard free energy change of a reaction (ΔG°) is related to standard enthalpy change of a reaction (ΔH°) and standard entropy change of a reaction (ΔS°) at constant temperature and pressure by the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \dots \dots \dots (2)$$

Whether a reaction can proceed in the desired direction or not depends on two factors, viz. the sign of the free energy change and the availability of a suitable reaction path. If the free energy is lowered by the reaction proceeding in the intended direction and a path is available, the necessary prerequisites exist for the reaction to proceed. If the free energy change is not favourable, the mere existence of a reaction path is not enough. Similar reasoning applies to the other case where the free energy change is favourable but the reaction path is either not available or not straightforward or when the chances of the reactants meeting each other are small.

Equilibrium Constant and Free Energy

For any chemical reaction at given temperature and pressure



in which b , c , d and e represent the number

of molecules of the reactants B and C, and products D and E taking part in the reaction, the change in free energy at a given temperature and pressure is given by the equation

$$\Delta G_T = \Delta G_T^\circ + RT \ln \frac{a_D^d \times a_E^e}{a_B^b \times a_C^c} \dots (3)$$

where a_E = activity of a constituent E; T = absolute temperature ($^\circ K$); and R = gas constant (1.987 cal./degree/mole). ΔG° is conventionally expressed in cal. per gram atom. When the reaction attains a state of equilibrium, the free energy change ΔG_T is zero, and, therefore,

$$\Delta G^\circ = -RT \ln \frac{a_D^d \times a_E^e}{a_B^b \times a_C^c} = -RT \ln K \dots (4)$$

$$\text{or } \log K = -\frac{\Delta G^\circ}{4.575T} \dots (4a)$$

where K is the equilibrium constant of the reaction. This equation shows the relation of standard free energy change ΔG° to the equilibrium constant (K) of a chemical reaction. K is a ratio which indicates the extent to which a chemical reaction can proceed. The high magnitude of K , therefore, indicates that the reaction proceeds substantially to the right-hand side of the equation. The unit in which K is expressed is generally related to the active mass (or activity). Change of the equilibrium constant (K) with temperature is given by the equation

$$\log K = -\frac{1}{4.575} \times \frac{\Delta G^\circ}{T} \dots (5)$$

If for any chemical reaction at a particular temperature ΔG° can be found, K can be determined, and vice versa. It is thus possible from equation (4) to calculate equilibrium activities for a reaction.

From equations (2) and (4) it follows that

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \dots (6)$$

which shows that the equilibrium constant of any temperature T can be calculated from

the known value of heat of reaction ΔH° and the value of change in entropy ΔS° , when the substances are in their standard states.

The variation of the equilibrium constant with temperature is expressed by van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \dots (7)$$

If ΔH° is positive, i.e. endothermic reaction, $\ln K$ or $-\Delta G^\circ$ becomes more negative and the reaction proceeds further with the rise of temperature. If ΔH° is negative, then $-\Delta G^\circ/T$ becomes more positive with the increase of temperature. The possibility of ΔH° changing sign with temperature should be considered. From equation (6)

$$\log K = -\frac{\Delta H^\circ}{4.575T} \text{ plus constant}$$

as the heat of the reaction does not change appreciably with temperature and pressure. When logarithm of the equilibrium constant is plotted against the reciprocal of absolute temperature, a straight line is obtained, the slope of which multiplied by 4.575 will give the heat of reaction in calories.

Thermodynamic data, therefore, provide means of ascertaining the possibility of any chemical reaction taking place under given conditions. It must be mentioned that the reaction rate will depend on factors such as the form of the reactants and is not predictable from thermodynamic considerations alone, e.g. the diffusion of the reactants and products from the zone of reaction may determine the rate of reaction. Metallurgical reactions usually take place at high temperatures at which diffusion rates are high. So, if the free energy change is favourable, a metallurgical reaction is expected to progress at a reasonable rate in the desired direction.

Activity

By activity is meant the effective concentration of a constituent, which may not always be equal to its concentration. Activ-

ity is always referred to a standard state. It represents the effective concentration in any desired state when compared to the effective concentration in the state chosen as the standard or reference state. In a large number of instances, the pure substance is taken to be the standard state. In such cases, if the solution obeys Raoult's law, the activity is equal to the mole or atom fraction. When considering dilute solutions, it is sometimes inconvenient to refer to the pure substance as the standard state. Hence, we have the infinitely dilute solution standard, and the 1 per cent solution (*vide* Chipman) standard. In dilute solutions, the activity is proportional to the concentration till the latter become excessive. This is expressed by Henry's law. Activity of a pure solid or liquid is conventionally considered as unity, and that of a gas as equal to its partial pressure.

The ratio of activity (a_i) to its concentration is called the activity coefficient (γ_i) where the concentration is defined by the mole fraction (N_i).

$$\gamma_i = \frac{a_i}{N_i} \dots\dots\dots (8)$$

These remarks can be generally applied to heterogeneous systems.

In equation (3), when the reactants and products are not in their standard states and, therefore, the activities are not unity, the free energy change of the reaction ΔG can be obtained by adding an activity correction to ΔG° . It follows from equation (3) that $\Delta G_T = \Delta G_T^\circ + RT \ln J_a$, where J_a is the activity function at temperature T . An activity correction chart has been shown with a $\Delta G^\circ/T$ diagram for chlorides (Fig. 4). The correction has to be multiplied by the number of molecules. This is to be added for products of reaction and subtracted for reactants. If a is less than unity, reciprocal of a to be added to ΔG_T° for reactants and subtracted for products.

The change in free energy with temperature at constant pressure can be expressed as

$$\Delta G^\circ = IT + \Delta H_o - \Delta aT \ln T - \frac{\Delta bT^2}{2} - \frac{\Delta cT^3}{6} \dots\dots (9)$$

where I and H_o are integration constants. The value of the other three constants a , b and c can be calculated from specific heat data of the constituents while H_o and I can be evaluated from one value of heat effect on the reaction and a known value of G° at a specified temperature respectively. It is thus possible to calculate the standard free energy change of a chemical reaction at a given temperature, but the equation is cumbersome.

Graphical Representation of Standard Free Energy Changes with Temperature

Standard free energies of formation of various compounds at different temperatures have been expressed in the form of equation (9) by Kelly¹.

Ellingham² plotted the standard free energy changes with temperature in a graphical form. From such a chart, one can directly see the conditions for a chemical reaction to occur. As H° and S° change only slightly with temperature, such a plot will result approximately in straight lines having a slope of S° , because of the relation

$$\frac{d\Delta G^\circ}{dT} = -\Delta S^\circ$$

If ΔG° is plotted downwards, as is common practice, the slope will be $-\Delta S^\circ$. With the abrupt change of entropy at transition, fusion, vaporization and sublimation temperatures, the slope is usually changed.

The standard free energy for chemical reaction is related to standard electrode potential (or decomposition voltage) of an electrolytic cell in which the reaction is carried out by the following equation:

$$\Delta G^\circ = -jnE^\circ F \dots\dots (10)$$

where E° = standard electrode potential in volts; F = faraday constant, 96,500 coulombs per mole; n = number of faradays per mole of reaction; and j = conversion factor from Joules to calories (= 0.239).

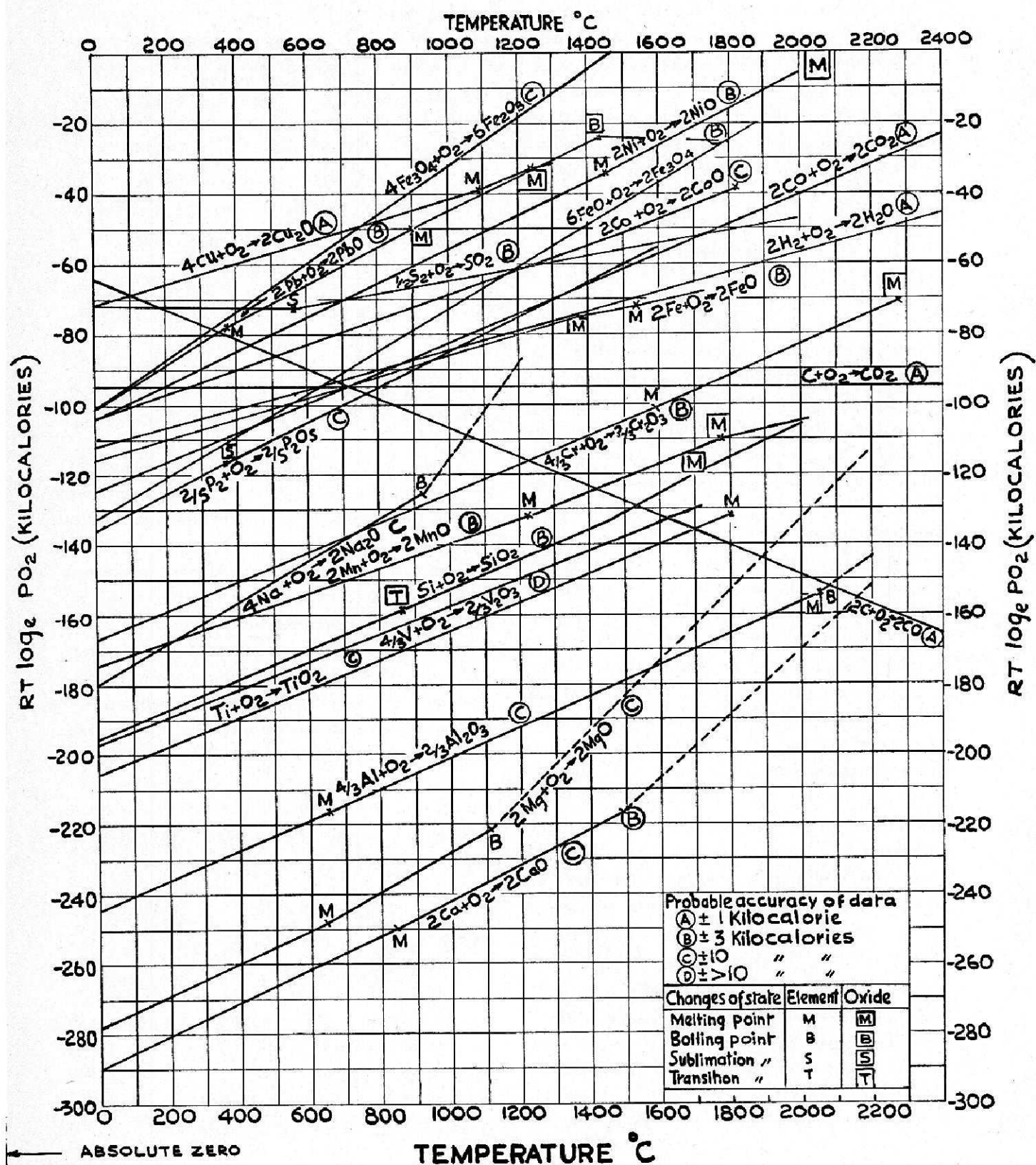
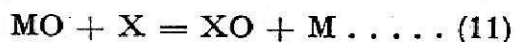


FIG. 1 — STANDARD FREE ENERGIES OF FORMATION AS A FUNCTION OF TEMPERATURE OF OXIDES INVOLVING ONE GRAM-MOLE OXYGEN (RICHARDSON AND JEFFES⁴)

It is, therefore, clear that the ordinate of the $\Delta G^\circ/T$ chart can represent ΔG° and E° , if n is constant for all the reactions given in a chart. In practice, due to internal resistance, over-voltage and polarization, voltages higher than the requisite decomposition voltage are necessary for electrolysis.

Standard Free Energy/Temperature Diagrams

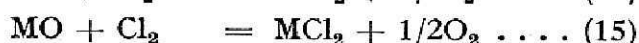
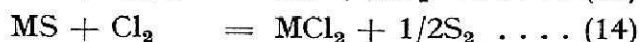
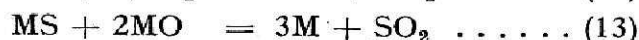
Figs. 1-9 show the dependence of standard free energies of formation of oxides³, sulphides⁴, chlorides⁵, fluorides⁶, sulphates⁷, carbonates⁷ and silicates⁸ on temperature. The application of these charts has been admirably described by Ellingham² and others^{3,5-7,9}. In each case, free energy change of the reaction in which 1 gram-mole of the gas O_2 , S_2 , Cl_2 , F_2 , N_2 , SO_3 and CO_2 or the compound SiO_2 reacts with requisite quantity of the metal or oxide has been represented, as it shows directly the relative stability of the compound or affinity for the gas. The further down a compound occurs in the chart, the more stable it is. When two reactions are compared, the vertical distance at a particular temperature separating the two characteristic lines represents the free energy change and, therefore, indicates the tendency of the element represented in the lower line to decompose the compound represented by the upper line. For example, if at a particular temperature T , the curve for oxidation of any element X is below that for element M , then the oxide of the element X is more stable than that of M and the reaction



will take place when the constituents are in their standard states. If, however, X forms an oxide of lower valency, the reverse reaction may be possible.

Thermodynamic data can be added or subtracted algebraically. The possibility of

oxidation of a sulphide, or of the chlorination of an oxide or a sulphide at any temperature T is shown by the free energy of formation of the oxide at T minus that of the sulphide at T , or the free energy of formation of the chloride at T minus the free energy of formation of the oxide or sulphide at T . In other words, feasibility of reactions like



can be predetermined by the use of the oxide, sulphide and chloride charts.

Applications to Metallurgy of Lead

The basic concepts of thermodynamics as applied to equilibrium in chemical reactions will now be applied to review the important chemical reactions in the roasting, smelting and purification of lead.

It can be seen from the $\Delta G^\circ/T$ diagram for oxides that the free energy of formation of CO becomes more negative with the rise in temperature and consequently it becomes theoretically possible to reduce all metallic oxides with carbon at very high temperatures. Due to the lower free energies of formation of sulphides like CS , CS_2 and H_2S compared to the oxides CO , CO_2 and H_2O , the reduction of metallic sulphides by carbon and hydrogen is, however, not possible. Sulphides of low stability can be reduced to metal either by the application of heat when at moderate temperature the free energy of formation becomes zero (e.g. of mercury sulphide) or by oxygen, which is adopted in the roast reaction method of obtaining lead to be described later. In such cases no reducing agent is required. The smelting of galena, like most of the sulphide ores of other metals,

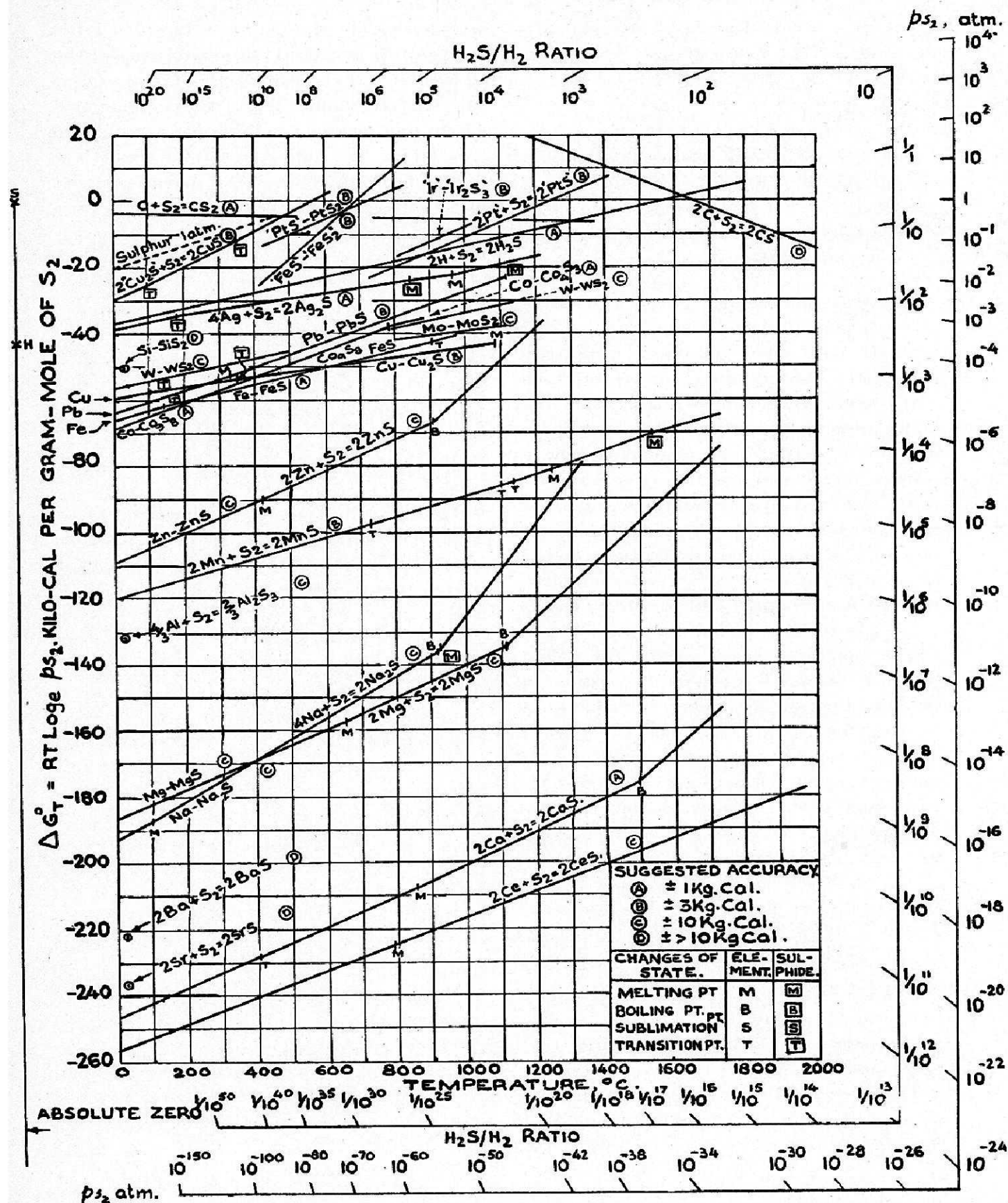


FIG. 2

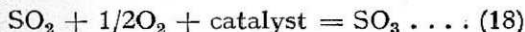
commonly involves roasting of the ore as the first stage.

General Aspects of Roasting

Some general aspects of roasting of sulphide concentrates have been described recently by Djingheuzian¹⁰. In oxidizing roasting, the ore concentrate is heated below its fusion point, to convert the sulphide into the oxide. The reaction may be expressed as



For the reaction to proceed substantially to the right, the free energy of the formation of the oxide MO should be higher than that of the sulphide MS, and the concentration of SO₂ in the roaster gases should be low to prevent the reverse reaction. Peretti¹¹ has mentioned that at temperatures commonly employed for roasting of sulphides of metals like copper, zinc and lead, the reaction $MS + \frac{3}{2}O_2 = MO + SO_2$ and the oxidation of sulphur to sulphur dioxide involve such large free energy changes that the SO₂/O₂ equilibrium ratios need not be considered. This will be later considered in relation to roasting of galena. Though the oxidation of the sulphide is the main chemical reaction aimed at, other side reactions usually take place and some of these reactions affect the production of a desirable calcine. In the presence of catalysts, SO₂ is converted into SO₃



SO₃ then reacts with the oxide MO to form sulphate



which is undesirable.

The roaster gas consists of a mixture of O₂, N₂, SO₂ and SO₃. In a mixture of gases, the partial pressure of each is, of course, proportional to its volume. The formation of MSO₄

will depend on the partial pressure of SO₃, temperature and on the characteristics of the oxide MO. If the partial pressure of SO₃ at the selected temperature is less than its equilibrium value, then MSO₄ will decompose into MO + SO₃ and more of the oxide will form. Conversely when the partial pressure of SO₃ is higher than the dissociation pressure of sulphate, SO₃ will combine with the oxide to form more sulphate till the partial pressure of SO₃ is reduced to equilibrium value. Thus the roasting reactions can be controlled by controlling the temperature and the composition of the gas in the roaster.

Roasting of Galena

The thermodynamical aspects of roasting of galena have been described by Wenner¹². But whereas he calculated the free energy data from equations, use has been made of appropriate $\Delta G^\circ/T$ charts in this review. In roasting, the following reactions are likely to take place:



The equilibrium constant of the reaction is

$$K_{20} = \frac{a_{\text{PbO}} \cdot p_{SO_2}}{a_{\text{PbS}} \cdot p_{O_2}^{1.5}} \dots (21)$$

Assuming that the activities of PbO and PbS are unity, the equilibrium constant becomes

$$K_{20} = \frac{p_{SO_2}}{p_{O_2}^{1.5}}$$

The change in free energy of reaction (20) can be found from the known values of standard free energies of formation of PbS, PbO and SO₂ and from the expression $\Delta G_{20} = -RT \ln K_{20}$, K₂₀ can be calculated. Other reactions are

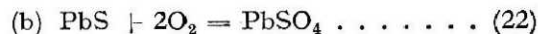


FIG. 3 — STANDARD FREE ENERGIES OF FORMATION/TEMPERATURE OF CHLORIDES INVOLVING ONE GRAM-MOLE OF CHLORINE GAS BETWEEN 0 AND -90 K. CAL. (KELLOG⁵)

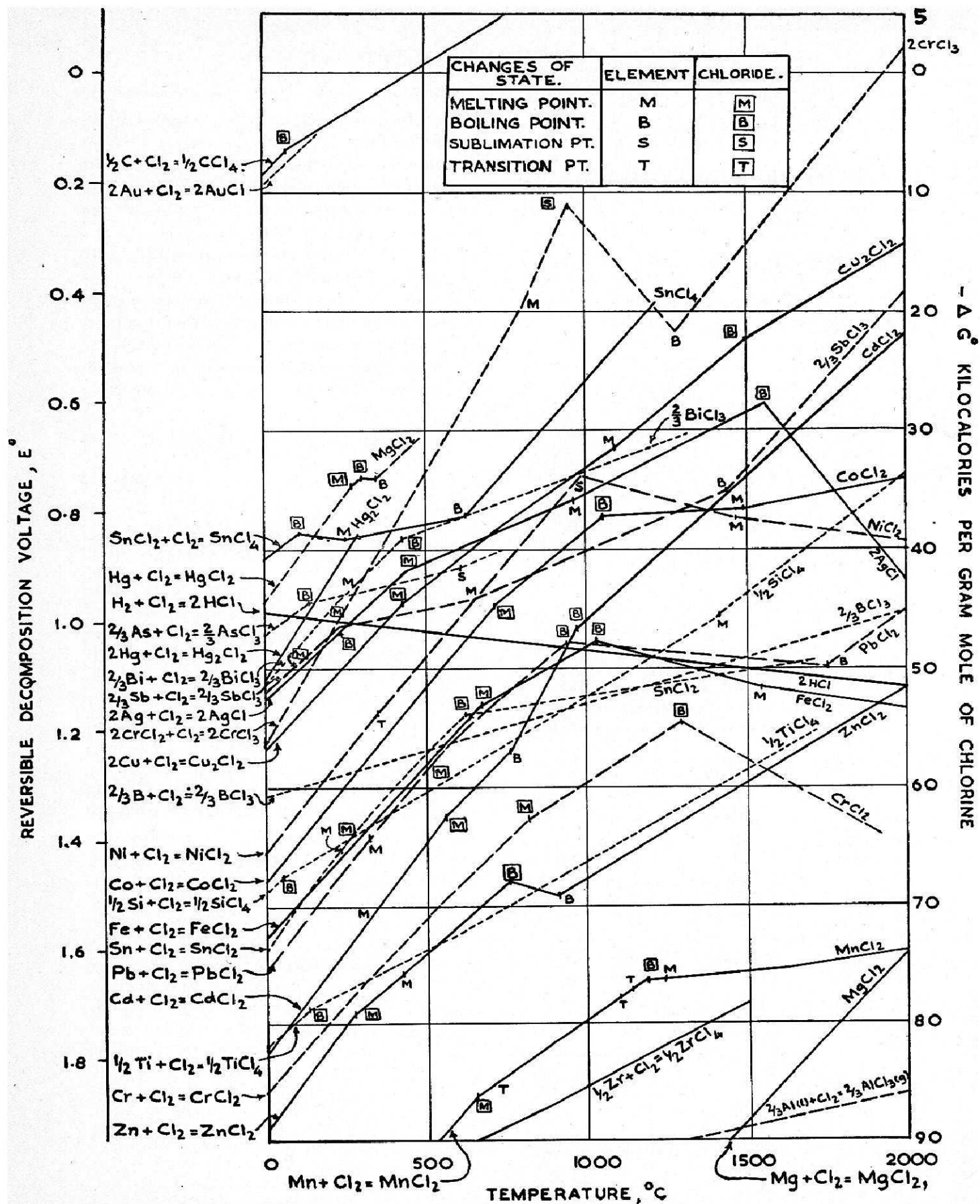


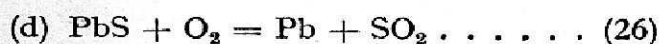
FIG. 3

For the reasons mentioned above

$$K_{22} = \frac{1}{pO_2^2} \dots \dots \dots (23)$$



$$K_{24} = \frac{pSO_2}{pO_2^{3.5}} \dots \dots \dots (25)$$



$$K_{26} = pSO_2/pO_2 \dots \dots \dots (27)$$



$$K_{28} = \frac{pSO_3}{pSO_2 \times pO_2^{0.5}} \dots \dots (29)$$



$$K_{30} = \frac{1}{pSO_3} \dots \dots \dots (31)$$

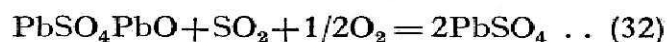
The approximate ΔG° values, as obtained from the appropriate $\Delta G^\circ/T$ diagram, and the calculated values of the equilibrium constants of these reactions at 600°, 700° and 800°C. are given in Table 1.

TABLE 1—FREE ENERGY OF FORMATION OF COMPOUNDS AND EQUILIBRIUM CONSTANTS OF REACTIONS (a) TO (d) DURING ROASTING OF GALENA

		TEMPERATURE, °C.		
		600	700	800
ΔG° PbS	cal.	—21500	—19500	—17500
ΔG° PbO	„	—32000	—29300	—27000
ΔG° PbSO ₄	„	—144280	—135700	—127130
ΔG° PbSO ₄	„	—180900	—169000	—158300
PbO*				
ΔG° SO ₂	„	—72000	—70000	—68000
(a) K_{20}		4.57×10^{20}	8.51×10^{17}	6.31×10^{15}
(b) K_{22}		5.9×10^{30}	1.3×10^{26}	2.14×10^{22}
(c) K_{24}		2.5×10^{52}	8.51×10^{44}	9.55×10^{38}
(d) K_{26}		4.4×10^{12}	2.2×10^{11}	2.0×10^{10}

*Calculated.

The high values of the equilibrium constants K_{20} , K_{22} , K_{24} and K_{26} show that the reactions (20), (22), (24) and (26) are thermodynamically feasible in the temperature range of 600°–800°C., and the reactions will proceed substantially to the right of the equation. The reaction $1/2S_2 + O_2 = SO_2$ has an equilibrium constant of 1.12×10^{18} at 825°C. PbO and SO₂ will, therefore, be stable phases where there is a minute partial pressure of oxygen. On the other hand, it can be shown from the free energy data that the basic lead sulphate formed in equation (24) should react with SO₂ and oxygen to form PbSO₄ thus:



which has an equilibrium constant of 5.01×10^5 at 800°C. It means that

$$pSO_2 \times pO_2^{0.5} = \frac{1}{5.01 \times 10^5} \dots \dots (33)$$

The partial pressure of oxygen is 0.21 atm. Substituting value of partial pressure of oxygen in the above equation, it can be seen that the partial pressure of SO₂ for the conversion of basic lead sulphate to lead sulphate is extremely low, which means that very low concentrations of SO₂ in the roaster gases in presence of oxygen can react with basic lead sulphate to form lead sulphate. Conversely high SO₂ concentrations in the presence of traces of oxygen will convert basic lead sulphate to lead sulphate. The roasted product will, therefore, consist of little unreacted lead sulphide and mainly of lead oxide and lead sulphate.

Smelting of Lead

The smelting of lead follows three methods, viz. (i) the reduction of lead oxide by carbon and carbon monoxide; (ii) reaction between

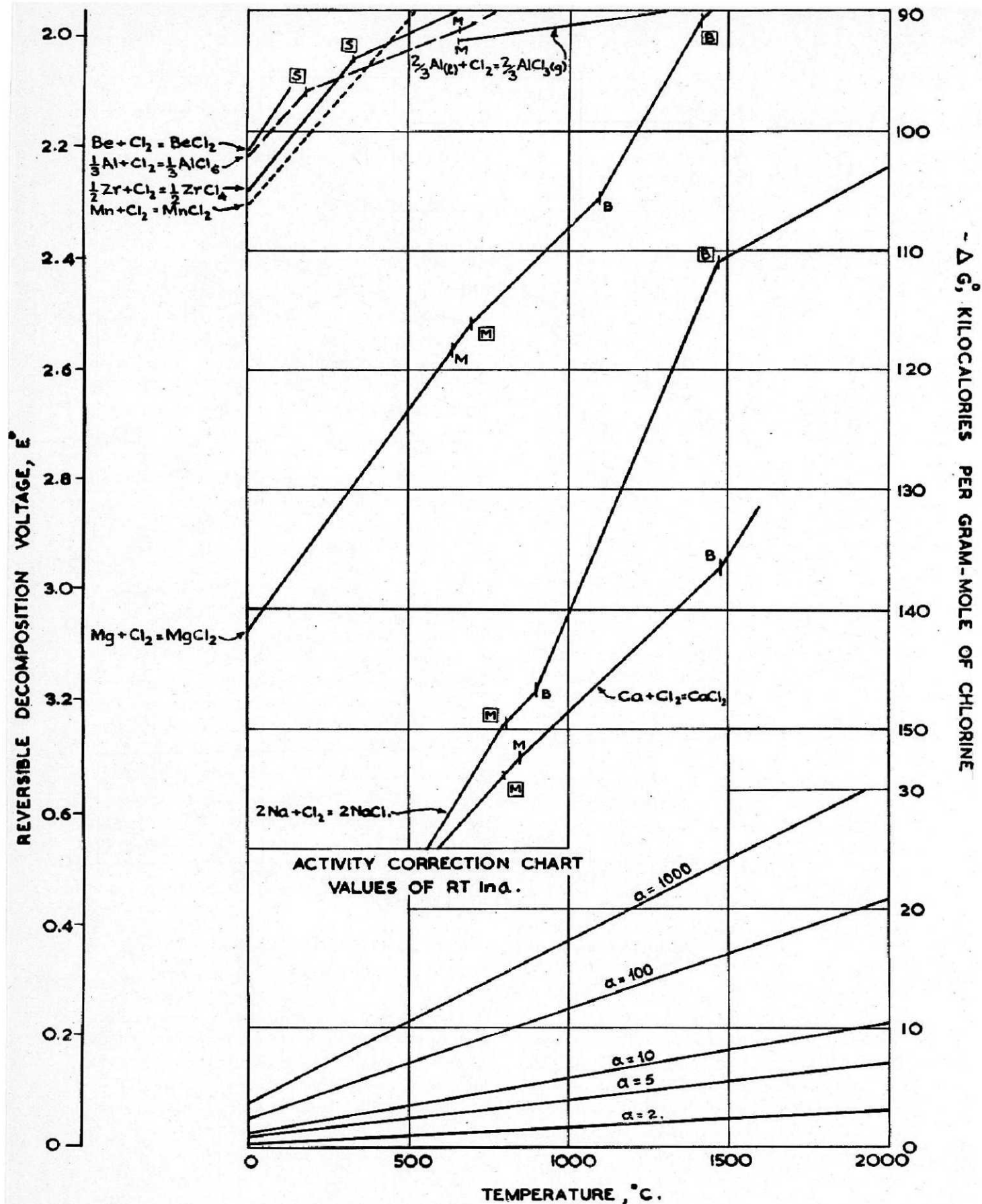


FIG. 4

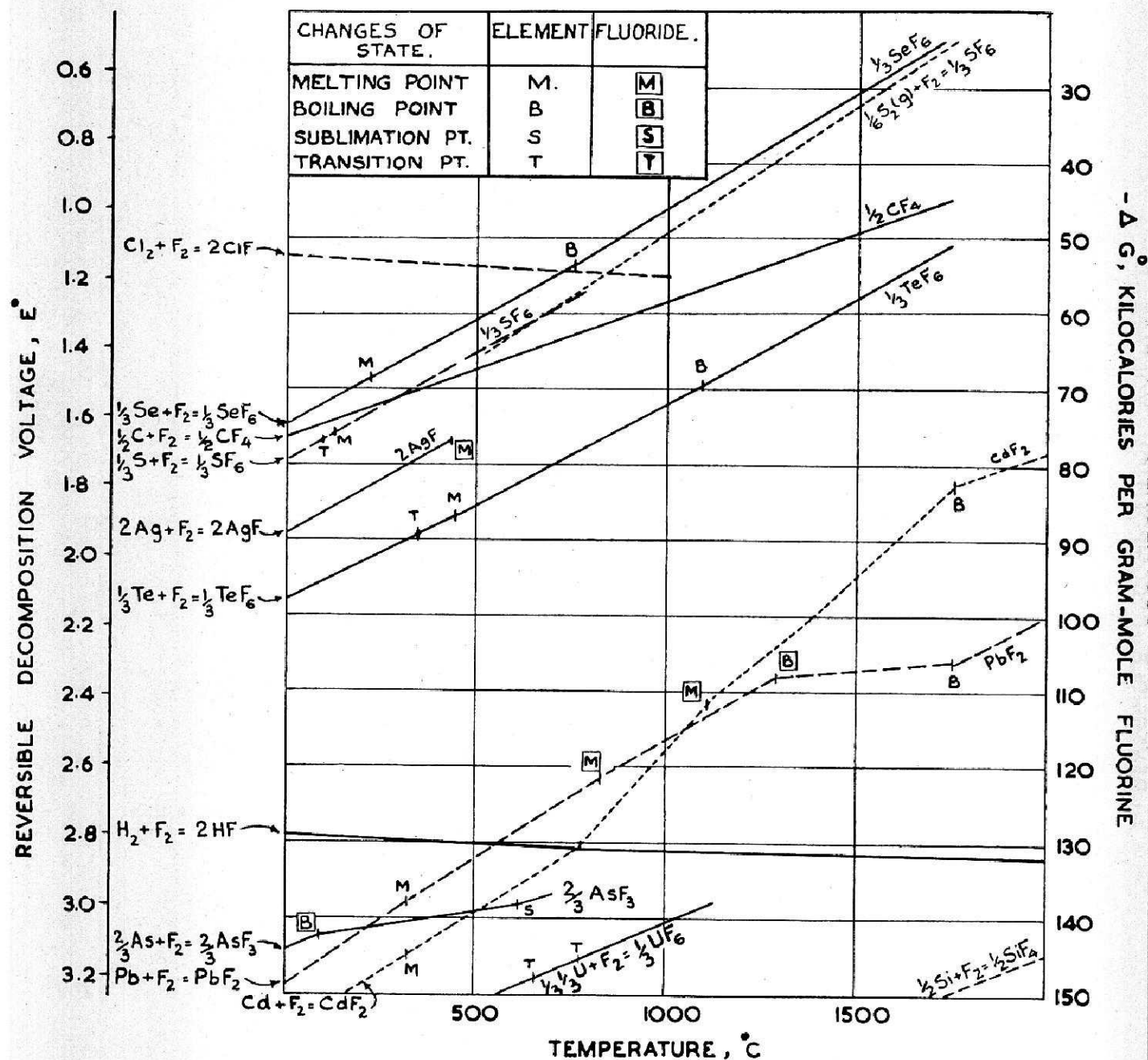


FIG. 5 — STANDARD FREE ENERGY OF FORMATION OF FLUORIDES AS A FUNCTION OF TEMPERATURE INVOLVING ONE GRAM-MOLE OF FLUORINE GAS BETWEEN -20 AND -150 K. CAL. (KELLOG⁶)

the sulphide and the oxide; and (iii) displacement of Pb from PbS by other metals. For the precipitation method, any metal whose position in the sulphide diagram is lower than PbS will be able to combine with sulphur, displacing lead from its sulphide. Iron is the chief element used for displacement. As the

reaction is reversible, complete decomposition is not possible. As regards the other two processes, argentiferous ores are treated in the blast furnace and high-grade non-argentiferous ores in reverberatory furnaces. In the $\Delta G^\circ/T$ diagram for the oxide, the $2C + O_2 = 2CO$ curve cuts that for $2Pb + O_2 = 2PbO$

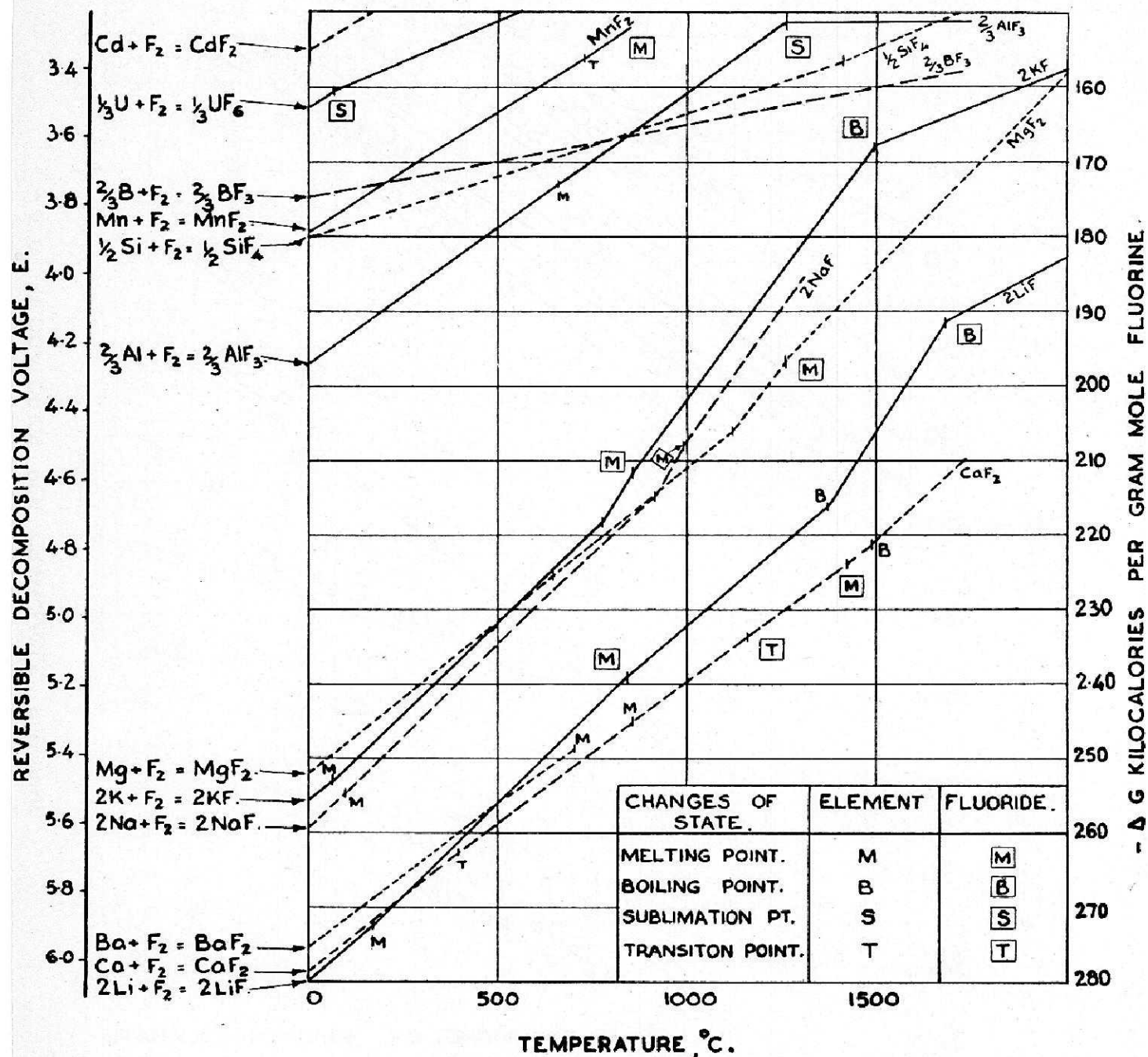
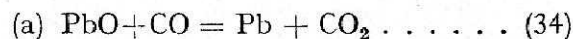
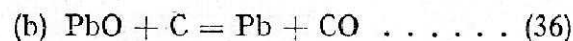


FIG. 6 — STANDARD FREE ENERGY OF FORMATION OF FLUORIDES AS A FUNCTION OF TEMPERATURE INVOLVING ONE GRAM-MOLE OF FLUORINE GAS BETWEEN -150 AND -280 K. CAL. (KELLOG⁶)

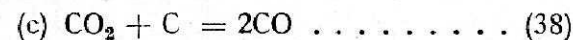
at about 200°C. , which means that the reducing effect of CO theoretically commences at that temperature. The reducing action of C commences at 400°C. and the rate of reduction is comparatively slow. The main reactions of the lead blast furnace and their equilibrium constants are as follows:



$$K_{34} = \frac{p\text{CO}_2}{p\text{CO}} \dots \dots \dots (35)$$



$$K_{36} = p\text{CO} \dots \dots \dots (37)$$



- ΔG° KILOCALORIES PER GRAM - MOLE OF SO₃ GAS

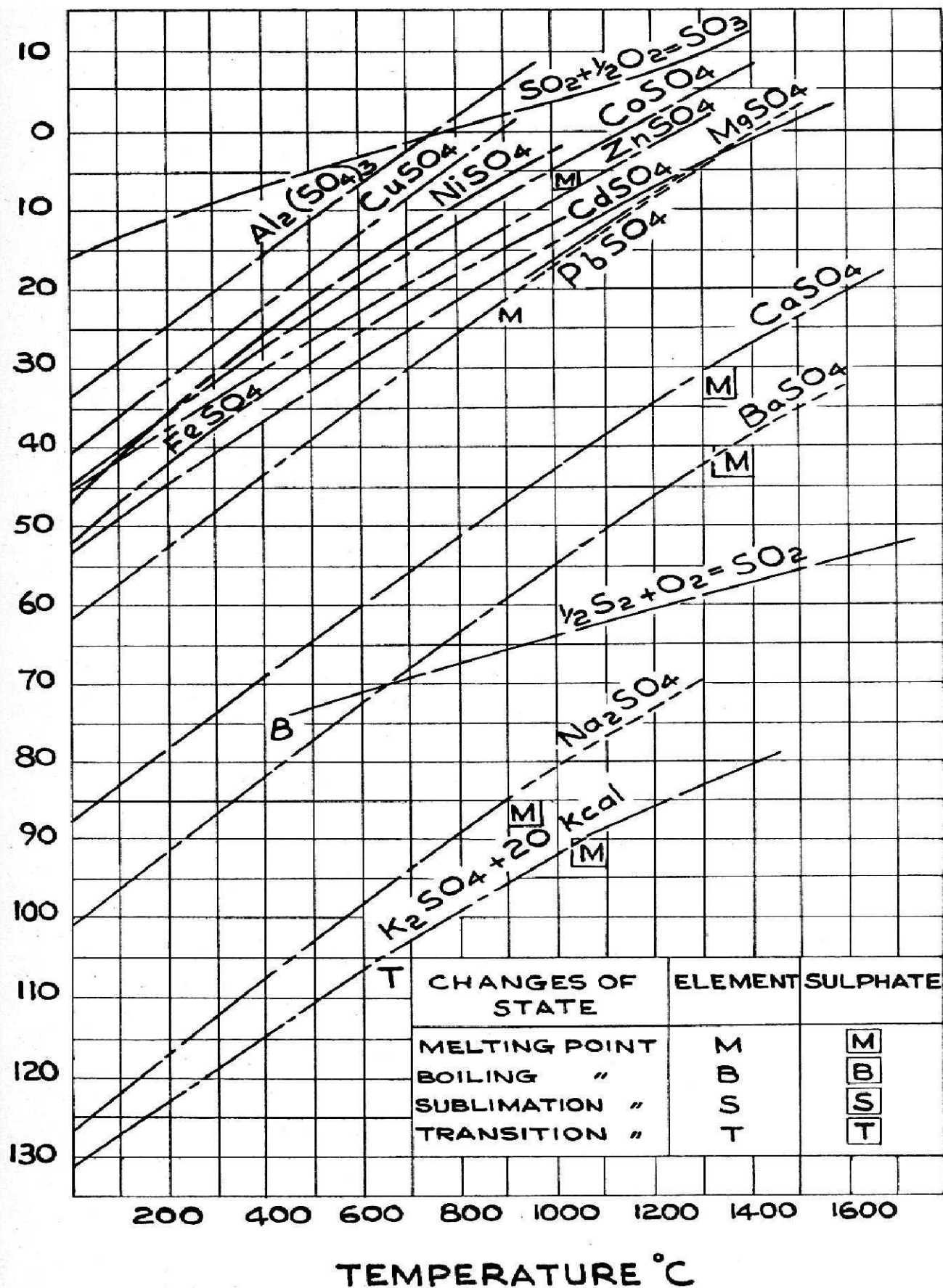
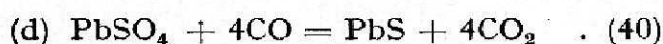
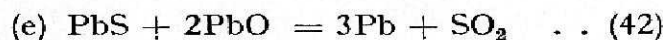


FIG. 7

$$K_{38} = \frac{p\text{CO}_2}{p\text{CO}} \dots \dots (39)$$



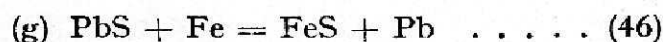
$$K_{40} = \frac{p\text{CO}_2^4}{p\text{CO}^4} \dots \dots (41)$$



$$K_{42} = p\text{SO}_2 \dots (43)$$



$$K_{44} = p\text{SO}_2^2 \dots \dots (45)$$



$$K_{46} = \frac{a_{\text{FeS}}}{a_{\text{PbS}}} \dots \dots (47)$$

All these reactions occur around 900°C. Reaction (36) is really a combination of the reactions represented by equation (34) and the producer gas reaction (38). The approximate values of free energies of formation of various compounds at 900°C. taken from the appropriate $\Delta G^\circ/T$ diagrams and the equilibrium constants of these reactions are given in Table 2.

Roast Reaction Process

The desirable reactions in the process are given in equations (42) and (44), but in the presence of excess of PbS or PbO than is required by equations (42) and (44), the excess remains unaltered, while with excess of PbSO₄ either a mixture of Pb and PbO, or PbO alone, results as shown in equations (48) to (51).

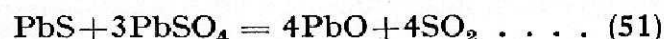
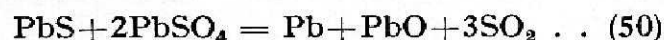
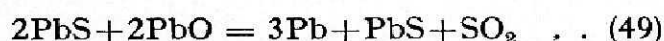
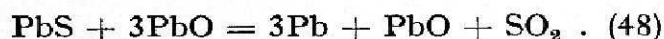


TABLE 2—FREE ENERGY OF FORMATION OF COMPOUNDS, EQUILIBRIUM CONSTANTS AT 900°, 1000° AND 1100°C. OF REACTIONS IN LEAD BLAST FURNACE

	TEMPERATURE, °C.		
	900	1000	1100
$\Delta G^\circ \text{ PbS cal.}$	-15200	-13000	-11500
$\Delta G^\circ \text{ CO } "$	-51500	-53000	-55500
$\Delta G^\circ \text{ CO}_2 "$	-94000	-94000	-94000
$\Delta G^\circ \text{ PbSO}_4^*$	-118600	-110000	-101000
$\Delta G^\circ \text{ PbO } "$	-24000	-22000	-19800
$\Delta G^\circ \text{ FeS } "$	-21500	-20000	-18600
$\Delta G^\circ \text{ SO}_2 "$	-66000	-64500	-63000
(a) K_{34}	3.2×10^3	2.2×10^3	1.1×10^3
(b) K_{36}	1.05×10^{13}	2.14×10^{12}	6.3×10^{11}
(c) K_{42}	2.0×10^{12}	3.1×10^{11}	2.0×10^{10}
(d) K_{42}	0.71	1.30	1.91
(e) K_{44}	4.5×10^{-1}	1.03	2.31
(f) K_{46}	1.17	1.26	1.13

$$^* \text{Pb(s)} + \text{S(s)} + 2\text{O}_2(\text{g}) = \text{PbSO}_4(\text{s}) \quad \Delta G_T^\circ = -219000 + 85.6 \text{ T. cal.}$$

TABLE 3—EQUILIBRIUM CONSTANTS OF THE CHEMICAL REACTIONS OF ROAST REACTION METHOD

EQUILIBRIUM CONSTANTS OF CHEMICAL REACTIONS	TEMPERATURE, °C.	
	800	900
K_{42}	0.21	0.71
K_{44}	2.0×10^{-2}	4.5×10^{-1}
K_{50}	—	2.14×10^{-6}
K_{51}	—	2.0×10^{-21}

The equilibrium constants of the reactions (42), (44), (50) and (51) at 800° and 900°C. are given in Table 3.

K_{42} has values of 0.71 at 900°C., 1.3 at 1000°C. and 1.91 at 1100°C. and the corresponding values of K_{44} are 4.5×10^{-1} , 1.03 and 2.31 respectively. These indicate that if the partial pressure of SO₂ attains these values,

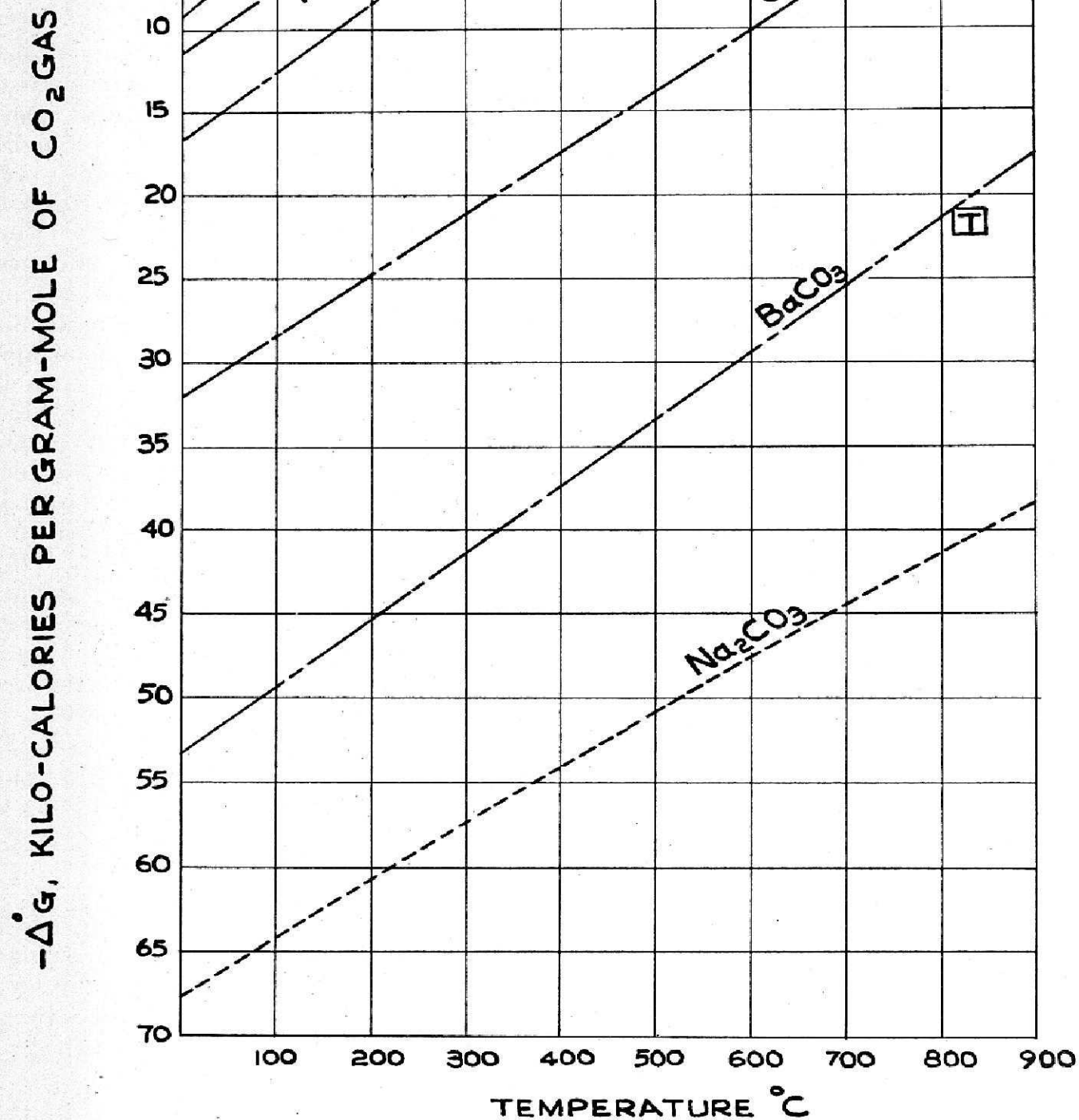


FIG. 8 — TEMPERATURE DEPENDENCE OF STANDARD FREE ENERGIES OF FORMATION OF CARBONATES FROM THE OXIDE AND CO_2 INVOLVING ONE GRAM-MOLE OF CO_2 GAS (OSBORN⁷)

the production of lead will stop. But as SO_2 is allowed to escape from the furnace, the partial pressure of SO_2 cannot attain any value excepting 4.5×10^{-1} so that the desired reactions will go to completion. For the same reason, reactions (50) and (51) will not proceed substantially to the right of the equations.

Refining of Lead

Besides lead, copper and iron, galena contains a large number of other metals like gold, silver, zinc, tin, arsenic, antimony, bismuth, nickel, cobalt, which need removal, with the sulphur, to obtain pure lead.

The elimination of impurities normally takes place in two main ways: volatilization of easily volatile oxides, like arsenic and antimony oxides, and slagging, in which the elements having higher free energy of formation of their oxides than that of lead oxide are readily oxidized and taken up by the slag. It can be seen with the aid of Fig. 1 that tin, zinc, sulphur, iron, nickel and cobalt are oxidized at a low temperature preferentially to lead and may thus be slagged off. Copper can only be partially removed by oxidation. It, however, forms an alloy of higher melting point than lead and, on slow melting, dross containing Cu, S, As and Pb separates out. As the free energy of formation of bismuth oxide is lower than that of lead oxide, removal of bismuth is not possible by either oxidation or vaporization (in a way similar to its removal from copper matte).

Removal of Bismuth

It is well known that Parkes's process does not remove bismuth, but that it can be removed by Pattinson's process, but at considerable cost. Betterton and Lebedeff¹³ have developed a process in which calcium, magnesium and antimony are used for the removal of bismuth. The principle is similar to that of Parkes's process in which partition of silver between alloys, rich in zinc and lead,

takes place. In this method, bismuth combines with calcium, magnesium and antimony forming a dross, and leaving lead which contains only 0.005 per cent Bi.

Removal of Zinc from Lead

From Parkes's process, lead contains 0.5-0.6 per cent zinc. The older practice was to pass air through molten lead kept at 1200°-1300°F. to oxidize zinc, because of higher free energy of formation of ZnO compared to lead oxide. But, in practice, oxidation of lead cannot be altogether prevented and 3-5 per cent lead is lost by oxidation. Betterton¹⁴ has described a method of purification by chlorine gas. In this process the loss of lead has been practically eliminated and zinc chloride is recovered as a valuable byproduct. The reaction is conducted under vacuum at a temperature of 350°-390°C. The reaction is exothermic, but ZnCl_2 does not volatilize until a temperature of 730°C. is attained. At the end of the operation, the lead contains about 0.005 per cent Zn and the 'crust' contains 2.5 per cent lead. Dezincing by chlorine evidently depends on the fact that the standard free energy curve for ZnCl_2 is below that of PbCl_2 . The standard free energy of formation of ZnCl_2 at 390°C. is -76,640 cal. and that of PbCl_2 is -61,550 cal. as shown in Fig. 3. If any PbCl_2 is formed, it will be decomposed by Zn according to the equation



in which the standard free energy change is -15,090 cal. at 390°C. Kellogg⁵ has calculated the residual zinc in lead treated in this way, on the assumption that equilibrium between the metal and chloride phases is attained.

$$\Delta G^\circ = -15090 = -RT \ln \frac{a_{\text{Pb}} \times a_{\text{ZnCl}_2}}{a_{\text{Zn}} \times a_{\text{PbCl}_2}} \dots (53)$$

As the final lead is of over 99.9 per cent purity, it can be assumed that $a_{\text{Pb}} = 1$. The final chloride has a mole fraction of 0.983. On the assumption that the solution

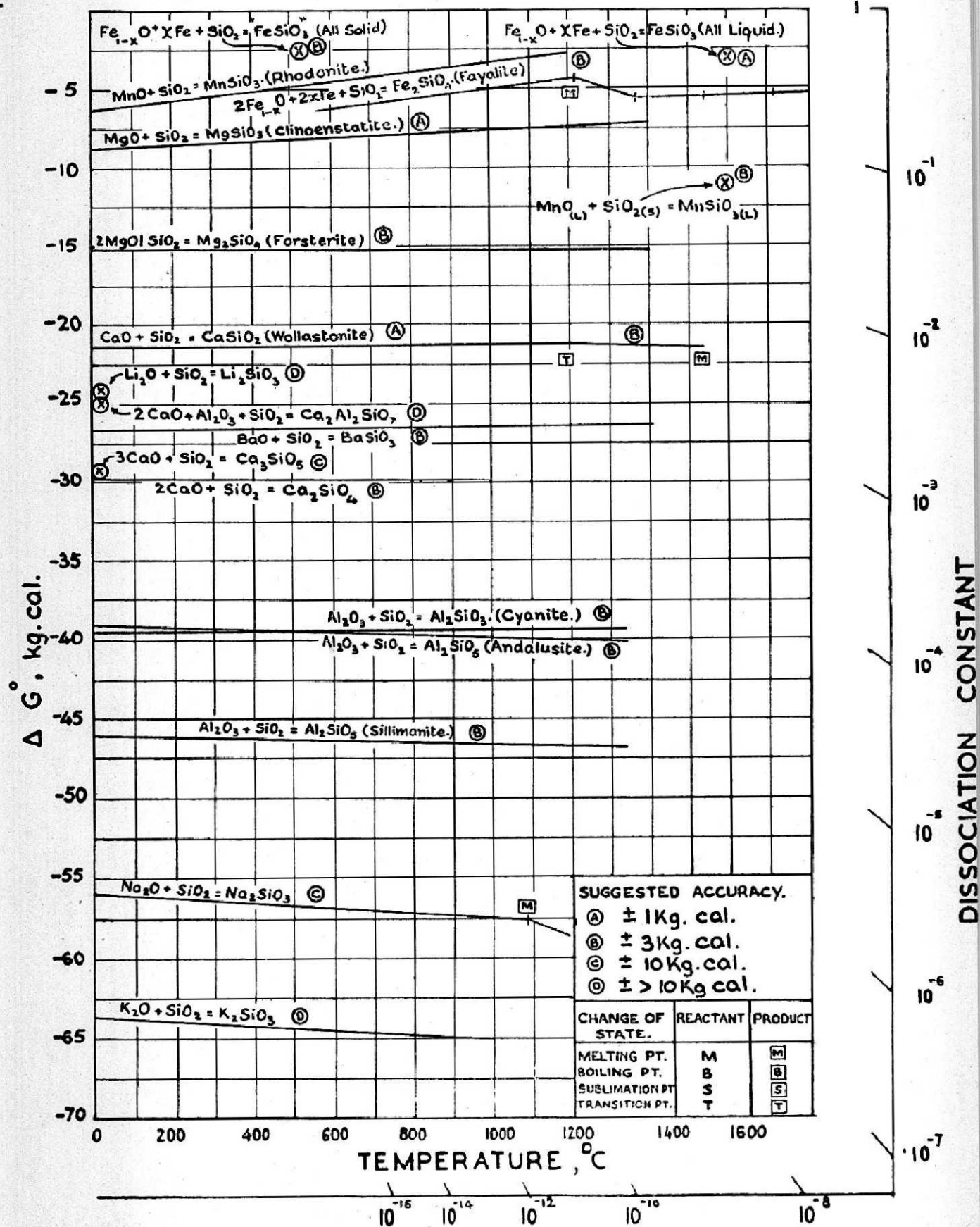


FIG. 9

of $\text{ZnCl}_2\text{-PbCl}_2$ is ideal, the activity of ZnCl_2 was taken as its mole fraction. Similarly, the activity of PbCl_2 was assumed as its mole fraction of 0.017 while the a_{Zn} accepted as the reported value of $29N_{\text{Zn}}$. Substituting these values in equation (47) Kellog⁵ found that under equilibrium conditions, 0.00066 per cent zinc should be present in the lead. In view of the assumptions made, the discrepancy between the theoretical value and that obtained in practice is not great.

Recently a vacuum distillation¹⁵ process for separating silver from silver-zinc alloy obtained from Parkes's process has been described. The principle of separation by vacuum distillation depends on the difference of vapour pressures of the metals concerned. As the vapour pressures of lead and zinc are much higher than that of silver, distillation under vacuum at 800°C . can separate lead and zinc from metallic silver.

Vacuum dezincing of desilverized lead bullion has also been developed at the St. Joseph Lead Company and the Broken Hill Associated Smelters (South Australia). This is carried out under a vacuum of 0.01-0.1 mm. mercury, when the zinc atoms from the bullion surface diffuse out to a neighbouring condensing surface. The design of the apparatus ensures that there is no resistance to the flow of zinc vapour apart from that due to the residual gas pressure within the vacuum dezincer. Davey¹⁶ has discussed the fundamental aspects of vacuum distillation processes with special reference to vacuum dezincing and has shown that the actual removal of zinc in practice has reasonably good agreement with theoretical calculations.

Summary

The application of thermodynamic principles to some of the chemical reactions involved in the metallurgy of lead has been made to

illustrate the importance of thermodynamics and free energy data in studying chemical reactions of value in extraction and refining of metals. It has been mentioned that chemical thermodynamics can predict the course of chemical reaction and enables to calculate the value of equilibrium constant. The application to practical problems depends on the availability of activity data. In this brief article it has not been possible to discuss all applications of physical chemistry to the extractive metallurgy of lead. The reproduction of standard free energy charts of various compounds in this paper should bring together for ready reference useful thermodynamic data scattered in the technical literature, which may be applied on similar lines to other cases than the metallurgy of lead extraction, provided the simplifying assumptions made in this treatment are, and remain, valid.

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The authors wish to record their indebtedness to those authorities in this field whose works have been referred to in the text. They are specially indebted to Richardson and Jeffes and Kellog and Osborn for their diagrams which have been reproduced.

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