

THERMODYNAMICS OF LEAD-SILICATE SLAGS SATURATED WITH SiO₂

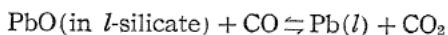
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I. Introduction

The binary system PbO-SiO₂ is the simplest of systems relating to important chemical properties of the slags formed in lead smelting in blast furnace. From this standpoint, an experimental study of this system has been started as the first step of a general research program on the thermodynamics of lead smelting. The equation for this study may be written as follows:



Then the equilibrium constant becomes equal to $K = P_{\text{CO}_2}/P_{\text{CO}}$. a_{PbO} , where a_{PbO} is activity of PbO. When the molten silicate is saturated with SiO₂, a_{PbO} is constant. In this study, $P_{\text{CO}_2}/P_{\text{CO}}$ was determined and from the values obtained, a_{PbO} was calculated by the equilibrium relation mentioned above.

II. Materials

Gases: CO₂ was generated in Kipp's apparatus by the reaction of hydrochloric acid on marble. CO was generated by the reaction of formic acid on heated sulphuric acid.

Lead monoxide: Lead monoxide was prepared by igniting the crystals of lead nitrate in air at 500° ~ 700°C; the latter were purified by the recrystallization of the commercial grade.

Silica: The powder of anhydrous SiO₂ was used.

Slag: The oxide mixture of lead monoxide 65% and silica 35% was melted in an alumina crucible lined by silica powder. In order to perfect the slag formation of the oxide mixture, the melt was stirred by bubbling CO₂ gas into it for 2 hrs before using as a slag in experimental measurement of the activity of PbO.

III. Experimental Procedure

The experimental arrangement is shown in Fig. 1. In what follows the description of each part is made.

A: a system for circulating the gas by raising and lowering the mercury reservoir.

B, C: a glass bulb for solidifying carbon dioxide by cooling it with liquid oxygen.

D: a glass bulb, the volume of which is known.

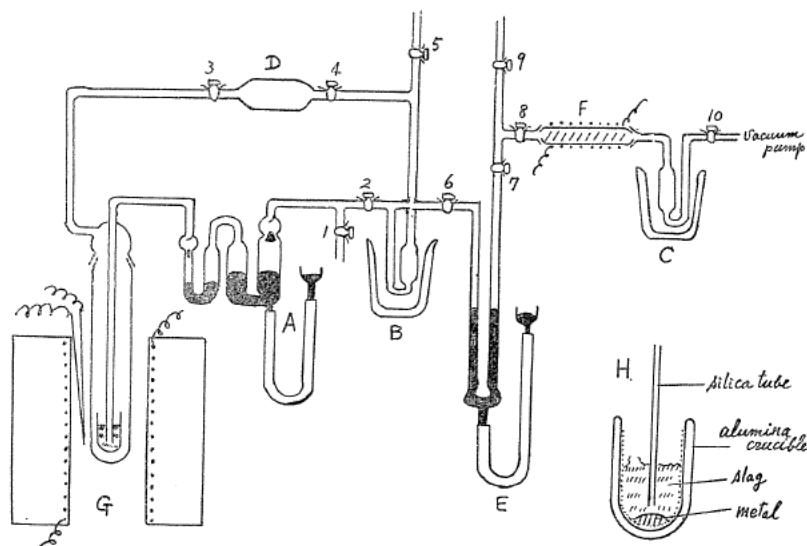


FIG. 1. Experimental arrangement.

E: a mercury manometer having mercury reservoir.

F: a net of cupper oxide contained in a quartz tube which was heated by electric furnace at about 600°C .

G: a reaction system consisting of a resistance furnace and a silica reaction tube (4×50 cm). A long silica tube, 3 mm in diam., was inserted in the reaction tube.

The alumina crucible containing ca. 15 gms of the slag prepared previously and ca. 1~2 gms of lead was placed in the reaction tube, and then the whole system was evacuated. When high vacuum was attained, the cocks 5 and 6 were closed and the gaseous mixture whose composition was near to the expected equilibrium value, was admitted into the reaction tube through the cock 1, and then the circulation system was made to operate and the reaction tube was heated to the operating temperature by the furnace whose temperature was controlled at constant temperature by hand regulation within $\pm 2^{\circ}\text{C}$.

The slag was stirred by the circulating gas bubbled into it as shown in Fig. 1, *H*. Each experiment usually lasted for 4 hrs, equilibrium being attained in the first 2 hrs in most tests.

Analysis of Gases: analysis was carried out for the gas enclosed in the bulb *D*. After the cocks 2, 3 and 4 were closed, and the mercury level in the manometer was lowered to the part of the leg, the bulbs *B*, *C* and the part connecting the both bulbs were evacuated. When high vacuum was attained, keeping evacuation, the cocks 5 and 9 were closed and bulbs *B* and *C* were cooled with liquid oxygen, and then the cock 4 was opened as slow as possible. In consequence, CO_2 contained in the gas was solidified in the bulb *B*, while CO was oxidized by heated cupric oxide and caught in the bulb *C*. Raising the mercury level in the manometer, CO_2 in the bulb *B* was vapourized and its pressure in the original volume was observed at the room temperature.

Having measured the pressure of CO₂, the bulb *B* was evacuated through the cock 5 to about 10⁻⁴ mm Hg, and then the gas in the bulb *C* was solidified in the bulb *B* by keeping evacuation and cooling it with liquid oxygen again. After high vacuum was attained, the pressure of CO₂ vapourized in the bulb *B* was observed. Since the ratio of the volume of *B* to that of *D* is known, the pressure of CO in the original volume can be calculated.

IV. Results

The results obtained are shown as a whole in Table 1. In Fig. 2, the relation

TABLE 1. Results of Experimental Measurement

Temp. °C	1/T 10 ⁴	P _{CO₂} mm Hg	P _{CO} mm Hg	log P _{CO₂} /P _{CO}	K	log K
780	9.497	434.9	0.301	3.1650	5,285	3.723
		635.0	0.600	3.0220		
		623.7	0.800	2.8915		
		249.7	0.351	2.8519		
820	9.149	532.1	0.849	2.7973	3,828	3.583
		492.7	0.600	2.9143		
		296.1	0.390	2.7917		
880	8.673	522.0	0.819	2.8041	2,692	3.430
		563.8	0.842	2.8258		
		563.8	0.876	2.8089		
		530.5	0.890	2.7753		
920	8.382	537.6	1.027	2.7193	1,837	3.264
		501.6	1.033	2.6863		
		564.5	1.270	2.6484		

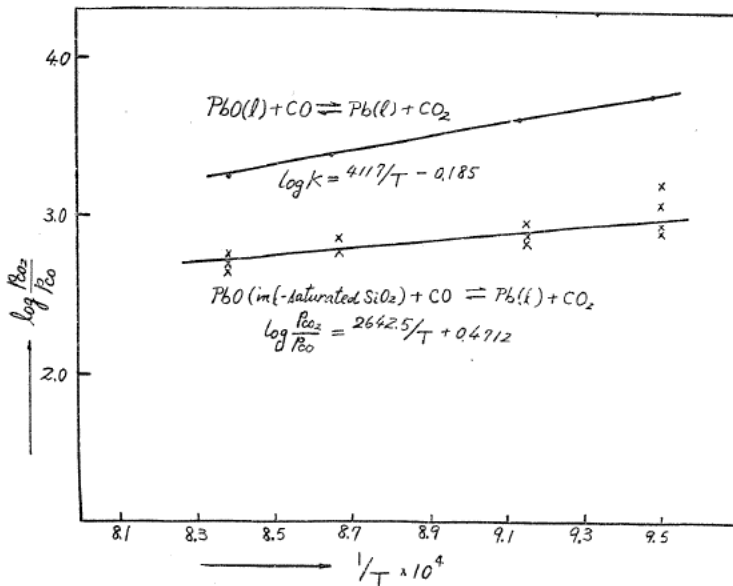
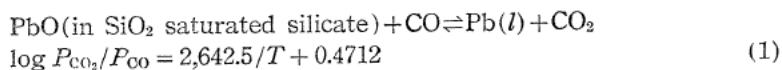
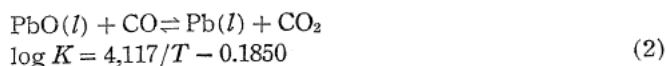


FIG. 2. Relation between log K_p and 1/T.

between $\log Kp$ and $1/T$ expressed by a straight line in the range of experimental temperature is shown, and the straight line thus obtained is expressed as follows:



Regarding to the equilibrium constant of reduction of the pure oxide by CO, W. Lange¹⁾ calculated the following equation:



From the equations (1) and (2), the activity of PbO in the SiO₂-saturated melt with reference to the pure oxide may be expressed by the following equation:

$$\log a_{\text{PbO}} = -1,474.5/T + 0.656 \quad (3)$$

From the phase diagram,²⁾ the relation of solubility of PbO (mol-fraction) with temperature is shown in Fig. 3 and the straight line obtained can be expressed as follows;

$$\log N_{\text{PbO}} = 298.1/T - 0.698 \quad (4)$$

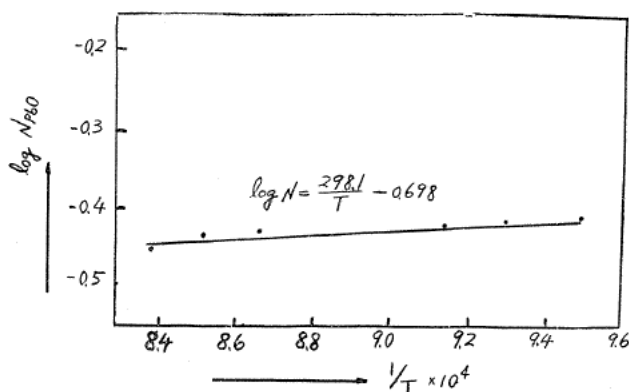


FIG. 3. Relation between mol fraction of PbO in lead-silicate saturated with SiO₂, and temperature.

Subtracting the equation (4) from (3), the activity coefficient of PbO may be expressed as follows:

$$\log \gamma_{\text{PbO}} = \log (a/N) = -1,773/T + 1.354 \quad (5)$$

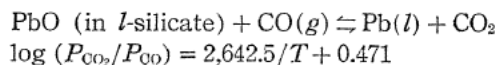
In Table 2, the experimental values with regard to the activity and the activity coefficient of PbO are compared with those calculated from the equations (3) and (5).

TABLE 2. Activity Coefficient of PbO in Lead-Silicate Saturated with SiO₂

$t^{\circ}\text{C}$	$a_{\text{exp.}}$	$a_{\text{calc.}}$	$\gamma_{\text{exp.}}$	$\gamma_{\text{calc.}}$
780	0.190	0.180	0.494	0.468
820	0.180	0.207	0.468	0.539
880	0.237	0.238	0.642	0.657
920	0.264	0.263	0.748	0.736

V. Summary

1. The reduction equilibrium of lead oxide in the lead-silicate saturated with SiO_2 by carbon monoxide was studied at several temperatures ranging from 780° to 920°C and the following equation for the relation between the equilibrium constant and the temperature was obtained.



2. The activity and the activity coefficient of lead monoxide in liquid lead-silicate saturated with SiO_2 were determined as follows:

$$\log a_{\text{PbO}} = -1,474.5/T + 0.656$$
$$\log \gamma_{\text{PbO}} = -1,773/T + 1.3537$$

References

- 1) W. Lange, Die thermodynamischen Eigenschaften der Metalloxyde (1949), 61.
- 2) F. P. Hall and H. Insley; Phase Diagrams for Ceramists. Amer. Cer. Soc. (1949), 157.