

DISTRIBUTION OF Cu AND Pb BETWEEN COPPER ALLOYS AND FLASH SMELTING SLAG

J. Botor, J. Czernecki, and A. Zaj'czkowski

Institute of Non-Ferrous Metals, Gliwice, Poland

Abstract

Equilibrium in the liquid metallic phase-slag phase heterogeneous system was examined. The Cu-Pb binary alloys and three-component Cu-Pb-Fe alloys were used. The slag phase were aluminium oxide saturated solutions: $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$, $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-FeO}_x$ and $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-FeO}_x$ type. Slag composition was close to that of slag from a single-stage flash smelting process sulphidic copper concentrates.

The examination was made at the temperature of 1673 K and the oxygen potential in a gaseous phase ranged from $2.70 \cdot 10^{-11}$ to $3.23 \cdot 10^{-7}$ atm. Composition of the alloys and aluminium oxide saturated slags were determined by chemical analysis. The results obtained were used to determine copper and lead distribution ratio between slag and metallic phases.

Introduction

Examination of thermodynamic equilibrium in heterogeneous liquid metallic phase-molten oxide phase systems is interesting both from scientific and applicational point of view. Metallurgical slags are a class of liquids whose properties and structure have not been yet sufficiently identified and therefore, they are still subject of intensive studies.

In copper extractive metallurgy, the fayallite $\text{SiO}_2 - \text{FeO} - \text{Fe}_2\text{O}_3$ type slags with an addition of Al_2O_3 , MgO and CaO are regarded as particularly interesting. They are present in most technologies for the copper production and therefore, they were subject of many studies [1-7]. On the other hand, there are very few reports on systematic investigation into the $\text{SiO}_2 - \text{CaO} - \text{Al}_2\text{O}_3$ type slags, which are produced e.g. during a single stage process of smelting Polish copper concentrates and are characterised by low iron content and considerable content of lead. The available literature data on these systems are very fragmentary and inconsistent [8-11]. Therefore, the present study was intended to systematically explore the equilibrium state in the systems composed of a liquid metallic phase (Cu-Fe-Pb) and the $\text{SiO}_2 - \text{CaO} - \text{Al}_2\text{O}_3$ type slag phase with MgO and FeO_x as additives. Positive results of the experiments which were planned to be carried out might contribute not only to solving an interesting scientific problem but also to improving technological conditions of the copper production process.

Experimental

Materials

The Cu-Pb master alloy was prepared from pure metals containing at least 99.96 mass. % Cu or Pb. Metals were melted in graphite crucibles under the protective atmosphere of argon, and the liquid metal obtained was kept at 1473 K for 30 minutes. Analytically pure silicon, calcium and aluminium oxides, pre-roasted at about 1473 K for two hours, were used to prepare slag. Next, 400 g weighed portions were rubbed and melted in corundum crucibles at about 1723 K or 1823 K in dependence on the silica content. The obtained slag contained 41.6-61.7 mass. % SiO_2 , 24.8-40.0 mass. % CaO , and 13.5-18.5 mass. % Al_2O_3 . Detailed chemical composition of the $\text{SiO}_2 - \text{CaO} - \text{Al}_2\text{O}_3$ slags, denoted ES, SD and EC, respectively, is shown in Table 1. In case of experiments with slags containing iron oxide and magnesium oxide, their appropriate amounts were earlier added to the pre-prepared $\text{SiO}_2 - \text{CaO} - \text{Al}_2\text{O}_3$ slags. These oxides were also analytically pure, the iron oxide was preliminary dried at about 473 K and magnesium oxide was roasted at about 1573 K. The gases used in the experiments were of the following purity : CO_2 – 99.7 vol. % minimum, CO - 99.0 vol. % minimum, and argon was of a “pure” class.

Equipment

A vacuum-tight electric furnace and a system for proportioning of $\text{CO}_2 + \text{CO}$, shown in Figs 1 and 2, were main components of the experimental installation. Their detailed specifications can be found in previous papers [12,13]. A vacuum-tight vertical pipe furnace was resistance-heated by means of the Kanthal Super 1800⁰C elements. The furnace was fitted with a programmable heating system, and the temperature was measured by the EL18 thermocouple located over the crucible with a sample examined. The sample was put on a crucible from sintered alumina, 40 mm in diameter and 60 mm high. The crucible was inserted into a shield crucible fixed on the alundum stand. A gas mixture of $\text{CO}_2 + \text{CO}$ was supplied over examined sample by a capillary tube. A gas proportioning system (Fig. 2) comprised a Balzers partial pressure controller consisting of two quadrupole spectrometers (QMS 064, QME 064 and QMA 064), two control valves (RME 010), gas agitator (M) and

flow controllers (RVG 040). The system enabled supplying determined amounts of gases to the agitation chamber in order to obtain required partial pressures of CO and CO₂. Before and after each experiment, the measuring circuit was scanned with the use of a manometer with an accuracy of 1 torr.

Collecting data

Experiments were made with eight slag types, whose chemical composition is shown in Table 1. About 30 g of metal alloy and from 30 g to 60 g of slag were used during each test. Equilibrium in the metal-slag system was reached within 39-60 hours depending on a slag mass. Next, the sample was rapidly quenched to the room temperature in the protective atmosphere of argon, a slag phase was separated from the metallic phase and samples for the chemical analysis were randomly taken.

The contents of lead and iron in the alloy were determined by AAS. The same analytical method was used to determine the contents of copper, lead and iron in the slag, and the content of aluminium oxide was determined by the complexometric method. For the two-phases GX slag, the calcium oxide content for each phase was determined by titration, and the contents of silicon oxide and magnesium oxide – by weighing. The contents of the latter oxides in the remaining slags were obtained from calculations based on the data on weighed amounts used to prepare the slag.

Distribution ratio

The distribution ratio of the metallic element (Me) between the slag and metallic phases $L_{Me}^{s/m}$ is defined as follows :

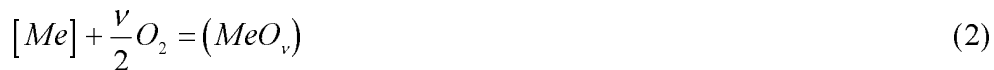
$$L_{Me}^{s/m} = \frac{(mass.\%Me)}{[mass.\%Me]} \quad (1)$$

where :

(mass. % Me) – Me content in the slag phase in mass. %,

[mass.% Me] – Me content in the metallic phase in mass. %

Assuming that Me is present in the slag phase in a form of oxides as a result of the chemical reaction :



where ν denotes stoichiometric coefficient, whose value depends on metal oxidation degree, the following equilibrium constant for the reaction (2) is obtained :

$$K_{\nu} = \frac{Q_{(MeO_{\nu})}}{Q_{[Me]}} = \frac{\gamma_{(MeO_{\nu})} \cdot x_{(MeO_{\nu})}}{\gamma_{[Me]} \cdot x_{[Me]} \cdot P_{O_2}^{\nu/2}} \quad (3)$$

Partial pressure of oxygen in the gaseous phase is determined by the following reaction:



The change of free enthalpy of the reaction (4) is [6]:

$$\Delta G^{\circ} = -282420 + 86.82 \cdot T \quad (5)$$

where T denotes absolute temperature in K.

The mole fractions can be calculated from the relationship:

$$x_{(Me)} = \frac{(mass.\%Me) / M_{Me}}{(n_T)} \quad (6)$$

and

$$x_{[Me]} = \frac{[mass.\%Me] / M_{Me}}{[n_T]} \quad (7)$$

where : n_T is the total number of moles in 100 g of the metallic [] or slag () phase, and M_{Me} is an atomic mass of the component Me.

The final relationship for the distribution ratio has the following form:

$$I_{Me}^{s/m} = \frac{\gamma_{[Me]} \cdot (n_T)}{[n_T]} \cdot \sum_v (P_{O_2}^{v/2} \cdot K_v) / \gamma_{(MeO_v)} \quad (8)$$

Results of measurements

The measurements were made at the temperature of 1673 ± 5 K and at the oxygen potential in the gaseous phase ranging from $2.70 \cdot 10^{-11}$ to $3.23 \cdot 10^{-7}$ atm. The molar ratio of the slag types examined $(X_{MgO} + X_{CaO}) / X_{SiO_2}$ ranged from 0.43 to 1.03, and the maximum content of iron was 7.5 mass. %. After the tests, the contents of lead and iron in the metallic phase, and the contents of copper, lead, iron and aluminium oxide in the slag phase was determined for each sample. Separation into two immiscible slag phases was observed at higher oxygen partial pressures in the five component $SiO_2 - CaO - Al_2O_3 - MgO - FeO_x$ slags, denoted GX. These phases, denoted GX' and GX'' had the chemical composition shown in Table 2.

The contents of particular components of the metallic and slag phases were used to calculate the distribution ratio. Equation (8) was used to determine metallic and oxidic components of the distribution ratio, denoted $I_{Me(Me)}^{s/m}$ and $I_{Me(MeO_v)}^{s/m}$, respectively, which are given in Tables 3 and 4. In the latter table, the oxygen potential is also given.

Discussion of results

The values of the distribution ratio of copper and lead between the metallic Cu-Pb and Cu-Pb-Fe phase and the slag phase were determined at the temperature of 1673 K and at the oxygen partial pressure ranging from $2.70 \cdot 10^{-11}$ to $3.23 \cdot 10^{-7}$ atm. The slag phase was of the $SiO_2 - CaO - Al_2O_3 - MgO - FeO_x$ type, and saturated with aluminium oxide. The molar ratio $(X_{MgO} + X_{CaO})/X_{SiO_2}$ ranged from 0.43 to 1.03, and the maximum iron content was 7.5 mass. %. Based on the experimental data, estimated values of metallic and oxidic components of the distribution ratio of copper and lead were determined. Equation (8) was used to determine both components of the distribution ratio showing for the oxidic component that copper was present in slag in a form of $CuO_{0.5}$ and lead -as PbO .

In case of the $SiO_2 - CaO - Al_2O_3$ type slags with the ES composition, the metallic component was close to zero in reference both to copper and lead, contrary to the EC type slag in which practically all metal contained in it had a metallic form. Analysis of the relationship between the X_{CaO}/X_{SiO_2} ratio and the value of oxidic component of the distribution coefficient showed that both $CuO_{0.5}$ and PbO are of alkaline character, which referred to PbO in greater degree than to $CuO_{0.5}$. The distribution coefficient values obtained in this study were several times lower than those reported in previous works [8,9].

In case of the $SiO_2 - CaO - Al_2O_3 - FeO_x$ type slag, copper and lead were present in a form similar to that in the ES, SD and EC type slags. The presence of iron in these slags

resulted in significant increase of copper and lead contents in a form of oxides, which can be concluded from comparison of the distribution coefficient values for the SN and SX slags and those for the SD slag.

In case of the $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-FeO}_x$ slag with the composition corresponding to that of GX slag, two separate slag phases are observed at the oxygen partial pressure over 10^{-8} atm. This observation is in agreement with earlier reports on the behaviour of this type of slag [13].

Moreover, significant effect of the iron content on the amount of copper and lead contained in a form of oxides in the slag phase has been found. When composition of the slag phase changes from SD to GS, the distribution coefficient for lead oxide increases by one order of magnitude and that for copper oxide practically does not change. This leads to the conclusion that lead oxide in the $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-FeO}_n$ type slag is more alkaline than $\text{CuO}_{0.5}$. Full thermodynamic analysis of the metal-slag systems examined will be presented in the paper which is already being prepared [14].

Acknowledgements

This research has been supported by the National Committee for Scientific Research (KBN) sponsored Project No. 7 T08B 023 10. The financial support is gratefully acknowledged.

References

1. J.M.Toguri, N.H.Santander: Metall.Trans. 3, 1972, 586
2. M.Nagamori, P.J.Mackey, P.Tarassoff: Metall.Trans.B. 6B, 1975, 295
3. M.Nagamori, P.J.Mackey: Metall.Trans.B. 8B, 1977, 39
4. J.Elliot, J.B.Sec, W.J.Rankin: Trans.Inst.Min.Metall., 87, 1978, C 204
5. T.Oishi, M.Kamuo, K.Ono, J.Moriyama: Metall.Trans.B, 14B, 1983, 101
6. H.G.Kim, H.Y.Sohn: Metall.Mater. Trans. B, 29B, 1998, 583
7. S.A.Degterov, A.D.Pelton: Metall.Mater. Trans. B. 30B, 1999, 661
8. M.Kucharski: Met.Technol., 11, 1979, 354
9. W.Ptak, J.Czernecki: Arch.Hutn., 26, 1981, 213
10. T.Pomianek, St.Sobierajski, Zb.Ćmieszek, J.Czernecki: IMN Reports, 7, 1978, 114
11. M.Kucharski: Arch.Metall., 32, 1987, 27
12. J.Botor, J.Kapryan, T.Mazur: Rudy Metale, 35, 1990, 190
13. A.Zaj'czkowski, J.Czernecki: Rudy Metale, 40, 1995, 174
14. A.Zaj'czkowski, J.Botor, J.Czernecki: Can.Metall.Q. (in preparation)

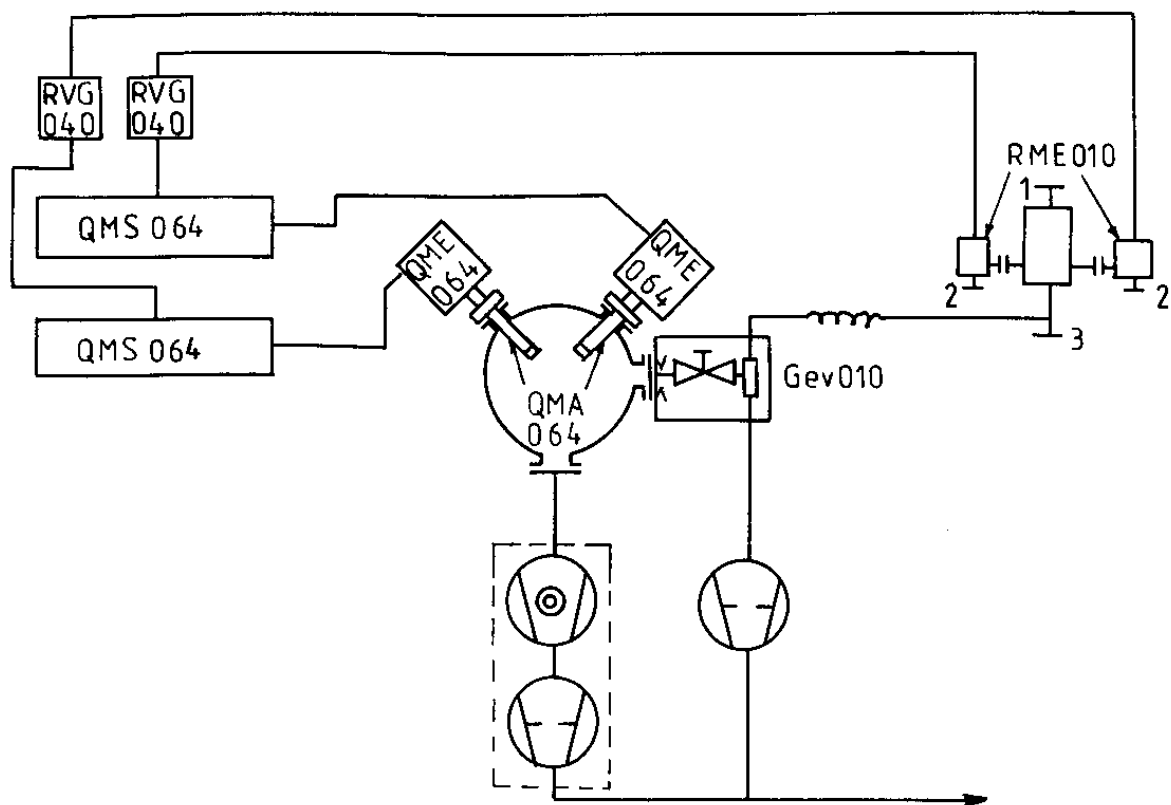


Fig. 1. Schematic diagram of the Balzer's partial pressure controller

1. Argon inlet, 2. CO, CO₂ inlet, 3. CO+CO₂+Ar outlet

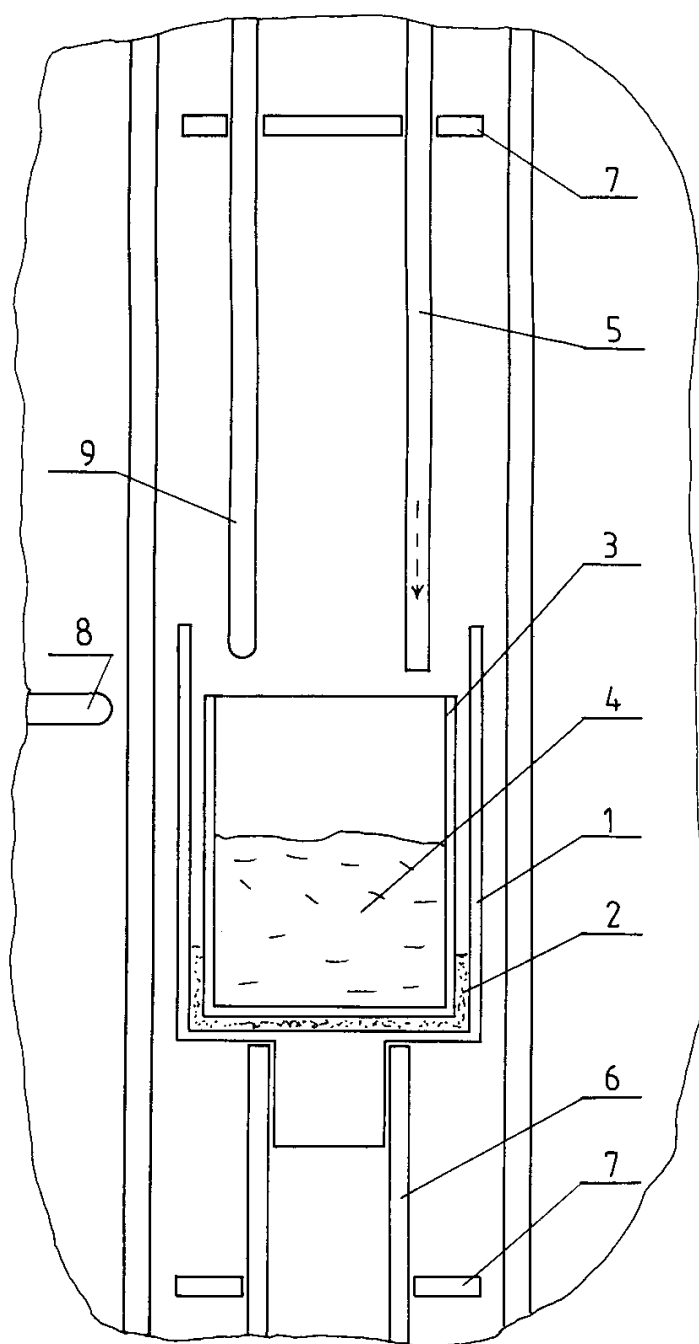


Fig. 2. Schematic diagram of a reaction chamber of the experimental apparatus

1. Shielding crucible, 2. Al₂O₃ powder, 3. Alundum crucible, 4. Sample, 5. Capillary, 6. Alundum stand, 7. Screens, 8. Control thermocouple, 9. Thermocouple

No.	Slag	Contents (in mass.%)				
		SiO ₂	CaO	Al ₂ O ₃	MgO	Fe ₂ O ₃
1	2	3	4	5	6	7
1	ES	61.70	24.80	13.50		
2	SD	47.90	35.60	16.60		
3	EC	41.60	40.00	18.50		
4	SN	44.43	33.02	15.40		7.15
5	SX	42.73	31.76	14.81		10.70
6	GS	50.15	20.16	17.39	12.30	
7	GF	46.72	18.72	16.14	11.42	7.15
8	GX	44.77	18.00	15.52	10.98	10.73

Table 1. Chemical composition of the slags

Table 2. Chemical composition of two phases of the GX type slag

Sample	Component	Contents in mass.% (GX')	Contents in mass.% (GX'')
1	2	3	4
GX 06	Cu	2.56	5.25
	Pb	0.16	1.23
	Fe	4.38	8.88
	Al ₂ O ₃	15.92	16.91
	SiO ₂	49.66	36.01
	CaO	18.57	14.15
	MgO	6.46	11.89
GX 07	Cu	0.82	2.13
	Pb	0.12	0.55
	Fe	4.69	9.69
	Al ₂ O ₃	16.97	17.32
	SiO ₂	48.30	35.96
	CaO	19.65	15.63
	MgO	9.12	14.20

Table 3. Values of the metallic component of the copper and lead distribution ratio

No	Type of		$L_{Cu(Cu)}^{s/m}$	$L_{Pb(Pb)}^{s/m}$
	slag	alloy		
1	2	3	4	5
1	ES	Cu-Pb	0	0
2	SD	Cu-Pb	$7.1E-4 \pm 1.25E-4$	$8.7E-3 \pm 1.56E-3$
3	EC	Cu-Pb	$8.6E-4 \pm 2.42E-4$	$5.2E-3 \pm 1.18E-3$
4	SN	Cu-Pb-Fe	0	0
5	SX	Cu-Pb-Fe	$2.8E-3 \pm 1.68E-3$	$14.6E-2 \pm 6.32E-2$
6	GS	Cu-Pb	$2.5E-4 \pm 1.65E-4$	$5.3E-3 \pm 1.79E-3$
7	GF	Cu-Pb-Fe	0	0
8	GX'	Cu-Pb-Fe	0	0
9	GX''	Cu-Pb-Fe	0	0

Table 4. Values of the oxidic component of the distribution ratio

No.	Sample	P_{O_2} / atm	$L_{Cu(CuO_{0.5})}^{s/m}$	$L_{Pb(PbO)}^{s/m}$
1	2	3	4	5
1	SD 01	$1.64 \cdot 10^{-08}$	8.184E-4	9.774E-4
2	SD 03	$2.67 \cdot 10^{-07}$	1.026E-3	2.520E-3
3	SD 05	$2.78 \cdot 10^{-11}$	2.477E-4	
4	SD 06	$4.54 \cdot 10^{-10}$	5.243E-5	5.410E-3
5	SD 09	$2.88 \cdot 10^{-09}$	2.809E-4	
6	SD 11	$4.20 \cdot 10^{-10}$	1.232E-4	
7	ES 01	$2.00 \cdot 10^{-08}$	2.957E-3	4.639E-2
8	ES 02	$1.85 \cdot 10^{-08}$	2.656E-3	3.223E-2
9	ES 03	$3.09 \cdot 10^{-07}$	9.168E-3	8.197E-2
10	ES 04	$2.94 \cdot 10^{-09}$	6.744E-4	5.140E-3
11	ES 06	$2.84 \cdot 10^{-11}$	5.522E-4	2.489E-3
12	ES 07	$5.18 \cdot 10^{-10}$	4.484E-4	9.091E-3
13	ES 10	$2.34 \cdot 10^{-09}$	3.546E-4	4.077E-3
14	SN 10	$2.57 \cdot 10^{-07}$	2.282E-2	5.252E-1
15	SN 11	$1.66 \cdot 10^{-08}$	4.312E-3	2.073E-2

Table 4. Continuation

Expt. No	Sample	P_{O_2} / atm	$L_{Cu(CuO_{0.5})}^{s/m}$	$L_{Pb(PbO)}^{s/m}$
1	2	3	4	5
16	SN 12	$2.78 \cdot 10^{-09}$	2.984E-3	1.146E-2
17	SN 13	$4.43 \cdot 10^{-10}$	5.593E-3	3.537E-2
18	SN 14	$2.71 \cdot 10^{-11}$	4.531E-4	6.731E-3
19	SX 04	$2.63 \cdot 10^{-07}$	2.125E-2	3.302E-1
20	SX 05	$1.68 \cdot 10^{-08}$	1.086E-2	5.575E-2
21	SX 06	$2.68 \cdot 10^{-09}$	1.053E-2	4.000E-3
22	SX 07	$4.30 \cdot 10^{-10}$	8.938E-4	
23	SX 08	$2.79 \cdot 10^{-11}$	3.569E-3	
24	SX 09	$3.01 \cdot 10^{-11}$	1.358E-3	2.143E-1
25	GS 01	$2.80 \cdot 10^{-11}$	3.822E-4	
26	GS 04	$2.72 \cdot 10^{-07}$	2.304E-3	1.184E-2
27	GS 05	$1.78 \cdot 10^{-08}$	8.757E-4	5.665E-3
28	GS 06	$2.84 \cdot 10^{-09}$	8.724E-4	4.700E-3
29	GS 07	$4.33 \cdot 10^{-10}$	2.787E-4	
30	GF 01	$2.99 \cdot 10^{-11}$	2.442E-3	8.844E-3

Table 4. Continuation

Expt. No	Sample	P_{O_2} / atm	$L_{Cu(CuO_{0.5})}^{s/m}$	$L_{Pb(PbO)}^{s/m}$
1	2	3	4	5
31	GF 03	$2.54 \cdot 10^{-09}$	3.993E-3	2.570E-2
32	GF 04	$1.74 \cdot 10^{-08}$	5.012E-3	4.000E-2
33	GF 05	$2.42 \cdot 10^{-07}$	1.261E-2	2.410E-1
34	GX' 01	$2.88 \cdot 10^{-11}$	2.678E-3	1.233E-2
35	GX' 02	$4.85 \cdot 10^{-10}$	3.997E-3	1.905E-2
36	GX' 03	$2.73 \cdot 10^{-09}$	7.668E-3	6.635E-2
37	GX' 05	$2.71 \cdot 10^{-07}$	3.402E-2	5.714E-1
38	GX' 06	$2.64 \cdot 10^{-07}$	2.572E-2	3.404E-1
39	GX' 07	$2.01 \cdot 10^{-08}$	8.337E-3	7.317E-2
40	GX'' 05	$2.71 \cdot 10^{-07}$	4.911E-2	2.476E-0
41	GX'' 06	$2.64 \cdot 10^{-07}$	5.275E-2	2.617E-0
42	GX'' 07	$2.01 \cdot 10^{-08}$	2.166E-2	3.354E-1