MOLTEN LITHIUM CARBONATE–SODIUM CARBONATE–POTASSIUM CARBONATE EUTECTIC: THE REACTION OF TEN MAIN GROUP ACIDIC OXIDES AND OXYANIONS

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ABSTRACT

    The reactions of ten main group acidic oxides and oxyanions with molten alkali metal carbonate eutectics have been studied by thermogravimetry. Products have been identified by IR and Raman spectroscopy and stoichiometries suggested for the several reactions as oxide is progressively incorporated. Ultimately the tetrahedral ortho-oxyanion was formed except with the less acidic oxides (As_2O_3, Sb_2O_3, SiO_2). Sulphite was partially oxidised by the carbon dioxide atmosphere to sulphate.

INTRODUCTION

The chemistry of molten alkali metal carbonates is at present very largely unknown, even though such melts when containing dissolved cyanide have been used for many years as baths for the carburizing of steel, and to some extent in preparative high temperature chemistry as highly basic solvents when the oxyanions of the less acidic oxidation states of transition metals are required. An important potential use which has received some attention in recent years is to act as the electrolyte of high temperature fuel cells. In addition to such applications, molten carbonates have definite interest in their own right as oxyanion melts of basic character.

Currently occasional measurements have been made in carbonate melts in the course of other investigations often as a comparison to the behaviour of the same reactant in another melt, while more systematic studies have been electrochemical and thus concerned with more dilute solutions. The major recent work has been carried out in the U.S. by Lorenz and Janz[1,2] and in the U.S.S.R. by Smirnov and his school[3-9]. The earlier work has been reviewed by Janz[10].

A systematic investigation of the inorganic chemistry of molten carbonates has now been started with this study of the reaction of acidic oxides and oxyanions of the main group elements. The results are compared on the one hand with those in

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the less basic and much lower melting nitrate and with the higher melting sulphate melts and on the other hand with the interaction, where known, of the acid with carbonate when both are dissolved in melts which act as relatively inert solvents, in practice mainly in alkali metal chloride melts.

EXPERIMENTAL

Materials

Aralar lithium carbonate, sodium carbonate and potassium carbonate (B.D.H.) were dried at 130°C for 4 h, cooled in a desiccator, mixed in the eutectic ratio (32.1:33.4:34.5 wt.%, respectively) and melted, in small quantities, in a platinum crucible at 500°C. The melt was kept under a carbon dioxide atmosphere for 5 h, solidified and finely ground in a dry box.

The acidic reagents of Analar ($K_2S_2O_8$, $K_2S_2O_5$, As_2O_3) or laboratory reagent quality ($NaPO_3$ insoluble form, $K_4P_2O_7$, As_2O_5, Sb_2O_3), all B.D.H., were dried at 120°C for 12 h. Phosphorus pentoxide (B.D.H.) and silica (Koch-Light) were used as received. Potassium pyrosulphate was prepared by heating Analar potassium persulphate to 250°C for 24 h (98.3% purity by titration).

Procedure

Reactions were carried out in 10 ml platinum or gold crucibles on a Stanton TR-1 thermobalance under a carbon dioxide atmosphere (flow rate 300 ml min^{-1})
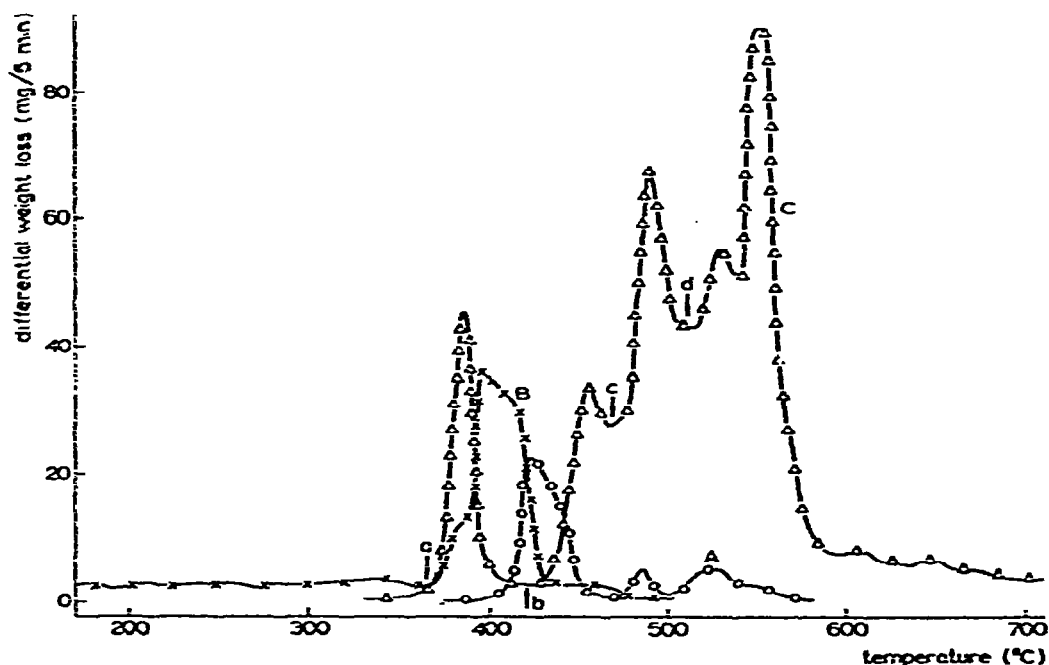

Fig. 1. Thermogravimetry of phosphates in lithium carbonate–sodium carbonate–potassium carbonate eutectic. Curve A, —O—O—O 0.88 m $K_4P_2O_7$; B, —×—×—× 0.56 m P_2O_5; C, —△—△—△ 8.4 m $NaPO_3$.

using a heating rate of 2° per minute. All reactants were "sandwich" mixed, a layer of powdered reactant being placed on a layer of melt and in turn covered with another layer of melt.

Infrared spectra were taken of powdered solidified reacted melts pressed into thin discs with potassium bromide, on a Unicam SP200 or a Perkin-Elmer 225 spectrometer. Raman spectra were obtained from the powdered reacted melts with a Cary-82 instrument using an argon laser.

RESULTS AND DISCUSSION

Potassium pyrophosphate reacted with the carbonate eutectic evolving carbon dioxide from 380°C, i.e. just below melting point of the pure eutectic, but probably the latter would be somewhat lowered when phosphates dissolved. Thermogravimetric analysis (Fig. 1, curve A) gave an average weight loss of 13.3% which corresponds to the stoichiometry

$$P_2O_7^{4-} + CO_3^{2-} \rightarrow 2\,PO_4^{3-} + CO_2 \tag{1}$$
(Calc. weight loss 13.3%)

The reacted solution solidified to an off-white solid which gave IR lines (Table 1) close to those of orthophosphate.

As would be expected phosphorus pentoxide was more strongly acidic and commenced reacting with the solid eutectic from 120°C but thermogravimetric analysis showed a very considerable increase in rate of carbon dioxide evolution (Fig. 1, curve B) which although below the melting point of the pure eutectic was probably at or close to the onset of melting. The loss at this point, marked (a), averaged 12.6% well below that calculated for formation of metaphosphate (31.0%), however, the total weight loss found (94.9%) was close to that calculated for eqn. (2), i.e. 93.0%

$$P_2O_5 + 3\,CO_3^{2-} \rightarrow 2\,PO_4^{3-} + 3\,CO_2 \tag{2}$$

The pale grey quenched melt (Table 1) gave somewhat similar IR bands as before. Sodium metaphosphate, as the insoluble form containing long chain polyphosphate anions, started to react at an intermediate temperature (350°C), the thermogram (Fig. 1, curve C) displaying a number of maxima. The overall weight loss averaged 43.4% which was close to that of stoichiometry

$$PO_3^- + CO_3^{2-} \rightarrow PO_4^{3-} + CO_2 \tag{3}$$
(Calc. weight loss 43.2%)

The pale grey quenched melt also showed IR bands similar to orthophosphate (Table 1) though differing from that found previously probably because of varying cations. The first and second minima of the thermograms (b and c on Fig. 1, curve C) at around 6.2 and 9.5% were not too far from those expected from the formation of penta- and tetraphosphate (8.6 and 10.8%) but the third minima (d) was much

TABLE 1

VIBRATIONAL SPECTRA OF PRODUCTS FROM REACTIONS WITH LITHIUM CARBONATE–SODIUM CARBONATE–POTASSIUM CARBONATE EUTECTIC

Reactant	Maximum temp. (°C)	Equation	IR	Raman (cm⁻¹)	Ref.
$K_4P_2O_7$	570	1	552 (br, s)		11,24
			888 (m)		
			927 (br, vs)		
			972 (s)		
			1020 (m)		
			1110 (br, s)		
P_2O_5	490	2	584 (s)		24
			605 (s)		
			889 (m)		
			1030 (br, s)		
P_2O_5	365		883 (m)		11
			1027 (br, vs)		
			1075 (s)		
$NaPO_3$	600	3	580 (br, s)	580 (45)	11,24
			680 (m)	941 (100)	
			887 (m)	1066 (60)	
			1035 (vbr, vs)		
$NaPO_3$	470		637 (w)	950 (30)	11
			756 (w)	1070 (100)	
			888 (w)	1171 (20)	
			1015 (br, s)		
			1095 (s)		
			1155 (br, w)		
			1305 (br, w)		
$NaPO_3$	430		471 (br, s)	694 (30)	11
			513 (s)	946 (25)	
			598 (s)	1055 (50)	
			700 (s)	1073 (100)	
			742 (m)	1157 (40)	
			887 (m)		
			1050 (br, s)		
			1090 (s)		
			1155 (s)		
			1290 (s)		
$K_2S_2O_8$	270	5	584 (br, s)	327 (65)	25
			540 (m)	517 (6)	
			790 (br, m)	748 (7)	
			1045 (s)	1056 (8)	
			1095 (s)	1101 (100)	
			1255 (s)		
			1287 (s)		
$K_2S_2O_8$	420		616 (vs)	986 (100)	24
			1110 (br, s)	1075 (23)	
				1094 (14)	
$K_2S_2O_7$	390	6	616 (vs)	455 (30)	24
			1110 (br, s)	620 (30)	
			1150 (s)	984 (100)	

Table 1 *(continued)*

Reactant	Maximum temp. (°C)	Equation	IR	Raman (cm^{-1})	Ref.
				1074 (45)	
				1091 (40)	
				1103 (30)	
				1147 (20)	
K$_2$S$_2$O$_3$	300	9	622 (s)	155 (40)	11
			700 (m)	987 (50)	
			964 (br, vs)	997 (40)	
			1105 (br, s)	1056 (95)	
				1076 (100)	
				1094 (50)	
K$_2$S$_2$O$_3$	400		617 (vs)	155 (60)	24
			1110 (br, vs)	454 (20)	
				623 (20)	
				985 (60)	
				995 (60)	
				1076 (100)	
				1097 (45)	
As$_2$O$_5$	460	10	687 (m)		11
			825 (br, s)		
As$_2$O$_3$	530	11	494 (br, m)		11
			685 (m)		
			822 (vbr, s)		
SiO$_2$	980		690 (m)		11
			830 (m)		
			1000 (br, s)		
SiO$_2$ in Na$_2$CO$_3$/K$_2$CO$_3$	1040		730 (w)		11
			940 (s)		
			1040 (s)		

Intensities: vs, very strong; s, strong; m, medium; br, broad, w, weak.

closer to the formation of pyrophosphate 21.1%, and the vibrational bands (Table 1) supported this[11].

$$2\,PO_3^- + CO_3^{2-} \rightarrow P_2O_7^{4-} + CO_2 \qquad (4)$$
(Calc. weight loss 21.6%)
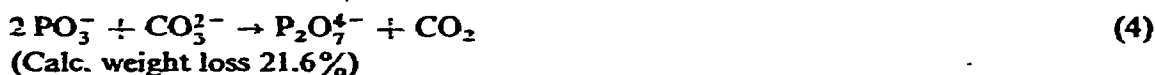
This acid–base behaviour is quite similar to that observed both in potassium nitrate at 350°C[12] and in sodium chloride–potassium chloride at 700°C[13], where pyrophosphate and orthophosphate were formed when sodium metaphosphate was neutralised with sodium carbonate, though in addition, in the former tripolyphosphate was formed initially and in the latter system the novel $(PO_3 \cdot 2O)^{5-}$ ion was claimed. An analogous neutralisation to pyro- and then orthophosphate had previously been found in alkali metal nitrate eutectics[14], but because of the lower basicity of the latter melts, the reactions occurred at higher temperatures.
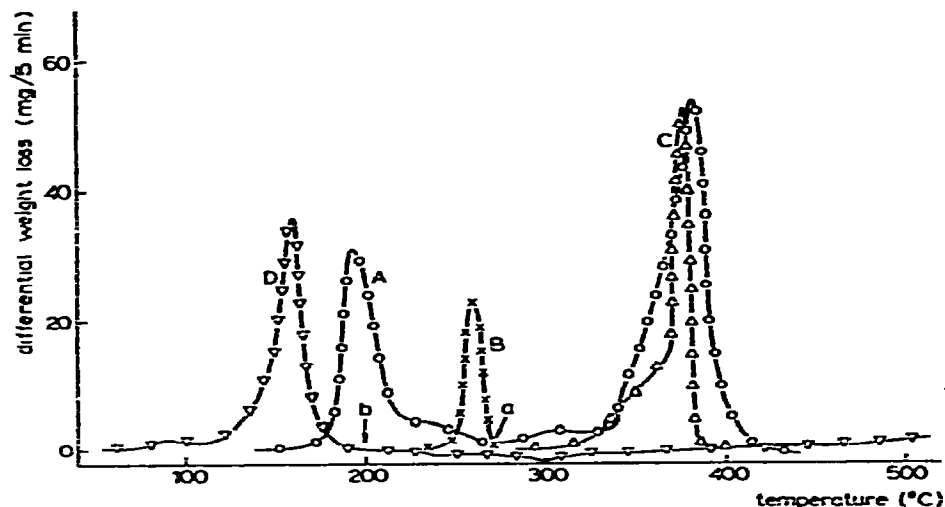
Fig. 2. Thermogravimetry of sulphur compounds in lithium carbonate–sodium carbonate–potassium carbonate eutectic. Curve A, —○—○—○ 1.1 m $K_2S_2O_8$; B, —×—×—× 0.45 g $K_2S_2O_8$ alone; C, —△—△—△ 1.6 m $K_2S_2O_7$; D, —▽—▽—▽ 1.9 m $K_2S_2O_5$.

Potassium persulphate reacted with two clear maxima (Fig. 2, curve A), the first corresponding to the loss of oxygen with the weight

$$K_2S_2O_8 \rightarrow K_2S_2O_7 \div \tfrac{1}{2} O_2 \tag{5}$$

(Calc. weight loss 5.95%)

loss to (a) being 6.0%. Some interaction with the melt seems likely as the temperature of thermal decomposition of the potassium persulphate without melt (Fig. 2, curve B) is some 60° higher. The second weight loss at or just below the melting point of the carbonate eutectic corresponded to the acid–base reaction

$$S_2O_7^{2-} \div CO_3^{2-} \rightarrow 2 SO_4^{2-} \div CO_2 \tag{6}$$

(Calc. weight loss 22.2%)

since the experimental loss was 22.4% and the white quenched melt gave vibrational bands like those found for sulphate (Table 1). A very similar reaction was found with potassium pyrosulphate (Fig. 2, curve C) with an experimental weight loss of 16.9% (Calc. for loss of CO_2 per $K_2S_2O_7$ 17.3%). In contrast, in a nitrate melt ($NaNO_3/KNO_3$ at 300°C) the reaction of pyrosulphate with carbonate has been reported to occur only to a small extent[16] while in a chloride melt (LiCl/KCl at 500°C) potassium persulphate was reduced directly[17] and pyrosulphate liberated sulphur trioxide.

$$S_2O_8^{2-} \div 2 Cl^- \rightarrow 2 SO_4^{2-} \div Cl_2 \tag{7}$$

$$Na_2S_2O_7 \rightarrow Na_2SO_4 \div SO_3 \tag{8}$$

Potassium *meta*-bisulphite initially reacted from 100°C with a loss of weight

(Fig. 2, curve D) which averaged 19.9% to (b) and corresponded to the formation of sulphite,

$$\dot{S}_2O_5^{2-} + CO_3^{2-} \rightarrow 2SO_3^{2-} + CO_2 \tag{9}$$

(Calc. weight loss 19.8%)

the vibrational bands of the white quenched melt (Table 1) being characteristic of sulphite (the solid also reducing acidic dichromate to chromium(III)). The gas evolution was followed by a slow weight gain which ceased at the melting point of the eutectic, at which point the quenched melt showed bands characteristic of sulphate as well as of sulphite. In agreement the weight gain from (b) of 4.5% was only a third of that required for complete formation of sulphate (Calc. for gain of O_2 per $K_2S_2O_5$ 14.4%).

The slow oxidation must be attributed to the carbon dioxide atmosphere having some difficulty in contacting the solid sulphite, though the sudden cessation on melting indicating that this gas had even more difficulty penetrating the melt, partly because of low solubility, a value of 0.1 mol l^{-1} is quoted for the ternary eutectic at 500°[15], and probably partly because of a slow solution step.

A reaction analogous to eqn. (9) has been reported in sodium nitrate–potassium nitrate at 300°C[16] though it was not found to go to completion. Oxidation of sulphite to sulphate in the presence of oxide by copper(II) and chromium(VI) oxide has also been reported[17], while the interaction of sulphur dioxide with molten carbonates has been the subject of several studies[18-20] where sulphite and sulphate were the products.
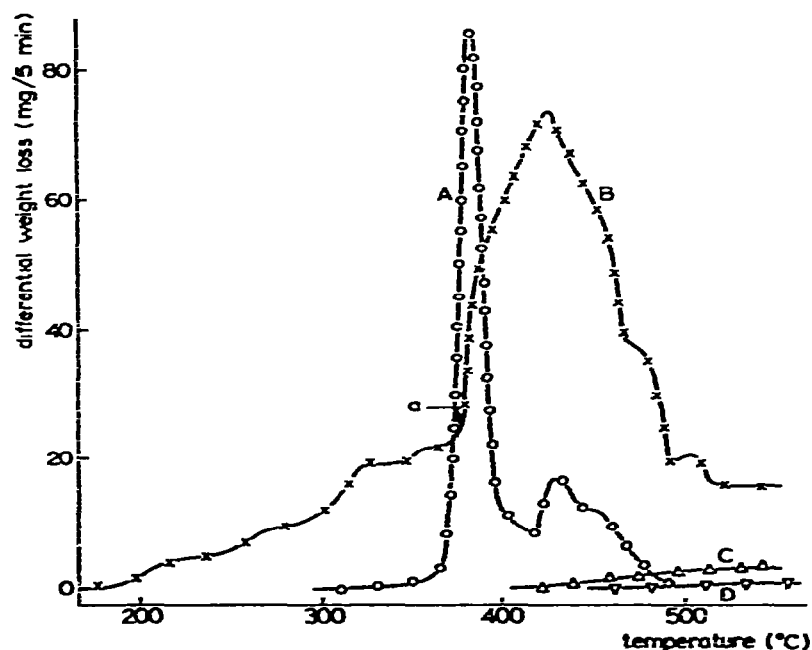

Fig. 3. Thermogravimetry of arsenic, antimony and silicon oxides in lithium carbonate–sodium carbonate–potassium carbonate eutectic. Curve A, —O—O—O 1.0 m As_2O_3; B, —×—×—× 3.7 m As_2O_3; C, —△—△—△ 0.61 m Sb_2O_3; D, —▽—▽—▽ 1.90 g melt alone.

Arsenic(V) oxide reacted rapidly probably with the molten, as opposed to solid, carbonate if some lowering of the eutectic melting point may be postulated (Fig. 3, curve A). The weight loss of 58.2% corresponded to that for the reaction

$$As_2O_5 + 3\,CO_3^{2-} \rightarrow 2\,AsO_4^{3-} + 3\,CO_2 \qquad (10)$$
(Calc. weight loss 57.5%)
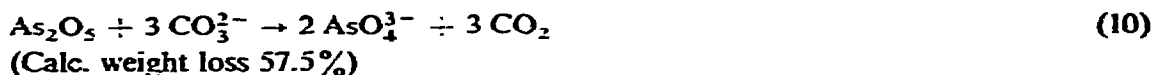
the creamy white quenched melt showing the absorptions (Table 1) of orthoarsenate. Arsenic(III) oxide reacted from a lower temperature with the solid carbonate (Fig. 3, curve B), but much more rapidly after melting, the weight loss of 44.4% being close to the formation of pyroarsenite, again illustrating the less acidic nature of this arsenic oxide as did the higher temperature of the maximum.

$$As_2O_3 + 2\,CO_3^{2-} \rightarrow As_2O_5^{4-} + 2\,CO_2 \qquad (11)$$
(Calc. weight loss 44.5%)

No comparisons are available for the reaction of these oxides with carbonate when dissolved in other melts, though arsenic(V) oxide is known to react as a Lux-Flood acid with molten nitrate forming metaarsenate which on titration with a base (sodium peroxide) formed the orthoarsenate[21].

In contrast antimony(III) oxide did not react, no weight loss being apparent to 430°C (Fig. 3, curve C) though some loss was observed at higher temperatures and at rates rather faster than a pure eutectic (Fig. 3, curve D) attributed to catalysis by the oxide. In molten potassium nitrate at 350°C the rate of reaction of antimony(V) oxide, expected to be more acidic than the lower oxide, was also found to be very slow even with added sodium peroxide[22].
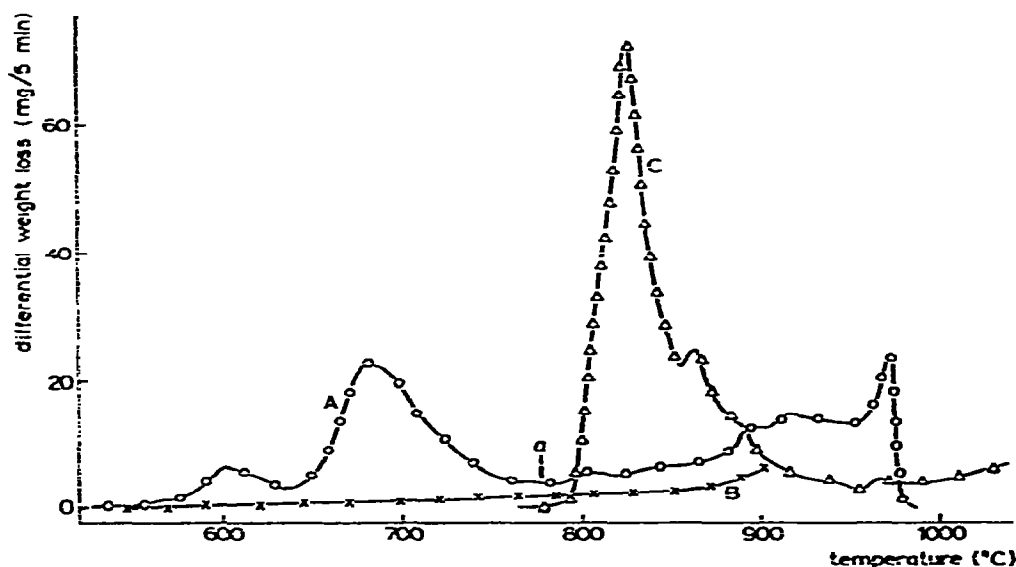

Fig. 4. Thermogravimetry of silica in carbonate eutectics. Curve A, —O—O—O— 1.1 m SiO₂ in Li₂CO₃/Na₂CO₃/K₂CO₃; B, —×—×—×— 1.90 g Li₂CO₃/Na₂CO₃/K₂CO₃; C —△—△—△— 1.9 m SiO₂ in Na₂CO₃/K₂CO₃.

The reaction of silica was also very slow (Fig. 4, curve A), not beginning until 510°C, well above the melting point. After the major maximum the weight loss, 73.2% at (a), corresponded closely to the formation of metasilicate

$$SiO_2 + CO_3^{2-} \rightarrow SiO_3^{2-} + CO_2 \tag{12}$$

(Calc. weight loss 73.25%)

Weight loss continued though more slowly probably to form orthosilicate ultimately but the overall weight loss was no longer diagnostic owing to thermal decomposition of the carbonate eutectic itself (Fig. 4, curve B). Electrochemical measurements have also shown the reaction to be slow[23], orthosilicate not being completely formed even after 6 h at 1100°C in sodium carbonate (O^{2-} to SiO_2 ratio equalled 1.8). In the sodium carbonate–potassium carbonate binary eutectic the rate of weight loss (Fig. 4, curve C) was initially much slower than in the ternary eutectic (curve A), the weight loss to 1000°C not quite reaching the value for formation of metasilicate, only averaging 63.7%.

REFERENCES

1 P. K. Lorenz and G. J. Janz, *J. Electrochem. Soc.*, 116 (1969) 1061.
2 P. K. Lorenz and G. J. Janz, *Electrochim. Acta*, 15 (1970) 1025, 2001.
3 T. I. Manukhima, I. N. Ozeryanaya and M. V. Smirnov, *Zashch. Met.*, 5 (1969) 228.
4 M. V. Smirnov, I. Y. Lyubimtseva and L. A. Tsvovkina, *Electrokhimiya*, 7 (1971) 566.
5 I. N. Ozeryanaya, L. A. Tsvovkima and M. V. Smirnov, *Zashch. Met.*, 8 (1972) 128.
6 O. P. Penyagina, I. N. Ozeryanaya, M. V. Smirnov, B. S. Shibanov, and N. D. Shamanova, *Zashch. Met.*, 8 (1972) 312.
7 M. V. Smirnov, L. A. Tsvovkina and I. U. Lyubimtseva, *Tr. Inst. Elect-okhim., Ural. Nauchn. Tsentr. Akad. Nauk S.S.S.R.*, 18 (1972) 122.
8 V. A. Oleinikova, L. A. Tsvovkina and M. V. Smirnov, *Tr. Inst. Electrokhim. Ural. Nauchn. Tsentr. Akad. Nauk S.S.S.R.*, 19 (1973) 65.
9 I. N. Ozeryanaya, T. I. Manukhina and O. P. Penyagina, *Fiz. Khim. Elektrokhim.*, 2 (1973) 94, 96.
10 G. J. Janz, *J. Chem. Educ.*, 44 (1967) 581.
11 R. A. Nyquist and R. O. Kagel, *Infrared Spectra of Inorganic Compounds*, Academic Press, New York, 1971.
12 A. M. Shams El Din, H. D. Taki El Din and A. A. El Hosary, *Electrochim. Acta*, 13 (1968) 407.
13 Y. K. Delimansky, V. I. Shapoval and O. G. Tsiklouri, *Ukr. Khim. Zh.*, 40 (1974) 8. .
14 D. A. Habboush and D. H. Kerridge, *Thermochim. Acta*, 10 (1974) 187.
15 P. K. Lorenz and G. J. Janz, *Electrochim. Acta*, 15 (1970) 1025.
16 M. Fredericks and R. B. Temple, *Aust. J. Chem.*, 25 (1972) 2319.
17 G. Delarue, *Bull. Soc. Chim. Fr.*, 1960, 906.
18 R. A. McIlroy and G. A. Attwood, *Environ. Sci. Technol.*, 7 (1973) 1022.
19 S. Y. Yosim, L. F. Grantham, D. E. McKenzie and G. C. Stegmann, *Adv. Chem. Ser.*, 127 (1973) 174.
20 R. D. Oldenkamp and E. D. Margolin, *Chem. Eng. Prog.*, 65 (1969) 73.

21 A. M. Shams El Din, A. A. El Hosary and A. A. A. Gerges, *J. Electroanal. Chem.*, 8 (1964) 312.
22 A. M. Shams El Din and A. A. El Hosary, *J. Electroanal. Chem.*, 7 (1964) 404.
23 E. Franks and A. Mukhergee, *J. Appl. Electrochem.*, 3, (1973) 179.
24 E. Steger and W. Schmidt, *Ber. Bunserges. Phys. Chem.*, 68 (1964) 102.
25 A. Simon and H. Wagner, *Z. Anorg. Allg. Chem.*, 311 (1961) 102.