

Vapour Pressure of Silicon Tetrafluoride above Mixtures of Fluorides and Silica

II. The System $\text{PbF}_2\text{—SiO}_2$

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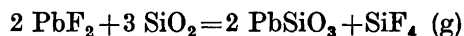
The vapour pressure of silicon tetrafluoride produced in the reaction between lead fluoride and silica in the solid state has been measured by means of the transport method. The results can be represented by the equation

$$R'T \log(p_{\text{SiF}_4}/\text{atm}) = 26\,700 - 19.6 T$$

in the temperature range 462–590°C. From X-ray investigations Pb_4SiO_6 was identified as the main product.

The phase relations of the reciprocal ternary system $\text{PbF}_2\text{—PbO—SiO}_2\text{—SiF}_4$ are only partly investigated. In the binary system PbO—SiO_2 Gellner, Creamer and Bunting¹ confirmed the existence of the three lead silicates, PbSiO_3 , Pb_2SiO_4 , and Pb_4SiO_6 , as later verified by Argyle and Hummel.² The X-ray patterns of the lead silicates are known.³

If other conceivable lead silicates and possible fluosilicates are absent in the relevant system it is reasonable to assume the following equilibrium established when a mixture of silica and lead fluoride is heated



This reaction between PbF_2 and SiO_2 is suggested by Lieser and Rosenbaum⁴ for the preparation of SiF_4 . The reaction is reported to proceed readily at temperatures above 380°C.

EXPERIMENTAL

The transport method was employed for the vapour pressure measurements. For details concerning the principles and the method the reader is referred to a previous paper.⁵ The apparatus used was identical with the one described as furnace B in the

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quoted paper.⁵ The silicon tetrafluoride was determined chemically. The gas was passed through a 10 % hydrofluoric acid solution contained in perspex cylinders, where the silicon tetrafluoride was dissolved, forming fluosilicic acid.

Chemicals. The following qualities were used in the present investigation: Lead fluoride, E. Merck, Suprapur quality. Silica, E. Merck, *pro analysi* washed and calcined.

The silica was ground in an agate mortar to pass No. 100 mesh sieve, then dried at 250° over night. The lead fluoride was dried the same way. The dried reagents were weighed in the desired ratio, thoroughly mixed, pressed into briquets which were broken into small lumps to prepare the charges for the equilibrium pressure measurements. Each charge weighed from 50 to 70 g. Two compositions were used, one with 85 weight % PbF_2 , and the other with 73 weight % PbF_2 . The extent of reaction did not in any case exceed 5 %.

Argon (99.99 % pure, supplied by Norsk Hydro-Elektrisk Kvælstofaktieselskab) was used as carrier gas.

RESULTS

The initial experiments to establish the optimal gas flow rate were carried out at 590°C. The results are presented in Fig. 1. The vapour pressure is

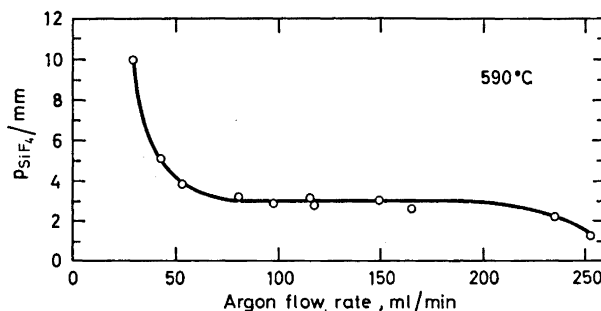


Fig. 1. Effect of flow rate on apparent vapour pressure at 590°C.

independent of the flow rate between 80 and 150 ml/min. From this a flow rate of 100 ml/min was chosen for the ensuing experiments.

The vapour pressure was measured at constant flow rate and varying temperatures between 460° and 590°C. Preliminary experiments established the non-existence of a liquid phase in this temperature range.

Results obtained are shown in Fig. 2. Using the method of least squares a straight line was fitted to the experimental points, the equation of which being

$$\log p_{\text{SiF}_4}/(\text{atm}) = 4.28 - 5830/T$$

From this the heat of reaction, ΔH_r° , is calculated to +26.7 kcal, and the entropy change ΔS_r° is +19.6 e.u./mole.

The reaction products in the solid phase were identified from X-ray diffraction patterns of samples heated in a stream of dry argon. In samples heated at 590°C for 6 h Pb_4SiO_6 was identified as the main product. The strongest line for Pb_2SiO_4 was also identified. Prolonged heating gave stronger X-ray pattern for this compound. Only in a sample containing 27 % SiO_2 ,

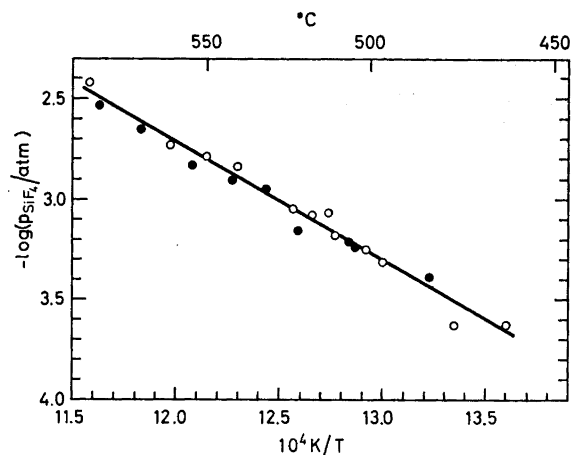


Fig. 2. Vapour pressure of SiF_4 above the system PbF_2 - SiO_2 . Open circles: 15 wt. % SiO_2 . Filled circles: 27 wt. % SiO_2 .

heated for 24 h at 600°C , was PbSiO_3 detected. Several unidentified strong lines in all the X-ray patterns examined indicate the presence of unknown reaction products, possibly some lead fluosilicate compounds.

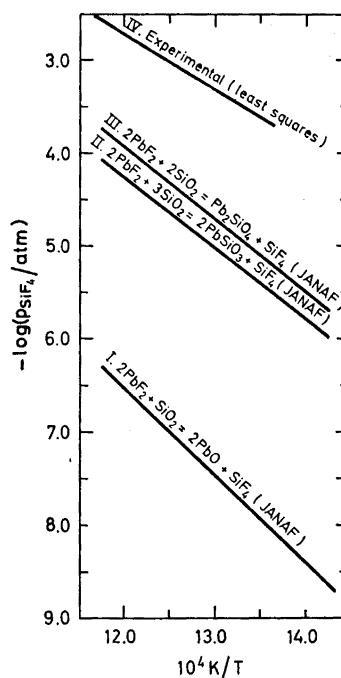


Fig. 3. Comparison between various calculated $\log p$ values and the experimental.

DISCUSSION

Whereas the equilibrium phases are expected to be PbF_2 , SiO_2 , PbSiO_3 , and SiF_4 , in fact no PbSiO_3 was detected in the X-ray diffractograms of the samples from the vapour pressure measurements. The question is, therefore, if one actually has investigated a true equilibrium, or just a metastable one. If the reaction had been allowed to proceed for sufficient time all lead silicate would of course be present as metasilicate in the end. The equilibrium measurements, however, lasted for a relatively short time.

Thermodynamic data for the relevant compounds except Pb_4SiO_6 are available in JANAF tables.⁶ For each of these reactions $\log p$ values may be calculated by means of the relation

$$\ln p = -\Delta G^\circ/RT$$

In Fig. 3. vapour pressure curves calculated for three different reactions are drawn together with the experimental values.

The fact that the experimental vapour pressure is higher than the calculated indicates that there is possibly a third equilibrium, however metastable, which governs the vapour pressure, provided that the thermodynamical data employed are reliable. This may involve, *e.g.*, the metastable phase Pb_4SiO_6 . The complexity of the lead-silicon-fluorine-oxygen system prevents the understanding of the actual reactions. The X-ray patterns of the reaction product show several unidentified lines, so that the formation of some lead fluosilicate complex cannot be excluded.

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