Vapour Pressure of Silicon Tetrafluoride above Mixtures

of Fluorides and Silica

I. The System CaF_2—SiO_2

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The vapour pressure of silicon tetrafluoride produced in the reaction between calcium fluoride and silica in the solid state in the temperature range 1107—1240°C has been measured by means of the transport method. The results can be expressed by the equation

$$R'T \log(p_{SiF_4}/\mathrm{atm}) = 48\,400 - 22.7\,T$$

From X-ray diffractograms $Ca_3Si_2O_7$ and Ca_2SiO_4 were identified together with $CaSiO_3$ as reaction products.

The system CaF_2—SiO_2 has been investigated by several authors, and treated in various ways. The most straightforward conception of the system is a simple binary system. Hillert [1] considered it as such, and found a eutectic at 1240°C at the composition 47 % SiO_2—53 % CaF_2 along with several ternary compounds.

In this system, however, silicon occurs together with fluorine, so that one has to take into account silicon tetrafluoride when discussing the system. Thus, at equilibrium there will be more than two phases present. In fact, the system will be found somewhere within the reciprocal ternary system SiO_2—CaF_2—SiF_4—CaO, although CaO most probably is not the fourth phase. As SiF_4 is volatile it is more practical to consider the system as a pseudo ternary system (Fig. 1). Each of the two binary joints SiO_2—CaO and CaO—CaF_2 is rather well known. Parts of the pseudo ternary phase diagram have also been investigated.[2,3] The part of the system which is relevant in this connection is SiO_2—CaF_2—$CaSiO_3$, as we will expect to find the reaction products at equilibrium in this region. The system is not well known, however. Bååk and Ölander [4] investigated the joint $CaSiO_3$—CaF_2, regarding it as a simple binary system with one eutectic. In the system CaF_2—$CaSiO_3$—Ca_2SiO_4

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the compound $3CaO \cdot 2SiO_2 \cdot CaF_2$ is reported as a defined, ternary compound,[5] corresponding to the mineral cuspidine.

It is concluded, then, that when SiO_2 and CaF_2 react, forming SiF_4, the fourth equilibrium phase at the outset must be $CaSiO_3$ as the system will be found inside the triangle $SiO_2-CaF_2-CaSiO_3$ in the phase diagram. The equilibrium reaction is thus

$$3 \; SiO_2 + CaF_2 = 2 \; CaSiO_3 + SiF_4(g) \qquad (1)$$

all components, except SiF_4, being in the solid state.

EXPERIMENTAL

Method. The equilibrium pressure of silicon tetrafluoride above mixtures of calcium fluoride and silica was measured by means of the transport method. An inert gas is passed at constant flow rate and pressure over the system at constant temperature.
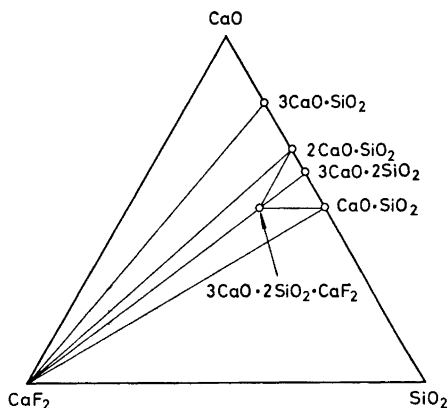

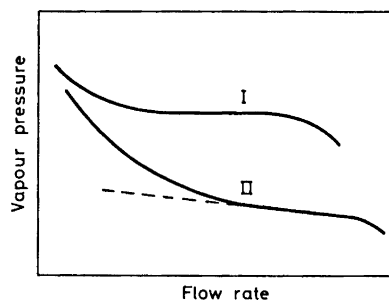Fig. 1. The pseudo-ternary system CaF_2-SiO_2-CaO, diagrammatical.

Fig. 2. Different types of vapour pressure/flow rate curves:

I: with a plateau (vapour pressure independent of flow rate)
II: with no horizontal part (vapour pressure in no region independent of flow rate).

The carrier gas transports the vapour being formed, out of the system to a region where the vapour either condenses, or otherwise is collected quantitatively. If one assumes ideal gases, and the carrier gas saturated with the vapour in question, the vapour pressure, p_v, is given according to Dalton's law by the equation

$$\frac{p_v}{p_t} = \frac{p_v}{p_v + p_c} = \frac{n_v}{n_v + n_c}$$

p_t being the total pressure of the system, p_c the pressure of the carrier gas, and n referring to the number of moles of each. Thus, if the molecular weight of the vapour is know, and the amount of carrier gas is known, the vapour pressure may be calculated.

The crucial point of these experiments is the saturation of the vapour. When a reaction in the solid state is involved, this is particularly critical. Saturation of the vapour may be checked in the following way: The vapour pressure above the system (or more correctly: the apparent vapour pressure) is measured at constant temperature, but at various flow rates. A diagram of vapour pressure as a function of the flow rate of the gas will then ideally appear as shown in Fig. 2 (curve I). If the flow rate drops below a certain value, the fraction of vapour molecules which is transported by means of gaseous diffusion will become of importance. The consequence is that the apparent vapour pressure is too high. On the contrary, if the flow rate is too high, the vapour becomes unsaturated, and the apparent vapour pressure is lower than the equilibrium pressure. Such a series of experiments indicates the optimum flow rate for the measurements.

Unfortunately, the diagram of the experimental vapour pressure as a function of the gas flow rate does not always show this ideal shape. At times it is found that the apparent vapour pressure varies with flow rate throughout the whole range. If the curve exhibits a part which is linear (although not horizontal) one may assume that extrapolation of this linear part to zero flow rate will give the correct equilibrium vapour pressure. This assumption cannot be given a rigid theoretical justification, but the extrapolation as mentioned is about the best one can do when the curve does not have a horizontal plateau.
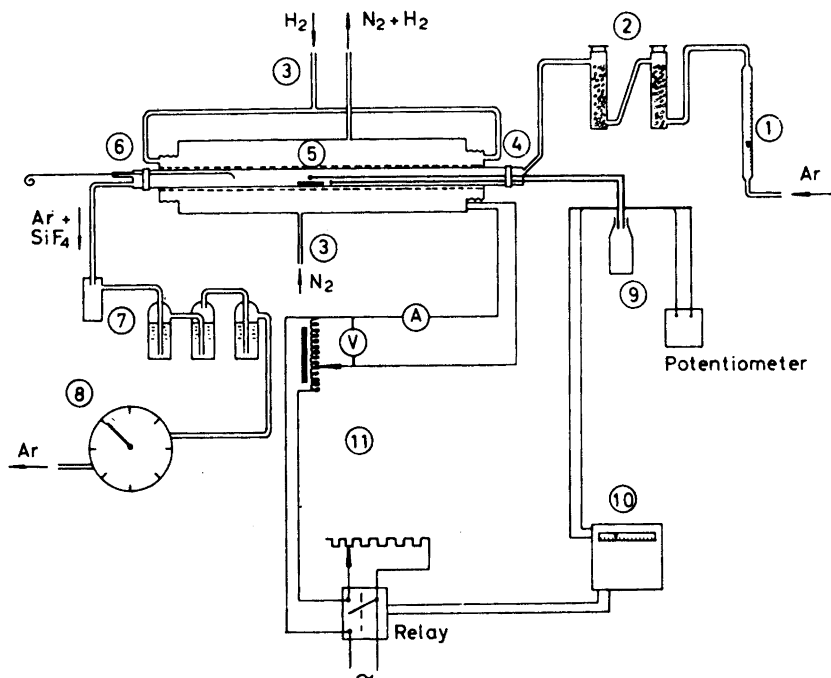

Fig. 3. Apparatus for transport measurements (furnace shown is type A, molybdenum windings).

1. Rotameter.
2. Purification train (Dehydrite).
3. Protective atmosphere for molybdenum windings.
4. Argon inlet to furnace. Thermocouples.
5. Reaction boat.

6. Gas outlet.
7. Absorbers for SiF$_4$.
8. Gas meter.
9. Thermocouple cold junctions.
10. Recording temperature controller.
11. Furnace power circuit.

Apparatus. The experiments were carried out in various ways, and various kinds of equipment were used.

In principle the apparatus used is identical with the one used by Grjotheim *et al.*[6] in studying aluminothermic reduction of magnesium. The general arrangement of the apparatus is shown in Fig. 3. Two different furnaces were used in the course of this work, both of them horizontally mounted tube furnaces. Furnace A had a tube of fused alumina and molybdenum windings, whereas furnace B had Inconel tube and Kanthal A windings. Both furnaces were gas tight, and the temperature was measured by means of a Pt/Pt10Rh thermocouple. The temperature in each furnace was kept constant to within ±3°C. This regulation was accomplished by means of a recording Kent controller for furnace A, and by means of a voltage stabilizer for furnace B.

In furnace A the charge was contained in a platinum boat, while in furnace B the charge filled the entire cross section of the tube, two steel shields keeping the charge together; see Fig. 4.

Fig. 4. Arrangement of charge in furnace.
(A) Charge in boat (furnace type A).

    1. Reaction tube;
    2. Platinum boat with charge;
    3. Thermocouple sheath (measuring thermocouple);
    4. Thermocouple sheath (regulating thermocouple).

(B) Plug charge (furnace type B), results in Fig. 5.
    1. Reaction tube;
    2. Charge;
    3. Radiation shields;
    4. Thermocouple sheath.
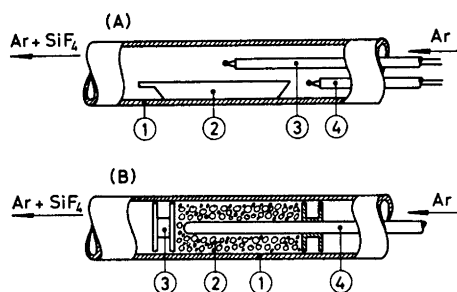
The determination of silicon tetrafluoride was done in two different ways. In most experiments it was determined chemically. The carrier gas was passed from the furnace through a series of polyethylene or perspex bottles filled with HF solution. The silicon tetrafluoride in the gas would then react with HF forming fluosilicic acid. After each experiment the amount of silicon in the solution was determined spectrophotometrically as SiO_2 using the molybdate method as modified by Langmyhr and Graff.[7]

It was also attempted to determine the amount of silicon tetrafluoride simply by measuring the weight loss of the charge as a result of the reaction. This gave results essentially in agreement with the chemical method.

Chemicals. The following qualities were used in the present investigation: Calcium fluoride, Baker analyzed reagent. Silica, E. Merck *pro analysi* grade, washed and calcined.

The silica was ground to pass No. 100 mesh sieve. The reagents were dried at 250°C over night before weighing and mixing in the desired ratio. The powder mixture was pressed into briquets, and subsequently broken into small lumps.

Argon (99.99 % pure, supplied by Norsk Hydro-Elektrisk Kvælstofaktieselskab) was used as inert carrier gas. Traces of moisture were removed by passing the gas through absorption towers filled with Dehydrite. The gas was measured quantitatively by means of a gas meter.

Three compositions of different $CaF_2 - SiO_2$ ratios were used. These contained, in weight per cent, 25 %, 50 %, and 77 % CaF_2, respectively. In no case the extent of reaction exceeded 5 % of the total charge, so that the content of neither SiO_2 nor CaF_2 was depleted.

RESULTS

The largest number of measurements were carried out at temperatures below 1240°C to be certain that all condensed phases were in the solid state. Samples heated above this temperature were partly melted.

Five series of experiments were carried out at various temperatures in Furnace B. In each series the same charge (50—60 g) was used throughout. At one temperature two series were performed in different ways (Fig. 5).
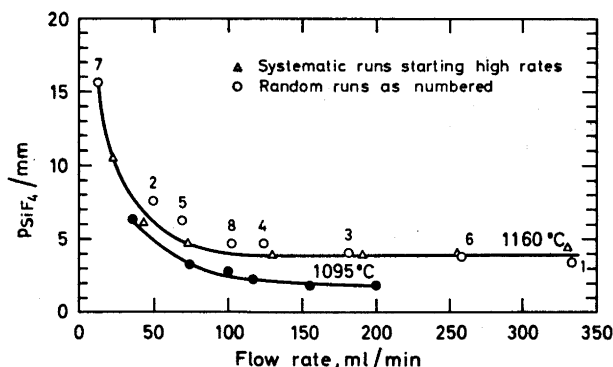

Fig. 5. Effect of flow rate on apparent vapour pressure at two temperatures: 1160°C (upper curve), and 1095°C (lower curve). Furnace type B, plug charge.

In the first series one started with the highest flow rate, continuing with lower flow rates in a systematic way. In the other series the flow rate was varied at random. Thus, at 1160°C the vapour pressure was found to be nearly constant in the region 80—330 ml/min. The equilibrium pressure here is 4.0 ± 0.5 mm.

In the molybdenum furnace experiments were carried out at various temperatures. The charge (5—6 g) was changed between each experiment.

Some of these experiments were made at various flow rates, the amount of silicon tetrafluoride being determined as weight loss of sample. The results are shown in Fig. 6. As the apparent vapour pressure varies with the gas flow rate over the whole range, the vapour pressure in each case is determined by extrapolation of the sloping line to zero, as discussed above.

The rest of the experiments in the molybdenum furnace were carried out at constant gas flow rate, 80 ml/min, and various temperatures.

The results are shown in Fig. 7. Applying the method of least squares a straight line may be fitted to the experimental points in the diagram. This line is represented by the equation

$$\log(p/\text{atm}) = 4.97 - 10\ 580/T$$

The measurements made at temperatures above 1240° (the eutectic) appear in the diagram, but they are not included in the thermodynamic discussion below.

The values obtained from extrapolation of the vapour pressure/flow rate diagram (Fig. 6) are included in Fig. 7. The agreement with the rest of the results is gratifying.

From this the heat of reaction, ΔH_r°, is calculated to 48.4 kcal/mole, and the entropy change ΔS_r°, 22.7 e.u./mole.
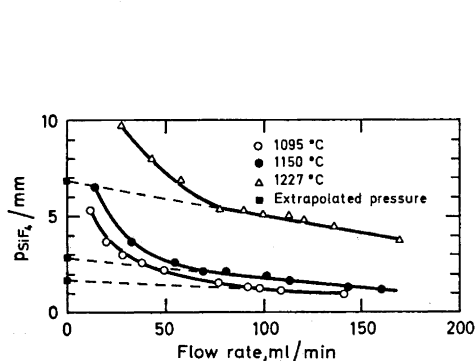
Fig. 6. Effect of flow rate on apparent vapour pressure at three different temperatures. Furnace type A, charge in platinum boat.
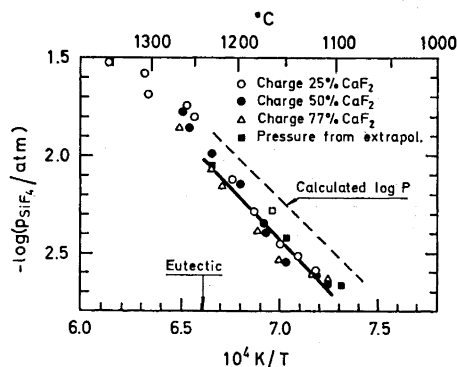
Fig. 7. Vapour pressure of SiF₄ above the system CaF₂—SiO₂.

Open circles: Furnace type A, charge 25 % CaF₂.
Filled circles: Furnace type A, charge 50 % CaF₂.
Triangles: Furnace type A, charge 77 % CaF₂.
Filled squares: Furnace type A, results obtained by extrapolation (Fig. 6), charge 25 % CaF₂.
Open square: Furnace type B, result obtained from "plateau", Fig. 5, charge 25 % CaF₂.

The reaction products both after vapour pressure measurements and after prolonged heating of samples under similar conditions, were investigated by means of X-ray diffractometry after quenching. The most important conclusions to be drawn from these investigations are:

1. Quartz in the reaction mixture is partly converted to tridymite.
2. No compound which could be identified as $3CaO.2SiO_2.CaF_2$ was found.
3. The reaction products were identified as a mixture of $Ca_3Si_2O_7$, α- and β-Ca_2SiO_4, and $CaSiO_3$.

DISCUSSION

The thermodynamic data used in the equilibrium calculations are taken from the following sources:
SiO_2, SiF_4: JANAF tables.[8]
CaO, CaF_2: Wicks and Block.[9]
$CaSiO_3$: Standard heat of formation: Kubaschewski et al.,[10] high temperature heat content and entropy: Kelley.[11],[12]
Calculation of ΔH_r° for reaction (1) from enthalpy data for the components gives 50.3 kcal/mole at 1500°K. Correspondingly entropy data for the compounds give an entropy change for the reaction of 29.0 e.u./mole.

"Third law" calculation of the enthalpy of the reaction gives 57.5 kcal/mole at the same temperature.

In the introduction to this paper it was assumed that calcium metasilicate is the only solid reaction product. Since this obviously is not so, according to the X-ray investigations, the question may arise whether one actually reaches equilibrium in the present measurements. The presence of several metastable phases implies the superposition of metastable equilibria, each contributing to the vapour pressure.

Calculation of the equilibrium vapour pressure of silicon tetrafluoride from the change in Gibbs free energy for reaction (1) (all phases having unit activity), gives the dashed line in Fig. 7. It has very nearly the same slope as the experimental line, although the absolute values of the vapour pressure are higher. The effect of the possible contribution to the vapour pressure by other equilibria than (1) would be to give even higher values than calculated. As the experimental values actually are lower it is not likely that equilibria other than (1) dominate.

However, it is a well-known fact that when calcium oxide and silica react in the solid state the first reaction products are disilicate and orthosilicate.[13] In the course of reaction they react further with silica forming metasilicate. These metastable equilibria are typical for silicate systems, and they may persist for long periods of time even at high temperature before thermodynamic equilibrium eventually is reached.

REFERENCES

1. Hillert, L. *Acta Chem. Scand.* **18** (1964) 2411.
2. Eitel, W. *Zement* **27** (1938) 455.
3. Mukerji, J. *J. Am. Ceram. Soc.* **48** (1965) 210.
4. Bååk, T. and Ölander, A. *Acta Chem. Scand.* **9** (1955) 1350.
5. Brisi, G. *J. Am. Ceram. Soc.* **40** (1957) 174.
6. Grjotheim, K., Herstad, O. and Toguri, J. M. *Can. J. Chem.* **39** (1961) 443.
7. Langmyhr, F. J. and Graff, P. R. *Anal. Chim. Acta* **21** (1959) 334 and 429.
8. *JANAF Thermochemical Tables,* edited by D. R. Stull, Thermal Res. Lab., Dow Chemical Co., Midland Mich; SiO_2 (cristobalite, high): June 30, 1967. (Third addendum); SiF_4: Sept. 30, 1963.
9. Wicks, C. E. and Block, F. E. *Bur. Mines Bull.* 605, Washington 1963.
10. Kubaschewski, O., Evans, E. L. and Alcock, C. B. *Metallurgical Thermochemistry,* 4th Ed., Pergamon 1967.
11. Kelley, K. K. *Bur. Mines Bull.* 584, Washington 1960.
12. Kelley, K. K. *Bur. Mines Bull.* 592, Washington 1961.
13. Jander, W. and Hoffmann, E. *Z. anorg. allgem. Chem.* **218** (1934) 211.

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