



Soviet-era science, translated into English

CHEMISTRY

Ya. I. Olshanskii

1957

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-195701.35988>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

CHEMISTRY

Ya. I. Olshanskii

EQUILIBRIUM OF TWO LIQUID PHASES IN THE SIMPLEST FLUOROSILICATE SYSTEMS

(Presented by Academician D. S. Korzhinskii, 31 January 1957)

The separation of fluorine-containing silicate melts into two immiscible liquids was first observed by D. P. Grigor'ev (1). The formation of two liquid phases in silicate melts containing phosphates and fluorides was discovered by V. V. Lapin (2) in the microscopic study of slags. Subsequently, Olsen and Med (3) and Fisher (4) studied separation in silicate melts containing fluorides.

In all these investigations, the formation of volatile SiF_4 ($2\text{CaF}_2 + \text{SiO}_2 = 2\text{CaO} + \text{SiF}_4$) greatly complicated experimentation and precluded the possibility of studying binary boundary systems SiO_2 –metal fluorides.

We made many attempts to carry out meltings of fluorosilicate melts in molybdenum crucibles sealed in quartz ampoules. The latter, however, even at comparatively low temperatures became plastic and ruptured. It was later found that SiO_2 reacts with SiF_4 .

V. A. Dunaevskii proposed carrying out the meltings in molybdenum crucibles fitted with molybdenum stoppers–rivets. It turned out that, with some skill, a molybdenum crucible (Fig. 1, A) can be riveted shut in such a way that evaporation of SiF_4 during heating of silicate–fluoride mixtures practically does not occur. The dimensions of the crucibles may vary within fairly wide limits, but the internal diameter must not be too large, since in that case riveting becomes difficult.

From 0.02 to 0.10 g of a finely ground mixture of fluoride and quartz was placed in a crucible, which was riveted shut and suspended in a furnace with a molybdenum heater (5). The temperature was measured with an optical pyrometer; heating (usually 5–15 min) was carried out in an atmosphere of hydrogen. Cooling was effected by dropping the crucible into the cold part of the furnace or simply by switching it off (the cooling rate of the furnace at 1700° was about 150° per second).

After heating, the crucible was weighed and broken open. Meltings with a weight loss of no more than 1.0–1.5% of the weight of the charge were considered

successful. The existence of two liquid phases in a given mixture was determined by microscopic examination of immersion preparations. If two liquid phases formed in the crucible at high temperature, then in the immersion preparations the same signs of two immiscible liquids were observed as in the separation of acidic silicate melts, first discovered by Greig (6). One of the liquids gives a low-refractive glass; the second liquid forms spherical or oval inclusions in it. These inclusions are almost always partly crystallized. Only the very smallest of them form pure glass. For mixtures whose composition was sufficiently far removed from the boundary of the field of equilibrium of two liquid phases, separation was —

was quite clearly detected. As, with increasing fluoride content, the composition of the mixture approached the boundary of the immiscibility region and the amount of liquid consisting mainly of silica decreased, microscopic examination became difficult. Small amounts of low-refractive glass with characteristic inclusions could remain unnoticed. In this connection, the concentration boundary of the immiscibility region could not be established with an accuracy greater than 2%.

From the summary of results given in Table 1 it is seen that the regions of two liquid phases in fluoride–silica systems are very large. They considerably exceed the corresponding immiscibility regions in oxide–silica systems. In the BaO–SiO₂ system two liquid phases are not formed; in the BaF₂–SiO₂ system a wide miscibility gap in the liquid state is observed. At the same time, in melts of various mixtures of silica and the fluorides of lithium, sodium, and aluminum, no signs of the formation of immiscible liquids were observed.

Likewise, as in ordinary silicate systems (7), the width of the immiscibility region in fluoride systems is related to the size and charge of the cations. The immiscibility region increases as the ratio of the cation radius to its charge decreases. Aluminum is an exception, which is apparently connected with its amphoteric character.

Table 1

Equilibrium of two liquid phases in systems silica–metal fluorides

Fluorides	Immiscibility boundary* (content of fluoride), wt. %	Immiscibility boundary* (content of fluoride), mol. %	Ratio of cation radius to valence, Å	Temperature of stratification boundary, °C
MgF ₂	92	92	0.375	1430
CaF ₂	94	92	0.505	1420
SrF ₂	95	90	0.59	not determined
BaF ₂	95	86	0.68	1460

Fig. 2. Region of two liquid phases in the system $CaO, CaF_2/SiO_2, SiF_4$

Figure 1: Fig. 2. Region of two liquid phases in the system $CaO, CaF_2/SiO_2, SiF_4$

Fluorides	Immiscibility boundary* (content of fluoride), wt. %	Immiscibility boundary* (content of fluoride), mol. %	Ratio of cation radius to valence, Å	Temperature of stratification boundary, °C
LiF	No immiscibility observed	No immiscibility observed	0.69	—
NaF	Same	Same	0.98	—
AlF ₃	» »	» »	0.190	—

* Composition of the liquid phase rich in cations.

Fig. 1. A —molybdenum crucible with quenching. **B** —molybdenum crucible for studying the interaction of SiO_2 and SiF_4

Table 1 gives the compositions of liquids containing much fluoride. As for the coexisting equilibrium liquids, some conclusions about their composition can be drawn from the following. Mixtures containing only 2-3% fluorides and 97-98% SiO_2 , after melting, had distinct signs of two liquid phases. Thus, one of the liquid phases consisted predominantly of SiO_2 and contained less than 2-3% fluorides of alkaline-earth metals. In immiscibility in such systems as $CaO-SiO_2$, $MgO-SiO_2$, one of the liquids consists mainly of SiO_2 and forms a glass with a refractive index of 1.461-1.462, which indicates the presence in it of a small amount of CaO or MgO (the refractive index of pure quartz glass is 1.459⁽⁶⁾). In our case, the glasses consisting mainly of SiO_2 had a significantly lower refractive index. Thus, after melting 90% SiO_2 + 10% CaF_2 , an acid glass with a refractive index of 1.442 was formed. Such a considerable decrease in the refractive index of the glass cannot be caused by dis-

by its dissolution of CaF_2 .^{*} The low refractive index of the glasses led us to suppose that the acidic liquids contain SiF_4 and that the systems studied are reciprocal ones (for example, $Ca, Si/F, O$). This is confirmed by the fact that the liquidus temperature in the region of immiscibility does not remain constant, as it should in binary systems, but decreases with increasing fluoride content. Mixtures containing 5-10% fluoride form two liquid phases only at 1600-1650° C. Table 1 gives the temperatures (1420-1460°) at which two liquid phases are formed from mixtures whose compositions lie near the boundary (on the fluoride side) of the immiscibility region.

Fig. 2. Region of two liquid phases in the system $CaO, CaF_2/SiO_2, SiF_4$

The formation of comparatively low-melting liquids from SiO_2 under the action of SiF_4 on it was also confirmed by a special experiment. A mixture of $CaF_2 + SiO_2$ (1) was poured onto the bottom of a molybdenum crucible (Fig. 1, B); above it was placed a small molybdenum crucible (2) with a small amount of ground quartz, the crucible not coming into contact with the charge containing CaF_2 . The crucible thus prepared was closed with a molybdenum rivet (3) and heated at 1460° for 1 hour. It turned out that the quartz in the small crucible melted from above and formed a glass with refractive index 1.445–1.452. Thus, the melting of quartz at 1460° (instead of 1715°) occurred as a result of the action of SiF_4 , formed when $CaF_2 + SiO_2$ was heated.

Melts in sealed molybdenum crucibles were used to determine the region of two liquid phases in the system $CaF_2—CaO—SiO_2$. Mixtures for melting were prepared from Ca_2SiO_4 , SiO_2 , and CaF_2 . The results are presented in Fig. 2 in the form of the reciprocal system $CaO, CaF_2/SiO_2, SiF_4$. The region of two liquids in the system $CaO—SiO_2$ is plotted according to Greig's data. The compositions of the liquid phases rich in CaO and CaF_2 were determined as a result of melts of various mixtures (along three sections of the system). The coexisting liquids, consisting mainly of SiO_2 , are plotted on the basis of the data given above so as to show a certain content of SiF_4 in them. The quantitative compositions of these liquids were not found. The diagram shows four tie-lines, for which the temperatures ($1530, 1490, 1460, \text{ and } 1420^\circ$) and the compositions of the liquids rich in CaO and CaF_2 were determined. The boundary line of the region of two liquids in the triangle $CaF_2—SiF_4—SiO_2$ was not determined. It is drawn with a dashed line in the way that seemed to us most probable.

Taking into account the similarity of the ions F^- and OH^- , it may be supposed that such aqueous-silicate systems as $H_2O—CaO—SiO_2$ or $Ca(OH)_2—CaO—SiO_2$ are constructed analogously to the reciprocal system presented above. Some confirmation of this assumption may be provided by the investigations of Tuttle and England (8), who observed the melting of quartz when it was heated to 1300° together with high-pressure water vapor (up to 2000 atm). On cooling, a glass of 98% $SiO_2 + 2\% H_2O$ was obtained. It is possible that the melt that formed this glass should be regarded as a solution of $SiO_2 + Si(OH)_4$.

* If a linear dependence of the refractive index on the content of CaF_2 in the glass is assumed, then the observed decrease in refraction could have been caused by the presence of 68% CaF_2 .

The series of melts of mixtures of $CaF_2 + Al_2O_3 + SiO_2$ that we carried out made it possible to determine the boundary of the region of two liquid phases in this system (approximately considering it ternary). It turned out that, as in the $CaO—Al_2O_3—SiO_2$ system, the presence of Al_2O_3 considerably reduces the region of two liquid phases. Mixtures of 25% $CaF_2 + 75\% SiO_2$ and 50% $CaF_2 + 50\% SiO_2$ form two liquids in the presence of, respectively, 7.5 and 10% Al_2O_3 , but become homogeneous after the addition of 10.0 and 15.0% Al_2O_3 . The configuration of the immiscibility region in the $CaF_2—Al_2O_3—SiO_2$ system

is analogous to that for $\text{CaO—Al}_2\text{O}_3\text{—SiO}_2$, but in the former system it is considerably larger than in the latter.

Institute of Geology of Ore Deposits,
Petrography, Mineralogy, and Geochemistry
Academy of Sciences of the USSR

Received
30 I 1957

REFERENCES

1. D. P. Grigor' ev, *Zap. Vseross. mineral. obshch.*, **64** [No. 1], 250 (1935).
2. V. V. Lapin, *Tr. Petrog. inst. AN SSSR*, No. 3, 247 (1938); *Tr. IGN AN SSSR*, issue 106, 28 (1949).
3. W. Oelsen, H. Maetz, *Mitt. K. W. Inst. f. Eisenforsch.*, **23**, 195 (1941).
4. R. Fischer, *Neues Jahrb. f. Mineral.*, **81**, No. 3, 315 (1950).
5. Ya. I. Ol' shanskii, *Izv. AN SSSR, ser. geol.*, No. 6, 128 (1951).
6. J. W. Greig, *Am. J. Sci.*, **13** (5), 1, 133 (1927).
7. O. A. Esin, *Izv. AN SSSR, OKhN*, **1948**, 561.
8. O. F. Tuttle, J. Z. England, *Bull. Geol. Soc. Am.*, **66**, 149 (1955).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.