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REPORT [redacted]
CD NO.

50X1-HUM

COUNTRY	USSR	DATE OF INFORMATION	1948
SUBJECT	Scientific - Chemistry, phase equilibria at high temperatures	DATE DIST.	9 Feb 1951
HOW PUBLISHED	Thrice-monthly periodical		
WHERE PUBLISHED	Moscow/Leningrad	NO. OF PAGES	5
DATE PUBLISHED	11 Mar 1949	SUPPLEMENT TO	[redacted]
LANGUAGE	Russian		

50X1-HUM

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SOURCE Doklady Akademii Nauk SSSR, Vol LXV, No 2, pp 167-170, [redacted] [redacted]

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NEW METHOD FOR DETERMINING THE INVARIANT EQUILIBRIUM OF PHASES AT HIGH TEMPERATURES

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Submitted 6 Dec 1948

/Digest. Figures referred to are appended./

At present two basic methods for the determination of equilibrium conditions at high temperatures between liquid and solid phases are being applied: Kurnakov's method of thermal analysis and the statistical method of chilling, which is used for the investigation of silicate systems.

Kurnakov's method yields excellent results when the liquid phases crystallize without excessive undercooling. A low viscosity of the liquid on melting, a high heat conductivity, and high heats of phase transformations are favorable factors contributing to the successful use of the method of thermal analysis. The statistical method of chilling, which is based on fixation of the liquid in the form of a glass by rapid chilling, is used successfully on substances which do not crystallize easily. In some cases neither of these two methods can be used effectively for a determination of the phase equilibrium. This refers to systems composed of substances which are aggressive at high temperatures, so that the system is contaminated due to the fact that the walls of the crucible or the protective sheath of the thermocouple dissolve in the liquid. For the same reason the method of chilling also cannot be used, an additional reason being that the aggressive melts have a strong tendency to crystallize, so that they do not form a glass even when chilled very rapidly.

In an investigation of sulfide-silicate systems, we have used a method based on capillary separation of the liquid phase (1). With the aid of this method, even the most aggressive melts can be handled. The application of the

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method in question to several very aggressive melts has been checked in the course of the work described at present. The proposed method can be used whenever a liquid which is in equilibrium with a solid phase wets the surface of the latter and has a high fluidity.

To determine the equilibrium between several solid phases and a liquid, a tablet consisting of a finely powdered, thoroughly homogenized mixture of the solid phases is prepared first. This tablet is placed on a porous plate made of one of the solid phases participating in the equilibrium. Upon heating of the tablet, the liquid formed as a result of the interaction of the solid phases soaks into the porous plate.

The temperature of formation of the liquid phase can be determined by keeping the tablet on the plate for a long time and raising the temperature gradually, then noting the temperature at which a spot formed by the liquid appears on the plate. The slower the heating is carried out, the higher will be the precision of the determined temperature.

A determination of the composition of the liquid in equilibrium can be made when no fewer than three components participate in the equilibrium. Let us assume that the composition of the liquid which is in equilibrium with the solid phases A, B, C, and D is to be determined. Then a tablet composed of A B + C + D and placed on a plate composed of A, to give an example, is heated at a temperature slightly higher than that corresponding to the equilibrium. A chemical analysis of the porous plate soaked in liquid will give the ratio of B:C:D: in the liquid. Repeating the experiment with a porous plate consisting of another solid phase, for instance B, we shall obtain the ratio A:C:D in the same liquid. The two ratios determined in this manner give the complete composition A:B:C:D of the equilibrium liquid.

Figure 1 is a schematic drawing of the apparatus in which determinations according to this method were carried out. The horizontal furnace 1 holds a long porcelain tube 2, the walls of which are impermeable to gas. The cold ends of the tube are equipped with rubber sleeves 3 and are stoppered. The protective sheath of the thermocouple 8 enters through the stopper at the left. The thermocouple and its sheath are placed high enough to leave room for support 4 holding the porous plate 5 and the tablet 6. Support 4 is a refractory cylinder cut along a plane parallel to the axis. The support can be easily moved in and out of the tube by means of a hook. The choice of the material for the support does not present any difficulties, because the dimensions of the porous plate and of the tablet can be always held within such limits that the liquid formed in melting does not soak completely through the porous plate.

Usually the support 4 was made of chamotte. The thermocouple Pt-Pt/Rh could be moved in the protective sheath and its hot connection 7 was placed above the tablet. By moving the thermocouple, the hottest spot in tube 2 could be determined. The tablet was placed in that spot. Glass tube 9 passes through the stopper at the right end. This tube is closed by a plane-parallel glass plate affixed to the end of the tube with an adhesive. The correctness of the tablet's position can be checked by looking through the glass plate. Before starting to heat the furnace, nitrogen was blown through tube 2. Passage of a slow current of nitrogen (0.5 liter per hour) was continued during the experiment. On drying and absorption of CO_2, the nitrogen was freed from admixtures of oxygen by passing it through copper /filings/ at 450-500° C and through a sodium-potassium alloy at 150-180° C. On leaving the tube, the nitrogen was passed through a Tishchenko flask filled with sulfuric acid, which resulted in a nitrogen pressure in the apparatus higher than the atmospheric. Tube 2 could be moved out of the apparatus without interrupting the flow of nitrogen, so that the tablet could be cooled rapidly.

Notwithstanding the careful purification of the nitrogen, complete absence of oxygen in the apparatus could not be achieved: small quantities of oxygen diffused into the apparatus due to the fact that the sealing of the latter was not completely hermetic. The presence of oxygen could be established by placing a shiny iron plate into the apparatus: this plate often became tinted as a result of oxidation.

The accuracy of the thermocouple was checked by determining the melting points of Cu, K_2SO_4, and Na_2SO_4 under the same conditions under which the tablet was heated.

For the purpose of checking the new method, the eutectic point of SiO_2 + Fe_2SiO_4 + Fe was determined. This eutectic point had already been determined by Bowen (2) by using the chilling method. The tablet was formed of chemically pure iron reduced with nitrogen, Fe_2SiO_4 prepared in an iron crucible, and amorphous SiO_2 calcined at 1100° C. These ingredients were thoroughly powdered and mixed and then formed into a tablet under addition of a small quantity of alcohol. To determine the eutectic point, the resulting tablet was heated on a porous plate prepared by sintering SiO_2 at 1300° C.

Formation of liquid in the tablet is clearly seen, because a greenish spot appears on the porous plate at the point of contact with the tablet and gradually spreads on the porous plate. Varying the composition of the tablet, one determines the lowest temperature at which a spot forms. The upper curve of Figure 2 shows the dependence of the temperature of appearance of the spot on the composition of the tablet. The content of metallic iron was kept constant at 19%.

The temperature curve exhibits a minimum at a composition of the tablet corresponding to the eutectic liquid. The minimum temperature on this curve corresponds to the eutectic point (1183° C), a result which agrees very well with the eutectic point of 1178° C found by Bowen according to the method of chilling. When a tablet the composition of which differs considerably from the eutectic is heated, formation of the spot occurs at temperatures considerably exceeding the equilibrium temperature, as can be seen from the curve. This is explained by the fact that in such tablets the quantity of liquid formed is insufficient to moisten the silicon dioxide plate. The curve near the minimum has a low enough slope, however, so that in the case of tablets the composition of which differs by 10-15% from the eutectic, the temperature difference does not exceed the range of experimental errors.

As has been mentioned already, complete freedom from oxygen could not be achieved notwithstanding thorough purification of the nitrogen. For that reason, the experiments were repeated in an iron crucible (cf. Figure 3), so that the penetration of noticeable quantities of oxygen to the tablet was prevented. Crucible 1 was closed by means of cover 2, and iron filings were placed on top of the cover. The crucible was placed in an apparatus similar to the one described above, except that it was in a vertical position. The thermocouple in its protective sheath was introduced into the crucible through opening 3 bored in the bottom of the crucible. Heating was carried out in a current of nitrogen, as before. The inner surface of the crucible always remained perfectly clean, because the oxygen was absorbed by the iron filings.

Analysis of the SiO_2 plate gave the relationship $FeO:Fe_2O_3 = 50.0$ or $Fe: O = 3.46$. To determine the relationship $SiO_2:O$ (where O is the oxygen combined with iron) in the liquid, a tablet having a composition near to the eutectic was heated on a porous iron plate prepared by sintering iron in a hydrogen atmosphere at 900° C. Analysis yielded the relationship $SiO_2:O = 2.48$. Thus, the composition of the eutectic liquid is $SiO_2:Fe:O = 2.48:3.46:1$, which also agrees well with Bowen's result (2.50:3.45:1).

From the point of view of the proposed procedure, the equilibrium Fe_2SiO_4 - SiO_2 - Fe - melt is not particularly favorable, because the melt saturated with SiO_2 has a rather high viscosity. Much more favorable are conditions with regard to the equilibrium FeS - FeO - Fe - melt, which was investigated by the same method. Porous plates were prepared from FeO or Fe, but it was also possible to use SiO_2 plates, because the presence of the SiO_2 plates does not result in a noticeable displacement of the equilibrium. The lower curve of Figure 2 gives the dependence of the temperature at which a spot begins to form on the composition of the tablet. (The quantity of Fe in the tablets is constant and amounts to 21%.) It can be seen from the curve that in this case the temperature of beginning spot formation is practically independent of the composition of the tablet within an extensive range.

For the investigation of equilibria, the following experimental technique is recommended. First, by using tablets consisting of equal quantities of all participating solid phases, the temperature and the composition of the equilibrium liquid are determined approximately for the purpose of orientation. Then, for an exact determination of the eutectic point, one should use a tablet composition which is close to that of the equilibrium liquid. It should not be too close, however, because otherwise the tablet will melt completely and soak into the porous plate together with suspended particles of solid phases.

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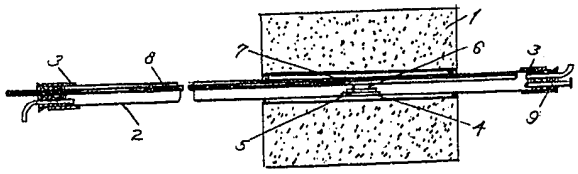

Figure 1. Apparatus Used for the Measurements

1. Furnace
2. Porcelain tube
3. Rubber sleeves
4. Support
5. Porous plate
6. Tablet
7. Hot connection of the thermocouple
8. Protective sheath of the thermocouple
9. Glass tube

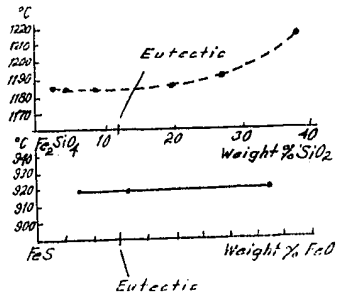

Figure 2. Temperature Dependence of Melting (as indicated by appearance of spot on the porous plate) on the Composition of the Tablet

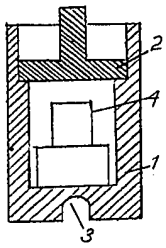

Figure 3. Iron Crucible

1. Crucible
2. Crucible cover
3. Hole for the insertion of thermocouple
4. Tablet

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