

PHASES IN THE PRODUCTS OF THE REACTION OF SULPHUR HEXAFLUORIDE WITH COPPER¹⁾

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The purpose of this paper is to follow the interaction of SF_6 with Cu in the region of pressures of 0.101325—2 MPa and temperatures ranging from room temperature of 298.15 K to the boiling temperature of copper. The system of the reaction products is thus heterogeneous, and on determining the composition of the system it is therefore necessary to concentrate on the selection of phases, since the number of phases should comply with the Gibbs phase rule.

I. INTRODUCTION

Some inner components of high voltage and very high voltage circuit breakers filled with sulphur hexafluoride — SF_6 are made of copper or may contain copper. SF_6 reacts with Cu already at temperatures of about 100°C [1].

The interaction of SF_6 with Cu should be studied from the viewpoint of the chemical equilibrium of the system in the ideal state, at constant pressure and temperature. The products of the interaction form a system of individual substances briefly denoted ($\text{SF}_6 + m\text{Cu}$), which may be present in the products of the reaction of one mole SF_6 with m moles of Cu after chemical equilibrium has been attained.

II. DESCRIPTION OF THE SYSTEM

We took into consideration all possible compounds — components of the system — whose heats of formation $\Delta_f H^\circ$ and the values of the thermodynamic potential $\Phi^\circ(T)$ are available in literature. They include the gases SF_6 , SF_5 , SF_4 , SF_3 , SF_2 , SF , S , S_2 , S_3 , S_4 , S_5 , S_6 , S_7 , S_8 , F [2], Cu , Cu_2 , CuF , CuF_2 [3], and the condensed components S [2], Cu, CuF , CuF_2 [3], CuS , Cu_2S [4].

Gases form a single phase, it is supposed that the condensed components

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$$h \leq M. \quad (1)$$

At constant temperature and pressure the Gibbs energy of the system is the function of the composition n_1, n_2, \dots, n_S and the equilibrium composition minimizes the Gibbs energy. This fact forms the basis of the calculation method of the equilibrium composition [6] used for the calculation of the composition of the system ($\text{SF}_6 + m\text{Cu}$).

III. DISCUSSION OF THE RESULTS

the coordinate axes, divide the first quadrant of the coordinates m , T into bounded areas of couples (m , T). The condensed phases occurring in ($S\text{F}_6 + m\text{Cu}$) in the respective area are written in Fig. 1. The initial and final points of some curves in Fig. 1 are marked with the capital letters of the alphabet. The position of the curves AB, CD, EZ, HL, FZ, ZI, ZK depends on the pressure; with increasing pressure the curves are shifted towards higher temperatures. The temperature corresponding to point B is the boiling temperature of sulphur for $p = 1$ MPa. In the line segment CD CuS/c decomposes to Cu_2S /c and to S/g [7]. Above the temperature corresponding to points E and H, respectively, there arises a vapour of CuF_2 and CuF in a considerable amount. In a similar way Cu_2S decomposes at temperatures above the point F.

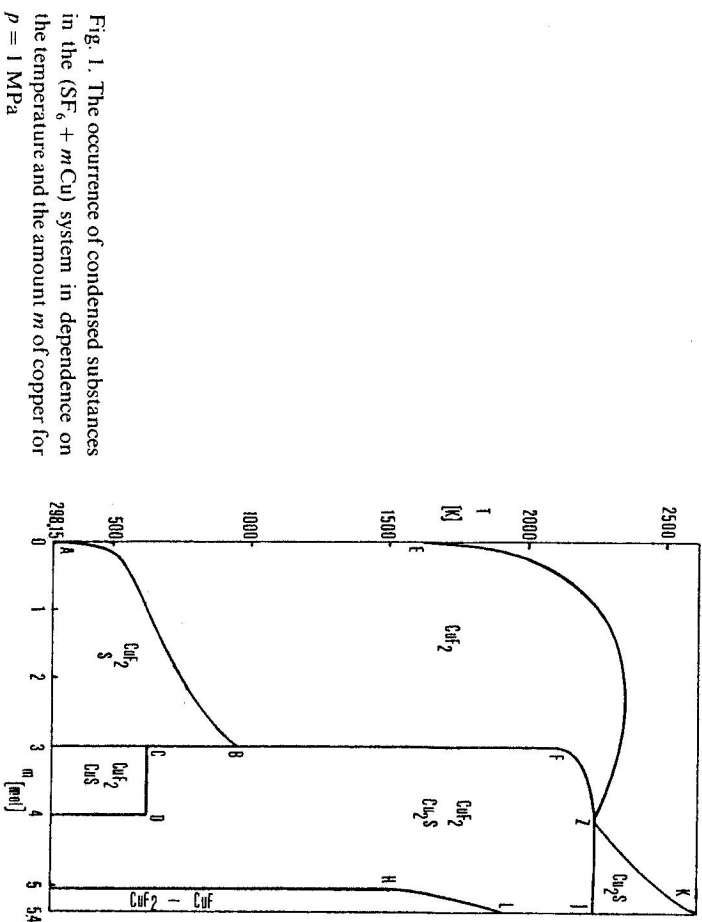


Fig. 1. The occurrence of condensed substances in the ($\text{SF}_6 + \text{mCu}$) system in dependence on the temperature and the amount m of copper for $p = 1 \text{ MPa}$

It is necessary to remark that in the system we do not assume the presence of $\text{Cu}_2\text{S/g}$, for which the values $\Phi^0(T)$, $\Delta_f H^0$ lacked, and the data upon the decomposition or evaporation of $\text{Cu}_2\text{S/c}$. For this reason we should take with reserve also the position of curve ZK. Very interesting is the information concerning the decomposition of CuF_3/c to CuF/c at the melting temperature

of $\text{CuF}_{2/2}\text{c}$ (1223 K) [8]. Calculations did not confirm this fact. Besides, [8] expresses doubts concerning the existence of CuF/c .

It follows from the results of the calculations that the decomposition SF_6 is caused by copper. During the decomposition of SF_6 there arise fluorine and sulphur and practically the whole content of copper reacts with them. We should add that the boiling temperature of copper for the pressure of 1 MPa equals 3454 K. Condensed copper appears in the system only for $m > 5.4$ mol. The maximum amount m_g of copper appearing in the gaseous components of the system increases with temperature. This dependence is illustrated in Fig. 2 for $p = 1$ MPa. With increasing pressure the curve in Fig. 2 is shifting towards lower amounts.

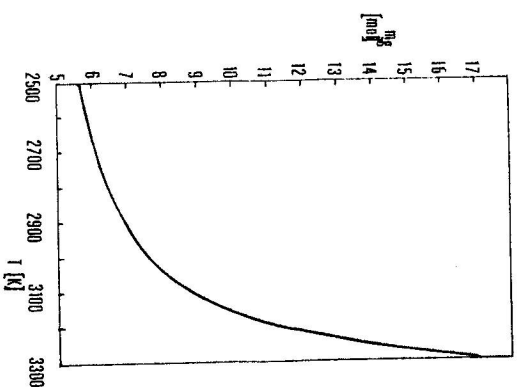


Fig. 2. Temperature dependence of the maximum amount m_g of copper in the gaseous phase of the system for $p = 1$ MPa

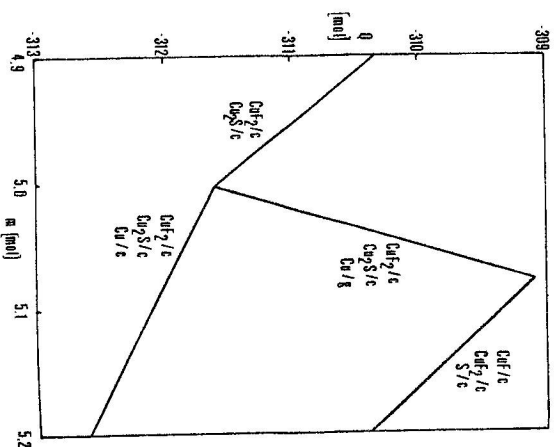
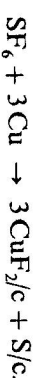


Fig. 3. The graph of function Q in the neighbourhood of the phase transition for $p = 1$ MPa

If a constant m is given ($0 \leq m \leq 5.4$), it is necessary, when interpreting the results of the equilibrium calculation, to take into account the rate of the chemical reactions at the temperature changes. More complicated is the interpretation of the calculation in the case of constant temperature and of a changing m . Let us denote $Q = G/RT$, where G is the Gibbs energy of the system

in equilibrium at the given temperature and pressure (R is the gas constant). The equilibrium composition as well as the calculation of the values $Q = Q(m)$ is the result of a numerical process, unstable for some values of m , e.g. for m_1, m_2, \dots At the points $m_1, m_2, \dots Q(m)$ appears either as a discontinuous function or is increasing in the neighbourhood of these points. For other values of m ranging from zero to 5.4 $Q(m)$ is a decreasing function. The points m_1, m_2, \dots will be further regarded as points of discontinuity and at a limiting transition we shall take into account only the points in which $Q(m)$ is decreasing. If m is nearing the value 3 from the left ($m \rightarrow 3 -$) and the temperature is below point B, then



In the system the gaseous phase disappears, while for $m \rightarrow 3 +$



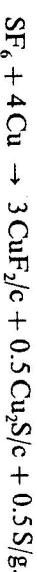
where in S/g we have included the molecules $\text{S}_1, \text{S}_2, \text{S}_3, \text{S}_4, \text{S}_5, \text{S}_6, \text{S}_7, \text{S}_8$. The difference

$$\lim_{m \rightarrow 3+} Q(m) - \lim_{m \rightarrow 3-} Q(m)$$

equals the difference of the Q values for S/g and S/c. The difference decreases with increasing temperature and above the boiling temperature of the sulphur equals 0. Similarly below point D for $m \rightarrow 4 -$



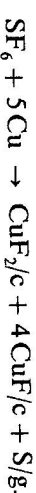
for $m \rightarrow 4 +$



Finally below point H for $m \rightarrow 5 -$ there is



for $m \rightarrow 5 +$



At each of the above points of discontinuity the limit of function $Q(m)$ from the right is always higher than the limit from the left. The minimum value of the function Q corresponds to the state of equilibrium. This might mean that with increasing m the system will reach the first point of discontinuity and the additional copper will not react. At the point of discontinuity the gaseous phase will completely disappear, the additional copper will evaporate as the equilibrium composition is calculated at constant temperature and pressure and the given pressure 1 MPa can be formed with gaseous copper. As an example in Fig.

3 we can see the graph of the function $Q(m)$ in the neighbourhood of the point $m = 5$ mol for $p = 1$ MPa and $T = 800$ K. In branch every of the graph the corresponding phases are indicated.

IV. CONCLUSION

It follows from the results of the calculation of the equilibrium composition at constant temperature and pressure that SF_6 reacts with Cu at all temperatures and pressures taken into consideration. The maximum amount m_g of Cu appearing in the gaseous components of the reaction of Cu with one mole of SF_6 is illustrated in Fig. 2 in dependence on the temperature for higher temperatures. The system of the reaction products is heterogeneous for lower temperatures. The occurrence of the condensed substances in the reaction products, which agrees with the Gibbs phase rule, depends on the amount m of copper and is evident from Fig. 1.

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ФАЗЫ В ПРОДУКТАХ РЕАКЦИИ SF_6 С Cu

Целью настоящей работы является изучение взаимодействия SF_6 с Cu в области давлений от 0,101325 до 2 МПа и в области температур, пробегавших от комнатных ее значений (298,15 К) до температуры кипения меди. Система продуктов этой реакции является неоднородной, поэтому для определения ее состава необходимо сосредоточиться на выборе фаз: поскольку число фаз должно подчиняться правилу фаз Гиббса.