

THERMODYNAMIC PROPERTIES OF THE PRODUCTS
OF REACTION OF SULPHUR HEXAFLUORIDE
WITH CARBON FOR TEMPERATURES UP TO
6000 K⁽¹⁾

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The interaction between the SF₆ extinguishing medium and carbon in HV and EHV circuit breakers is dealt with. It is assumed that the products of interaction form a closed ideal system in local equilibrium. The composition, enthalpy and heat capacity are determined for a constant pressure of this system.

I. INTRODUCTION

The inner components of some types of circuit breakers using an SF₆ extinguishing medium are of carbon. The products of the reaction of SF₆ with carbon affect the properties of the extinguishing medium. The products of the reaction of one mole of SF₆ with m moles of C form a system $S = S(m)$ of individual substances - components of the system. Thermodynamic properties of S are determined uniquely if the chemical potentials μ_i of all the components of the system are known as functions of independent variables T (temperature), p (pressure), n_1, n_2, \dots, n_N (amounts of the components), where N is the number of components [1]. It is further assumed that S is an ideal closed system in a state of local thermodynamic equilibrium. The system components are the following gases: S, S₂, S₃, S₄, S₅, S₆, S₇, S₈, SF, SF₂, SF₃, SF₄, SF₅, SF₆, F, F₂, C, C₂, C₃, C₄, C₅, CF, CF₂, CF₃, CF₄, C₂F, C₂F₂, C₂F₃, C₂F₄, C₂F₅, C₂F₆, CS, CS₂, e⁻, S⁻, S₂⁻, F⁻, F₂⁻, C⁻, C₂⁻, SF⁻, SF₃⁻, SF₅⁻, C⁺, C₂⁺, S⁺, S₂⁺, F₂⁺, SF⁺, FSSF, SSF₂, S₂F₁₀ and condensed sulphur S/c. For the amount m of carbon is assumed to be less than of equal to 1 mol. According to [2] it is therefore not necessary to consider condensed carbon in S .

1) Contribution presented at the 8th Symposium on Elementary Processes and Chemical Reactions in Low Temperature Plasma. STARÁ LESNÁ, May 28-June 1, 1990

2) Vysoké učení technické v Brně, Božetěchova 2, 612 66 BRNO, CSFR

II. COMPOSITION OF SYSTEM S

The composition is given by the amounts n_1, n_2, \dots, n_N , with n_N assumed to be the amount of S/c. For a given p, T the equilibrium composition of the system S minimizes the Gibbs energy of the system [3]

$$\begin{aligned}
 G &= \sum_{i=1}^N n_i \mu_i, \\
 \mu_N &= \Delta_f H_N^\circ - T \Phi_N^\circ(T); \\
 \mu_i &= \Delta_f H_i^\circ - T \Phi_i^\circ(T) + RT \ln(p \cdot x_i), \quad i = 1, 2, \dots, N-1; \\
 p &= \frac{p}{p^\circ}, \quad p^\circ \text{ is standard pressure;} \\
 x_i &= \frac{n_i}{\sum_{k=1}^{N-1} n_k}, \quad i = 1, 2, \dots, N-1;
 \end{aligned} \tag{1}$$

R is the universal gas constant, $\Delta_f H_i^\circ$ is the standard heat of formation of the i th component, $\Phi_i^\circ(T)$ is its standard Gibbs thermodynamic potential (determined by partition function). The values $\Delta_f H_i^\circ$ and $\Phi_i^\circ(T)$ have been taken from [4-7]. For the chemical potential μ_N the dependence of the condensed sulphur volume on pressure is neglected, which is a justified assumption if pressures of up to 2 MPa are considered [8]. The minimum Gibbs energy G is bound by the closed quality of S , i.e. the total amount of sulphur, fluorine and carbon in S does not change and equals 1, 6 and m mol, respectively. For the calculation of the composition there was used the method described in [9].

The composition of S is further expressed by dimensionless numbers x_i (relation (1)), which for gaseous components are molar fractions, and x_N is the relative amount of S/c for 1 mol of gaseous components. Fig. 1 gives the composition of S for $m=1$ mol, $p=1$ MPa, $300 \leq T \leq 1500$ K. It can be seen from Fig. 1 that all the carbon reacts with fluorine, giving CF_4 . The same conclusion also holds for other values of p, m . The composition in the temperature range up to 1500 K has been given because it is affected by a change in the input data with regard to [2]. Also the amount of the component S_2F_{10} , which was not considered in [2], should not be neglected.

The results of the calculation of the equilibrium composition do not, however, provide any information on the rate of possible reactions. It is likely that CF_4 is formed when fluorine from dissociated SF_6 reacts with carbon vapour. CF_4 formed in this way is then a component of the extinguishing medium even at low temperatures. The amount of condensed sulphur depends on m ; e.g. for $p=1$ MPa S/c does not occur in S if $m \leq 0.01$ mol. The magnitude of m also affects the molar

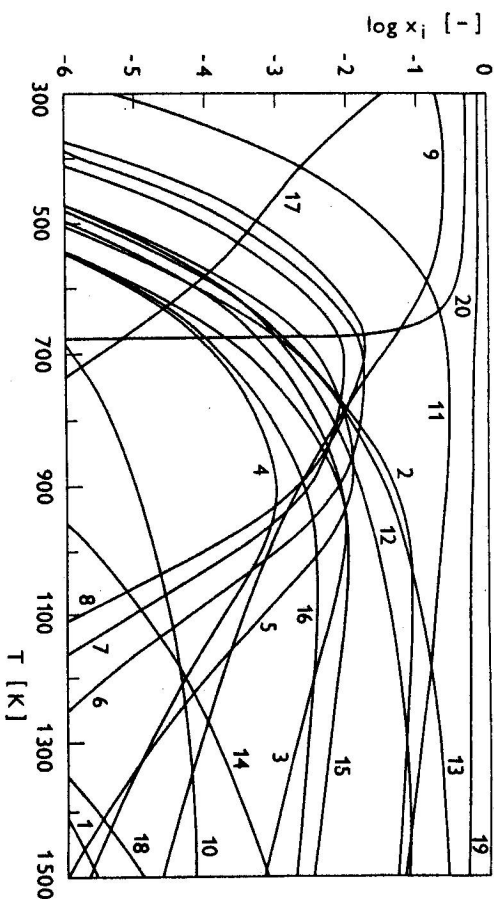


Fig. 1. Composition of S for $p=1$ MPa, $m=1$ mol; 1 - S , 2 - S_2 , 3 - S_3 , 4 - S_4 , 5 - S_5 , 6 - S_6 , 7 - S_7 , 8 - S_8 , 9 - SF_6 , 10 - SF_5 , 11 - SF_4 , 12 - SF_3 , 13 - SF_2 , 14 - SF , 15 - SSF_2 , 16 - $SFSF$, 17 - S_2F_{10} , 18 - F , 19 - CF_4 , 20 - S/c .

fraction of free electrons x_e in S , as can be seen in Fig. 2. For a constant m and T x_e decreases with increasing pressure.

III. THERMODYNAMIC PROPERTIES

Formulae for the calculation of thermodynamic properties of an ideal heterogeneous system are known from literature. The input data for the calculation of the thermodynamic properties of system S are the equilibrium composition x_1, x_2, \dots, x_N , the partial derivative of the composition with respect to p, T , and the standard thermodynamic functions of the system components, which are determined by the partition function. Owing to the limited length of this paper we shall only deal with the specific enthalpy h and the equilibrium specific heat capacity at the constant pressure c_p .

$$h = \frac{1}{M} \sum_{i=1}^N x_i l_i^0, \tag{2}$$

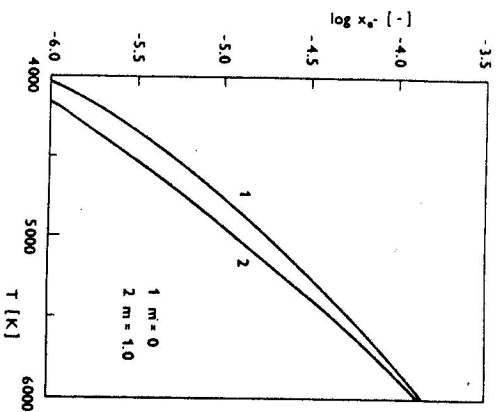


Fig. 2. Dependence of molar fraction of free electrons on T for $p=1$ MPa.

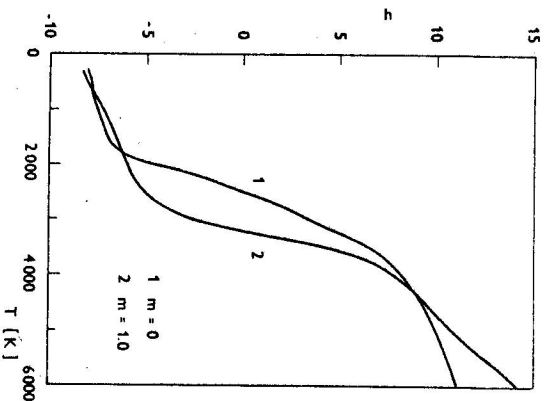


Fig. 3. Dependence of specific enthalpy h on temperature for $p = 1$ MPa, $[h] = \text{MJkg}^{-1}$.

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p, \quad (3)$$

$$M = \sum_{i=1}^N x_i M_i,$$

M_i is the molar mass of the i th component,

$$I_i^0(T) = \Delta_f H_i^0 + T^2 \frac{\partial \Phi_i^0}{\partial T}$$

is the standard total enthalpy of the i th component. For a given system $S(m)$ both h and c_p are functions of p, T . Fig. 3 gives the dependence of h on T for $p=1$ MPa, $m=0$ and 1 mol. Figs 4 and 5 give the temperature dependence of c_p for $p=1$ MPa and for different m . The discontinuities of c_p in Fig. 4 are due to the disappearance of S/c. In addition to these discontinuities, c_p and also h must exhibit discontinuities due to the phase transition in the substance S/c. It follows from relations (3) and (2) that

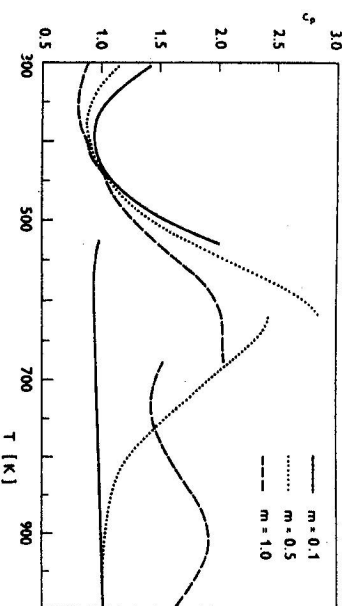


Fig. 4. Dependence of specific heat capacity c_p at constant pressure on temperature, for $p=1$ MPa; $[c_p]=\text{kJkg}^{-1}\text{K}^{-1}$.

where $\partial I_i^0/\partial T$ is the standard molar heat capacity at constant pressure C_{pi} of the i th component. The discontinuities in $C_{pi}(T)$ must of necessity show in the discontinuities in c_p . Fig. 6 illustrates the dependence $C_{pN}(T)$ of the condensed sulphur as found in [5]. Marked on the axis T are the temperatures in which the function $C_{pN}(T)$ is discontinuous or has no derivative with respect to T . The discontinuities in c_p which are due to the discontinuities in $C_{pN}(T)$ are small and they are neglected in Fig. 4.

IV. CONCLUSION

The composition and some thermodynamic properties of SF_6 contaminated with carbon are published for the first time in this article not only for the gaseous phase but also for the condensed phase.

Evaporated carbon reacts with fluorine from dissociated SF_6 and forms a stable gas CF_4 [10]. At low temperature the system S contains, in addition to SF_6 and CF_4 , condensed sulphur and its vapour, SF_4 , and a highly toxic substance S_2F_{10} [11] (see Fig. 1). The temperature dependence of c_p is discontinuous at a temperature at which condensed sulphur disappears and at the temperatures of phase transitions of condensed sulphur. This fact must be taken into account when using c_p in mathematical models of processes taking place in the circuit breaker. SF_6 itself dissociates up to a temperature of 3000 K while CF_4 starts dissociating

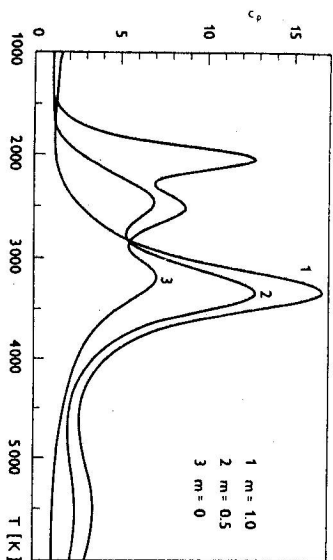


Fig. 5. Dependence of specific heat capacity c_p at constant pressure on temperature, for $p=1$ MPa; $[c_p]=\text{kJkg}^{-1}\text{K}^{-1}$.

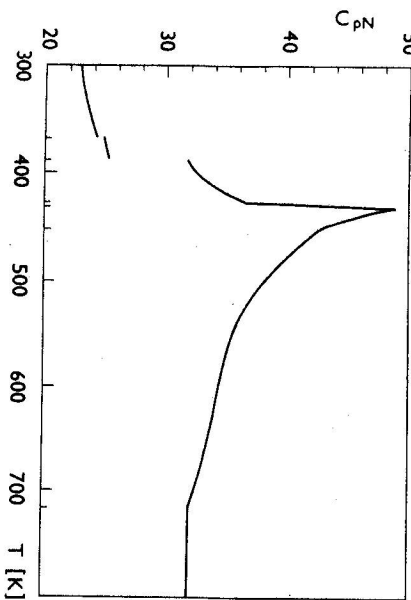


Fig. 6. Standard molar heat capacity at constant pressure $C_{p,m}$ of condensed sulphur; $[C_{p,m}]=\text{Jmol}^{-1}\text{K}^{-1}$.

only at temperatures of over 3000 K. The result is that SF_6 can accumulate more energy than SF_6 with C approximately to a temperature of 4000 K while above this temperature it is SF_6 with C that accumulates more energy (see Fig. 3). The molar fraction of free electrons decreases with increasing m (Fig. 2).

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Received October 18th, 1990

Accepted for Publication March 5th, 1991

ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА ПРОДУКТОВ РЕАКЦИИ SF_6 УГЛЕРОДОМ ПРИ ТЕМПЕРАТУРАХ ДО 6 000 К

В работе обсуждается взаимодействие гасящего средства SF_6 выключателя высокого и сверхвысокого напряжения с углеродом. Предполагается, что в результате взаимодействия возникает изолированная идеальная сетка, которая находится в равновесии. Определены состав, энтропия и теплоемкость при постоянном давлении такой сетки.