NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.
VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES
ON THE EXISTENCE OF GASEOUS SULPHIDES OF THE TRANSITION ELEMENTS

TECHNICAL DOCUMENTARY REPORT No. WADD-TR-60-782, PART IV

MAY 1962

DIRECTORATE OF MATERIALS AND PROCESSES
(MATERIALS CENTRAL)
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

(Prepared under Contract No. AF 61(052)-225 by the Universite Libre de Bruxelles, Brussels, Belgium; R. Colin, P. Goldfinger, and M. Jeunehomme, Authors)
NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified requesters may obtain copies of this report from the Armed Services Technical Information Agency, (ASTIA), Arlington Hall Station, Arlington 12, Virginia.

This report has been released to the Office of Technical Services, U.S. Department of Commerce, Washington 25, D.C., in stock quantities for sale to the general public.

Copies of this report should not be returned to the Aeronautical Systems Division unless return is required by security considerations, contractual obligations, or notice on a specific document.
FOREWORD

This report was prepared by the University of Brussels, Brussels, Belgium under USAF Contract No. AF 61(052)-225. The Contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials", Task No. 735001, "Non-Graphitic". The work was administered under the direction of the Directorate of Materials and Processes, Deputy Commander/Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer. This report covers work done from April 1961 to April 1962.

WADD Technical Report 60-782, Parts I, II, III, V, VI have already been published, Parts VII and VIII are in preparation.
ABSTRACT

Thermodynamic considerations permit us to predict the mode of vaporization of transition element sulphides. MnS is the only clear case where the gaseous sulphide molecule has an appreciable concentration in the saturated vapor. This is confirmed by a mass spectrometric investigation which gave us the measurement $D_g (MnS) = 65 \pm 5$ Kcal/mole.

PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

FOR THE COMMANDER:

W. C. RANKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Laboratory
Directorate of Materials and Processes
ON THE EXISTENCE OF GASEOUS SULPHIDES OF THE TRANSITION ELEMENTS

The Dissociation Energy of Gaseous MnS

It is very important to obtain information on the lattice energy, $\Delta H_0^0[\text{at}]$, of solids, and dissociation energies, $D_0^0$, of gaseous molecules of whole groups of compounds such as homonuclear molecules (1), oxides (2), sulphides (3) etc. and to study the variation of these properties, or ratio of these magnitudes, $\Delta H_0^0[\text{at}]/D_0^0 = \alpha$, as a function of the electronic structure of the constituting atoms. An interesting case is that of the sulphides of transition elements.

The simplest discussion of the mechanism of vaporization of solid sulphides $[\text{MeS}]$ can be based on three processes:

\[
[M\text{eS}] \rightarrow \text{Me} + \frac{1}{2} \text{S}_2 \quad (1)
\]
\[
[M\text{eS}] \rightarrow [\text{Me}] + \frac{1}{2} \text{S}_2 \quad (2)
\]
\[
[M\text{eS}] \rightarrow \text{MeS} \quad (3)
\]

(condensed phases, solid and liquids, are marked by square brackets $[]$, gases without brackets). Complications that occur when instead of reaction (2) stoichiometric compounds...
such as $[\text{Me}_2\text{S}]$ or non stoichiometric solids $[\text{Me}_x\text{S}_y]$ are formed are not discussed here in detail. Association of $S_2$ is not discussed, dissociation shall be mentioned.

Which of the processes (1) or (2) predominates is seen immediately by considering the equilibrium

$$S_2 + 3[\text{Me}] \iff 2[\text{MeS}] + \text{Me} \quad (4)$$

and the magnitude

$$A = 3\Delta H^0_{\text{vapMe}} + D^0_0(S_2) - 4\Delta H^0_{\text{atMeS}} + T\Delta \text{f} \{2[\text{MeS}] + \text{Me} - S_2 - 3[\text{Me}]\} \quad (5)$$

where $\Delta H^0_{\text{vapMe}}$ is the heat of vaporization of one atom-gram $[\text{Me}]$, $\Delta H^0_{\text{atMeS}}$ the heat necessary to transform one half molecule-gram $[\text{MeS}]$ in the constituting gaseous atoms, $D^0_0(S_2) = 100$ kcal$^3$ the dissociation energy of $S_2$ and $\Delta \text{f}$ the difference in free energy functions of the substances given in the braces $\{ \}$.

If $A > 0$ process (2) predominates and

$$-RT\ln\left(\frac{p(\text{Me})}{p(S_2)}\right) = A = \Delta H^0_{\text{vapMe}} + T\Delta \text{f} \quad (6)$$

For the first row of transition elements sulphides$^{(4,5)}$

$\Delta \text{f} \approx -5$ e.u.; the dominant term is the enthalpy difference which from FeS to CuS lies in the narrow limits $\Delta H^0_{\text{vap}}(6) \approx 24 \pm 3$ kcal (well within error limits) i.e. $p(\text{Me})/p(S_2) \approx 10^{-4}$ at 1000°K and $10^{-2}$ at 2000°K. In this case the relation

$$-RT\ln\left(\frac{p(S_2)}{p(\text{MeS})}\right) = D^0_0(\text{MeS}) + 2\Delta H^0_{\text{atMeS}} - D^0_0(S_2) - 2\Delta H^0_{\text{vapA}}$$

$$+ T\Delta \text{f} \{2[\text{Me}] + S_2 - \text{MeS} - [\text{MeS}]\} \quad (7)$$
is obtained from the equilibrium

\[ \text{MeS} + [\text{MeS}] \rightleftharpoons \text{S}_2 + 2[\text{Me}] \]  

(8)

\( \Delta_{\text{f,e}} \) is again small, about + 3 e.u.; from a comparison of oxides and sulphides one obtains \( D_0^0(\text{MeS}) \approx 60 \) to 70 kcal and \( \Delta H_0^0(7) \approx -40 \) to -50 kcal for FeS, CoS, CuS. Thus \( p(\text{MeS})/p(S_2) \) increases with increasing temperature but even at 2000*K reaches only \( \text{10}^{-3} \) to \( \text{10}^{-4} \). This is not easily reconciled with Hsiao and Schlechten's (6) results indicating 20 to 54% Fe and Co transfer in the vaporization of FeS and CoS; these results would mean that \( D_0^0(\text{MeS}) \approx 100 \) kcal. An explanation might be in the terms of more complicated gaseous sulphides such as \( \text{Fe}_2\text{S}_3 \), \( \text{Fe}_2\text{S}_3 \), or gaseous polymers. Finally

\[ -RT \ln \frac{p(S_2)}{p(S)} \approx D_0^0(S_2) + \Delta H_0^0[\text{vapMe}] - 2\Delta H_0^0[\text{MeS]} \] 

leads to \( p(S_2) \approx 10 \) to 100 \( p(S) \). If \([\text{Me}] \) reacts with \([\text{MeS}] \) to give stoichiometric or non stoichiometric compounds \( p(S_2)/p(\text{Me}) \) is even larger.

In the first row of transition elements MnS is the only clear case of \( A < 0 \) (eq.5), with \( \Delta H_0^0 = -64 \); at the end of this row for ZnS and GaS \( \Delta H_0^0 = -99 \) and -59 kcal respectively. For the oxides \( \Delta H_0^0 \) is strongly negative with the exception of CuO (+ 6 kcal), where however probably the actual process is

\[ [\text{CuO}] \Rightarrow \frac{1}{2} [\text{Cu}_2\text{O}] + \frac{1}{2} \text{O}_2. \] 

For negative \( \Delta H_0^0 \), i.e. process (1)
the ratio \( \frac{p(S_2)}{p(\text{MeS})} \) is obtained from the equilibrium:

\[
\text{MeS} \rightleftharpoons \frac{1}{3} \text{[MeS]} + \frac{1}{3} S_2 + \frac{2}{3} \text{Me}
\]  

(9)

and

\[
-RT \ln \frac{p(S_2)}{p(\text{MeS})} = D^o(\text{MeS}) - \frac{2}{3} \Delta H^o(\text{MeS}) - \frac{1}{3} D^o(S_2) + \frac{2}{3} RT \ln 2 + T \Delta \text{f} \left\{ \frac{1}{3} \text{[MeS]} + \frac{1}{3} S_2 + \frac{2}{3} \text{Me} - \text{MeS} \right\}
\]  

(10)

For \( \text{MeS} \) an estimate similar to that above, gives

\[-\log p(S_2)/p(\text{MeS}) \propto -6500/T + 1.5\]

using the mass spectrometric vaporization technique described previously. Experiments were carried out with \( \text{MnS} \) between 1800° and 1900°K: at 1850°K

\[\log p(S_2)/\log p(\text{MnS}) = 2.1\]

From eq. (10) \( D^o(\text{MnS}) = 65 \pm 5 \text{ kcal} \)

was obtained. For this third law method free energy functions of \( \text{MnS} \) were calculated from \( r_e = 2.1 \text{ Å} \) and \( \omega_e = 540 \text{ cm}^{-1} \), the data from were taken for Mn and \( S_2 \). Further \( \Delta H^o_{298} \text{[MnS]} = 49.0 \pm 0.5 \text{ kcal} \) (8, 9, 4); \( \Delta H^o_{298} \text{[MnS]} = 18.7 \pm 0.3 \text{ e.u.} \) (10) and

\[C_p \text{[MnS]} = 11.4 + 1.8 \times 10^{-3} T\]

yield \( \log p(\text{Mn}) = -3.00 \pm 0.35 \); pressure calibrations by complete vaporization of weighed samples yield \(-3.44\). Also

\[-RT \ln p(S)/p(S_2) \approx \frac{2}{3} \left\{ D(S_2) - \Delta H^o(\text{atMnS}) \right\}\]

is in agreement with experiment.

For \( \text{VS}, \text{TiS}, \text{CrS} \) there are no data, however

\[\Delta H^o(\text{atMeO}) - \Delta H^o(\text{atMeS}) = 16.5 \pm 2 \text{ kcal for Ca, Mn, Co, Ni};\]

assuming this difference to be constant \( \Delta H^o \) of eq. (6) is for these three sulphides \(-70 \pm 10 \text{ kcal}\). Assuming \( D^o(\text{MeO}) - D^o(\text{MeS}) \approx 30 \text{ kcal} \)
as for oxides and sulphides of group II$^A$, IV$^B$ and Mn one finds: 

$$-\log(p(S_2)/p(MeS)) \approx -3300/T + 1.5 \text{ and } P(S) \approx 10p(S_2);$$

a favorable situation for observing gaseous sulphides.

For the two other rows of transition elements it seems difficult to make predictions, for the rare earths however one would expect to find gaseous sulphides since $\Delta H^0_{vapMe}$ is relatively low and $D^0_o(MeO)$ high$^{(12)}$. 
REFERENCES.

1. G.Verhaegen, F.E.Stafford, P.Goldfinger, M.Ackerman, XVIIIth International Congress of Pure and Applied Chemistry, Montreal, Canada, 6-12 August 1961, to be published.

2. R.Colin, P.Goldfinger, to be published.


Aeronautical Systems Division, Div/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio

Unclassified report
Thermodynamic considerations permit us to predict the mode of vaporization of transition element sulphides. MnS is the only clear case where the gaseous sulphide molecule has an appreciable concentration in the saturated vapor. This is confirmed by a mass spectro-

metric investigation which gave us the measurement \( D_0^0 \) (MnS) = 65 ± 5 kcal/mole.

Aeronautical Systems Division, Div/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio

Unclassified report
Thermodynamic considerations permit us to predict the mode of vaporization of transition element sulphides. MnS is the only clear case where the gaseous sulphide molecule has an appreciable concentration in the saturated vapor. This is confirmed by a mass spectro-

metric investigation which gave us the measurement \( D_0^0 \) (MnS) = 65 ± 5 kcal/mole.
Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio


Unclassified report

Thermodynamic considerations permit us to predict the mode of vaporization of transition element sulphides. NoS is the only clear case where the gaseous sulphide molecule has an appreciable concentration in the saturated vapor. This is confirmed by a mass spectro-

metric investigation which gave us the measurement $D^0_\text{h}(\text{NoS}) = 65 \pm 5 \text{ kcal/mole}$. 

---

Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio


Unclassified report

Thermodynamic considerations permit us to predict the mode of vaporization of transition element sulphides. NoS is the only clear case where the gaseous sulphide molecule has an appreciable concentration in the saturated vapor. This is confirmed by a mass spectro-

metric investigation which gave us the measurement $D^0_\text{h}(\text{NoS}) = 65 \pm 5 \text{ kcal/mole}$. 

---

1. Manganese sulphide
2. Mass Spectroscopy
I. AFSC Project 7350, Task 735001
II. Contract AF 61(002)-225
III. Université de Bruxelles, Bruxelles, Belgium
IV. R. Colin, P. Goldfinger, M. Jeunhomme
V. Aval fr ONS
VI. In ASTIA collection
Unclassified report
Thermodynamic considerations permit us to predict the mode of vaporization of transition element sulphides. MnS is the only clear case where the gaseous sulphide molecule has an appreciable concentration in the saturated vapor. This is confirmed by a mass spectro-
metric investigation which gave us the measurement $D_0^{\text{MnS}} = 65 \pm 5$ kcal/mole.

1. Manganese sulphide
2. Mass Spectroscopy
I. AFSC Project 7350, Task 735001
II. Contract AF 61(052) - 225
III. Université de Bruxelles, Brusse, Belgium

IV. R. Colin,
F. Goldfinger
M. Jeunehomme
V. Avel fr ONS
VI. In ASIA collection

Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab.
Wright-Patterson AFB, Ohio

Unclassified report
Thermodynamic considerations permit us to predict the mode of vaporization of transition element sulphides. MnS is the only clear case where the gaseous sulphide molecule has an appreciable concentration in the saturated vapor. This is confirmed by a mass spectro-
metric investigation which gave us the measurement $D_0^{\text{MnS}} = 65 \pm 5$ kcal/mole.

1. Manganese sulphide
2. Mass Spectroscopy
I. AFSC Project 7350, Task 735001
II. Contract AF 61(052) - 225
III. Université de Bruxelles, Brusse, Belgium

IV. R. Colin,
F. Goldfinger
M. Jeunehomme
V. Avel fr ONS
VI. In ASIA collection