FOREWORD

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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_0^0 (MnS) = 65 ± 5 Kcal/mole.

PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

FOR THE COMMANDER:

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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, $\Delta H_0^0[at]$, 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, $\Delta H_0^0[at]/D_0^0 = \alpha$, 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 $[MeS]$ can be based on three processes:

$$[MeS] \rightleftharpoons Me + 1/2\ S_2 \qquad (1)$$

$$[MeS] \rightleftharpoons [Me] + 1/2\ S_2 \qquad (2)$$

$$[MeS] \rightleftharpoons MeS \qquad (3)$$

(condensed phases, solid and liquids, are marked by square brackets $[\ ]$, gases without brackets). Complications that occur when instead of reaction (2) stoichiometric compounds

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such as $[Me_2S]$ or non stoichiometric solids $[Me_xS_y]$ 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

$$S_2 + 3\,[Me] \rightleftharpoons 2\,[MeS] + Me \qquad (4)$$

and the magnitude

$$A = 3\Delta H_0^0[vapMe] + D_0^0(S_2) - 4\Delta H_0^0[atMeS] + T\Delta fef\left\{2\,[MeS] + Me - S_2 - 3[Me]\right\} \qquad (5)$$

where $\Delta H_0^0[vapMe]$ is the heat of vaporization of one atom-gram $[Me]$, $\Delta H_0^0[atMeS]$ the heat necessary to transform one half molecule-gram $[MeS]$ in the constituting gaseous atoms, $D_0^0(S_2)$ = 100 kcal$^{(3)}$ the dissociation energy of S_2 and Δ fef the difference in free energy functions of the substances given in the braces $\{\}$.

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

$$-RT\ln p(Me)/p(S_2) = A = \Delta H_0^0 + T\Delta fef \qquad (6)$$

For the first row of transition elements sulphides$^{(4,5)}$ $\Delta fef \approx -5$ e.u. ; the dominant term is the enthalpy difference which from FeS to CuS lies in the narrow limits $\Delta H_0^0(6) \approx +24 \pm 3$ kcal (well within error limits) i.e. $p(Me)/p(S_2) \approx 10^{-4}$ at 1000°K and 10^{-2} at 2000°K. In this case the relation

$$-RT\ln p(S_2)/p(MeS) = D_0^0(MeS) + 2\Delta H_0^0[atMeS] - D_0^0(S_2) - 2\Delta H_0^0[vapA]$$
$$+ T\Delta fef\left\{2\,[Me] + S_2 - MeS - [MeS]\right\} \qquad (7)$$

is obtained from the equilibrium

$$\mathrm{MeS} + [\mathrm{MeS}] \rightleftharpoons \mathrm{S_2} + 2[\mathrm{Me}] \qquad (8)$$

Δfef is again small, about + 3 e.u.; from a comparison of oxides and sulphides one obtains $D_0^0(\mathrm{MeS}) \approx 60$ to 70 kcal and $\Delta H_0^0(7) \approx -40$ to -50 kcal for FeS, CoS, CuS. Thus $p(\mathrm{MeS})/p(\mathrm{S_2})$ increases with increasing temperature but even at 2000°K reaches only 10^{-3} to 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 $D_0^0(\mathrm{MeS}) \approx 100$ kcal. An explanation might be in the terms of more complicated gaseous sulphides such as $\mathrm{Fe_2S}$, $\mathrm{Fe_2S_3}$ or gaseous polymers. Finally $-RT\ln p(\mathrm{S})/p(\mathrm{S_2}) \approx D_0^0(\mathrm{S_2}) + \Delta H_0^0[\mathrm{vapMe}] - 2\Delta H_0^0$ at $[\mathrm{MeS}]$ leads to $p(\mathrm{S_2}) \approx 10$ to $100\ p(\mathrm{S})$. If $[\mathrm{Me}]$ reacts with $[\mathrm{MeS}]$ to give stoichiometric or non stoichiometric compounds $p(\mathrm{S_2})/p(\mathrm{Me})$ 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 ΔH_0^0 is strongly negative with the exception of CuO (+ 6 kcal), where however probably the actual process is $[\mathrm{CuO}] \rightleftharpoons 1/2\ [\mathrm{Cu_2O}] + 1/2\ \mathrm{O_2}$. For negative ΔH_0^0, i.e. process (1) the ratio $p(S_2)/p(MeS)$ is obtained from the equilibrium:

$$MeS \rightleftharpoons 1/3[MeS] + 1/3\ S_2 + 2/3\ Me \qquad (9)$$

and

$$-RT\ln p(S_2)/p(MeS) = D^o_o(MeS) - 2/3\Delta H^o_o[atMeS] - 1/3D^o_o(S_2) + 2/3RT\ln 2$$
$$+ T\Delta\ fef\left\{1/3[MeS] + 1/3\ S_2 + 2/3\ Me - MeS\right\} \qquad (10)$$

For MeS an estimate similar to that above, gives $-\log p(S_2)/p(MeS) \approx -6500/T + 1.5$ using the mass spectrometric vaporization technique described previously(7) experiments were carried out with MnS between 1800° and 1900°K: at 1850°K $\log p(S_2)/\log p(MnS) = 2.1$ From eq.(10) $D^o_o(MnS) = 65 \pm 5$ kcal was obtained. For this third law method free energy functions of MnS were calculated from $r_e = 2.1$ A and $\omega_e = 540\ cm^{-1}$, the data from(5) were taken for Mn and S_2. Further $\Delta H^{o\,f}_{298}[MnS] = 49.0 \pm 0.5$ kcal(8,9,4); $S^o_{298}[MnS] = 18.7 \pm 0.3$ e.u.(10) and $C_p[MnS] = 11.4 + 1.8 \times 10^{-3}T$(11) yield $\log p(Mn) = -3.00 \pm 0.35$; pressure calibrations by complete vaporization of weighed samples yield − 3.44. Also $-RT\ln p(S)/p(S_2) \approx 2/3\left\{D(S_2) - \Delta H^o_o[atMnS]\right\}$ is in agreement with experiment.

For VS, TiS, CrS there are no data, however $\Delta H^o_o[atMeO] - \Delta H^o_o[atMeS] = 16.5 \pm 2$ kcal for Ca, Mn, Co, Ni ; assuming this difference to be constant ΔH^o_o of eq.(6) is for these three sulphides -70 ± 10 kcal. Assuming $D^o_o(MeO) - D^o_o(MeS) \approx 30$ kcal as for oxides and sulphides of group II^A, IV^B and Mn one finds: $-\log p(S_2)/p(MeS) \approx -3300/T + 1.5$ 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 $\Delta H^o_o[\text{vapMe}]$ is relatively low and $D^o_o(\text{MeO})$ high(12).

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