The results of the computations for this particular case indicate that the separation is enhanced by the use of alternating currents, particularly at high applied voltage, and with frequencies higher than the reciprocals of the relaxation times of the reactions. Direct current also achieves separation; however, experimental considerations (for example, the necessity of using very long columns and the probable blurring effect of electrophoretic anomalies due to conductivity and $p$H changes in the boundary region[5]) weigh against its use.

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## Existence of Gaseous Sulphides of the Transition Elements: Dissociation Energy of Gaseous MnS

IT is of interest to obtain data 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[2], etc., and to study the variation of these properties, or the 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 [MeS] can be based on three processes:

$$[\text{MeS}] \rightleftharpoons \text{Me} + 1/2\ \text{S}_2 \tag{1}$$

$$[\text{MeS}] \rightleftharpoons [\text{Me}] + 1/2\ \text{S}_2 \tag{2}$$

$$[\text{MeS}] \rightleftharpoons \text{MeS} \tag{3}$$

(Condensed phases, solid and liquid, 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. Though association of $\text{S}_2$ is not discussed, dissociation is considered.

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

$$\text{S}_2 + 3[\text{Me}] \rightleftharpoons 2[\text{MeS}] + \text{Me} \tag{4}$$

and the magnitude

$$A = 3\Delta H_0^0[\text{vap.Me}] + D_0^0(\text{S}_2) - 4\Delta H_0^0[\text{at.MeS}] + T\Delta fef\{2[\text{MeS}] + \text{Me}-\text{S}_2-3[\text{Me}]\} \tag{5}$$

where $\Delta H_0^0$[vap.Me] is the heat of vaporization of one atom-gm. [Me], $\Delta H_0^0$[at.MeS] the heat necessary to transform one half molecule-gm. [MeS] in the constituting gaseous atoms, $D_0^0(\text{S}_2) = 100$ kcal. (ref. 3) the dissociation energy of $\text{S}_2$ and $\Delta fef$ the difference in free energy functions of the substances given in the braces {}.

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

$$-RT\ln p(\text{Me})/p(\text{S}_2) = A = \Delta H_0^0 + T\Delta fef \tag{6}$$

For the first row of transition element 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), that is, $p(\text{Me})/p(\text{S}_2) \approx 10^{-4}$ at 1,000° K. and $10^{-2}$ at 2,000° K. In this case the relation

$$-RT\ln p(\text{S}_2)/p(\text{MeS}) = D_0^0(\text{MeS}) + 2\Delta H_0^0[\text{at.MeS}] - D_0^0(\text{S}_2) - 2\ \Delta H_0^0[\text{vap.Me}] + T\ \Delta fef\{2[\text{Me}] + \text{S}_2 - \text{MeS} - [\text{MeS}]\} \tag{7}$$

is obtained from the equilbrium:

$$\text{MeS} + [\text{MeS}] \rightleftharpoons \text{S}_2 + 2\ [\text{Me}] \tag{8}$$

$\Delta fef$ is again small, about + 3 e.u.; from a comparison of oxides and sulphides one obtains $D_0^0(\text{MeS}) \approx$ 60–70 kcal. and $\Delta H_0^0(7) \approx -40$ to $-50$ kcal. for FeS, CoS, NiS, CuS. Thus $p(\text{MeS})/p(\text{S}_2)$ increases with increasing temperature but even at 2,000° K. reaches only $10^{-3}$–$10^{-4}$. This is not easily reconciled with Hsiao and Schlechten's[6] results indicating 20–54 per cent 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 given in the terms of more complicated gaseous sulphides such as $\text{Fe}_2\text{S}$, $\text{Fe}_2\text{S}_3$ or gaseous polymers. Finally $-RT\ln p(\text{S})/p(\text{S}_2) \approx D_0^0(\text{S}_2) + \Delta H_0^0[\text{vap.Me}] - 2\Delta H_0^0[\text{at.MeS}]$ leads to $p(\text{S}_2) \approx 10$ to $100\ p(\text{S})$. If [Me] reacts with [MeS] to give stoichiometric or non-stoichiometric compounds $p(\text{S}_2)/p(\text{Me})$ is even larger.

In the first row of transition elements MnS is the only clear case of $A < 0$ (Equation 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 $[\text{CuO}] \rightleftharpoons 1/2\ [\text{Cu}_2\text{O}] + 1/2\ \text{O}_2$. For negative $\Delta H_0^0$, that is, process (1), the ratio $p(\text{S}_2)/p(\text{MeS})$ is obtained from the equilibrium:

$$\text{MeS} \rightleftharpoons 1/3\ [\text{MeS}] + 1/3\ \text{S}_2 + 2/3\ \text{Me} \tag{9}$$

and

$$-R\text{T}\ln p(\text{S}_2)/p(\text{MeS}) = D_0^0(\text{MeS}) - 2/3\ \Delta H_0^0[\text{at.MeS}] - 1/3\ D_0^0(\text{S}_2) + 2/3RT\ln 2 + T\Delta fef\{1/3[\text{MeS}] + 1/3\ \text{S}_2 + 2/3\ \text{Me} - \text{MeS}\} \tag{10}$$

For MnS an estimate similar to that above gives $-\log p(\text{S}_2)/p(\text{MeS}) \approx -6{,}500/T + 1{\cdot}5$. Using the mass spectrometric vaporization technique described previously[7] experiments were carried out with MnS between 1,800° and 1,900° K.: at 1,850° K. $\log p(\text{S}_2)/\log p(\text{MnS}) = 2{\cdot}1$. From equation (10) $D_0^0(\text{MnS}) = 65 \pm 5$ kcal. was obtained. For this third law method free-energy functions were calculated from $r_e = 2{\cdot}1\ A$ and $\omega_e = 540$ cm.$^{-1}$; the data from ref. 5 were taken for Mn and $\text{S}_2$. Further $\Delta H_{298}^0[\text{MnS}] = 49{\cdot}0 \pm 0{\cdot}5$ kcal.[8,9,4] $S_{298}^0[\text{MnS}] = 18{\cdot}7 \pm 0{\cdot}3$ e.u. (ref. 10) and $C_p[\text{MnS}] = 11{\cdot}4 + 1{\cdot}8 \times 10^{-3}T$ (ref. 11) yield $\log p(\text{Mn}) = -3{\cdot}00 \pm 0{\cdot}35$; pressure calibrations by complete evaporation of weighed samples yield $-3{\cdot}44$. Also $-RT\ \ln p(\text{S})/p(\text{S}_2) \approx 2/3\{D(\text{S}_2) - \Delta H_0^0[\text{at.MnS}]\}$ is in agreement with experiment.

For VS, TiS, CrS there are no data: however, $\Delta H_0^0[\text{at.MeO}] - \Delta H_0^0[\text{at. MeS}] = 16{\cdot}5 \pm 2$ kcal. for Ca, Mn, Co, Ni; assuming this difference to be constant $\Delta H_0^0$ of equation (6) is for these three sulphides $-70 \pm 10$ kcal. Assuming $D_0^0(\text{MeO}) - D_0^0(\text{MeS}) \approx 30$ kcal. as for oxides and sulphides of groups II$^A$, IV$^B$ and Mn one obtains: $\log p(\text{S}_2)$

$p(\text{MeS}) \approx -3{,}300/T + 1{\cdot}5$ and $p(\text{S}) \approx 10p(\text{S}_2)$: a favourable 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 $\Delta H_0^0$[vap.Me] is relatively low and $D_0^0$(MeO) high[12].

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## Reactions of Gaseous Hydroxyl Radicals

VERY little is known of the rates of reaction of hydroxyl radicals. The most extensive work is that of Avramenko and Lorentso[1], but that has been critically reviewed by Steacie[2]. In the present work the homogeneous decomposition of hydrogen peroxide was used as a source of hydroxyl radicals[3], and the relative rates at which hydroxyl radicals react with methane, formaldehyde and carbon monoxide were estimated. The method was checked by independent experiments wherein methane was oxidized thermally at 500° C. to formaldehyde, carbon monoxide and carbon dioxide.

When, using helium as a carrier gas, hydrogen peroxide was decomposed in the presence of methane and carbon monoxide, the competing reactions were:

$$\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O} \tag{1}$$

and

$$\text{CO} + \text{OH} = \text{CO}_2 + \text{H} \tag{2}$$

In the presence of small amounts of oxygen, hydrogen atoms were removed by the chain ending reaction

$$\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M} \tag{3}$$

whereas methyl radicals were converted to ethane and a little formaldehyde. Under these conditions:

$$\frac{k_1}{k_2} = \frac{2\text{C}_2\text{H}_6 + \text{CH}_2\text{O}}{\text{CO}_2} \times \frac{\text{CO}}{\text{CH}_4}$$

The CO/CH$_4$ ratio was varied by a factor of 50 yet the values of $k_1/k_2$ remained constant. Even at temperatures as low as 400° C. where heterogeneous decomposition of hydrogen peroxide predominates, it was found that carbon monoxide and methane were homogeneously oxidized according to reactions 1 and 2.

When methane and oxygen were added to the gas stream most of the methyl radicals formed reacted with oxygen to give formaldehyde, which reacted further according to the reactions:

$$\text{OH} + \text{CH}_2\text{O} = \text{HCO} + \text{H}_2\text{O} \tag{4}$$

$$\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2 \tag{5}$$

The results are detailed below.

| | 400° C. | 450° C. | 525° C. | 600° C. | 650° C. |
|---|---|---|---|---|---|
| $k_1/k_2$ | 0·83 | 1·10 | 2·1 | 2·7 | 3·4 |
| $k_4/k_1$ | — | — | 33 | 27 | 22 |

In the oxidation of methane it was found that the relative rates of oxidation of methane and formaldehyde were proportional to their relative concentrations when surface oxidations were eliminated. Under these conditions, throughout reactions involving a considerable range of mixture strengths, reactions 4 and 1 seemed to predominate in the oxidation. A value of 35 ± 10 was obtained for $k_4/k_1$ at 500° C.

The variation of $k_1/k_2$ with temperature gives 7 kcal./mole for $E_1 - E_2$, which is consistent with the value of 10–30 for $k_1/k_2$ determined at about 1,800° K. by Westenberg and Fristrom[4]. It explains why less carbon dioxide is formed in the oxidation of rich methane/oxygen mixtures at higher temperatures.

The ratio of the stearic factors $P_1/P_2$ must be about 100. This can be understood if the hydroxyl radical has to approach along the axis of the carbon monoxide molecule to give the linear carbon dioxide molecule.

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## Synthesis of a Protected Octapeptide Analogue of Hypertensin II

IN order to investigate whether the basicity of the amino-acid residue at position 2 in hypertensin II has any strong bearing on its biological activity or affects the balance of oxytocic and pressor properties of this hormone, the histidine[1]–hypertensin analogue[2] was synthesized in this laboratory. I used the procedure for histidyl peptides[1], which also leads to the synthesis of the im. benzyl analogue. The latter might spread light on the biological significance of the imidazole ring of histidine.

In an earlier communication[2] the synthesis of a protected heptapeptide, carbobenzoxy-im. benzyl-L-histidyl-L-valyl-L-tyrosyl-L-iso-leucyl-im. benzyl-L-histidyl-L-prolyl-L-phenylalanine methyl ester, and its corresponding benzyl ester was reported. I now wish to record the synthesis of a protected octapeptide with the amino-acid sequence asp.his.val.tyr.ileu.his.pro.phe.

In view of the sensitivity of the aspartyl bond[3] and in order also to diminish the danger of racemization.