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## VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES

### PART XVII. THERMODYNAMIC STUDY OF TIN SELENIDE AND TIN TELLURIDE USING A MASS SPECTROMETER

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AIR FORCE MATERIALS LABORATORY  
RESEARCH AND TECHNOLOGY DIVISION  
AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 7350, Task No. 735001

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Universite Libre de Bruxelles, Brussels, Belgium;  
R. Colin and J. Drowart)

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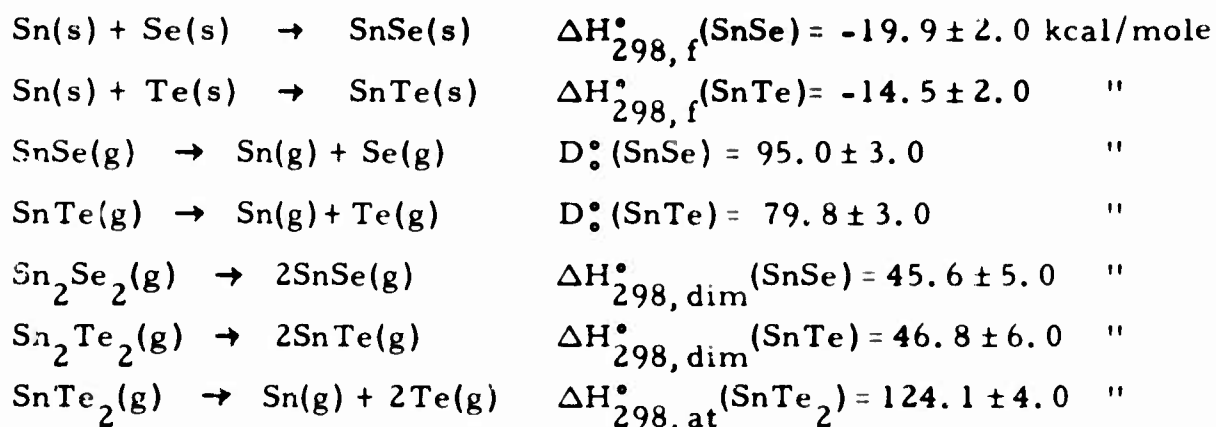
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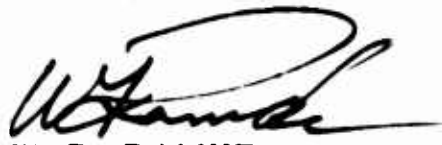
## ABSTRACT

In a mass spectrometric investigation of the vapor in equilibrium with solid SnSe and solid SnTe, a number of reaction enthalpies were measured which combined with known thermochemical data yield:



The dissociation energies are compared to the available spectroscopic data.

This technical documentary report has been reviewed and is approved.



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# THERMODYNAMIC STUDY OF TIN SELENIDE AND TIN TELLURIDE USING A MASS SPECTROMETER

## INTRODUCTION

Mass spectrometric studies of the vaporization of Group IV (Me)-Group VI (X) compounds or systems include those of  $\text{SiO}_2$  and  $\text{SiO}_2 + \text{Si}^{(1)}$ ,  $\text{GeO}_2^{(2)}$ ,  $\text{PbSe}^{(3)}$ ,  $\text{PbTe}^{(3)}$ ,  $\text{SnS}^{(4)}$  and  $\text{PbS}^{(4)}$ . These investigations have shown the presence in the gas phase of  $\text{MeX}_2$  molecules and  $(\text{MeX})_n$  polymers in addition to the spectroscopically well known  $\text{MeX}$  molecules<sup>(5)</sup>.

The composition of the saturated vapor of other group IV-group VI compounds have now been studied mass spectroscopically in this laboratory<sup>(6)</sup>. This paper reports the details of the study of  $\text{SnSe}$  and  $\text{SnTe}$ .

The total pressure of both tin selenide and telluride have been measured by Nesterova, Pashinkin and Novoselova<sup>(7)</sup> and Hirayama, Ichikawa and De Roo<sup>(8)</sup> using classical techniques. In both cases the evaporation was carried out below the known melting points<sup>(9)</sup>. A standard heat of formation  $\Delta H_{298, f}^\circ = -14.6 \pm 0.3$  kcal/mole has been obtained for  $\text{SnTe(s)}$  by McAteer and Seltz<sup>(10)</sup>.

The spectroscopic data<sup>(11)</sup> for  $\text{SnSe(g)}$  and  $\text{SnTe(g)}$  include the vibrational frequencies of the ground state and of several excited states. For one of the electronically excited states of  $\text{SnSe}$ , the E state, a precise value for the convergence limit is known. A graphical extrapolation gives 4.41 eV., while estimates of the onset of continuous absorption gives 4.54 eV. On the assumption that the E state dissociates into a pair of ground state atoms

$^3P + ^3P$ , Vago and Barrow<sup>(11)</sup> had proposed a value for the dissociation energy of SnSe,  $D'_0(\text{SnSe}) = 4.54 \text{ eV}$ . For SnTe there are no well known convergence limits. For the E state there seems to be a region of continuous absorption which leads to a convergence limit of 4.07 eV. Vago and Barrow state<sup>(11)</sup> however ... "since we have not been able to put forward a satisfactory vibrational analysis for the E-X system..., this estimate... must be treated with considerable reserve". Nevertheless those authors proposed a value for the dissociation energy  $D'_0(\text{SnTe}) = 4.1 \text{ eV}$  based both on this convergence limit and the linear Birge-Sponer extrapolation for the ground state.

The purpose of this study was to establish the nature of the atomic and molecular species composing the saturated vapor of SnSe and SnTe, to determine their stability and in particular that of the SnX molecules in order to compare the thermochemical value of the dissociation energies with the convergence limits of the excited states observed spectroscopically.

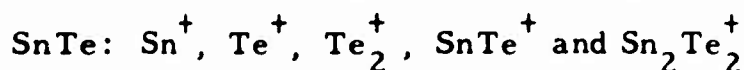
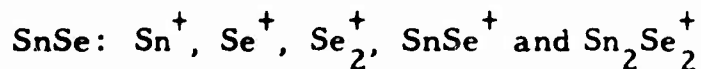
## EXPERIMENTAL PROCEDURE

The main features of the mass spectrometer and Knudsen effusion cell as well as the experimental procedure have been described previously previously<sup>(4, 12-15)</sup>. For the present study a small quartz cell with an effusion orifice of  $0.48 \cdot 10^{-2} \text{ cm}^2$  was used. After evaporation the cell showed no signs of reaction with the samples. The temperatures were measured with a Pt-PtRh (10%) thermocouple.

## RESULTS

### A. Composition of the Vapors.

The atomic and molecular ions, identified from their mass and isotopic distribution, characteristic of the SnSe and SnTe systems were



Relative ion intensities for nominal 33 eV electrons were respectively

at the average temperatures of the experiments:

$$\text{SnSe}(870^\circ\text{K}) : 4.6 \times 10^{-2}; 9.3 \times 10^{-3}; 3.5 \times 10^{-4}; 1; 4.4 \times 10^{-3}$$

$$\text{SnTe}(910^\circ\text{K}) : 6.3 \times 10^{-2}; 2.1 \times 10^{-2}; 4.1 \times 10^{-3}; 1; 4.0 \times 10^{-3}; 6.9 \times 10^{-3}$$

The interception of the molecular beam<sup>(15)</sup> showed that these ions were formed from neutral species originating from the cell. Ionization efficiency curves were measured for several of these ions and the linear extrapolation method used to obtain approximate appearance potentials, the energy scale being calibrated with the known appearance potential of water<sup>(16)</sup>.

In the SnSe system, the relative intensities and appearance potentials showed that  $\text{SnSe}^+$  and  $\text{Sn}_2\text{Se}_2^+$  are parent ions. The appearance potential of  $\text{SnSe}^+$  ( $9.7 \pm 0.5$  eV) can be compared to the ionization potentials of the isoelectronic diatomic molecules  $\text{As}_2$ :  $11 \pm 0.3$  eV,<sup>(17)</sup> and  $\text{Sb}_2$ :  $8.4 \pm 0.3$  eV<sup>(18)</sup>. In the same manner the appearance potential of  $\text{Sn}_2\text{Se}_2^+$  ( $9.8 \pm 0.5$  eV) can be compared to the ionization potentials of  $\text{As}_4$ :  $9.0 \pm 0.5$ <sup>(17)</sup> and  $\text{Sb}_4$ :  $7.7 \pm 0.3$ <sup>(18)</sup>. The  $\text{Se}_2^+$  ion can be attributed to direct ionization of  $\text{Se}_2$  molecules present in the vapor and not to fragmentation of  $\text{Sn}_2\text{Se}_2$  by analogy with the behavior under electron impact of  $\text{Sn}_2\text{S}_2$ <sup>(4)</sup>. The presence of  $\text{Se}_2$  molecules in the gas phase is further sustained by thermodynamic calculations to be presented below. From the comparison of the measured appearance potentials of  $\text{Sn}^+$  ( $12.8 \pm 0.5$  eV) and  $\text{Se}^+$  ( $12.7 \pm 0.5$  eV) with the ionization potentials of tin (7.30 eV)<sup>(19)</sup> and selenium (9.73 eV)<sup>(19)</sup> it was concluded that these ions are fragment ions. The saturated vapor of SnSe is thus mainly composed of SnSe molecules and small quantities of  $\text{Sn}_2\text{Se}_2$  and  $\text{Se}_2$  molecules.

The ionization efficiency curve of the  $\text{Te}^+$  ion in the SnTe system showed that two processes lead to the formation of this ion. The first appearance potential of  $\text{Te}^+$  ( $9.5 \pm 1.0$  eV) agrees within experimental error with the ionization potential of tellurium<sup>(19)</sup> (9.95 eV) and was

therefore attributed to direct ionization of atomic tellurium. The second ( $12.1 \pm 1.0$  eV) was due to the fragmentation of SnTe. The measured appearance potential of the  $\text{SnTe}^+$  ion,  $9.1 \pm 0.5$  eV shows it to be a parent ion. Although no appearance potential were measured, it can be concluded that  $\text{Sn}_2\text{Te}_2^+$  and  $\text{Te}_2^+$  are also parent ions. The  $\text{SnTe}_2^+$  ions were considered as parent ions on the basis that the usual fragmentation<sup>(4)</sup> of  $\text{Me}_2\text{X}_2$  dimers of the group IV-group VI molecules by electron impact yields  $\text{Me}_2\text{X}^+$  and  $\text{Me}_2^+$  ions. The ion intensity of  $\text{SnTe}_2^+$  was also larger than that of the  $\text{Sn}_2\text{Te}_2^+$  ions. It should be noted that the  $\text{SnTe}_2$  molecule is of the same general formula as the well known  $\text{CO}_2$ ,  $\text{CS}_2$  and  $\text{SiO}_2$ <sup>(1)</sup> molecules and that other group IV-group VI molecules of this type have been identified<sup>(20)</sup>:  $\text{SiS}_2$ ,  $\text{SiSe}_2$ ,  $\text{SiTe}_2$  and  $\text{GeTe}_2$ . The saturated vapor above SnTe is thus mainly composed of SnTe with small concentrations of  $\text{Sn}_2\text{Te}_2$ ,  $\text{Te}_2$ ,  $\text{SnTe}_2$  molecules and Te atoms. Both with SnSe and SnTe, when the samples were completely vaporized, small quantities (approximately 1% of the initial sample) of metallic Sn were left in the evaporation cell.

#### B. Pressure Data.

In order to obtain absolute values of the pressures, vaporizations were carried out quantitatively. Weighted samples of either SnSe or SnTe (about 100 mgrs) were therefore vaporized completely and the ion intensity of the main component (SnSe or SnTe) of the vapor integrated with time. The contribution of the minor species to the weight-loss is negligible in both cases. Partial pressures of the minor species were derived from the relation<sup>(15)</sup>

$$\frac{P_1}{P_2} = \frac{I_1^+ \sigma_2 \gamma_2 T_1}{I_2^+ \sigma_1 \gamma_1 T_2} \quad (1)$$

where  $P$  is the partial pressure,  $I^+$  the ion intensity,  $\sigma$  the ionization cross section,  $\gamma$  the secondary electron multiplier efficiency and  $T$  the

absolute temperature.

Table I gives the  $\sigma$  and  $\gamma$  values used. For atomic species the  $\sigma$  values used were those calculated by Otvos and Stevenson<sup>(21)</sup>. For symmetric diatomic molecules the ionization cross section was taken as 1.6 times the value for the corresponding atom as shown to hold for  $\text{Se}_2$  and  $\text{Te}_2$ <sup>(22, 23)</sup> and other dimers<sup>(24, 25)</sup>. For other molecules the sum of 0.8 times the ionization cross section of the constituent atoms was used. The secondary multiplier efficiency  $\gamma$  was estimated from the calibration curve of a multiplier analogous to the one used in this work<sup>(26)</sup> and molecular effects on the first dynode of the electron multiplier were taken into account as suggested by Stanton, Chupka and Inghram<sup>(27)</sup>.

The vapor pressure of SnSe and SnTe are summarized in Fig. 1. and 2. and compared to vapor pressure determinations by Nesterova, Pashinkin and Novoselova<sup>(7)</sup> and Hirayama, Ichikawa and DeRoo<sup>(8)</sup>

TABLE I. Relative ionization cross section and multiplier efficiencies.

| Molecule or atom                | Cross section | Multiplier efficiency |
|---------------------------------|---------------|-----------------------|
| Se                              | 29.6          | 0.48                  |
| SnSe                            | 35.5          | 0.41                  |
| Sn <sub>2</sub> Se <sub>2</sub> | 56.8          | 0.32                  |
| Te                              | 25.6          | 0.51                  |
| Te <sub>2</sub>                 | 41.0          | 0.37                  |
| SnTe                            | 41.1          | 0.38                  |
| SnTe <sub>2</sub>               | 53.4          | 0.25                  |
| Sn <sub>2</sub> Te <sub>2</sub> | 65.8          | 0.27                  |

### C. Enthalpy of Sublimation and Formation.

#### 1. SnSe

A second law treatment of the various experiments shown in fig. 1 led to an average value for the heat of sublimation:

$\Delta H_{900, \text{subl}}^{\circ}(\text{SnSe}) = 48.6 \pm 5.0$  kcal/mole, compared with the literature values 42.0<sup>(7)</sup> and 48.0<sup>(8)</sup> kcal/mole at similar temperatures. An

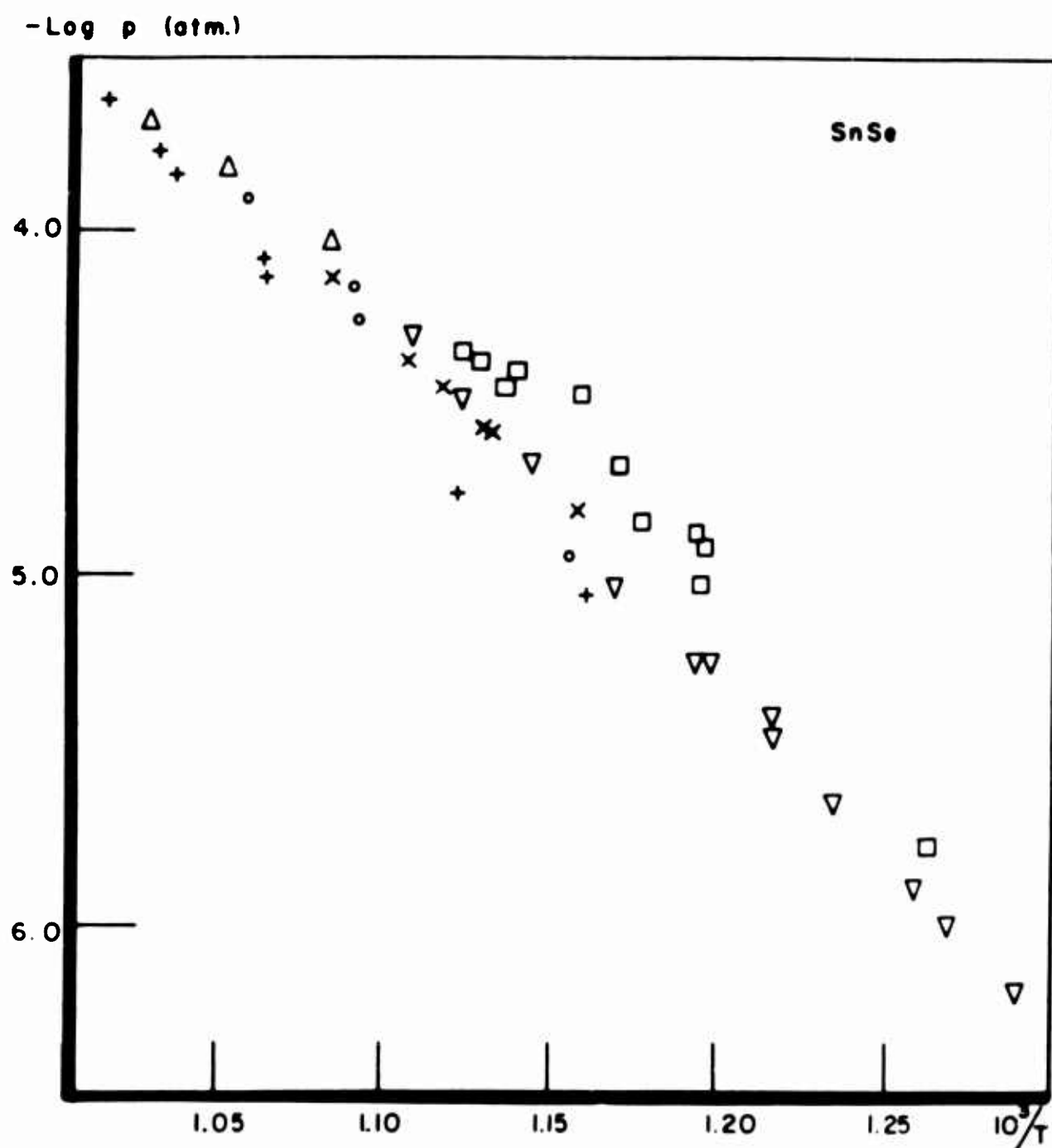


Fig. 1. Vapor pressure of SnSe

Nesterova, Pashinkin and Novoselova<sup>(7)</sup>

Hirayama, Ichikawa and De Roo<sup>(8)</sup>

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+ This work exp. n° 65.10

This work exp. n° 65.11

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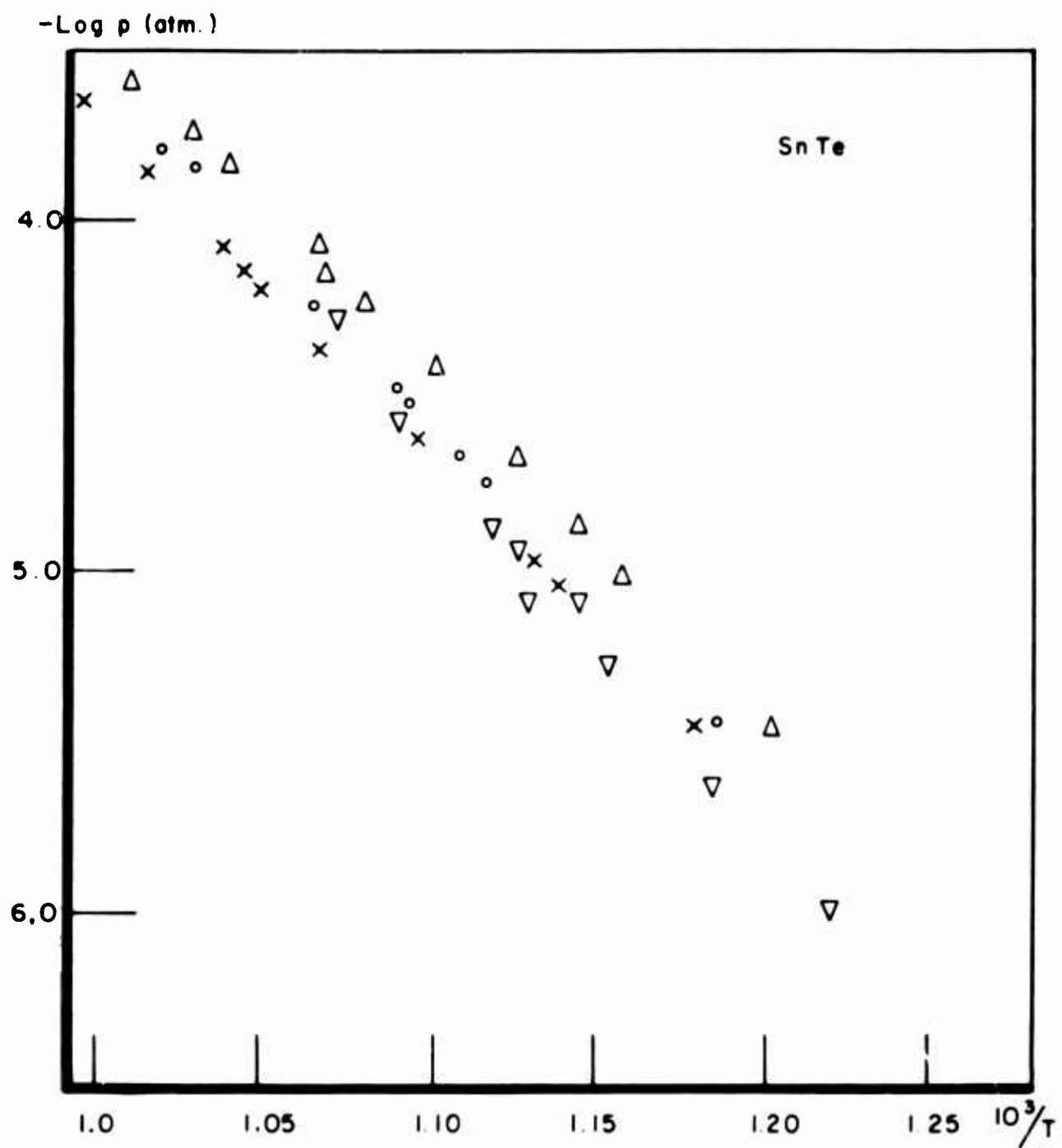


Fig. 2. Vapor Pressure of SnTe

Nesterova, Pashinkin and Novoselova<sup>(7)</sup>

Hirayama, Ichikawa and De Roo<sup>(8)</sup>

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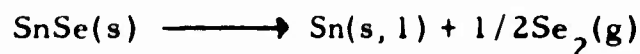
estimate of the difference in heat content  $H_{900}^{\circ} - H_{298}^{\circ}$  was made for solid SnSe by using approximation methods described by Kubaschewski and Evans<sup>(28)</sup>, while the corresponding quantity for gaseous SnSe is known<sup>(29)</sup> from spectroscopic data<sup>(5)</sup>. Whence

$$\Delta H_{298, \text{subl.}}^{\circ} (\text{SnSe}) = 50.3 \pm 6.0 \text{ kcal/mole}$$

Since absolute values of the pressure of SnSe were determined, a third law treatment could be applied provided an estimate of the free energy function -  $\left( \frac{G_T^{\circ} - H_{298}^{\circ}}{T} \right)$  of solid SnSe be made. By comparison with other IV-VI compounds a value of the entropy  $S_{298}^{\circ} (\text{SnSe(s)}) = 22.5 \text{ e. u.}$  was derived. This leads to the estimated free energy function values given in Table II which gives also literature values<sup>(29, 31)</sup> for the other gaseous and solid species encountered in this study. In Table III, the third law values of  $\Delta H_{298, \text{subl.}}^{\circ} (\text{SnSe})$  are given; the mean value  $51.0 \pm 2.5 \text{ kcal/mole}$  is in agreement with the second law value.

A similar third law treatment of the pressure data of Nexterova, Pashinkin and Novoselova<sup>(7)</sup> leads to a value of  $51.5 \pm 2.5 \text{ kcal/mole}$ , and of the pressure data of Hirayama, Ichikawa and De Roo<sup>(8)</sup> to  $51.0 \pm 2.5 \text{ kcal/mole}$ .

From the  $\text{Se}_2$  partial pressures, the enthalpy change for the reaction



was calculated. The values obtained are given in Table IV.

TABLE II. Free energy functions  $-\left(\frac{G_T^\circ - H_{298}^\circ}{T}\right)$  in cal/degree/mole

|                                     | 800°K | 900°K | 1000°K | ref.   |
|-------------------------------------|-------|-------|--------|--------|
| Sn(s, l)                            | 16.1  | 16.8  | 17.6   | 29     |
| SnSe(s)                             | 26.8  | 28.0  | 29.0   | -      |
| SnSe(g)                             | 64.0  | 64.7  | 65.3   | 27, 28 |
| Se <sub>2</sub> (g)                 | 63.4  | 64.0  | 64.6   | 29     |
| Sn <sub>2</sub> Se <sub>2</sub> (g) | 86.3  | 87.8  | 89.2   | -      |
| Te(g)                               | 45.4  | 45.8  | 46.2   | 29     |
| SnTe(s)                             | 28.6  | 29.8  | 30.7   | 28     |
| SnTe(g)                             | 65.7  | 66.5  | 67.2   | 27, 28 |
| Te <sub>2</sub> (g)                 | 67.2  | 68.0  | 68.6   | 29     |
| Sn <sub>2</sub> Te <sub>2</sub> (g) | 90.7  | 92.2  | 93.6   | -      |
| SnTe <sub>2</sub> (g)               | -     | -     | 85.9   | -      |

By combining the average value  $\Delta H_{298}^\circ = 37.0 \pm 1.5$  kcal/mole with the heat of sublimation of Se<sub>2</sub>,  $\Delta H_{298, \text{subl.}}^\circ(\text{Se}_2) = 34.2 \pm 2.0$  kcal/mole<sup>(31)</sup> a value of the enthalpy of formation of solid SnSe is obtained:  $\Delta H_{298, f}^\circ(\text{SnSe}) = -19.9 \pm 2.0$  kcal/mole which can be compared to the estimated value  $-16.5 \pm 2.0$  kcal/mole given by Kubaschewski and Evans<sup>(28)</sup>.

TABLE III. Enthalpy of sublimation of SnSe

| Exper. n° | T°K | -log p (SnSe)<br>(atm) | $\Delta \left\{ - \left( \frac{G_T^\circ - H_{298}^\circ}{T} \right) \right\}$ | $\Delta H_{298, \text{subl.}}^\circ$<br>(kcal/mole) |
|-----------|-----|------------------------|--------------------------------------------------------------------------------|-----------------------------------------------------|
| 65.08     | 792 | 5.79                   | 37.2                                                                           | 50.4                                                |
|           | 835 | 4.94                   | 37.1                                                                           | 49.9                                                |
|           | 836 | 4.90                   | 37.1                                                                           | 49.7                                                |
|           | 871 | 4.50                   | 36.9                                                                           | 50.1                                                |
|           | 853 | 4.69                   | 37.0                                                                           | 50.4                                                |
|           | 876 | 4.43                   | 36.8                                                                           | 50.0                                                |
|           | 887 | 4.38                   | 36.8                                                                           | 50.4                                                |
|           | 884 | 4.39                   | 36.8                                                                           | 50.3                                                |
|           | 879 | 4.47                   | 36.8                                                                           | 50.3                                                |
|           | 848 | 4.85                   | 37.0                                                                           | 50.2                                                |
|           | 837 | 5.04                   | 37.1                                                                           | 50.3                                                |
| 65.10     | 861 | 5.06                   | 37.0                                                                           | 51.8                                                |
|           | 890 | 4.78                   | 36.8                                                                           | 52.0                                                |
|           | 936 | 4.16                   | 36.6                                                                           | 52.3                                                |
|           | 937 | 4.10                   | 36.6                                                                           | 52.1                                                |
|           | 961 | 3.86                   | 36.5                                                                           | 52.0                                                |
|           | 965 | 3.80                   | 36.4                                                                           | 52.0                                                |
|           | 979 | 3.64                   | 36.4                                                                           | 51.9                                                |
| 65.11     | 864 | 4.96                   | 37.0                                                                           | 51.5                                                |
|           | 912 | 4.27                   | 36.6                                                                           | 51.1                                                |
|           | 914 | 4.18                   | 36.6                                                                           | 50.9                                                |
|           | 942 | 3.92                   | 36.5                                                                           | 50.6                                                |
| 65.12     | 920 | 4.05                   | 36.6                                                                           | 50.8                                                |
|           | 948 | 3.84                   | 36.5                                                                           | 51.3                                                |
|           | 969 | 3.70                   | 36.4                                                                           | 51.7                                                |
|           |     |                        | mean:                                                                          | 51.0                                                |

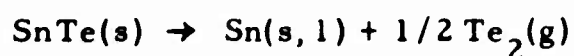
TABLE IV. Enthalpy change for the reaction  $\text{SnSe(s)} \rightarrow \text{Sn(s, l)} + 1/2\text{Se}_2(\text{g})$

| Exper. N° | T°K | $-\log p (\text{Se}_2)$<br>(atm) | $\Delta \left\{ - \left( \frac{G_T^\circ - H_{298}^\circ}{T} \right) \right\}$ | $\Delta H_{298}^\circ$<br>(kcal/mole) |
|-----------|-----|----------------------------------|--------------------------------------------------------------------------------|---------------------------------------|
| 65.11     | 976 | 7.36                             | 20.9                                                                           | 36.8                                  |
|           | 989 | 7.17                             | 20.9                                                                           | 36.9                                  |
| 65.12     | 949 | 7.83                             | 20.9                                                                           | 36.9                                  |
|           | 968 | 7.69                             | 20.9                                                                           | 37.3                                  |
| mean      |     |                                  |                                                                                | 37.0                                  |

## 2. SnTe.

The enthalpy of sublimation  $\Delta H_{900, \text{subl.}}^\circ (\text{SnTe})$  obtained by a second law treatment is:  $\Delta H_{900, \text{subl.}}^\circ (\text{SnTe}) = 46.4 \pm 5.0$  kcal/mole, compared to the literature values  $44.9^{(7)}$  and  $51.4^{(8)}$  kcal/mole at similar temperatures. Estimating as for SnSe the heat content,  $H_{900}^\circ - H_{298}^\circ$  for solid SnTe, a value  $\Delta H_{298, \text{subl.}}^\circ (\text{SnTe}) = 48.1 \pm 6.0$  kcal/mole was obtained. The value obtained by a third law treatment (Table V) is  $\Delta H_{298, \text{subl.}}^\circ (\text{SnTe}) = 52.1 \pm 2.0$  kcal/mole. Preference is given to the third law value on account of the fact that the entropy of solid SnTe is known<sup>(30)</sup>  $S_{298}^\circ = 24.2 \pm 0.1$  e. u. and that the estimate of the free energy function of SnTe(s) is therefore reduced to that of the heat capacity between 900° and 298°K. A similar third law treatment of the pressure data of Nesterova, Pashinkin and Novoselova<sup>(7)</sup> and Hiriyama, Ichikawa and De Roo<sup>(8)</sup> leads respectively to a values of  $52.6 \pm 2.0$  and  $52.8 \pm 2.0$  kcal/mole.

The enthalpy change for the reaction

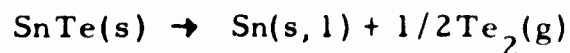


were also calculated and is given in Table VI. Using the enthalpy of sublimation  $\Delta H_{298, \text{subl.}}^\circ (\text{Te}_2) = 39.6 \pm 2.0 \text{ kcal/mole}^{(33)}$ , the heat of formation  $\Delta H_{298, f}^\circ (\text{SnTe})$  was computed to be  $\Delta H_{298, f}^\circ (\text{SnTe}) = -14.5 \pm 2.0 \text{ kcal/mole}$ , in agreement with the value obtained by McAteer and Seltz<sup>(10)</sup>,  $\Delta H_{298, f}^\circ (\text{SnTe}) = -14.6 \pm 0.3 \text{ kcal/mole}$ . This agreement is a confirmation of the free energy function used for SnTe(s).

TABLE V. Enthalpy of sublimation of SnTe.

| Exper. N° | T°K | -log p (SnTe)<br>(atm) | $\Delta \left\{ - \left( \frac{G_T - H_{298}}{T} \right) \right\}$ | $\Delta H_{298, \text{subl.}}^\circ$<br>(kcal/mole) |
|-----------|-----|------------------------|--------------------------------------------------------------------|-----------------------------------------------------|
| 65.06     | 872 | 5.24                   | 36.8                                                               | 53.0                                                |
|           | 915 | 4.52                   | 36.7                                                               | 52.4                                                |
|           | 917 | 4.47                   | 36.7                                                               | 52.4                                                |
|           | 894 | 4.74                   | 36.7                                                               | 52.1                                                |
|           | 844 | 5.44                   | 36.9                                                               | 52.1                                                |
|           | 939 | 4.24                   | 36.6                                                               | 52.6                                                |
|           | 902 | 4.66                   | 36.7                                                               | 52.3                                                |
|           | 971 | 3.84                   | 36.5                                                               | 52.4                                                |
|           | 981 | 3.79                   | 36.5                                                               | 52.8                                                |
|           |     |                        |                                                                    |                                                     |
| 65.09     | 936 | 4.14                   | 36.6                                                               | 52.0                                                |
|           | 962 | 3.83                   | 36.6                                                               | 52.1                                                |
|           | 938 | 4.06                   | 36.6                                                               | 51.7                                                |
|           | 908 | 4.41                   | 36.7                                                               | 51.6                                                |
|           | 887 | 4.68                   | 36.7                                                               | 51.9                                                |
|           | 864 | 5.02                   | 36.8                                                               | 51.6                                                |
|           | 832 | 5.46                   | 36.9                                                               | 51.5                                                |
|           | 874 | 4.87                   | 36.8                                                               | 51.6                                                |
|           | 926 | 4.23                   | 36.6                                                               | 51.8                                                |
|           | 972 | 3.73                   | 36.5                                                               | 52.1                                                |
|           | 990 | 3.59                   | 36.5                                                               | 52.4                                                |
|           |     |                        |                                                                    |                                                     |
|           |     |                        | mean                                                               | 52.1                                                |

TABLE VI. Enthalpy change for the reaction



| Expr N° | T°K | -log p (Te <sub>2</sub> )<br>(atm) | $\Delta \left\{ - \left( \frac{G_T^\circ - H_{298}^\circ}{T} \right) \right\}$ | $\Delta H_{298}^\circ$ (I)<br>(kcal/mole) |
|---------|-----|------------------------------------|--------------------------------------------------------------------------------|-------------------------------------------|
| 65.06   | 939 | 6.93                               | 21.0                                                                           | 34.6                                      |
|         | 971 | 6.19                               | 21.0                                                                           | 34.2                                      |
|         | 981 | 6.14                               | 21.0                                                                           | 34.4                                      |
| 65.09   | 936 | 6.65                               | 21.0                                                                           | 33.9                                      |
|         | 962 | 6.33                               | 21.0                                                                           | 34.1                                      |
|         | 972 | 6.25                               | 21.0                                                                           | 34.3                                      |
|         | 990 | 5.9                                | 21.0                                                                           | 34.7                                      |
| mean:   |     |                                    |                                                                                | 34.3                                      |

## D. Dissociation Energy of Gaseous SnSe and SnTe.

Dissociation energies  $D_{298}^\circ$  of both SnSe and SnTe derived from the thermochemical cycles given in Table VII, using the heats of formation and sublimation obtained in this work and the previously mentioned values for the heats of sublimation of Se<sub>2</sub> and Te<sub>2</sub> and  $D_{298}^\circ(\text{Te}_2) = 52.5 \pm 2.0$  kcal/mole<sup>(3, 22)</sup>. The dissociation energy of Se<sub>2</sub>,  $D_{298}^\circ(\text{Se}_2) = 75.4 \pm 2.0$  kcal/mole was obtained in a recent mass spectrometric study<sup>(32)</sup> by a third law procedure.

$D_0^\circ$  value are:

$$D_0^\circ(\text{SnSe}) = 95.0 \pm 3.0 \text{ kcal/mole or } 4.12 \pm 0.13 \text{ eV.}$$

$$D_0^\circ(\text{SnTe}) = 79.8 \pm 3.0 \text{ kcal/mole or } 3.46 \pm 0.13 \text{ eV.}$$

TABLE VII. Dissociation energies of SnSe and SnTe from thermochemical cycle ( $\Delta H_{298}^\circ$  value in kcal/mole)

|                                                        | Se              | Ref | Te              | Ref   |
|--------------------------------------------------------|-----------------|-----|-----------------|-------|
| $\text{SnX(g)} \rightarrow \text{SnX(s)}$              | $-51.0 \pm 2.0$ | --  | $-52.1 \pm 2.0$ | —     |
| $\text{SnX(s)} \rightarrow \text{Sn(s)} + \text{X(s)}$ | $+19.9 \pm 2.0$ | —   | $+14.5 \pm 0.5$ | —     |
| $\text{Sn(s)} \rightarrow \text{Sn(g)}$                | $+72.0 \pm 0.6$ | 31  | $+72.0 \pm 0.6$ | 31    |
| $\text{X(s)} \rightarrow 1/2 \text{X}_2(\text{g})$     | $+17.1 \pm 1.0$ | 31  | $+19.8 \pm 1.0$ | 31    |
| $1/2 \text{X}_2(\text{g}) \rightarrow \text{X(g)}$     | $+37.7 \pm 1.0$ | 32  | $+26.3 \pm 1.0$ | 3, 22 |
| $\text{SnX(g)} \rightarrow \text{Sn(g)} + \text{X(g)}$ | $+95.7 \pm 3.0$ |     | $+80.5 \pm 3.0$ |       |

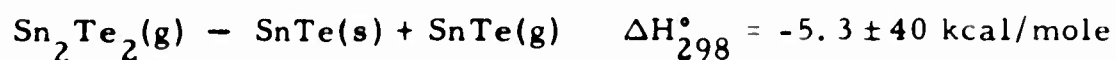
E. Stability of gaseous dimers  $\text{Sn}_2\text{Se}_2$  and  $\text{Sn}_2\text{Te}_2$  and of gaseous  $\text{SnTe}_2$

In order to obtain values for the enthalpy of dimerization of SnSe and SnTe, values of the free energy function of these dimers were taken from an interpolation vs molecular weight of the free energy functions of the isoelectronic molecules  $\text{As}_4$  and  $\text{Sb}_4$ <sup>(31)</sup>. This implies that the moments of inertia are roughly the same and that the decrease in symmetry number for  $\text{Me}_2\text{X}_2$  compensates for an increase in the vibration frequencies. The values used are given in Table II.

The enthalpy of dimerization of SnSe was calculated from various experiments as shown in Table VIII. The mean value  $46.5 \pm 5.0$  kcal/mole combined with  $D_{298}^\circ(\text{SnSe})$  leads to an atomization energy of  $\text{Sn}_2\text{Se}_2$ :

$$\Delta H_{298, \text{at}}^\circ(\text{Sn}_2\text{Se}_2) = 237.9 \pm 10 \text{ kcal/mole}$$

The dimerization enthalpy of  $\text{Sn}_2\text{Te}_2$  was obtained from the reaction



whence  $\Delta H_{298, \text{at}}^{\circ}(\text{Sn}_2\text{Te}_2) = 217.8 \pm 11 \text{ kcal/mole}$

$$\Delta H_{298, \text{dim}}^{\circ}(\text{SnTe}) = 46.8 \pm 6.0 \text{ kcal/mole}$$

The free energy function of  $\text{SnTe}_2$  was calculated assuming a linear Te-Sn-Te structure by analogy with  $\text{CS}_2$  and  $\text{CO}_2$ <sup>(33)</sup>. The vibrational frequencies of the three normal vibrations, one of which is doubly degenerate ( $\omega_2$ ) were calculated to be  $\omega_1 = 180 \text{ cm}^{-1}$ ,  $\omega_2 = 89 \text{ cm}^{-1}$  and  $\omega_3 = 335 \text{ cm}^{-1}$  assuming the stretching force constant  $k_1$  of the Sn-Te to be identical to the one on the diatomic SnTe molecule; the bending force constant  $k_\delta$  was estimated on the basis that

$$\frac{k_\delta}{l^2 k_1} = (3.5 \pm 0.3) 10^{-2} \text{ cm}^{-2} \text{ which holds for } \text{CS}_2 \text{ and } \text{CO}_2^{(33)}$$

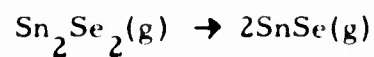
$l$  is the internuclear distance). The ground state was also assumed to be nondegenerate as for  $\text{CO}_2$  and  $\text{CS}_2$ . The free energy function calculated in this manner at  $1000^\circ\text{K}$  is given in Table II. Table IX gives the enthalpy change for the reaction



leading to an atomization enthalpy

$$\Delta H_{298, \text{at}}^{\circ}(\text{SnTe}_2) = 124.1 \pm 4.0 \text{ kcal/mole.}$$

TABLE VIII. Enthalpy of dimerization of SnSe



| Exp. N° | T°K | -log p (SnSe)<br>(atm) | -log p (Sn <sub>2</sub> Se <sub>2</sub> )<br>(atm) | $\Delta \left\{ -\left( \frac{G_T^\circ - H_{298}^\circ}{T} \right) \right\}$ | $\Delta H_{298, \text{dim}}^\circ$<br>(kcal/mole) |
|---------|-----|------------------------|----------------------------------------------------|-------------------------------------------------------------------------------|---------------------------------------------------|
| 65.08   | 955 | 3.77                   | 6.02                                               | 41.5                                                                          | 46.2                                              |
|         | 965 | 3.81                   | 6.10                                               | 41.5                                                                          | 46.9                                              |
| 65.10   | 937 | 4.10                   | 6.44                                               | 41.5                                                                          | 46.4                                              |
|         | 961 | 3.86                   | 6.11                                               | 41.5                                                                          | 47.0                                              |
|         | 979 | 3.64                   | 6.05                                               | 41.5                                                                          | 46.2                                              |
| 65.11   | 942 | 3.92                   | 6.26                                               | 41.5                                                                          | 46.9                                              |
|         |     |                        |                                                    | mean                                                                          | 46.5                                              |

TABLE IX. Enthalpy change for the reaction



| Exp. N° | T°K | -log p (SnTe <sub>2</sub> )<br>(atm) | -log p (SnTe)<br>(atm) | -log (Te <sub>2</sub> )<br>(atm) | $\Delta \left\{ -\left( \frac{G_T^\circ - H_{298}^\circ}{T} \right) \right\}$ | $\Delta H_{298}^\circ$<br>kcal/mole |
|---------|-----|--------------------------------------|------------------------|----------------------------------|-------------------------------------------------------------------------------|-------------------------------------|
| 65.06   | 881 | 6.32                                 | 3.79                   | 6.14                             | 15.6                                                                          | 17.7                                |
| 65.09   | 990 | 6.06                                 | 3.59                   | 5.88                             | 15.6                                                                          | 17.2                                |
|         |     |                                      |                        |                                  | mean:                                                                         | 17.5                                |

## DISCUSSION

SnSe and SnTe molecules.

The thermochemical values of the dissociation energy of SnSe and SnTe can be compared to the spectroscopically determined convergence limit of the excited E state of the molecules. It has been postulated<sup>(34, 35)</sup> that the E state of all the group IV-group VI MeX molecules are analogous and correlate with the same atomic products. It has already been concluded<sup>(35)</sup>, on the basis of the agreement between the convergence limits for this state and the Birge-Sponer value for the dissociation energy of the ground state, that this state correlates with  $\text{Me}(^3\text{P}) + \text{X}(^3\text{P})$ . Recent rotational analysis showed for  $\text{PbO}^{(36)}$ ,  $\text{PbS}^{(37)}$  and  $\text{SnO}^{(38)}$  that for E state of these molecules the most probable correlation is  $\text{Me}(^3\text{P}_1) + \text{O}(^3\text{P}_1)$ . Likewise the comparison of thermochemical and spectroscopic data showed<sup>(4)</sup> that for SnS and PbS the most likely correlations are  $\text{Me}(^3\text{P}_1) + \text{S}(^3\text{P}_{1,0})$ , the accuracy of the thermochemical data making it impossible to distinguish between  $\text{S}(^3\text{P}_1)$  and  $\text{S}(^3\text{P}_0)$  sublevels of sulfur, the separation of which is only of 0.02 eV. The rotational analyses for  $\text{PbO}^{(36)}$  and  $\text{PbS}^{(37)}$  favor however the  $\text{Me}(^3\text{P}_1) + \text{O}(^3\text{P}_1)$  correlation. For SnSe the subtraction of several combinations of the excitation energies of the  $^3\text{P}$  sublevels of Sn and Se from the well established convergence limit of the E state at  $4.54 \pm 0.06$  eV would yield a value of the dissociation energy which is in agreement within the error limits with the thermochemical value  $D^\circ(\text{SnSe}) = 4.12 \pm 0.13$  eV. These combinations include the  $\text{Sn}(^3\text{P}_1) + \text{Se}(^3\text{P}_1)$  combination which leads to a value of  $D^\circ(\text{SnSe}) = 4.08$  eV. This agreement may be used to suggest a selected dissociation energy  $D^\circ(\text{SnSe}) = 4.10 \pm 0.10$  eV. Using for SnTe the "assumed" convergence limit of the E state at 4.07 eV, the  $\text{Sn}(^3\text{P}_1) + \text{Te}(^3\text{P}_1)$  correlation yields a value of  $D^\circ(\text{SnTe}) = 3.28$  eV compared to the thermochemical value  $D^\circ(\text{SnTe}) = 3.46 \pm 0.13$  eV.

SnTe<sub>2</sub> molecule.

The SnTe<sub>2</sub> molecule is analogous to the well known CO<sub>2</sub> molecule of which two analogous were already known: CS<sub>2</sub> and SiO<sub>2</sub><sup>(1)</sup>. Until now

TABLE X. Stability of group IV-group VI molecules (kcal/mole)

|                         | $\Delta H_{\text{at}}^{\circ}(\text{MeX}_2)$ | ref | $D_{\text{e}}^{\circ}(\text{MeX})$ | ref      | $\Delta H_{\text{at}}^{\circ}(\text{MeX}_2)/D_{\text{e}}^{\circ}(\text{MeX})$ |
|-------------------------|----------------------------------------------|-----|------------------------------------|----------|-------------------------------------------------------------------------------|
| CO/CO <sub>2</sub>      | 381.5                                        | 28  | 256.2                              | 40       | 1.49                                                                          |
| CS <sub>2</sub> /CS     | 272.0                                        | 39  | 173.6                              | 39       | 1.57                                                                          |
| SiO <sub>2</sub> /SiO   | 302.8                                        | 1   | 191.9                              | 28<br>41 | 1.58                                                                          |
| SiS <sub>2</sub> /SiS   | 230.4                                        | 20  | 147.0                              | 42       | 1.57                                                                          |
| GeTe <sub>2</sub> /GeTe | 137.1                                        | 20  | 92.7                               | 20       | 1.48                                                                          |
| SnTe <sub>2</sub> /SnTe | 123.2                                        | -   | 79.8                               | -        | 1.55                                                                          |

other molecules of this type, observed in mass spectrometric investigations<sup>(20)</sup> similar to the one reported here are: SiS<sub>2</sub>, SiSe<sub>2</sub>, SiTe<sub>2</sub> and GeTe<sub>2</sub>. The stabilities of these molecules were estimated by assuming again that they are analogous in structure as well as in nature of the electronic state to CO<sub>2</sub>. The values of the enthalpies of atomization  $\Delta H_{\text{at}}^{\circ}(\text{MeS}_2)$  are given in Table X as well as the dissociation energy of the corresponding MeX molecules. It is interesting to observe that for these molecules the ratio  $\Delta H_{\text{at}}^{\circ}(\text{MeX}_2)/D_{\text{e}}^{\circ}(\text{MeX})$  is reasonably constant for all the molecules detected to this day. The mean value 1.54 permits to predict with a good approximation the stability of the not yet observed group IV-group VI MeX<sub>2</sub> molecules.

Sn<sub>2</sub>Se<sub>2</sub> and Sn<sub>2</sub>Te<sub>2</sub> molecules

The dimerization energies of SnSe and SnTe, 46.5 and 46.8 kcal/mole

respectively are very close to those of the analogous molecules  $\text{SnS}^{(4)}$  48.7 and  $\text{PbS}^{(4)}$ , 44.8 kcal/mole. This approximate constancy of the dimerization energy, as well as the fact that the group IV-group VI dimers, and the homonuclear group V tetratomic molecules are isoelectronic had already been used<sup>(4)</sup> to propose a close (tetragonal or tetrahedral) rather than a linear structure for the dimeric group IV-group VI molecules.

It is further to be noted that the dimerization energies are for these, as for several other molecules of this type, quite close to the heat of sublimation of the monomer from the lattice, implying that similar types of interaction are responsible for the stability of the polymeric molecules and of the lattice.

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