

1. Bender, M. L. and Kézdy, F. J. *Ann. Rev. Biochem.* **34** (1965) 49.
2. v. Hofsten, B., van Kley, H. and Eaker, D. *Biochim. Biophys. Acta* **110** (1965) 585.
3. v. Hofsten, B. and Reinhammar, B. *Biochim. Biophys. Acta* **110** (1965) 599.
4. v. Hofsten, B. and Tjeder, C. *Biochim. Biophys. Acta* **110** (1965) 576.
5. Engström, L. *Biochim. Biophys. Acta* **52** (1961) 49.

Received August 24, 1966.

Thermodynamic Properties of Stannous Sulfide Around 900°C

ARNE W. ESPELUND

Metallurgisk Institutt, Norges tekniske høgskole, Trondheim, Norway

The equilibrium relations found between the condensed phases of the system Sn—SnS are in good agreement as reported in Ref. 1, shown in Fig. 1. However, determination of the stability of SnS and vapour pressures in the system has presented difficulties because of the high escaping tendency and the complexity of the gas phase. There are great discrepancies between some results reported in the literature,²⁻⁴ and it was found worth-while to investigate the system.

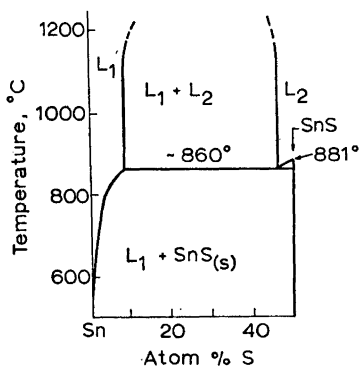


Fig. 1. The phase diagram Sn—SnS.

The experiments were performed at constant temperature on a sample composed of the two phases metallic tin and tin sulfide in contact with each other held in a crucible in a vertical tube furnace. Purified hydrogen was passed through the sample. The gas had a double function: it would react with the sulfide and transport the resulting hydrogen sulfide as well as gaseous tin sulfide away from the hot zone. The tin sulfide condensed in a cooler region. The remaining gas passed through absorption tubes containing NaOH ("Ascarite") and finally through an integrating flow meter.

The presence of two condensed phases in the crucible throughout the experiment ensured constancy of activities.

The hydrogen gas was bubbled through the upper sulfide layer of the charge. Results for experiments at flow rates varying from about 50 to 120 ml H₂ (NTP)/min showed no systematic variation, indicating completion of reaction.

During the heating and cooling of the reactor the gas was passed in the direction opposite to normal to ensure that the results would represent the period with constant temperature only.

After completion of each run the condensate of SnS needles was carefully collected and weighed, the weight increase of the absorption tubes noted and the amount of hydrogen gas registered.

In Fig. 2 are shown the results for the reaction

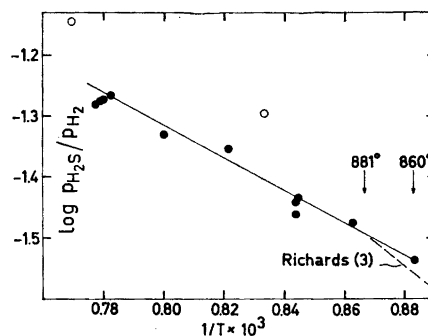
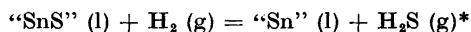


Fig. 2. Ratios of H₂S/H₂-pressures above the binary mixture "Sn"—"SnS". Open circles: calculated from Kellogg's values. Filled circles: present work.

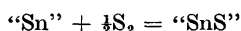


in a conventional plot with $\log (p\text{H}_2\text{S}/p\text{H}_2)$ against reciprocal absolute temperature between the monotectic temperature 860°C and about 1000°C. The points are best represented by the linear equation

$$\log (p\text{H}_2\text{S}/p\text{H}_2) = -2670/T + 0.817$$

corresponding to $\Delta H_T^\circ = 12.2$ kcal.

Combination with accepted values⁵ for the free energy change of formation of H_2S leaves as net result for



$$\Delta G_T^\circ = 15.54 T - 33\,800 \text{ cal } (1133 - 1270^\circ\text{K})$$

The apparent SnS pressure was found to vary between 16 mm (912°C) and 57 mm (990°C). According to Colin and Drowart⁶ there is some association in the gas phase, so that under these conditions the pressure of the dimer Sn_2S_2 may be about 5% of the total. However, no great accuracy is claimed for these figures obtained because of the relatively crude method of collecting the condensate.

Richards' data³ for the reaction between SnS and H_2 , obtained in the range 500–675°C and extrapolated to the melting point of pure SnS (881°C) are also shown in Fig. 2. Combination with the present results renders $\Delta S^\circ = 4.0$ cal/°C mole as the entropy of fusion of SnS, a probable figure for a diatomic species.

Richards' measurements, however, refer to almost pure metal and sulfide phases, different from the compositions at higher temperatures because of the increasing tendency to mutual solubility. No activity data are available for this system. However, assuming validity of Raoult's law, neither a_{Sn} nor a_{SnS} will be significantly less than 1.0 referred to the pure phases. Furthermore, being in the numerator and the denominator of the equilibrium constant, respectively, they will tend to cancel each other.

In Fig. 2 is also included another set of values for two temperatures, based on values suggested by Kellogg⁷ and the

values for formation of H_2S used before. The difference in terms of $\log K$ is approximately 0.1, corresponding to a correction term for activities $a_{\text{Sn}}/a_{\text{SnS}} = 1.25$. Whether this is real or the result of experimental error cannot be proved by this investigation.

The figures obtained for the vapour pressure of SnS above this binary mixture "Sn"—"SnS" are in good agreement with the results of Richards,³ Klushin and Chernykh,⁸ and Colin and Drowart⁶ above pure SnS, indicating little change in activity due to the dilution with tin.

The conclusion is reached that the figures for the vapour pressure of sulfur in this composition region given by Albers and Schol⁵ appear to be too high.

Note added in proof. The author has become aware of the comprehensive contribution by Dr. Hans Rau, "Thermodynamische Messungen an SnS" (*Ber. Bunsenges.* **69** (1965) 731), in which among several data the $\text{H}_2\text{S}/\text{H}_2$ -ratios above solid SnS and liquid "Sn" are reported. The value at the melting point agrees well with the value presented above.

Acknowledgements. The author would like to thank professor T. Rosenqvist for good advices and *Norges tekniske hogskoles fond* for financial support.

1. Elliott, R. P. *Constitution of Binary Alloys, First Supplement*, McGraw, New York 1965.
2. Hsiao, C. M. and Schlechten, A. W. *J. Metals* **4** (1952) 65.
3. Richards, A. W. *Trans. Faraday Soc.* **51** (1955) 1193.
4. Albers, W. and Schol, K. *Philips Res. Rep.* **16** (1961) 329.
5. Kubaschewski, O. and Evans, E. L. *Metallurgical Thermochemistry*, Pergamon, New York 1958.
6. Colin, R. and Drowart, J. *J. Chem. Phys.* **37** (1962) 1120.
7. Kellogg, H. H. *Trans. Met. Soc. AIME* **236** (1966) 602.
8. Klushin, D. N. and Chernykh, V. Ya. *Zh. Neorgan. Khim.* **5** (1960) 1409.

Received August 2, 1966.

* Non-stoichiometric phases are marked with " ".