Dissociation of Manganous Sulphide at High Temperatures & the Study of Its Reaction with Carbon*

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The dissociation of manganous sulphide has been studied between 1746° and 1850°K employing transpiration technique. Since the dissociation is quite small even on prolonged heating (3 hr), longer time, it could not be of much use to calculate the thermodynamic parameters. The reaction of MnS with carbon has been carried out in the temperature between range 1657° and 1823°K. The heat of reaction is found to be 158.5 ± 2.9 kcal mole⁻¹ at 1740°K. Employing the C_p values available in the literature, the value for the heat of reaction (ΔH_r) at 298°K is found to be 168.4 ± 2.9 kcal mole⁻¹. Using this value, the heat of formation ΔH_{f298} for MnS has been calculated by second law method and found to be $\Delta H_{f298} = -46.6 \pm 2.9$ kcal mole⁻¹ which compares well with that ($\Delta H_{f298} = -5.5 \pm 7.6$ kcal mole⁻¹) obtained from Third Law. These values compare favourably with that reported in the literature (-49 kcal mole⁻¹).

REFRACTORY sulphides offer a fertile field for future development, despite their susceptibility to oxidation at elevated temperatures. Manganous sulphide[1] can be considered to be on the border line between refractory sulphides and non-refractory sulphides, since its melting point is high (1893°K) and is fairly volatile in vacuum at 1648°K. In connection with the studies on MnS-C system, Wiedemeir and Schäfer[2] have emphasized the importance of vaporization of MnS.

A number of workers[2,3] have studied the dissociation pressures of MnS(C), employing effusion method and mass spectrometric study.

While studying the sublimation, Gilles[3] observed the formation of small quantities of MnS⁺ and MnS₂⁺ and MnS₃⁺ and reported the dissociation energy of MnS(g) as 71 ± 4 kcal. mole⁻¹. Wiedemeir and Schäfer[4] employed the Knudsen effusion method to vaporize MnS in molybdenum crucibles. In order to study reaction (1)

$$MnS(c) + C(c) = Mn(g) + CS(g) \qquad \ldots(1)$$
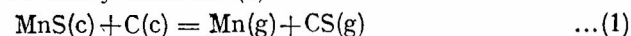
information about reaction (2)

$$MnS(c) = Mn(g) + \tfrac{1}{2}S_2(g) \qquad |\ldots(2)$$

was necessary. They further showed that reactions (1) and (2) were indeed predominant. Reactions (1) and (2) have now been investigated using transpiration technique.

Materials and Methods

Manganous sulphide was prepared by passing carbon disulphide vapours over manganese sulphate monohydrate (AR, Sarabhai Merck) kept in a silica boat in a tube furnace at 1023°K for ~4 hr. Nitrogen gas was bubbled through liquid carbon disulphide kept at 298°K to carry CS₂ vapours to react with the sulphate. The manganous sulphide

formed was cooled in nitrogen atmosphere. The sample was ground and purified by heating at 673°K under hydrogen atmosphere, thus removing the excess sulphur. The sulphide was subjected to chemical[5] and X-ray analyses. The chemical analysis is in good agreement with the corresponding theoretically calculated values. The 'd' spacings compared well with those of MnS reported earlier[6]. Purified argon gas was used as a carrier gas. Impurities like oxygen, nitrogen, carbon dioxide and moisture were removed by methods described by Rao[7]. In addition light lanthanon sesquisulphides[8] (i.e. Sm₂S₃ and Nd₂S₂) kept at about 773°K were used to remove traces of oxygen (partial pressure of oxygen in argon gas was 10^{-19} atm.).

The furnace was constructed[9] by winding a platinum rhodium (13%) wire (diam. 1·5 mm) on a recrystallized alumina tube (length 55 cm, int. diam. 3·5 cm) (Morgan Refractories, UK). The furnace cone was enclosed in a rectangular box made of light refractory bricks. The box was heated by connecting the heating elements to the mains through a voltage stabilizer. An alumina tube (length 75 cm, int. diam. 2·5 cm) both ends of which were connected to ground silica joints with a refractory cement, was used as the reaction tube. A molybdenum boat contained in an alumina boat was employed.

Temperatures of the hot zone, in which the sample was located, were measured by means of (a) Pt-Pt/Rh-13% thermocouple and (b) an optical pyrometer (disppearing filament type, Polish make, type EP-5). Thermocouple as well as pyrometer were calibrated by standard methods as described by Bockris[10]

Procedure — Pure solid MnS was weighed in a molybdenum boat contained in an alumina boat placed in a glass capsule which was tightly closed. The operation of transforming MnS to the

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boat was carried out in a dry box in an inert atmosphere.

Having attained the required temperature, the reaction tube was flushed with purified argon gas. After adjusting the argon gas rate to a desired value, the molybdenum boat containing the sulphur free MnS placed in an alumina boat (in order to avoid the reaction between molybdenum and mullite) was introduced from the down stream end and kept in the colder zone of the furnace for about 30 min. The tube was then moved so that the boat could be located in the hot zone. The experiment was conducted for a definite time (3 hr) after which the heating was stopped and the tube moved so that the boat got into the colder part of the furnace. The boat was allowed to cool to room temperature in argon atmosphere. The sintered mass of the sulphide was weighed after cooling. The experimental data are presented in Table 1.

In all these experiments it was observed that there was no change in colour of the green MnS. X-ray powder patterns of the mass after experimental run revealed only the presence of MnS.

Reaction between MnS and carbon — The materials and apparatus are similar as described above. A weighed quantity of green purified MnS was mixed with excess graphite powder and placed in a graphite boat contained in an outer alumina boat. The operations were conducted in a dry box in an inert atmosphere. The rest of the experimental details are the same as given above. The sintered mass containing MnS and graphite was removed and analysed for manganese by bismuthate method and sulphur content by wet process. From the quantities of Mn and S the loss in weight of MnS was found out.

Results

The sublimation of MnS is too small at the temperatures listed in Table 1, even if the experiment

was carried out for a long time (3 hr). The weight loss data could not be of much value as it could well be due to experimental errors involved in the transpiration technique. When these studies were carried out using a graphite boat the loss in weight of the sulphide was substantial indicating a reaction between the boat material and the sulphide. It was, therefore, decided to study the reaction of MnS with carbon at high temperatures. The results of the study are given in Table 2.

Treatment of the data — In the study of the reaction of MnS with carbon over the temperature range 1657-1822°K the experimental weight loss was used to calculate the vapour pressure of Mn(g)/CS(g) employing Eq. (3)

$$p = n \frac{RT_r}{V_r} \qquad ...(3)$$

where p = pressure in atmosphere
n = number of moles of MnS
R = gas constant
V_r = volume of the argon in litres at temperature T_r°K.

The equilibrium constant K_p can be calculated from Eq. (4)

$$K_p = p \text{ of } Mn(g) \times p \text{ of } CS(g) \qquad ...(4)$$

The free energies and heats of reaction at various temperatures were calculated employing Eq. (5)

$$\Delta G° = RT \ln k \qquad ...(5)$$

The free energy functions for CS(g) were taken from JANAF tables and[12] for Mn and graphite were taken from Stull and Sinke[13] and free energy functions for MnS(c) were calculated from heat contents and entropies tabulated by Kelley[14] and by King[15]. The free energies and calculated Third Law heats for the reaction have been summarized in Table 2.

Employing the Vant Hoff's equation, the heat of reaction (ΔH_r) has been determined from the plot of log K vs 1/T. The slope of the line obtained by the method of least squares gave a value for the heat of reaction $\Delta H_{1740} = 158.5 \pm 2.9$ kcal mole^{-1}. This value represents the mean over the temperature range studied and does not include the C_p values. The value for ΔH_{r298} could be calculated applying Kirchoff's law (Eq. 6).

$$\Delta H_{r298} = \Delta H_{1740} - \int_{1740}^{298} \Delta C_p \, dT \qquad ...(6)$$

where ΔC_p is change in heat capacities of products

TABLE 1 — DISSOCIATION OF MnS

No.	Temp. °K	Rate of flow of argon (litre/hr)	Loss of MnS mg
1	1746	4·40	1·5
2	1774	4·35	2·0
3	1798	4·00	2·5
4	1821	3·80	4·5
5	1850	4·13	6·5

TABLE 2 — TRANSPIRATION DATA FOR THE REACTION MnS(c) + C(c) = Mn(g) + CS(g)

Temp. °K	Rate of argon (litre/hr)	Loss of MnS(c) mg	$pMn(\times 10^4)$ atm.	$Kp(\times 10^7)$	—Log K_p	ΔF kcal mole^{-1}	Δfef kcal mole^{-1}	$T\Delta fef$ kcal mole^{-1}	ΔH_{298} kcal mole^{-1}
1657	3·60	6·0	1·561	0·2436	7·6133	57·70	68·64	113·73	171·43
1734	2·70	10·5	3·643	1·327	6·8771	54·57	68·47	118·72	173·29
1752	2·88	15·0	4·879	2·380	6·6234	53·10	68·34	119·73	173·23
1773	2·52	16·5	6·133	3·761	6·4247	52·12	68·40	121·27	173·39
1793	2·52	21·0	7·811	6·101	6·2146	50·98	58·54	122·89	173·87
1808	2·94	24·0	7·649	5·850	6·2328	51·57	68·27	123·43	175·00
1810	2·04	33·0	1·515	2·295	5·5392	46·71	68·27	123·56	170·27
1822	3·00	42·0	1·311	1·718	5·7650	48·09	68·33	124·51	172·61

and reactants. Thus the value for ΔH_{f298} is 168.4 ± 2.9 kcal mole^{-1}. The corresponding Third Law value is 172.9 ± 2.6 kcal mole^{-1}.

Heat of formation of MnS — The heat of formation ΔH_{f298} of MnS(c) has been calculated from the heat of reaction at 298°K.

$$\Delta H_r = \Delta H_f \text{ Mn(g)} + \Delta H_f\text{CS(g)} - \Delta H_f \text{ MnS(c)}$$
$$-\Delta H_f \text{ C(c)} \qquad \qquad ...(7)$$

Hence $\Delta H_{f298} = (-168.4 \pm 2.9) + 66.73 + (55.0 \pm 5.0)$ $= -46.6 \pm 2.9$ kcal mole^{-1} and the corresponding Third Law value is -51.1 ± 7.6 kcal mole^{-1}. The values for heat of formation of Mn(g) and CS(g) were taken from Stull and Sinke[13] and JANAF[12] tables respectively.

Entropy of the reaction — The entropy of the reaction was calculated by the least squares method and was found to be 60.2 ± 1.6 e.u. at 1740°K.

Acknowledgement

References

1. CAMPBELL, I. E., *High temperature technology* (John Wiley, New York), 1956, 187.
2. WIEDEMEIR, H. & SCHÄFER, H., *Z. anorg. allg. Chem.*, **326** (1964), 235.
3. WIEDEMEIR, H. & GILLES, P. W., *J. chem. Phys.*, **42** (1965), 2765.
4. WIEDEMEIR, H. & SCHÄFER, H., *Z. anorg. allg. Chem.*, **326** (1964), 230.
5. HILL, S. D., CLEILAND, C. A., ADAMS, ARNE LANDSBERG & BLOCK, F. E., *J. chem. Engng Data*, **14** (1969), 84.
6. *Standard X-ray diffraction powder pattern*, N.B.S. Circular No. 539, Vol. IV (United States Dept. of Commerce), 1955, 11.
7. BHOGESWARA RAO, D. & DADAPE, V. V., *J. phys. Chem.*, **70** (1966), 1349.
8. ATCHAYYA, M. & DADAPE, V. V., *J. Less common Metals*, **13** (1967), 559.
9. THOMAS, J. RHODES, *Industrial instruments for measurement and control* (McGraw-Hill, New York), 1941, 257, 329.
10. BOCKRIS, J. O'M., WHITE, J. L. & MACKENZIE, J. D., *Physicochemical measurements and high temperatures* (Butterworths, London), 1959, 22; 28.
11. VOGEL, A. I., *A text book of quantitative inorganic analysis* (The English Language Book Society and Longman), 1961, 299, 466.
12. STULL, D. R. *et al.*, *JANAF thermochemical tables*, PB 168 370 (Dow Chemical Co., Midland, Michigan), Aug. 1965.
13. STULL, D. R. & SINKE, G. C., *Thermodynamic properties of the elements* (American Chemical Society, Washington DC), 1956, 127.
14. KELLEY, K. K. & KING, E. G., *Contribution to the data on theoretical metallurgy*, Bulletin 584 (US Bureau of Mines, Washington), 1960, 119.
15. KELLEY, K. K. & KING, E. G., *Contributions to the data on theoretical metallurgy*, Bulletin 592 (US Dept. of Interior, Bureau of Mines), 1961, 64.