

THE INFLUENCE OF THE STRUCTURE OF MOLYBDENUM DISULPHIDE ON ITS REACTIVITY*

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The equilibrium in the system Mo–MoS₂–H₂S–H₂ was studied between 569.4 and 1 276.8 K. The equilibrium gaseous mixture was analyzed by an iodometric method, the solid phase was studied by X-ray powder diffraction. The structure of MoS₂ changed in the course of measurements from a "poorly crystalline" form at lower temperatures to a "well crystalline" one with a small number of stacking faults at higher temperatures. The poorly crystalline form is more reactive than the well crystalline one. For the formation of the well crystalline form of MoS₂ a Gibbs-energy equation, ΔG^0 (J mole⁻¹) = -390 100 + 176.7T, was derived. It is in excellent agreement with the equation derived from the data obtained by fluorine calorimetry.

For a long time, molybdenum disulphide has been a basis for some of the most widely used hydrocarbon processing catalysts. It has been also used as a lubrication additive. These applications arise in part from its highly anisotropic physical properties, which are due to its crystal structure.

Another manifestation of the anisotropic and macromolecular nature of MoS₂ is its preparation and characterization in a "poorly crystalline" form^{1,2}. In the course of the thermal decomposition of the moist MoS₃, (NH₄)₂MoS₄ etc., gases (sulphur, H₂O, H₂S, NH₃ etc.) are liberated and at about 620–670 K the crystallization of Mo_{1-x}S₂ (x ≅ 0.17) sets in. The crystallites tend to orientate themselves with their largest surfaces in parallel planes. The orientations of the crystallites around the Z axis are, however, random. After further heating the crystallites grow with the loss of sulphur, and they orientate themselves with respect to their neighbours. At 770 K the parallel and antiparallel stacking of adjacent layers occurs almost at random, but gradually the antiparallel stacking begins to dominate, and at about 1 100 K the product may be described as hexagonal MoS₂ with stacking faults. In order to obtain hexagonal MoS₂ in a degree of crystallinity comparable to that of nature molybdenite a prolonged annealing at about 1 300 K should be necessary.

It was observed that the stacking faults may function as the centres of enhanced

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reactivity^{3,4}. From this point of view we judged our results of the equilibrium measurements in the system Mo-MoS₂-H₂S-H₂.

EXPERIMENTAL

Chemicals. The molybdenum disulphide used for this study was prepared by thermal decomposition of ammonium tetrathiomolybdate in the stream of pure and dry hydrogen. The thiomolybdate was prepared from ammonium molybdate (*p.a.* purity grade, fa Lachema) by the method of Krüss⁵. Two samples of MoS₂ were prepared. One was obtained by the decomposition of ammonium thiomolybdate at the temperature of 670 K (Sample 1). The decomposition at 670 K and subsequent annealing at about 1070 K in the stream of hydrogen for a period of five hours yielded the other one (Sample 2).

The other chemicals used for the analytical purposes were *p.a.* purity grade preparations made in Czechoslovakia.

Analytical method. The equilibrium gas mixture was passed into a 2.9M-NaOH solution, where hydrogen sulphide was absorbed. Sodium sulphide thus obtained was oxidized with KIO₃ in a strongly alkaline solution using a modified Bethge's method⁶⁻⁸.

The structure of the solid phase was examined by X-ray powder diffractography. Diffractograms were taken by means of Geigerflex fy Rigaku-Denki diffractometer. Copper K_α radiation ($\lambda = 154.178$ pm) was used throughout. The measurements were carried out in the region $\theta = 1$ to 44°.

Equilibrium apparatus and procedure. The apparatus used for the equilibrium measurements was essentially the same as that used in the previous studies⁹⁻¹¹. Purified and dried hydrogen was passed through a layer of MoS₂ in a quartz reactor held at a constant temperature. On leaving the reactor the equilibrium gas mixture was analyzed for the contents of H₂S (see above).

RESULTS AND DISCUSSION

The equilibrium measurements extend over the temperature range 569.4 to 1 276.8 K. The results, *i.e.* the values of the ratio of equilibrium pressures of H₂S and H₂, for the reaction



are listed in Table I (in the order in which they were obtained) and shown in Fig. 1, in which the logarithms of the ratio $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ are plotted against $1/T$, T being the temperature in K (the arrows in Fig. 1 indicate points obtained after a reduction of temperature). Two samples of MoS₂ were used to obtain these points and the results from both of them agree within the limits of experimental errors. The results of the experiments in which the equilibrium was approached from the side of higher as well as lower H₂S/H₂ ratios agreed, thus satisfying an important criterion for true equilibrium measurements.

Fig. 1 suggests to divide the experimental results into three groups. The first one includes the measurements the temperature of which did not exceed 800 K. The points obtained after raising the temperature above 800 K (but not higher than

900 K) as well as the points obtained by the following measurements at temperatures lower than 800 K belong to the second group. The third group comprises the results of the measurements at temperatures above 900 K.

The powder diffractograms of the samples corresponding to the particular temperature regions are reproduced in Fig. 2. In Table II the ascertained diffraction lines together with the lines reported for 2 H-MoS₂ in literature (ref.^{1,2}) are surveyed.

The first group of experiments was carried out with MoS₂, the diffractogram of which is shown in Fig. 2a. The diffractions are here in the form of wide, vague bands; this corresponds to the beginning of the arranging and orientation of the crystallites around the Z axis. The main part is constituted apparently by still one-layer randomly orientated crystallites of Mo_{1-x}S₂ ($x \approx 0.17$). On heating above 800 K the crystallites

TABLE I
Equilibrium results for MoS₂ hydrogen reduction

<i>T</i> , K	$p_{\text{H}_2\text{S}}/p_{\text{H}_2}$	<i>T</i> , K	$p_{\text{H}_2\text{S}}/p_{\text{H}_2}$
Sample 1			
742.8	$2.935 \cdot 10^{-5}$	868.0	$1.080 \cdot 10^{-4}$
746.1	$3.167 \cdot 10^{-5}$	868.2	$8.573 \cdot 10^{-5}$
746.1	$3.106 \cdot 10^{-5}$	846.3	$5.622 \cdot 10^{-5}$
746.3	$3.094 \cdot 10^{-5}$	902.3	$1.286 \cdot 10^{-4}$
703.7	$1.187 \cdot 10^{-5}$	735.2	$5.973 \cdot 10^{-6}$
703.8	$1.302 \cdot 10^{-5}$	790.0	$2.429 \cdot 10^{-5}$
671.9	$4.403 \cdot 10^{-6}$	839.7	$3.721 \cdot 10^{-5}$
672.1	$3.748 \cdot 10^{-6}$	1 081.6	$7.355 \cdot 10^{-4}$
626.4	$8.369 \cdot 10^{-7}$	1 167.8	$2.125 \cdot 10^{-3}$
569.4	$1.444 \cdot 10^{-7}$	1 080.5	$8.118 \cdot 10^{-4}$
682.7	$6.450 \cdot 10^{-6}$	1 276.8	$8.087 \cdot 10^{-3}$
793.3	$8.618 \cdot 10^{-5}$	981.5	$2.703 \cdot 10^{-4}$
793.5	$8.542 \cdot 10^{-5}$	778.7	$2.017 \cdot 10^{-5}$
587.9	$2.847 \cdot 10^{-7}$		
Sample 2			
724.3	$6.556 \cdot 10^{-6}$	740.9	$8.575 \cdot 10^{-6}$
724.6	$6.775 \cdot 10^{-6}$	715.9	$4.417 \cdot 10^{-6}$
724.6	$6.834 \cdot 10^{-6}$	714.3	$4.428 \cdot 10^{-6}$
722.2	$6.821 \cdot 10^{-6}$	717.2	$5.728 \cdot 10^{-6}$
722.3	$6.847 \cdot 10^{-6}$	768.3	$1.521 \cdot 10^{-5}$
741.4	$1.008 \cdot 10^{-5}$	768.5	$1.774 \cdot 10^{-5}$
741.0	$7.624 \cdot 10^{-6}$	768.5	$1.241 \cdot 10^{-5}$
741.0	$9.684 \cdot 10^{-6}$		

lose a part of the sulphur atoms and tend to orientate themselves. Fig. 2*b* represents the diffractogram of a sample corresponding to this temperature region. The sharpness of the (00*l*) type of diffractions demonstrates the presence of more-layer crystallites developed by stacking around the *Z* axis. Parallel and antiparallel orientations of the adjacent layers occur almost at random, which gives rise to the observation of the diffractions (103) and (105) in the form of broad and weak bands. The loss of some sulphur atoms as well as the orientation of crystallites is an irreversible change and therefore the measurements made now at the temperatures below 800 K (in Fig. 1 they are denoted by the arrows) gave results belonging to the second and not to the first group. The results of the measurements with Sample 2 (in Fig. 1 they are denoted by full circles) fall into this category as well.

The third group consists of the measurements performed at temperatures above 900 K. The diffractogram is presented in Fig. 2*c*. All more intensive diffractions

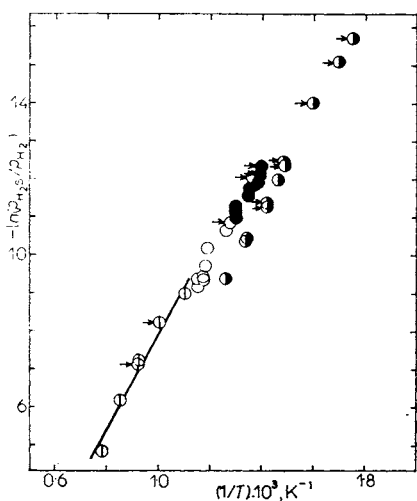


FIG. 1

Experimental data on the equilibrium reduction $1/2 \text{MoS}_2(\text{s}) + \text{H}_2(\text{g}) = 1/2 \text{Mo}(\text{s}) + \text{H}_2\text{S}(\text{g})$. The dependence of $\ln(p_{\text{H}_2\text{S}}/p_{\text{H}_2})$ on $1/T$. \odot Sample 1, the first measurements, the temperature of which did not exceed 800 K, \circ sample 1, the points obtained after the heating above 800 K but not higher than 800 K, \diamond sample 1, the measurements performed at temperatures above 900 K, \bullet sample 2. The arrows denote the points obtained after the reduction of temperature

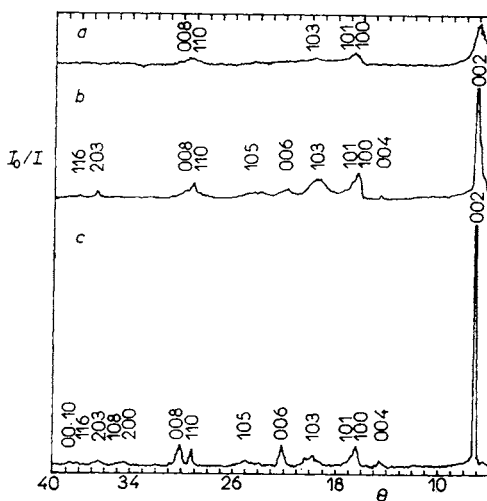


FIG. 2

Powder diffractograms of MoS_2 (see Table II). *a* Sample gained by the decomposition of $(\text{NH}_4)_2\text{MoS}_4$ at 670 K, *b* subsequent to annealing to 1 070 K, *c* subsequent to annealing to 1 250 K

tabulated for hexagonal MoS₂ (ref.¹²) are observed here. The sharpness of the (00*l*) type of diffractions together with their occurrence up to high values of *l* (e.g. (00·10)) makes it clear that the inspected sample contains more-layer crystallites formed by stacking around the *Z* axis, in which the antiparallel orientation is prevailing, i.e. hexagonal MoS₂ with only a small number of stacking faults.

Experimental data belonging to the third group were used for evaluating the following quantities characterizing the system Mo–MoS₂–H₂S–H₂:

The equation

$$\ln K = 4.687 - 12\,560/T, \quad (1)$$

with constants determined by the least squares method, representing the data on

TABLE II

Evaluation of the powder diffractograms of MoS₂ obtained under different conditions

<i>I</i> / <i>I</i> ₀ of the observed diffraction lines Sample ^a			Literary values for 2 H–MoS ₂ (ref. ¹²)		
<i>a</i>	<i>b</i>	<i>c</i>	<i>θ</i>	(<i>hkl</i>)	<i>I</i> / <i>I</i> ₀
16	46	100	7·18	(002)	100
—	2	3	14·48	(004)	4
2	6	9	16·30	(100)	16
3	5	6	16·70	(101)	10
1	2	5	20·19	(103)	45
3	4	11	22·04	(006)	14
—	1	2	24·84	(105)	25
—	—	—	27·94	(106)	4
3	6	7	29·10	(110)	12
2	3	9	29·98	(008)	12
—	—	—	31·34	(107)	2
—	1	2	34·16	(200)	2
—	—	1	35·00	(108)	4
—	2	2	36·30	(203)	6
—	—	1	37·90	(116)	4
—	—	1	38·70	(00·10)	2
—	—	—	38·96	(109)	2
—	—	—	40·00	(205)	4
—	—	—	44·26	(118)	6
—	—	—	44·26	(118)	6

^a The way of the sample treatment, see Fig. 2.

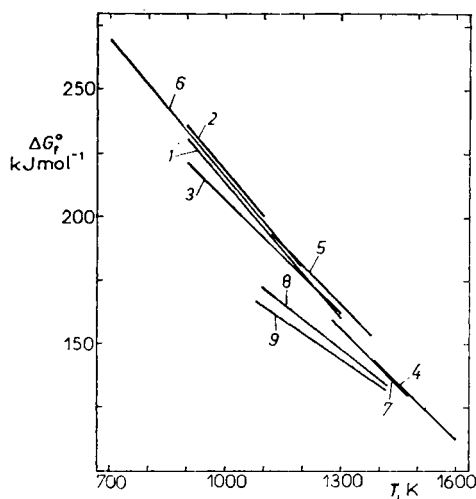


FIG. 3

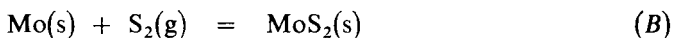
The temperature dependence of the standard Gibbs energy change for the reaction $\text{Mo(s)} + 1/2 \text{S}_2(\text{g}) = \text{MoS}_2(\text{s})$. 1 ΔG^0 (J mole^{-1}) = $-390\,100 + 176.8T$; this work, the reduction of molybdenum disulphide by hydrogen in a flow apparatus in temperature range 900–1 277 K, 2 ΔG^0 (J mole^{-1}) = $-399\,300 + 181.1T$; Schaefer and Gokcen¹⁷ by measuring the Gibbs energy change for the reversible cell $\text{Pt, MoS}_2, \text{MoO}_2, \text{SO}_2$ (101.325 kPa) | ZrO_2 | O_2 (1.135 kPa), Pt with overall cell reaction $\text{MoS}_2(\text{s}) + 3 \text{O}_2(\text{g}) = \text{MoO}_2(\text{s}) + 2 \text{SO}_2(\text{g})$ at temperatures 900–1 100 K, 3 ΔG^0 (J mole^{-1}) = $-354\,400 + 147.6T$; Pouillard and Perrot¹⁸, determination of the Gibbs energy of MoS_2 and Mo_2S_3 formation for controlled chemical potentials of S derived from $\text{H}_2\text{S}/\text{H}_2$ ratios in temperature range 900–1 300 K, 4 ΔG^0 (J mole^{-1}) = $-352\,400 + 150.7T$; combination of Hager and Elliot's data¹⁹ for the formation of Mo_2S_3 and Stubbles and Richardson's data²¹ on the hydrogen reduction of Mo_2S_3 ; temperature interval 1 365–1 610 K, 5 ΔG^0 (J mole^{-1}) = $-368\,600 + 156.2T$; Larson and Elliot²⁰, determination of the Gibbs energy of MoS_2 formation by a reversible electromotive-force cell employing stabilized zirconia as the electrolyte (similar to ref.¹⁷) in temperature interval 1 051–1 372 K, 6 ΔG^0 (J mole^{-1}) = $-397\,000 + 181.1T$; calculated from O'Hare's value for the standard enthalpy of MoS_2 formation gained by the fluorine bomb calorimetry¹⁵ and Frederickson and Chasanov's relative enthalpy and relative Gibbs energy values, gained by drop calorimetry¹⁶, 7 ΔG^0 (J mole^{-1}) = $-360\,700 + 156.9T$; Stubbles and Richardson²¹, a study of the reactions $2/3 \text{Mo(s)} + \text{H}_2\text{S(g)} = 1/3 \text{Mo}_2\text{S}_3(\text{s}) + \text{H}_2(\text{g})$ at 1 123–1 473 K and $\text{Mo}_2\text{S}_3(\text{s}) + \text{H}_2\text{S(g)} = 2 \text{MoS}_2(\text{s}) + \text{H}_2(\text{g})$ at 1 273–1 473 K using a radiochemical method, 8 ΔG^0 (J mole^{-1}) = $-300\,700 + 116.6T$; Zelikman and Krein²², investigation of the hydrogen reduction of MoS_2 employing a circulation apparatus at temperatures 1 073–1 373 K, 9 ΔG^0 (J mole^{-1}) = $-280\,400 + 104.9T$; Parravano and Malquori²³; at temperatures 1 078–1 373 K they studied the equilibrium of $\text{H}_2\text{S}-\text{H}_2$ mixture with molybdenum and its lowest sulphide which they believed to be MoS_2 ; however, McCabe²⁴ and Stubbles and Richardson²¹ have subsequently demonstrated that Mo_2S_3 , and not MoS_2 , is the lowest sulphide in the equilibrium with Mo. As a result, the data of Parravano and Malquori may be erroneous

equilibrium reduction (A) over the temperature range 900 to 1 300 K and the standard Gibbs energy equation for the reaction (A), applicable over the given temperature range,

$$\Delta G^0 = 104\,500 - 39.0T \quad (\text{J mole}^{-1}). \quad (2)$$

The constants in this equation are $\Delta H^0 = 104.4 \text{ kJ mole}^{-1}$ and $\Delta S^0 = 39.0 \text{ J K}^{-1} \cdot \text{mole}^{-1}$ for the reaction (A).

The Gibbs-energy equation for the formation of solid molybdenum disulphide from gaseous diatomic sulphur and solid molybdenum, can be derived by taking account of the thermodynamic data for the formation of hydrogen sulphide¹³:



$$\Delta G^0 = -390\,100 + 176.8T \quad (\text{J mole}^{-1}). \quad (3)$$

The values of $-390.1 \text{ kJ mole}^{-1}$ for ΔH^0 and $176.8 \text{ J K}^{-1} \text{ mole}^{-1}$ for ΔS^0 , which are given by two terms of equation (3) for the temperature interval 900–1 300 K, may be compared with the values of $-397.0 \text{ kJ mole}^{-1}$ and $181.1 \text{ J K}^{-1} \text{ mole}^{-1}$, calculated from the standard enthalpy of $\text{MoS}_2(\text{s})$ formation¹⁵, relative enthalpy and relative Gibbs energy of $\text{MoS}_2(\text{s})$, determined from calorimetric measurements¹⁶, and tabulated values for $\text{H}_2\text{S}(\text{g})$ (ref.¹³) and $\text{Mo}(\text{s})$ (ref.¹⁴). Taking into account that the uncertainty in the enthalpy of MoS_2 formation itself has the value of $\pm 5 \text{ kJ mole}^{-1}$ (ref.¹⁵), we may consider our results to be satisfactorily congruent with the values obtained by the calorimetric measurements.

The third law treatment of the experimental data led to the value $-273.2 \text{ kJ mole}^{-1}$ for the enthalpy of formation of solid molybdenum sulphide from solid molybdenum and solid rhombic sulphur. This value is in very good agreement with the value of $-275.3 \pm 5 \text{ kJ mole}^{-1}$, determined by fluorine bomb calorimetry¹⁵.

Fig. 3 shows the Gibbs energy of molybdenum disulphide formation from solid molybdenum and gaseous diatomic sulphur (reaction (B)) as a function of temperature. Our results are compared here with the results of other workers (see the legend to Fig. 3). This figure as well as the foregoing text show that our data are in an excellent agreement with the values obtained by fluorine bomb calorimetry. It can be seen from Fig. 1 that the values of the ratio $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ over the system Mo– MoS_2 ascertained experimentally at temperatures below 900 K are higher than its values we would obtain from equation (1) (Fig. 1, the full line) on presumption of its applicability in this temperature region. This fact may be regarded as a corroboration of the presumption that the “poorly crystalline” form of MoS_2 is more reactive than the “well crystalline” one.

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