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Equilibrium Measurements in the Mo–C–H System

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RECEIVED MAY 10, 1952

Equilibrium data for the reaction: $2\mathrm{Mo} + \mathrm{CH_4} = \mathrm{Mo_2C} + 2\mathrm{H_2}$ have been obtained in the temperature range 447–682°. The solid phases present were confirmed by means of X-ray spectrograms. Equilibrium data for the reaction: $\mathrm{Mo_2C} + \mathrm{CH_4} = 2\mathrm{MoC} + 2\mathrm{H_2}$ have been determined in the temperature range 663–825°. In the temperature range studied, both $\mathrm{Mo_2C}$ and MoC are thermodynamically stable with respect to carbon and molybdenum.

Molybdenum forms two carbides[2] having the stoichiometric formulas $\mathrm{Mo_2C}$ and MoC. According to Tutiya,[2] $\mathrm{Mo_2C}$ is formed by the action of carbon monoxide on molybdenum at 450–600°, whereas another carbide, assumed to be MoC, is formed at 750–800°.

Schenck, Kurzen and Wesselcock[3] studied the action of methane on molybdenum catalysts at 700 and 850°, the samples containing a varying amount of carbon. In general, on samples containing less carbon than that corresponding to $\mathrm{Mo_2C}$ (5.89% carbon corresponds to $\mathrm{Mo_2C}$), the $\mathrm{H_2/CH_4}$ ratio at equilibrium was much higher than that for the $\mathrm{C{-}H_2{-}CH_4}$ system, whereas on samples containing more than about 6% carbon, the $\mathrm{H_2/CH_4}$ ratio was somewhat less than that for the $\mathrm{C{-}H_2{-}CH_4}$ system. In discussing the equilibrium data of Schenck, Kelley[4] selected values obtained on samples having 5.8 to 10.7% carbon and assigned them to the reaction

$$\mathrm{Mo} + \mathrm{CH_4} = \mathrm{Mo_2C} + 2\mathrm{H_2},\ K_1 = (\mathrm{H_2})^2/\mathrm{CH_4} \quad (1)$$

This assignment of the equilibrium constants to reaction (1) by Kelley appears to be erroneous because the carbon content was such as to correspond to a mixture of $\mathrm{Mo_2C}$ and MoC and all of the values at 700° and several at 850° were obtained from the methane side.

For the purpose of clarifying the data of Schenck and correcting the calculations of Kelley, values of the equilibrium constants for reaction (1) were measured in the temperature range 447–682°. In addition, equilibrium values were obtained for a sample of molybdenum carbide containing 7.6% carbon by weight. It is believed that the latter values represent the reaction

$$\mathrm{Mo_2C} + \mathrm{CH_4} = 2\mathrm{MoC} + 2\mathrm{H_2},\ K_2 = (\mathrm{H_2})^2/\mathrm{CH_4} \quad (2)$$

Experimental

A sample of $\mathrm{MoO_3}$ was reduced to metallic Mo at 550° in a stream of dry hydrogen. The sample was then carbided with carbon monoxide at 450° to a carbon content of 3.7% by weight. X-Ray examination of this sample showed $\mathrm{Mo_2C}$ and Mo to be the main constituents. Several faint lines in addition to those for $\mathrm{Mo_2C}$ and Mo were also present. These lines were not those of any known oxide or carbide of molybdenum, though five of the six spurious lines agreed with those for $\mathrm{Mo_2N}$. They may possibly result from the trace of nitrogen probably present in both the hydrogen used in reduction and in the carbon monoxide used in carbiding.

In preparing an $\mathrm{Mo_2C{-}MoC}$ sample, the molybdenum was first carbided at 450° to 5.4% carbon. Then the temperature was raised gradually to 680°, and the sample was carbided to a carbon content of 7.6% by weight. The purpose of carbiding to approximately $\mathrm{Mo_2C}$ before raising the temperature was to prevent, if possible, the formation of free carbon by reaction of carbon monoxide with metallic molybdenum. An X-ray pattern of the sample taken at this point showed $\mathrm{Mo_2C}$ and also a pattern agreeing with MoC.[5] A second X-ray sample was taken after the 850° run; its pattern was identical to that of the first sample, and indicated the presence both of $\mathrm{Mo_2C}$ and MoC.

The apparatus and procedure were the same as those described in a previous paper[6] and involved the circulation of a $\mathrm{CH_4{-}H_2}$ mixture over the $\mathrm{Mo{-}Mo_2C}$ or $\mathrm{Mo_2C{-}MoC}$ systems until equilibrium was obtained. The platinum–platinum, 10% rhodium thermocouple used for temperature measurement was calibrated by the Gulf Research & Development Company Laboratory against the freezing points of zinc, aluminum and copper.

Results and Discussion

The results obtained for reaction (1) are shown in Table I and in Fig. 1, while those for reaction (2) are shown in Table II and in Fig. 1. Also in Fig. 1 are shown the results of Schenck for reaction (1), and the two points which represent the average of Schenck's results for reaction (2) at 700 and 850°.

$\mathrm{Mo_2C}$ and MoC are both stable thermodynamically with respect to molybdenum and carbon. From Fig. 1, using the present data, at 950°K. the free energy change for reaction (1) is −12,172 cal./mole, while that for reaction (2) is −869 cal./mole. At the same temperature, the free energy of formation of methane from carbon (β-graphite) and hydrogen is 3310 cal./mole.[7] From these data the free energy for the reaction

$$\mathrm{Mo} + \mathrm{C}\ (\beta\ \text{graphite}) = \mathrm{MoC} \quad (3)$$

is −3,211 cal./mole and the free energy for the reaction

$$2\mathrm{Mo} + \mathrm{C} = \mathrm{Mo_2C} \quad (4)$$

is −8,862. Thus, if the equilibrium constant for the sample containing 7.6% carbon is assumed to be for reaction (2), one must conclude that both $\mathrm{Mo_2C}$ and MoC are thermodynamically stable with respect to their elements at 950°K. However, the free energy change is favorable for MoC to react at this temperature with any free molybdenum that might be present to form $\mathrm{Mo_2C}$ by the reaction

$$\mathrm{MoC} + \mathrm{Mo} = \mathrm{Mo_2C},\ \Delta F^\circ_{950^\circ\mathrm{K.}} = -5651\ \text{cal./mole} \quad (5)$$

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[1] U. S. Bureau of Mines, Bruceton, Pa.

[2] H. Tutiya, *Bull. Inst. Phys. Chem. Res.* (*Tokyo*), **11**, 1150 (1932).

[3] Schenck, Kurzen and Wesselcock, *Z. anorg. Chem.*, **203**, 159 (1931).

[4] K. K. Kelley, Bureau of Mines Bulletin No. 407 (1937).

(5) There is no doubt that the X-ray lines of the present sample were due to MoC even though the X-ray patterns of MoC and MoN [G. Hägg, *Z. physik. Chem.*, **B7**, 354 (1930)] are almost identical. MoC has a hexagonal structure with $a = 2.901$ and $C = 2.786$. MoN also has a hexagonal structure, the values of a and C being 2.860 and 2.804, respectively.

(6) L. C. Browning and P. H. Emmett, THIS JOURNAL, **73**, 581 (1951).

(7) F. D. Rossini, *et al.*, Circular of the National Bureau of Standards C461 (1946).

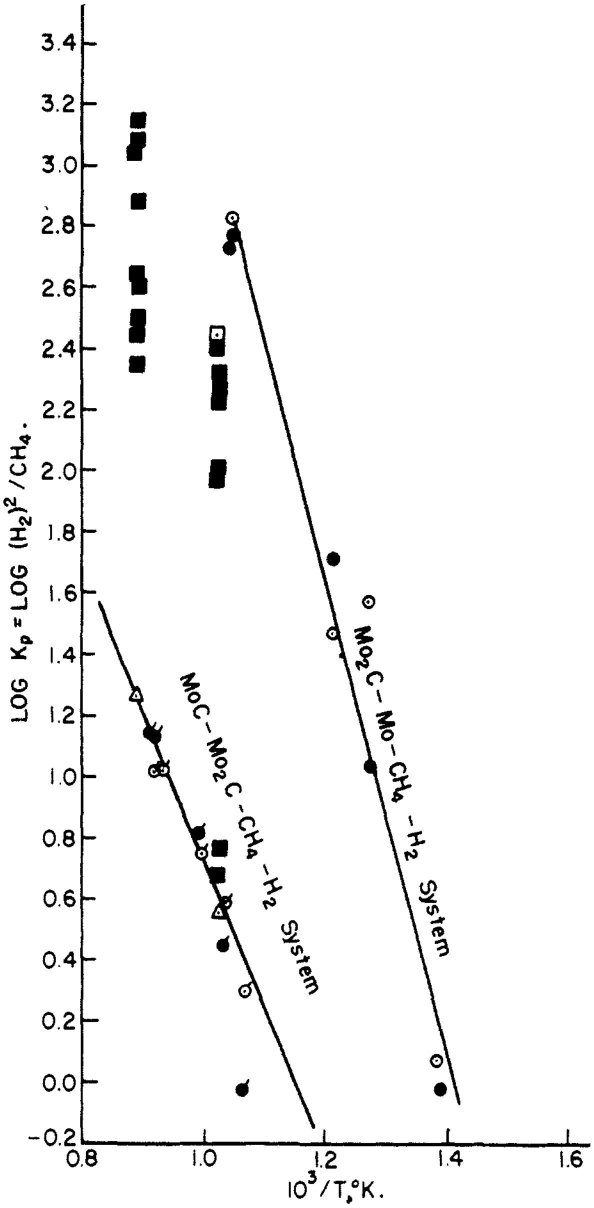

Fig. 1.—log of K_p *vs.* $10^3/T$ for the Mo–C–H_2 system and the C–H_2–CH_4 system: ⊙, author's data for reaction (1); ⊘, author's data for reaction (2); ⊡, Schenck's data for reaction (1); △, average values of Schenck's data for reaction (2). Solid symbols are for approaches to equilibrium from the CH_4 side; open symbols, from the hydrogen side.

and also for it to form free carbon by the reaction

$$2MoC = Mo_2C + C, \Delta F°_{950°K.} = -2441 \text{ cal./mole} \quad (6)$$

The agreement of the present data with those of Schenck appears quite good for reaction (2) and fairly good for reaction (1). Certainly both his data and ours indicate that at 950°K. Mo_2C as well as MoC are thermodynamically stable with respect to Mo and C.

As pointed out above, Kelley's values for the equilibrium constant $(H_2)^2/CH_4$ are well chosen except that they should apparently be applied to reaction (2).

Table I

Equilibrium Constants for the Reaction $2Mo + CH_4 = Mo_2C + 2H_2$

Expt. No.	Temp., °C.	Composition of initial gas, % H_2		Composition of equilibrated gas, % H_2		Total pressure, atm.	K_p, atm.
		H_2	CH_4	H_2	CH_4		
1	546.7	82.5	17.5	98.97	1.03	0.5336	50.7
2	546.7	100.0	0.0	98.38	1.62	.4842	29.1
3	512.2	79.6	20.4	95.27	4.73	.5692	10.9
4	511.6	100.0	0.0	98.60	1.40	.5586	38.9
5	447.0	60.9	39.1	70.98	29.02	.5350	0.93
6	448.6	75.4	24.6	74.96	25.04	.5279	1.18
7	681.7	95.0	5.0	99.90	0.10	.5723	545
8	678.8	93.5	6.4	99.85	.15	.8780	591
9	678.8	100.0	0.0	99.87	.13	.8837	649

Table II

Equilibrium Constants for the Reaction $Mo_2C + CH_4 = 2MoC + 2H_2$

Expt. No.	Temp., °C.	Composition of initial gas, %		Composition of equilibrated gas, %		Total pressure, atm.	K_p, atm.
		H_2	CH_4	H_2	CH_4		
1	662.8	100.0	0.0	78.25	21.75	0.7064	1.99
2	663.6	68.2	31.8	65.87	34.13	.7529	0.96
3	736.9	77.2	22.8	91.60	8.40	.6362	6.43
4	734.9	100.0	0.0	90.60	9.40	.6553	5.70
5	689.6	50.3	49.7	82.50	17.50	.7305	2.83
6	693.6	100.0	0.0	88.19	11.81	.5984	3.95
7	820[a]	98.2	1.8	96.5	3.5	.3842	10.43
8	798[a]	98.0	2.0	93.6	6.4	.6434	10.50
9	820[a]	87.7	12.3	94.5	5.5	.7382	13.30
10	825[a]	86.9	13.1	95.0	5.0	.6684	13.33

[a] Temperatures were controlled manually for these runs. Temperatures given were observed when equilibrated gas sample was removed from catalyst for analysis. In each case, the catalyst temperature had been drifting downward for several hours at the rate of 2° per hour.

In conclusion, a few peculiarities of the Mo–Mo_2C system should, perhaps, be mentioned. As stated previously, the reaction of carbon monoxide with molybdenum at temperatures of 450–480° stops after carburization to Mo_2C has occurred. In several instances, X-ray samples taken immediately after this carbiding showed only molybdenum to be present, in spite of the fact that the weight increase corresponded to full carburization to Mo_2C. Heat treatment at 530° of one of these samples for a period of 72 hours caused a complete disappearance of molybdenum lines, and the appearance of Mo_2C lines. Possibly free carbon is initially formed and reacts with the molybdenum to form Mo_2C at higher temperatures. However, on this basis, one's inability to obtain a weight increase of more than that corresponding to Mo_2C is difficult to explain.

Acknowledgment.—Thanks are due to Dr. L. Alexander and Dr. R. Collin of the Chemical Physics Department for taking and interpreting the X-ray spectrograms mentioned in this investigation. We also wish to acknowledge the help of William Starnes who made runs 7, 8, 9 and 10 shown in Table II for the system Mo_2C–MoC–CH_4–H_2.

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