of a mixture 2.01×10^{-3} M in sulfate and 3.63×10^{-4} M bisulfate by about 1.5 units. With stronger hydrogen bond donors, like p-bromophenol, the effect is much greater. This phenol is such a weak acid that it cannot react with sulfate by proton transfer. Here the acid–base reaction is due practically entirely to hydrogen bonding. The presence of 0.1 M p-bromophenol in the above mixture decreases the pa_H by 7.5 units. Hence the shape of the neutralization curve of bisulfate with tetraalkylammonium hydroxide is affected by water and alcohol and to a much greater extent by p-

bromophenol or phenol. In the presence of a carboxylic acid proton transfer with the sulfate ion occurs. However, heteroconjugation will be the most important reaction. It can be predicted that a carboxylic acid not only greatly affects the neutralization curve of a bisulfate but that the sulfate formed will greatly affect the neutralization curve (or the effective strengths) of the carboxylic acid. At present we are studying the systems bisulfate–sulfate–acetic acid and sulfate–acetic acid–acetate. The results will be communicated in a subsequent paper.

Equilibrium Measurements in the Molybdenum–Carbon–Hydrogen System

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Abstract: Equilibrium values for the reaction of molybdenum with methane to form Mo_2C and hydrogen have been determined over the temperature range 450–650°. The results yield values for the free energy of formation of Mo_2C in good agreement with those reported by Gleiser and Chipman. The data previously reported by Browning and Emmett are in error, apparently because of contamination of the equilibrating system with a small amount of molybdenum oxide.

The equilibrium for the reaction

$$2Mo + CH_4 \rightleftharpoons Mo_2C + 2H_2 \tag{1}$$
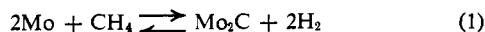
was measured by Browning and Emmett[1] on a sample of Mo_2C prepared by carbiding molybdenum with carbon monoxide. The resulting data are shown by curve 2 of Figure 2. A few years ago Gleiser and Chipman[2] pointed out that the data of Browning and Emmett lead to an impossibly high entropy change (about 26 eu) for the reaction

$$2Mo + C \rightleftharpoons Mo_2C \tag{2}$$
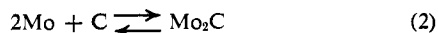
They also showed that equilibrium measurements in a system containing Mo_2C, MoO_2, CO, and CO_2 in the temperature range 1200–1300° gave values for the free energy of formation of Mo_2C involving a small reasonable entropy change. In view of these facts we decided to redetermine the equilibrium for reaction 1.

The most obvious source of error in the measurements of Browning and Emmett was the possible contamination of the carbide sample with molybdenum oxide with the resulting inclusion of some water vapor, carbon dioxide, or carbon monoxide in the fraction called methane in the analysis of the final methane–hydrogen mixture. Accordingly, it was decided to prepare the Mo_2C by carbiding with methane under such partial pressure conditions as to exclude the formation of free carbon and also with the complete absence of any contamination due to oxygen.

Experimental Section

The equipment used is drawn schematically in Figure 1. It was so arranged that a methane–hydrogen mixture of known composition could be circulated over a sample of Mo or a mixture of Mo_2C and Mo. The molybdenum was obtained by reducing in hydrogen a sample of molybdenum trioxide powder (Baker "Analyzed" reagent). The powdered trioxide was supported on a quartz sinter in a quartz reactor. A quartz rod loosely fitting in a hole bored through the sinter was flattened on top to close off the hole during the reduction of the oxide and the equilibration of the metal–metal carbide system with the circulating methane–hydrogen mixture. In the bottom of the rod at a point below the furnace was imbedded a piece of soft iron. It was then possible, by use of a magnet, without interrupting the gas circulation to shake down samples of the molybdenum and its various compounds into a Pyrex capillary for X-ray examination. The temperature in the reactor could be closely controlled by a platinum resistance wire feeding a thyratron unit. Temperature was measured by a Pt—Pt-10% Rh thermocouple unit. It was controlled during a run to an accuracy of ±1°.

A four-way stopcock made it possible to close off the reactor from the exterior system. The latter consisted of the related circulating pump, inlet valves for hydrogen and methane, a vacuum line, manometer, trap, and a system of stopcocks which made it possible to flush a small constant volume of the gas mixture being circulated to a thermal conductivity cell without interrupting the circulation. The separation of the reactor and the exterior system in this way enabled one to mix methane and hydrogen in any desired concentration before bringing the gas mixture into contact with the molybdenum sample.

The hydrogen gas was diffused through a palladium–silver alloy thimble before entering the apparatus; the methane was taken directly from a tank (Matheson CP quality).

A liquid nitrogen trap was introduced into the circulating system to remove any traces of water vapor or carbon dioxide that might arise from traces of oxygen present as impurities. If any carbon monoxide were present it would be removed by reactions with the metallic molybdenum to form carbon dioxide and molybdenum carbide. The continual freezing out of any carbon dioxide would assure the absence of carbon monoxide since the reaction of carbon monoxide and Mo is known to be rapid over the temperature range
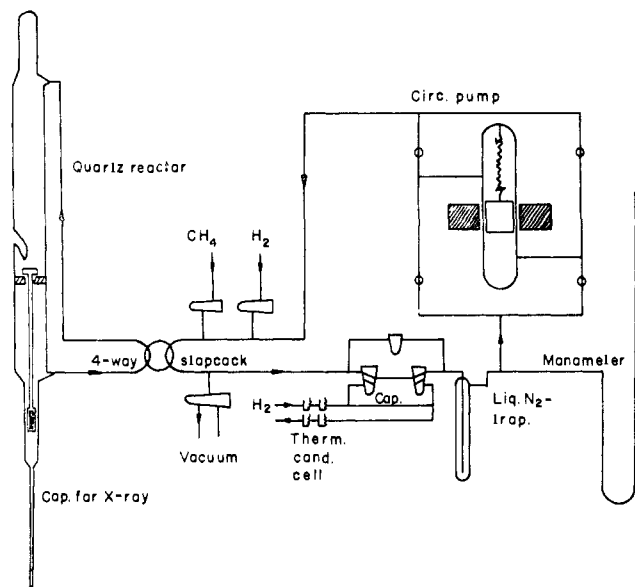
(1) L. C. Browning and P. H. Emmett, *J. Amer. Chem. Soc.*, **74**, 4773 (1952).

(2) M. Gleiser and J. Chipman, *J. Phys. Chem.*, **66**, 1539 (1962).

Figure 1. Equipment used for equilibrium measurements in the system Mo–CH₄–H₂; see detailed explanation in the text.

studied. The vapor pressure of methane at −195° is about 10 mm. This is much higher than any equilibrium values (about 0.1 mm or less) with which we were concerned. Therefore, the liquid nitrogen trap would have no influence on the methane–hydrogen equilibrium mixture in contact with the Mo–Mo₂C system.

Molybdenum trioxide (3 g) was reduced with hydrogen (60 cc/min) for 7 days at 550°, the last 4 days of the reduction being carried out with hydrogen diffused through the palladium–silver alloy thimble. Partial carbiding of the sample up to about a 1% carbon content was carried out with a mixture of hydrogen and methane at 550°, the pressure of methane never exceeding 50 mm in a total pressure of about 500 mm. This kept the methane concentration well below the equilibrium value for the hydrogen–carbon–methane system reported by Rossini[3] and by Browning and Emmett.[4] Free carbon as well as oxides of molybdenum were thus avoided.

Since a few measurements were also made on the reaction

$$Mo_2C + CH_4 = 2MoC + 2H_2 \qquad (3)$$
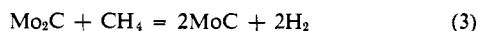
it was necessary to prepare an Mo₂C–MoC mixture. This was done by carbiding the Mo₂C with methane at 625°. When the pressure at the end of each carbiding cycle started to increase owing to the formation of MoC when practically all the Mo was used up, the partial pressure of methane was raised slowly until equilibrium with respect to reaction 3 was attained. The rise in the methane pressure started at about 5.5% carbon, but steady equilibrium could not be reached until about 5.8% carbon was incorporated. This is in good agreement with the theoretical amount of carbon in MoC, 5.89%. Further carbiding to about 6.5% carbon was done at 680°, using initial methane pressures about 40 mm above the equilibrium pressures. The rate of reaction to form MoC was considerably slower than the rate of formation of Mo₂C.

Results and Discussion

The experimental data for the equilibrium constant $(H_2)^2/(CH_4)$ for reaction 1 are plotted logarithmically against $1/T$ as curve 1 in Figure 2. The equilibrium points reached from the high methane side are shown by the open circles; those from the high hydrogen side, by the solid circles. Some of the points were obtained from starting mixtures containing as much as 50 mm of methane at a total pressure of 500 mm. Others were obtained by starting with pure hydrogen. Still other points were obtained by shifting the temperature up or

(3) F. Rossini, National Bureau of Standards Circular, No. C461, U. S. Government Printing Office, Washington, D. C., 1946.
(4) L. C. Browning and P. H. Emmett, *J. Amer. Chem. Soc.*, 73, 581 (1951).

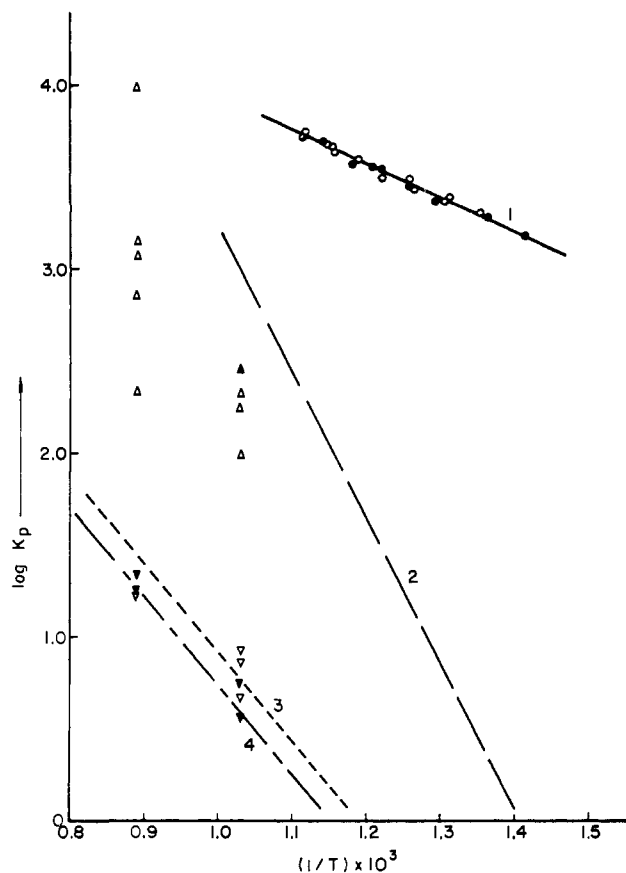Figure 2. Log K_p as a function of $1/T$: curve 1, author's data on reaction 1; curve 2, Browning and Emmett's data[1] on reaction 1; △, data from Schenck, *et al.*,[6] for reaction 1; ▽ data from Schenck, *et al.*,[6] for reaction 3; curve 3, Browning and Emmett's data[4] for reaction 4; curve 4, Browning and Emmett's data[1] for reaction 3; open symbols, equilibrium reached from the high CH₄ side; closed symbols, equilibrium reached from the high H₂ side. Equilibrium pressures are in atmospheres.

down and reequilibrating the gas mixture with the molybdenum–molybdenum carbide system. Equilibrium pressures of methane varied from 0.06 to 0.02 mm. The experimental error in the thermal conductivity analysis of the hydrogen–methane system is estimated to be about the size of the experimental points in curve 1, Figure 2. The line representing the data is drawn in accordance with a least-squares method. Two separate sets of data originating from separate readings of the equilibrium pressures of the methane differed by about 2.5% in the slope of the line.

The standard free-energy change for reaction 1 can be expressed by the equation

$$\Delta F^\circ = 8410 - 26.44T$$

Adding the standard free energy for the formation of methane from graphite by the reaction

$$C + 2H_2 \rightleftharpoons CH_4 \qquad (4)$$

the standard free energy of formation of Mo₂C from molybdenum and graphite in the 600–900°K range can be expressed by the linear equation

$$\Delta F^\circ = -12,030 - 1.44T$$

In Figure 3, curve 1, is given the plot of this equation representing the authors' data. As curve 2 is shown the

plot of the data obtained by Gleiser and Chipman[2] from reactions involving the equilibration of a mixture of MoO_2 and Mo_2C with CO and CO_2. The data of Gleiser and Chipman and the authors' data thus yield curves for the free energy of formation of Mo_2C from graphite and molybdenum in excellent agreement with each other.

In curve 3 are plotted values for the free energy of formation of Mo_2C as calculated by Pankratz, Weller, and King[5] from the third law with the help of heat capacity data. Their curve differs from that of the authors and of Gleiser and Chipman by about 1000–1400 cal even though they estimate the uncertainty of their calculation to be about 700 cal. On the basis of the excellent agreement between the authors' data and those obtained by Gleiser and Chipman by an entirely different set of reactions, we are inclined to believe the experimental values as represented by curves 1 and 2 of Figure 3 are preferable to the calculated values for the variation of the free energy of formation of Mo_2C with temperature. Specifically, the experimental error of the authors' data appear to be equivalent to about ±100 cal in the value for the standard free energy of formation of Mo_2C.

A few experimental points for reaction 3 were also obtained on the sample of carbide containing about 6.5% carbon. The points scattered around the equilibrium data given by Browning and Emmett[1] for reaction 3. It should be noted, however, that their curve for reaction 3 is almost identical with that given by Rossini[3] for reaction 4, the carbon-methane-hydrogen equilibrium. It is, therefore, felt that considerable uncertainty must remain in regard to the standard free energy of formation of MoC.

The present study did not seem to be complete without attempting to show that the data of Browning and Emmett[1] were those to be expected from carbiding the molybdenum with carbon monoxide. To this end, a sample of molybdenum produced in the usual way by the reduction of molybdenum trioxide by hydrogen was carbided to 3% carbon with pure carbon monoxide, in accordance with the description given by Browning and Emmett. After the sample was pumped and flushed several times with pure hydrogen, some equilibrium points were taken at 596 and 539° both from the hydrogen side and from the methane side without the liquid nitrogen trap being used. Thermal conductivity analysis yielded gas compositions equal approximately to those found by Browning and Emmett. However, when a Dry Ice-acetone trap was added to the circulating system, the equilibrium constant increased above the curve corresponding to the Browning and Emmett results. The constant rose still more when a liquid nitrogen trap was included in the circulating system. Clearly, therefore, the results of Browning and Emmett were in error due to the presence of molybdenum oxide in the original sample. The matter was not pursued further.

The examination by X-rays of our sample for the Mo-Mo_2C as prepared by carbiding with methane showed lines corresponding to Mo and to Mo_2C plus some faint lines fitting those for SiO_2. These latter
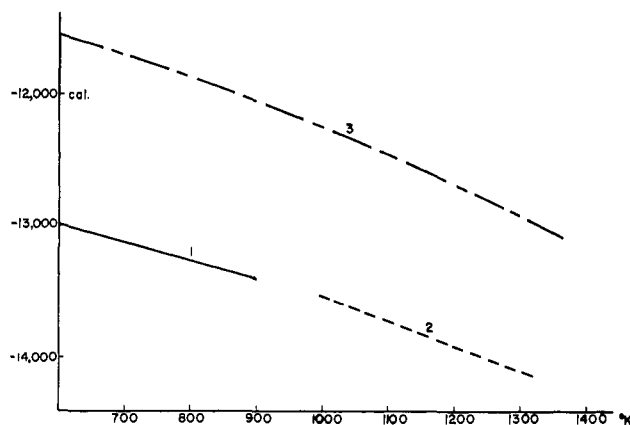

Figure 3. Standard free-energy change for reaction 2 as a function of temperature: curve 1, author's data; curve 2, data from Chipman, et al.; curve 3, data from Pankratz, et al.[5]

were presumably due to small particles from the quartz sinter collected in the X-ray sample accidentally.

The only previous equilibrium data for reactions 1 and 3, aside from those of Browning and Emmett, were published by Schenck, Kurzen, and Wesselkock.[6] Typical values from their work are shown in Figure 2. They analyzed for methane by a combustion method depending upon the formation and measuring of carbon dioxide from the combustion. Clearly, if any traces of oxygen or water vapor got into the system, it would have resulted in formation of CO or CO_2, both of which would have been reported as methane. Actually, these authors admit that some oxygen contamination did occur in transferring their reduced molybdenum to the equilibrium apparatus. If the removal of this oxygen contamination by their subsequent static hydrogen reduction was incomplete, their equilibrium points for reaction 1 would, as observed, be expected to be on the low side of the true equilibrium curve.

It should also be noted that they, in their static system, measured the composition of the gas phase by removing most of it from the reactor and analyzing for hydrogen and methane. Depending upon the detailed arrangement of the apparatus, some error due to thermal diffusion might also have been involved. It would have been in the direction of lowering the equilibrium constant slightly. The data of Schenck and his co-workers for reaction 3 are in good agreement with the data of Browning and Emmett for this same reaction and with the few points taken in the present work with careful exclusion of any molybdenum oxide. Unfortunately, Kelley[7] used data for reaction 3 from the work of Schenck and coworkers but mislabeled it as representing data for reaction 1.

As pointed out above, the data of Schenck and coworkers, those of Browning and Emmett, and also those of the present work for reaction 3 combine to yield a curve for equilibrium values that is common to all three sets of data. Unfortunately, the curve is not far removed from and is parallel to the equilibrium curve for reaction 4 as given by the data of Rossini[3] for the case in which the carbon phase is β-graphite.

(5) L. B. Pankratz, W. W. Weller, and E. G. King, U. S. Bureau of Mines, Report of Investigation 6861, Mines Bureau, Pittsburgh, Pa., 1966.

(6) R. Schenck, F. Kurzen, and H. Wesselkock, Z. Anorg. Allgem. Chem., 203, 159 (1931).

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It is even closer to an equilibrium curve observed by Browning and Emmett[4] for reaction 4 when the carbon is presumably amorphous and is formed by the decomposition of metallic carbides at low temperature. This latter curve is shown as curve 3 in Figure 2. The difference between the curves is so small that one might suspect that the real equilibrium measured is that of reaction 4 with the carbon in a slightly more active form than the β-graphite. Similar deviations are reported by Troesch[8] on carbon supported on Ni, and by Leitnaker[9] on a U–C system. Although the formation of

MoC phases is reported by Tutiya,[10] by Clougherty, et al.,[11] and established on X-rays of samples of Mo carbided to 7.6% C by Browning and Emmett,[1] the true equilibrium for reaction 3 must still be in doubt because of the difficulty in separating it from complications by reaction 4. The equilibrium for reaction 1, however, is, we believe, accurately defined by curve 1, Figure 2.

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(9) J. M. Leitnaker, Symposium on Thermodynamics of Nuclear Material, Vienna, 1967.

(10) H. Tutiya, *Bull. Inst. Phys. Chem. Res.* (Tokyo), **11**, 1150 (1932).
(11) E. V. Clougherty, K. H. Lothrop, and J. A. Kafalas, *Nature*, **191**, 1194, 4794 (1961).

Molecular Orbital Calculation on Some Group I, II, and III Methyl Compounds[1]

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Abstract: The methyl compounds of the group I, II, and III elements display some interesting variations in structure. Some of the compounds are electron deficient in the sense that they form polymeric species through the delocalization of one or more bonding pairs. Examples of the latter are $((CH_3)_3Al)_2$, $(CH_3Li)_4$, and $((CH_3)_2Be)_x$. By contrast other compounds such as $(CH_3)_3B$ and $(CH_3)_2Zn$ are monomers showing little or no tendency toward association. An attempt has been made to understand the bonding factors which are responsible for the variations in structure of the methyl compounds of lithium, beryllium, boron, and aluminum largely on the basis of charge-iterated extended Hückel molecular orbital calculations. CNDO–SCF calculations were also performed on CH_3Li and $(CH_3Li)_4$.

The methyl compounds of the group I, II, and III elements display some interesting variations in structure. Some of these compounds are electron deficient in the sense that they form polymeric species through the delocalization of one or more bonding pairs. Examples of the latter are the trimethylaluminum dimer,[2] the dimethylberyllium polymer,[3] and the methyllithium tetramer.[4] By contrast, other methyl compounds such as trimethylboron[5] and dimethylzinc[6] are monomers showing little or no tendency toward association.

In the present paper we report the results of semiempirical molecular orbital calculations on some of these molecules. Our basic objective was to understand the bonding fractors which are responsible for these variations in structure. We were also interested in the validity of the concept of hyperconjugation, particularly in the case of $(CH_3)_3B^7$ since it has been

argued[8] that this effect should be enhanced in this molecule due to C^-–B^+ polarity of the σ bond. Previously, Rundle[9] has described a simplified MO treatment of $(CH_3)_6Al_2$ and indicated that the bridge bonding in this species can be described as a combination of tetrahedral orbitals from aluminum and carbon or equivalently as a "methylated double bond."

More recently extended Hückel calculations have been performed on this molecule[10a] and $(CH_3)_3B$.[10b] Rough estimates have been made[4] for the MO energies of the lithium–carbon skeleton of $(CH_3Li)_4$, and the hypothetical methyllithium dimer has been the subject of an LCAO–SCF treatment.[11]

Methods of Calculation

Two types of Hückel molecular orbital calculations were performed on the following molecules: CH_3Li, $(CH_3Li)_4$, $(CH_3)_2Be$, $(CH_3)_3B$, $(CH_3)_6B_2$, $(CH_3)_3Al$, and $(CH_3)_6Al_2$. In addition CNDO self-consistent field calculations were performed on CH_3Li and $(CH_3Li)_4$.

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