

Fig. 1.—Bond lengths and angles in $\text{Rh}(\text{CO})_2\text{Cl}$.

least squares⁸ resulted in a final discrepancy factor of $R_1 = 6.7\%$ for 239 observed reflections.

The principal features of the structure are given in Fig. 1. Two essentially planar $\text{Rh}(\text{CO})_2\text{Cl}$ groups intersect at an angle of 124° . The resulting dimers apparently are linked by direct Rh-Rh bonds to form infinite chains. A Rh-Rh distance of 3.31 Å. is consistent with X-ray data for other metal-metal bonds⁹⁻¹¹ which involve the coupling of unpaired electrons. In order to explain the compound's diamagnetism in the solid state we propose a second so-called bent metal-metal bond as indicated in Fig. 1 which would result from the overlap of d^2sp^3 hybridized σ -type orbitals at an angle of approximately 56° . Evidently in solution the weak metal-metal bonds break to give dimeric molecules. The interatomic distances and angles are in accord with the proposed octahedral environment about each Rh atom. Semi-quantitative molecular orbital arguments¹² for bent metal-metal bonding involving primarily p orbitals have been presented for $\text{Co}_2(\text{CO})_6\text{-C}_2(\text{C}_6\text{H}_5)_2$.^{13,14}

Our work on $\text{Rh}(\text{CO})_2\text{Cl}$ suggests that bent metal-metal bonding involving octahedral hybridization occurs in $\text{Co}_2(\text{CO})_8$ ¹⁵ and $\text{Co}_2(\text{CO})_9\text{C}_2\text{H}_2$.¹⁶ In fact octahedral coordination rather than square pyramidal coordination¹⁷ readily can be rationalized from the structural results for $\text{Fe}_2(\text{CO})_9$,¹⁸ $\text{Fe}_2(\text{CO})_9\text{-C}_2\text{Me}_2$,^{18,19} and $\text{Fe}_3(\text{CO})_9[(\text{C}_6\text{H}_5)_2\text{C}_2]_2$.²⁰

On the basis of infrared and dipole moment measurements Hieber and Beck²¹ proposed that di-

(8) W. R. Busing and H. Levy, "A Crystallographic Least Squares Refinement Program for the I.B.M. 704," Oak Ridge National Laboratory, 1959.

(9) L. F. Dahl and D. L. Wampler, *J. Am. Chem. Soc.*, **81**, 3150 (1959).

(10) L. F. Dahl, E. Ishishi and R. E. Rundlc, *J. Chem. Phys.*, **26**, 1750 (1957).

(11) F. C. Wilson and D. P. Shoemaker, *ibid.*, **27**, 809 (1957).

(12) D. A. Brown, *J. Chem. Phys.*, **33**, 1037 (1960).

(13) H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, R. Markby and I. Wender, *J. Am. Chem. Soc.*, **76**, 1457 (1954).

(14) W. G. Sly, *ibid.*, **81**, 18 (1959).

(15) G. G. Sumner, H. P. Klug and L. E. Alexander, abstracts of papers, National Meeting of the American Crystallographic Association, Washington, D. C., January, 1960.

(16) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 156 (1959).

(17) O. S. Mills and G. Robinson, *ibid.*, 421 (1960).

(18) A. A. Hock and O. S. Mills, *ibid.*, 233 (1958).

(19) O. S. Mills, private communication.

(20) R. P. Dodge and V. Schomaker, private communication.

(21) W. Hieber and W. Beck, *Z. anorg. u. allgem. Chem.*, **305**, 265 (1960).

meric compounds of the type $[\text{Fe}(\text{CO})_2\text{X}]_2$ ($\text{X} = \text{S}, \text{Se}, \text{SC}_2\text{H}_5, \text{SeC}_2\text{H}_5$) possess chalcogen bridges and non-planar configurations. Our results support this proposal, and we furthermore believe that these compounds possess bent metal-metal bonds.

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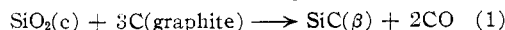
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THE FREE ENERGY OF SILICA

Sir:

Experimental data on certain metallurgical reactions at high temperatures point to an error in the presently accepted value for the free energy of SiO_2 . Four distinct groups of data lead to the same conclusion.

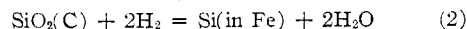
I.—Kay and Taylor¹ have repeated the earlier measurements of Baird and Taylor² on the reaction



According to their measurements the equilibrium pressure of CO reaches 1 atm. at 1800°K . Using the accepted values³ for the free energy of SiO_2 and CO, the equilibrium data lead to a free energy of SiC which is less negative by 5 kcal. than that found by Humphrey, Todd, Coughlin and King.⁴ The data of the latter investigators have received experimental confirmation in the work of Chipman, Fulton, Gokcen and Caskey⁵ and more recently that of Kirkwood and Chipman⁶ using measurements of the solubility of SiC in molten iron and lead, respectively. The agreement suggests that the equilibrium of reaction (1) be used to calculate the free energy of SiO_2 rather than the reverse calculation which has been reported by Smiltens.⁷

Using the tabulated data of Humphrey, *et al.*,⁴ for the free energy of β -SiC and the accurately known data for CO, the free energy of formation of SiO_2 at 1800°K . is -138.4 kcal. Coughlin³ gives -133.35 for cristobalite and essentially the same figure for the other crystalline forms. The equilibrium data thus lead to a result which is 5 kcal. more negative than the "third-law" value.

II.—When a molten Fe-Si alloy is equilibrated with an atmosphere of H_2 and H_2O in a silica crucible, equilibrium (2) may be established



(1) D. A. R. Kay and J. Taylor, *Trans. Faraday Soc.*, **56**, 1372 (1960).

(2) J. D. Baird and J. Taylor, *ibid.*, **54**, 526 (1958).

(3) J. P. Coughlin, U. S. Bureau of Mines Bulletin 542 (1954).

(4) G. L. Humphrey, S. S. Todd, J. P. Coughlin and E. G. King, Bur. Mines Rept. Inv. 4888 (1952).

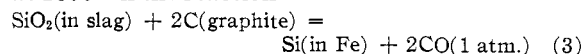
(5) J. Chipman, J. C. Fulton, N. Gokcen and C. R. Caskey, *Acta Met.*, **2**, 439 (1954).

(6) D. H. Kirkwood and J. Chipman, paper submitted to *J. Phys. Chem.*

(7) J. Smiltens, *J. Phys. Chem.*, **64**, 368 (1960).

If independent values of the activity of Si were available, the equilibrium constant would fix the free energy of SiO_2 . An effort was made by Chipman and co-workers⁵ to fix this activity by distribution measurements between Fe and Ag. The experiments were done at 1420° at which temperature the lower limit of the liquid field has a mole fraction $N_{\text{Si}} = 0.14$. The equilibrium measurements were made at higher temperatures and lower concentrations. Extrapolation of the activity coefficient data could be made to agree with the free energy change in reaction (2) only by neglecting the distribution results at the lowest concentrations and adopting an unsatisfactory relation between $\log \gamma_{\text{Si}}$ and N_{Si} . The accepted value of ΔF^0 for SiO_2 led to $\log \gamma_{\text{Si}} = -2.14$ at 1873° K. and infinite dilution. A more satisfactory extrapolation of the distribution data gives $\log \gamma_{\text{Si}} = -3.4$ at 1420° , which is corrected by means of the known⁵ partial molal enthalpy of Si (-28.5 kcal.) to give $\log \gamma_{\text{Si}} = -3.0$ at 1873° K. More recently Matoba, Gunji and Kuwana⁸ have made direct measurements on reaction (2), at low concentrations of Si. Their data with the above activity coefficient give a free energy of formation of -138.5 kcal. at 1873° K. An uncertainty of ± 2 kcal. is inherent in the activity coefficient. This is to be compared with -130.0 kcal. in the tables.

III.—The activity of SiO_2 in metallurgical slags such as $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ solutions at $1500\text{-}1700^\circ$ has been studied by a number of investigators with grossly discrepant results. The four published experimental studies cover somewhat different ranges of concentration, but these overlap sufficiently in the binary system CaO-SiO_2 to permit comparison at $N_{\text{SiO}_2} = 0.45$. Fulton and Chipman⁹ determined equilibrium concentrations at 1600° in the reaction



They used the activity coefficient of Si in the molten alloy which had been determined⁵ and the accepted free energies of SiO_2 and CO to calculate a_{SiO_2} . Their value at $N_{\text{SiO}_2} = 0.45$ was 0.040. Baird and Taylor² and more recently Kay and Taylor¹ applied reaction (1) to slags and reported results at 1550° from which the interpolated activities of SiO_2 at $N_{\text{SiO}_2} = 0.45$ were 0.16 and 0.14, respectively. Yang, McCabe and Miller¹⁰ used effusion measurements to obtain the activity of silica at 1637° . Interpolation to $N_{\text{SiO}_2} = 0.45$ gives $a_{\text{SiO}_2} = 0.28$. The direct measurements of the activity of SiO_2 are seen to yield values which are four to seven times as large as those obtained through reaction (3) and the accepted free energy of SiO_2 . A four-fold correction in the equilibrium constant of this reaction would raise the activity coefficient by a factor of 4 and would require an adjustment of -5 kcal. in the free energy of formation of SiO_2 .

(8) S. Matoba, K. Gunji and T. Kuwana, *Tetsu to Haganē*, **45**, 229 (1959); *Stahl und Eisen*, **80**, 299 (1960).

(9) J. C. Fulton and J. Chipman, *Trans. Am. Inst. Min. Met. Pet. Engrs.*, **200**, 1136 (1954).

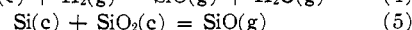
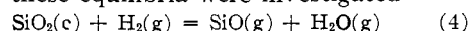
(10) L. Yang, C. L. McCabe and R. Miller, "The Physical Chemistry of Steelmaking," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 63.

IV.—Professor Wagner, in a private communication, has pointed out that the chemical potential of SiO_2 in a slag mutually saturated with Ca_2SiO_4 and CaSiO_3 may be calculated from the free energies of these compounds. The value so calculated confirms the results of Taylor and co-workers and is about 5 kcal. less negative than that interpolated from reaction (3) and the "third-law" free energy of SiO_2 .

Research is in progress which is aimed at securing more accurate data on the several equilibria mentioned. Present accuracy is in all cases better than that corresponding to a discrepancy of 5 kcal. It is not easy to understand so large an error in the heat of formation or in the entropy of SiO_2 , the latter amounting to $R \ln 4$. There are apparently no reasons for suspecting a zero-point entropy on structural grounds. On the other hand, the third-law value of ΔF^0 in reaction (1) is independent of the heat of formation of SiO_2 since that value is used in obtaining the heat of formation of SiC. Thus the discrepancy in this case could be either in the entropy of SiO_2 or in an equal error in two independent heats of combustion.

The fact that crystalline silicates require the same correction is readily understandable if the error is in ΔH . If, however, we have to add $R \ln 4$ to the entropy of SiO_2 , it must be added not only for all the crystalline forms of silica but also for the silicates. Thus one cannot look for an entropy anomaly in the arrangements of SiO_4 tetrahedra but only within this structure. Clearly the problem requires theoretical attention as well as improved accuracy of measurement.

V. Addendum.—Since the foregoing considerations were initially set forth, the writer has seen an unpublished paper by Ramstad and Richardson¹¹ in which these equilibria were investigated



Combination of the results with the known free energy of formation of H_2O gave the free energy of formation of SiO_2 . This was more negative by 3.8 ± 2 kcal. at 1700° K. than the third-law values listed in Coughlin's tables.³

(11) H. F. Ramstad and F. D. Richardson, "Silicon Monoxide," Feb., 1961, meeting, The Metallurgical Society of AIME.

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CONCERNING THE STABILITY OF SOME
SUBSTITUTED CYCLOPROPENYL RADICALS;
EVIDENCE FROM POLAROGRAPHY OF THE
CORRESPONDING CATIONS

Sir:

The high stability of derivatives of the two-pi-electron cyclopropenyl cation¹ and the instability of a derivative of the four-pi-electron cyclopropenyl anion² are evidence for the "magic number" effect predicted by molecular orbital theory for such systems³; the same theory predicts that cyclo-

(1) R. Breslow and H. Höver, *J. Am. Chem. Soc.*, **82**, 2644 (1960). and references therein.

(2) R. Breslow and M. Battiste, *Chem. and Ind.*, 1143 (1958).

(3) Cf. S. L. Manatt and J. D. Roberts, *J. Org. Chem.*, **24**, 1336 (1959).