silver is in the +1 oxidation state is shown by its diamagnetism ($X_m = -194 \times 10^{-6}$). Stabilization of Ag(II) by (AO) should occur, for the structure would be planar and have the extra energy of the hydrogen bond. However, treatment with H_2O_2 or $S_2O_8{}^{=}$ does not appear to oxidize $[Ag(AO)_2]^{+1}$.

Palladium(II) in dilute acid solution rapidly forms compounds of the type $[Pd(AO)Cl_2]^0$ with all of the (AO)'s studied. In neutral media a second ligand is added which predominantly attaches *cis*. It has been shown[11] that $[Pd(AO)_2-H]ClO_4$ and $[Ni(AO)_2-H]ClO_4$ are isomorphous with one axis of the former's unit cell slightly enlarged. Platinum(II) slowly forms the intermediate $[Pt(AO)Cl_2]^0$ in acid solution and in neutral solution $[Pt(AO)_2\text{-}H]^{+1}$ may be isolated. In this case, however, the yield of the *cis* form is low and the *trans* may be present but difficult to isolate. In every Pt(II) or Pd(II) compound containing two (AO) groups the characteristic infrared absorption of the hydrogen bond was observed, and was absent in all mono-chelated complexes.

The action of free (AO) on $[Co(H_2O)_6](ClO_4)_2$ in water lowers the *p*H and yields a slightly soluble brown precipitate of $[Co(AO)_2-H]ClO_4$ which oxidizes rapidly with air to give a mixture of Co(III) compounds. The octahedral coördination compounds of Co(III) can be prepared using essentially the same procedures as for the corresponding ethylenediamine compounds. However, unlike the ethylenediamine and (DMG) compounds there is no evidence that a tris-(AO) compound exists and *p*H changes do not rupture the hydrogen bond as they appear to do in the $[Co(DMG)_2-2H\ X_2]^{-1}$ series.

The properties of the cobalt-(AO) compounds suggest that the (AO)'s have a planar configuration and that the monodentate ligands assume *trans* positions. Sterically, the formation of a hydrogen bond would appear to be impossible if this were not the case. In addition the green color of $[Co(AO)_2-HCl_2]^0$ is similar to many other *trans*-dichloro Co(III) compounds as opposed to the purple *cis* isomers. Attempts to prepare *cis* isomers by procedures analogous to those used in the ethylenediamine series have been unsuccessful.

Acknowledgment.—The author expresses his appreciation to George F. Svatos for the infrared spectra measurements.

STORRS, CONNECTICUT

[11] L. Katz and M. Kay, private communication.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, AND THE DIVISION OF MINERAL TECHNOLOGY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Dissociation Pressures of the Tantalum Silicides[1,2]

BY CLIFFORD E. MYERS AND ALAN W. SEARCY

RECEIVED AUGUST 27, 1956

The dissociation pressures of the tantalum silicides have been measured by the Knudsen effusion method. Phase modifications in the temperature ranges covered were established by quenching experiments and X-ray diffraction investigation. The heats of dissociation were combined with the heat of vaporization of silicon to obtain, for the heats of formation per silicon atom at 298°K.: $4.5TaSi_{0.22_2\pm0.03}$, −34.4 kcal.; Ta_2Si, −29.3 kcal.; $1.67TaSi_{0.60\pm0.08}$, −26.7 kcal.; and $^1/_2TaSi_2$, −11.6 kcal.

The silicides of tantalum[3-5] have been shown by Kieffer, Benesovsky, Nowotny and Schachner[6] to have melting points in excess of 2000°. From a consideration of the trends in stability of carbides, nitrides and other related compounds as well as from stabilities demonstrated in high temperature chemical reaction,[7] the silicides of tantalum could be predicted to be among the most stable of all silicides from a thermodynamic standpoint. Because of the expected high stabilities, measurement of heats and free energies of formation of the tantalum silicides seemed of particular interest. Accordingly, stabilities of all four of the stable tantalum silicide phases: $TaSi_{0.22_2\pm0.03}$, Ta_2Si, $TaSi_{0.60\pm0.08}$ and $TaSi_2$ have been determined from Knudsen effusion[8] measurements of the silicon dissociation pressures by means of apparatus and techniques outlined by Searcy and McNees.[9] (A fractional formula such as $TaSi_{0.22_2}$ or $TaSi_{0.60}$ is used when the ideal structure is unknown, or when there is evidence that the actual structure may be different from the ideal. For Ta_2Si and $TaSi_2$ the actual phase compositions apparently are those corresponding to ideal crystal structures.) A high temperature quenching furnace was used to determine which modifications of the various phases were stable in the temperature range of the dissociation pressure measurements.

Phase Studies

A $TaSi_2$ phase has been known for many years.[3,4] Additional tantalum silicides of compositions $TaSi_{0.22_2\pm0.03}$, Ta_2Si and $TaSi_{0.60\pm0.08}$ were more recently reported both by Brewer, Searcy, Templeton and Dauben[5] and by Nowotny, Schachner, Kieffer

---

(1) From a thesis by Mr. Myers in partial fulfillment of the requirements for the Ph.D. degree at Purdue University.

(2) This research was supported by the Office of Naval Research.

(3) O. Hönigschmid, *Monatsh.*, **28**, 1017 (1907).

(4) H. J. Walbaum, *Z. Metallkunde*, **33**, 378 (1941).

(5) L. Brewer, A. W. Searcy, D. H. Templeton and C. H. Dauben, *J. Am. Ceram. Soc.*, **33**, 291 (1950).

(6) R. Kieffer, F. Benesovsky, H. Nowotny and H. Schachner, *Z. Metallkunde*, **44**, 242 (1953).

(7) L. Brewer and O. Krikorian, *J. Electrochem. Soc.*, **103**, 38 (1956).

(8) M. Knudsen, *Ann. Physik*, [4] **28**, 999 (1909).

(9) A. W. Searcy and R. A. McNees, Jr., THIS JOURNAL, **75**, 1578 (1953).

and Benesovsky.[10] However, the last two investigations yielded different modifications for $TaSi_{0.22}$ and $TaSi_{0.60}$. Nowotny's modification of $TaSi_{0.60}$ ($D8_8$ type, ideal formula M_5Si_3) was shown by Brewer and Krikorian[7] to be stabilized by a small percentage of carbon. More recently, Parthe, Nowotny and Schmid[11] have found yet another modification of $TaSi_{0.60}$. The structure of the $TaSi_{0.60}$ modification found by Brewer and coworkers has been reported recently by Parthe, Lux and Nowotny.[12]

In the present research, mixtures of tantalum and silicon powders, in atomic ratios corresponding to the formulas of the known tantalum silicides, were heated over a wide range of temperatures and cooled at various rates according to techniques developed earlier in this Laboratory.[13,14]

Experimental

All samples were prepared by direct synthesis. Tantalum metal was obtained as 200 mesh powder from Fansteel Metallurgical Company. Silicon was obtained from Union Carbide and Carbon Company. Spectrographic analysis showed the only impurity in either the tantalum or the silicon to be a trace of iron. The reactions were carried out in tantalum and molybdenum crucibles.

Results and Conclusions.—From consideration of the data obtained and of the results of previous studies,[5,10,11] the high temperature equilibrium modifications of the tantalum silicides can be established. Only Brewer's modification[5] of $TaSi_{0.22}$ was observed. The different modification reported by Nowotny and co-workers[10] was found by those workers in samples heated to a higher temperature than those reached in this study. However, Nowotny and co-workers cooled their samples slowly, and the modification they observed is probably formed during slow cooling below 1520°, the lowest temperature at which the stability of $TaSi_{0.22}$ was investigated in this research. Thus, it is probable that Brewer's modification of $TaSi_{0.22}$ is the equilibrium high-temperature form.

The form of Ta_2Si reported in earlier research[5] was the only one observed and is apparently stable over at least the range from 1000–2000°.

The modification of $TaSi_{0.60}$ previously reported by Brewer and co-workers[5] was the only form of this phase observed in the present research. Nowotny's modification has been shown by Brewer and Krikorian[7] to be stabilized by carbon. The modification of $TaSi_{0.60}$ reported by Parthe, Nowotny and Schmid[11] was prepared from a molten copper solution by these workers at a lower temperature than those used here. Thus Brewer's modification[5] of $TaSi_{0.60}$ is apparently the stable high-temperature form of this composition, and Parthe's modification[11] of $TaSi_{0.60}$ either is a low temperature form or is metastable.

No new modification of $TaSi_2$ was observed in the present work. The previously observed form[3,4] is evidently stable over a wide temperature range.

Dissociation Pressure Measurements

Experimental.—The dissociation pressure of $TaSi_{0.22}$ was measured in a tantalum effusion cell, and the dissociation pressures of Ta_2Si, $TaSi_{0.60}$ and $TaSi_2$ were measured in a tungsten effusion cell. Experimental arrangements were the same with either a tantalum or tungsten cell. Each cell was placed in two concentric graphite crucibles which were surrounded by 5 mil tantalum radiation shields. The cover of a cell had four parts: a lid made from 5 mil tungsten or tantalum sheet with the effusion orifice drilled through it, a second lid of tantalum, $^1/_{16}$ inch thick, with a tapered hole somewhat larger than the orifice in the thin lid, a graphite disk with a still larger tapered hole, and a tantalum radiation shield. A vapor beam was defined by the orifice through the innermost 5 mil lid. The inner graphite crucible, its contents and the two inner lids of the effusion cell were weighed as a unit before and after each run to determine the weight loss of silicon vapor through the orifice. Weighings were made to 0.01 mg. on an Ainsworth, type F. D. I., microbalance. Empty cells were heated before making measurements until the background weight changes had been reduced either to zero or to a constant known value, never more than 0.35 mg./hr. When the background weight changes were not zero, the effusion weight losses were corrected for the weight loss of the cell itself.

Temperatures were measured with a Leeds and Northrup disappearing filament optical pyrometer which had been calibrated against a standard tungsten ribbon lamp. Observed temperatures were corrected for the light absorbed by the viewing window. Corrections were made on the calculated pressure for the length to radius ratio of the orifice[15] and for thermal expansion.

Results

Good agreement in pressures calculated from measurements using hole areas differing more than a factor of two demonstrates that essentially equilibrium pressures were obtained within the cell. Heats of dissociation at 298°K. were obtained from the vapor pressure data both by a calculation of the slope of a least squares solution of a plot of $-R \ln P$ *vs.* $1/T$ and by combination of estimated $(F^\circ - H^\circ_{298})/T$ data with the individual pressure data to obtain ΔH°_{298} values from each separate experimental value. Calculations by the latter method are summarized in Tables I–IV. For estimation of $(F^\circ - H^\circ_{298})/T$ values the entropy and heat capacity per tantalum atom were assumed to be the same whether the atom was in the pure metal or in a silicide phase.

Silicon atoms were estimated to have the same entropy in the silicide phases as in elemental solid silicon at the melting point. C_p for silicon in a silicide phase at 298°K. was estimated to be 1 cal. mole^{-1} deg.$^{-1}$ greater than in the solid element and at the melting point ($1412 \pm 2°$)[16] was estimated to be the same as in the solid element. C_p per gram atom of silicon in each silicide was estimated to average 7.3 cal. mole^{-1} deg.$^{-1}$ between the melting point of silicon and 2500°K. The heat content and entropy changes of solid silicon between 298 and 1200°K. were obtained from the table of Kelley.[17] Comparison of Kelley's heat content data with those of Olette[16] yields 6.74 cal. mole^{-1} deg. as an average for C_p between 1200°K. and the melting point of silicon. The entropy of solid silicon at 298°K. was obtained from Brewer.[18]

---

(10) H. Nowotny, H. Schachner, R. Kieffer and F. Benesovsky, *Monatsh.*, **84**, 1 (1953).

(11) E. Parthe, H. Nowotny and H. Schmid, *ibid.*, **86**, 385 (1955).

(12) E. Parthe, B. Lux and H. Nowotny, *ibid.*, **86**, 859 (1955).

(13) J. H. Carpenter and A. W. Searcy, THIS JOURNAL, **78**, 2079 (1956).

(14) J. H. Carpenter, M.S. Thesis, Purdue University, 1953.

(15) P. Clausing, *Ann. Physik*, [5] **12**, 961 (1932).

(16) M. Olette, Institute de Recherches de la Siderurgie, Sainte Germain en Laye, France, private communication.

(17) K. K. Kelley, Bureau of Mines Bull. 476 (1949).

(18) L. Brewer, Paper No. 3 in "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1950.

TABLE I

HEAT OF THE REACTION: $4.5TaSi_{0.22_2} = 4.5Ta + Si(g)$

T (°K).	$P_{Si} \times 10^7$ (atm.)	$-(F^\circ - H^\circ_{298}/T)_{Si(g)}$ (cal./deg.)	$-(F^\circ - H^\circ_{298}/T)_{Si(c)}$[a] (cal./deg.)	$\Delta F^\circ/T$ (cal./deg.)	ΔH°_{298} (kcal.)
2233	2.62	45.95	11.19	30.12	144.9
2235	5.38	45.96	11.20	28.69	141.8
2259	2.90	46.00	11.25	29.92	146.1
2283	4.78	46.05	11.32	28.92	145.3
2309	7.14	46.10	11.38	28.12	145.1
2329	10.5	46.15	11.44	27.36	144.6
2329	11.1	46.15	11.44	27.25	144.3
2391[b]	34.7	46.27	11.59	24.98	142.6
2401[b]	37.5	46.29	11.62	24.83	142.9
2432	39.4	46.35	11.69	24.73	144.4
2441	46.1	46.37	11.71	24.42	144.2
2445	47.7	46.38	11.74	24.35	144.2
2488[b]	78.4	46.47	11.83	23.37	144.3
				Av.	144.2

[a] $[(F^\circ - H^\circ_{298})/T]_{Si(c)}$ is the estimated contribution of Si to the solid phase. [b] Data for hole of 0.00964 cm.^{2} area, Clausing constant = 0.852. Other data for 0.02036 cm.^{2} hole, Clausing constant = 0.922.

TABLE II

HEAT OF REACTIONS: $9/5Ta_2Si = 18/5TaSi_{0.22_2} + Si(g)$

T (°K.)	$P_{Si} \times 10^7$ (atm.)	$-(F^\circ - H^\circ_{298}/T)_{Si(g)}$ (cal./deg.)	$-(F^\circ - H^\circ_{298}/T)_{Si(c)}$[a] (cal./deg.)	$\Delta F^\circ/T$ (cal./deg.)	ΔH°_{298} (kcal.)
2216	7.57	45.92	11.15	28.01	139.1
2241[b]	11.2	45.97	11.21	27.23	138.9
2262	17.5	46.01	11.27	26.34	138.2
2300	27.5	46.09	11.36	25.45	138.4
2316	42.8	46.13	11.40	24.57	137.3
2324	37.1	46.14	11.42	24.85	138.4
2346	50.9	46.18	11.48	24.22	138.2
2373[b]	52.1	46.23	11.54	24.18	139.7
2387	92.1	46.26	11.58	23.04	137.8
2419	112	46.33	11.66	22.66	138.7
2420	97.9	46.33	11.66	22.92	139.3
				Av.	138.6

[a] $-[(F^\circ - H^\circ_{298})/T]_{Si(c)}$ is the estimated contribution of Si to the solid phase. [b] Data for hole of 0.0212 cm.^{2} area, Clausing constant = 0.929. Others, hole of 0.00811 cm.^{2} area, Clausing constant = 0.946.

TABLE III

HEAT OF REACTION: $10TaSi_{0.60} = 5Ta_2Si + Si(g)$

T (°K.)	$P_{Si} \times 10^7$ (atm.)	$-(F^\circ - H^\circ_{298}/T)_{Si(g)}$ (cal./deg.)	$-(F^\circ - H^\circ_{298}/T)_{Si(c)}$[a] (cal./deg.)	$\Delta F^\circ/T$ (cal./deg.)	ΔH°_{298} (kcal.)
2033	4.70	45.56	10.69	28.96	129.8
2105	12.3	45.70	10.87	27.04	130.2
2147	17.9	45.78	10.98	26.30	131.2
2161[b]	17.3	45.81	11.01	26.36	132.2
2213[b]	47.8	45.92	11.15	24.35	130.8
2238	55.0	45.97	11.21	24.07	131.7
2271	73.1	46.03	11.29	23.50	132.3
2304	138	46.10	11.37	22.29	131.4
2313[b]	189	46.11	11.39	21.62	130.3
				Av.	131.1

[a] $-[F^\circ - H^\circ_{298}/T]_{Si(c)}$ is the estimated contribution of Si to the solid phase. [b] Hole area 0.00802 cm.^{2}, Clausing correction 0.881. Other data 0.0212 cm.^{2}, Clausing correction 0.929.

TABLE IV

HEAT OF REACTION: $5/7TaSi_2 = 5/7TaSi_{0.60} + Si(g)$

T (°K.)	$P_{Si} \times 10^6$ (atm.)	$-(F^\circ - H^\circ_{298}/T)_{Si(g)}$ (cal./deg.)	$-(F^\circ - H^\circ_{298}/T)_{Si(c)}$[a] (cal./deg.)	$\Delta F^\circ/T$ (cal./deg.)	ΔH°_{298} (kcal)
1903	1.21	45.32	10.37	27.09	118.1
1912	1.80	45.34	10.39	26.28	117.1
2004	4.73	45.52	10.92	24.36	118.2
2011	5.08	45.52	10.64	24.21	118.8
2013	4.55	45.53	10.65	24.44	119.4
2037[b]	8.19	45.57	10.70	23.28	118.5
2050[b]	8.92	45.60	10.73	23.11	118.9
2054	9.29	45.60	10.74	23.02	118.9
2118	23.1	45.73	10.90	21.21	118.7
2141	30.4	45.78	10.97	20.67	118.8
2164[b]	68.4	45.82	11.02	19.06	116.6
				Av.	118.4

[a] $-[(F^\circ - H^\circ_{298})/T]_{Si(c)}$ is the estimated contribution of Si to the solid phase. [b] Hole area 0.00755 cm.^{2}, Clausing correction 0.796. Others, area 0.0168 cm.^{2}, Clausing correction 0.94.

The $(F^\circ - H^\circ_{298})/T$ data for silicon gas were calculated from the work of Katz and Margrave[19] using $(H^\circ_{298} - H^\circ_0)$ for silicon gas given by Brewer.[18]

Least square results for the heats of dissociation to one mole of silicon gas at 298°K. were for $TaSi_{0.222}$, 148.5 kcal.; for Ta_2Si, 135.8 kcal.; for $TaSi_{0.60}$, 120.2 kcal.; for $TaSi_2$, 116.1 kcal. An average of the values obtained by the two methods is considered the best that can presently be calculated. These averages are 146.4 ± 2.2 for $TaSi_{0.222}$, 137.2 ± 1.4 for Ta_2Si, 125.6 ± 5.5 for $TaSi_{0.60}$ and 117.2 ± 1.2 for $TaSi_2$.

These heats of dissociation were combined with the heat of vaporization of silicon at 298°K., 112 ± 3 kcal. per mole,[20] to give the standard heats of formation of the tantalum silicides at 298.15°K. Values of the heats of formation per silicon atom at 298°K. are $4.5TaSi_{0.22_2}$, −34.4 kcal.; Ta_2Si, −29.3; $1.67TaSi_{0.60}$, −26.7; $^1/_2TaSi_2$, −11.6. The uncertainty in each of these values is estimated to be a maximum of ±5 kcal. Much of this uncertainty is due to ignorance of the true values for entropies; when these heats are used in calculations of free energies at temperatures near those of the original measurements, the uncertainties are estimated to be only 2 to 3 kcal.

The heats of formation of the tantalum silicides found in this research are well within the upper and lower limits for the heats of formation established by Brewer and Krikorian[7] and in fair agreement with the values −25.3 kcal. for $1.67TaSi_{0.60}$, and −13.9 kcal. for $^1/_2TaSi_2$ found by Robins and Jenkins by direct measurement of the heats of formation.[21]

LAFAYETTE, IND.
BERKELEY, CAL.

---

(19) T. J. Katz and J. L. Margrave, *J. Chem. Phys.*, **23**, 983 (1955).

(20) S. G. Davis and A. W. Searcy, unpublished data, University of California.

(21) D. A. Robins and I. Jenkins, *Acta Met.*, **3**, 598 (1955).