action rate constants for higher polymers have not been determined. Thus, although the molybdate curve for a given mixture of polysilicic acids is quantitatively reproducible, it gives only a qualitative picture of the relative distribution of monomer, dimer, and higher polymers.

It is of interest to note that the degree of polymerization of 4.7 of polysilicic acid from 3.25 ratio sodium silicate corresponds to a molecular weight of 282 on an anhydrous SiO_2 basis. Earlier work by Iler[11] indicated such silicic acid to have a number average molecular weight of around 200, while Debye and Nauman[12–14] found, in solutions of 3.3 ratio sodium silicate, a molecular weight of 325 by light scattering.

[11] R. K. Iler, *J. Phys. Chem.*, **57**, 604 (1953).

[12] P. Debye, *ibid.*, **53**, 1 (1949).

[13] P. Debye and R. Nauman, *J. Chem. Phys.*, **17**, 664 (1949).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Preparation and Properties of Molybdenum–Germanium Compounds[1,2]

BY ALAN W. SEARCY AND ROBERT J. PEAVLER[3]

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An X-ray diffraction investigation has established the existence of the phases Mo_3Ge_2, Mo_2Ge_3, α-$MoGe_2$ and β-$MoGe_2$ in addition to the phase Mo_3Ge which has already been reported. The high temperature form of $MoGe_2$ is tetragonal with unit cell dimensions $a = 3.313 \pm 0.003$ Å. and $c = 8.195 \pm 0.005$ Å. It belongs to space group D_{4h}^{17}–I 4/mmm. Reactivities of the molybdenum germanides toward some common reagents are reported.

The germanides of transition metals have received little attention until very recently. Apparently there is still no published information on the chemical properties of any transition metal–germanium compounds, although a few transition metal–germanium phase diagrams have been studied.

The available information shows that germanides of the transition metal often have compositions and structures similar to those of the silicides of the same transition metals.

Since the molybdenum silicides have recently been shown to be stable and high melting compounds,[4] it seemed of interest to investigate the nature of molybdenum–germanium compounds.

The remark by Wallbaum[5] that $MoGe_2$ does not have the same crystal structure as $MoSi_2$ is apparently the only reference to any molybdenum germanide compound prior to our own investigations. We have recently reported the preparation of Mo_3Ge and the determination of its structure.[6]

Experimental.—Samples for X-ray diffraction analysis were prepared by heating thoroughly mixed germanium and molybdenum powders in carbon crucibles. The molybdenum was obtained from Fansteel Metallurgical Corporation in the form of 200 mesh powder. The germanium was obtained from Eagle–Picher Company both in lump form and in the form of 200 mesh powder. Spectrographic analysis of the germanium showed it to contain essentially no metallic impurity, but the powder was found by X-ray diffraction investigation to contain a few per cent. germanium dioxide. Two series of samples were made: a series prepared by heating to 980° in a resistance-heated nickel tube furnace under an atmosphere of argon, and a second series prepared by heating to 1350° in an induction furnace under vacuum.

Molybdenum powder gave negligible weight losses when heated alone under conditions comparable to those of our preparative runs. Germanium powder lost a few milligrams per 100 mg. under the same conditions. The compositions of the molybdenum–germanium alloys after heating were calculated by assuming that the small weight losses that occurred were due exclusively to vaporization of germanium, perhaps as germanium monoxide. Substitution of crushed lump germanium reduced losses of germanium to 5 or 6 mg. for heating periods of 6 hr. at 980°. For samples heated at 1350°, excessive loss of germanium was avoided by covering the crucibles with tight-fitting lids. These lids were drilled with $^1/_{32}$-inch holes to allow the escape of non-condensable gases. When lids were used, the loss of germanium at 1350° was never more than 2 mg. per hour even for samples of high germanium content. Samples prepared at 980° were all cooled at a rate of about 100° per hour while samples prepared at 1350° were cooled from 1350 to 700° in 3 or 4 min.

X-Ray diffraction patterns of the powdered products were obtained in a camera of 114.57 mm. diameter. Copper Kα radiation (wave length $\alpha_1 = 1.540522$Å, $\alpha_2 = 1.544367$ Å) was used.

Discussion.—Examination of the variation in diffraction patterns with composition revealed the existence of four molybdenum–germanium phases in the set of samples heated to 980°. The pressence of three or more phases in a sample after heating would constitute evidence that equilibrium had not been reached. Samples which had been heated for at least one-half hour at 980° never yielded diffraction patterns of more than two phases. Maximum intensities of the four phases were obtained at compositions $MoGe_{0.35 \pm 0.05}$, $MoGe_{0.7 \pm 0.1}$, $MoGe_{1.5 \pm 0.2}$ and $MoGe_{2.1 \pm 0.25}$. The phases were, therefore, identified as Mo_3Ge, Mo_3Ge_2 (or Mo_5Ge_3), Mo_2Ge_3 and $MoGe_2$. Details of this method of fixing phase compositions are presented in previous publications.[4,6]

Samples of less than 60 atomic % germanium which had been prepared at 1350° were indistinguishable from those prepared at 980°, but samples of more than 60 atomic % germanium always yielded the pattern of a new phase. Since the maximum intensities for the pattern of this phase were always obtained along with a pattern of the phase identified as $MoGe_2$, the new phase was

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[1] From a thesis presented by Robert J. Peavler in partial fulfillment of the requirements for the Ph.D. degree.

[2] Work supported by the Metallurgy Branch of the Office of Naval Research.

[3] Purdue Research Foundation Fellow 1950–1952.

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

[5] H. J. Wallbaum, *Naturwissenschaften*, **32**, 76 (1944).

[6] A. W. Searcy, R. J. Peavler and H. J. Yearian, THIS JOURNAL, **74**, 566 (1952).

presumed to be a high temperature form of $MoGe_2$ whose complete transformation to the low temperature form was prevented by the rapid rate at which the samples were cooled.[7] The crystal structure of this high temperature phase (designated β-$MoGe_2$) was determined and the structure confirms our conclusion that the phase composition is $MoGe_2$. The formula Mo_3Ge for the phase of composition $MoGe_{0.35 \pm 0.05}$ was also confirmed by determination of the crystal structure of the phase.[6]

The diffraction patterns of Mo_3Ge_2, Mo_2Ge_3 and the low temperature form of $MoGe_2$ (α-$MoGe_2$) could not be fitted into any cubic, tetragonal or hexagonal lattice from powder diffraction data; however, the lines of the Mo_3Ge_2 pattern showed a one-to-one correspondence in position with the lines reported by Brewer, Searcy, Templeton and Dauben for Mo_3Si_2, and it seems certain that Mo_3Ge_2 and Mo_3Si_2 have the same crystal structure. Diffraction data for Mo_3Ge_2, Mo_2Ge_3 and α-$MoGe_2$ are presented in Table I.

TABLE I

DIFFRACTION DATA FOR Mo_3Ge_2, Mo_2Ge_3 AND α-$MoGe_2$

vs, very strong; s, strong; w, weak; vw, very weak

Mo_3Ge_2		Mo_2Ge_3		α-$MoGe_2$	
d, Å.	Visual intensity	d, Å.	Visual intensity	d, Å.	Visual intensity
3.302	vw	4.980	w⁻	3.561	w⁻
2.487	w⁻	3.766	m⁻	3.180	w
2.445	w⁻	2.986	w	2.607	w
2.386	m	2.458	s	2.547	w⁻
2.338	vw	2.339	vs	2.473	m⁺
2.311	vw	2.300	s⁻	2.333	w⁺
2.218	m⁺	2.090	s⁺	2.297	vw
2.192	s	2.028	w⁻	2.248	s⁺
2.146	vs	1.880	w	2.145	vw
2.021	s	1.842	s	2.118	vw
1.823	vw	1.787	w⁻	2.077	vs
1.746	vw	1.713	vw	2.050	w⁻
1.711	vw	1.623	w⁻	2.028	w⁻
1.687	vw	1.606	w⁻	1.893	w⁺
1.552	w⁻	1.570	w	1.766	vw
1.519	vw	1.532	vw	1.752	vw
1.466	w⁻	1.495	w⁺	1.724	w⁺
1.423	w⁻	1.470	w⁺	1.656	vw
1.416	w⁻	1.430	vw	1.551	vw
1.404	w⁻	1.414	w⁻	1.532	vw
[a]		[b]		[c]	

[a] 32 additional lines. [b] 39 additional lines. [c] 24 additional lines.

The lines of the β-$MoGe_2$ diffraction pattern were obtained by subtracting the known pattern of α-$MoGe_2$ from a diffraction photograph of a mixture of α- and β-$MoGe_2$. The β-$MoGe_2$ lines could be fitted readily to a tetragonal lattice in which $a = 3.313 \pm 0.003$ Å., $c = 8.195 \pm 0.005$ Å., and $c/a = 2.473$. The observed reflections were all readily indexed. Reflections are observed only when $h + k + l = 2n$, though no other systematic absences are evident. The observed reflections are consistent with the space group D_{4h}^{17}–I 4/mmm. The experimental density of the mixture of α- and β-$MoGe_2$ that showed the strongest pattern of β-$MoGe_2$ was 6.9 g. cm.$^{-3}$. The calculated density of β-$MoGe_2$ if two molecules are assumed to be present per unit cell is 8.91 g. cm.$^{-3}$.

Intensities of the reflections were calculated from the equation

$$I = CpF^2 \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

where C is a constant, p is the probability factor, F is the scattering factor and θ is the diffraction angle. These calculations gave excellent agreement with observed intensities with the atom positions as

2 Mo in (b): $0, 0, 0;\ {}^1/_2, {}^1/_2, {}^1/_2;$

4 Ge in (e): $0, 0, Z;\ 0, 0, \bar{Z};\ {}^1/_2, {}^1/_2, {}^1/_2 + Z;\ {}^1/_2, {}^1/_2, {}^1/_2 - Z.\ Z = {}^1/_3$

TABLE II

DIFFRACTION DATA FOR β-$MoGe_2$

vs, very strong; s, strong; m, medium; w, weak; vw, very weak

h	k	l	d, Å.	$\sin^2\theta$ Obsd.	$\sin^2\theta$ Calcd.	I Visual	I (10^4) Calcd.
0	0	2	4.0823	0.0357	0.0353	w⁻	12
1	0	1	4.0634	.0633	.0629	w⁻	19
1	1	0	2.3429	.1083	.1083	vs	160
1	0	3	2.1090	.1336	.1335	vs	230
0	0	4	....	....	.1416	...	1
1	1	2	....	....	.1436	...	2
2	0	0	1.6565	.2166	.2164	s	44
1	1	4	....	....	.2499	...	1
2	0	2	....	....	.2517	...	1
1	0	5	....	....	.2746	...	1
2	1	1	....	....	.2793	...	2
0	0	6	1.3658	.3186	.3176	w⁺	14
2	1	3	1.3022	.3505	.3499	s⁺	88
2	0	4	....	....	.3580	...	1
1	1	6	1.1807	.4264	.4259	m⁻	32
2	2	0	1.1713	.4332	.4328	w⁺	31
2	2	2	....	....	.4681	...	1
1	0	7	....	....	.4864	...	1
2	1	5	....	....	.4911	...	1
3	0	1	....	....	.4957	...	1
2	0	6	1.0546	.5343	.5340	m⁻	25
3	1	0	1.0474	.5417	.5410	m⁻	24
0	0	8	....	....	.5664	...	1
3	0	3	1.0245	.5662	.5663	m⁻	23
2	2	4	....	....	.5744	...	1
3	1	2	....	....	.5763	...	1
1	1	8	....	....	.6747	...	1
3	1	4	....	....	.6826	...	1
2	1	7	....	....	.7028	...	1
3	0	5	....	....	.7075	...	1
3	2	1	....	....	.7118	...	1
2	2	6	0.8907	.7491	.7504	m⁻	24
1	0	9	0.8788	.7681	.7687	m⁻	24
2	0	8	....	....	.7828	...	1
3	2	3	0.8714	.7826	.7824	m⁺	51
3	1	6	0.8318	.8589	.8586	s⁻	62
4	0	0	[a]	....	.8656	...	62
0	0	10	....	....	.8822	...	1
4	0	2	....	....	.9009	...	1
3	0	7	....	....	.9192	...	1
3	2	5	....	....	.9236	...	1
4	1	1	....	....	.9285	...	1
3	3	0	0.7812	.9738	.9738	w	21
2	1	9	0.7767	.9851	.9851	s	72

[a] Coincides with a line of α-$MoGe_2$.

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(7) ADDED IN PROOF.—β-$MoGe_2$ is a metastable phase formed during cooling. At 1095 ± 20° α-$MoGe_2$ disproportionates to Mo_2Ge_3 and liquid germanium (A. W. Searcy and John H. Carpenter, unpublished data).

The high temperature form of $MoGe_2$ is therefore isostructural with $MoSi_2$[8] and $ReSi_2$.[9] Diffraction data for β-$MoGe_2$ are summarized in Table II.

No shift in lattice constants of any of the molybdenum–germanium phases was observed as the compositions of the samples were varied. It therefore appears that all the molybdenum–germanium phases in this system have narrow ranges of homogeneity.

Samples that contained less than 67 atomic % germanium gave no indication of melting when heated to 1350°. All eutectic temperatures for samples containing less than 67 atomic % germanium are therefore believed to lie above that temperature. Samples of composition Mo_3Ge did not melt on being heated to 1750°.

The chemical behavior of the molybdenum germanides toward some common reagents was studied. All the phases show similar chemical properties. In general, they do not react quickly with ordinary non-oxidizing acids or with solutions of bases. Sulfuric, hydrochloric and hydrofluoric acids, concentrated or dilute, hot or cold, showed no immediate reaction, though concentrated sulfuric acid, in contact with molybdenum germanides for a week turned blue. Boiling 20% sodium hydroxide or concentrated ammonium hydroxide caused no immediate attack, nor was any reaction observable after the solution had stood for a week in the cold. Oxidizing agents, however, readily attack the molybdenum germanides; a 30% hydrogen peroxide solution or cold nitric acid, either concentrated or dilute, dissolved the germanides readily. Yellow solutions were formed with either oxidizing agent. Mo_2Ge_3 and $MoGe_2$ yielded white residues, presumably of GeO_2, after attack by nitric acid or hydrogen peroxide, but the phases of lower germanium content were dissolved completely. A fused nitrate and carbonate mixture attacked the germanides with almost explosive violence. Fused pyrosulfate dissolved them rapidly to form a clear yellow melt.

The molybdenum germanides resemble the molybdenum silicides in several ways. Mo_3Ge, β-$MoGe_2$ and apparently Mo_3Ge_2, are isostructural with known molybdenum silicides. There is no known molybdenum silicide with a formula corresponding to Mo_2Ge_3, however. The molybdenum germanides, like the silicides, are high melting compounds. The molybdenum germanides, on the other hand, are not as stable toward oxidizing agents as the corresponding silicides; furthermore, the germanides cannot be expected to show the resistance to high temperature oxidation that some silicides display.

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[8] W. H. Zachariasen, *Z. physik. Chem.*, **128B**, 39 (1927).

[9] H. J. Wallbaum, *Z. Metallkunde*, **33**, 378 (1941).

[CONTRIBUTION FROM AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Stability Constants of Cadmium Chloride Complexes: Variation with Temperature and Ionic Strength[1]

BY CECIL E. VANDERZEE AND HAROLD J. DAWSON, JR.

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Stability constants for the complex species $CdCl^+$, $CdCl_2$ and $CdCl_3^-$ at constant ionic strengths 0.5, 1, 2 and 3 have been determined by a potentiometric method at 0, 25 and 45°. Extrapolation to zero ionic strength was made using a form of the Hückel equation. All of the complexes are formed endothermally, the values of ΔH becoming more positive for the higher complexes and lower ionic strengths. With increasing ionic strength, ΔS values decrease rapidly at first, then level off and increase slowly at higher ionic strengths.

Complex ion formation in cadmium chloride solutions has been the subject of several investigations. Leden[2] has made a study of the stability constants for various cadmium halide complexes at 25° in solutions at constant ionic strength 3, and gives an extensive summary of references to previous work. Recently King,[3] studying the effect of chloride ion upon the solubility of cadmium ferrocyanide, reported stability constants for the cadmium chloride complexes at ionic strength 3 for temperatures 0, 25 and 47.5°, and evaluated the heats of formation for the complexes $CdCl^+$, $CdCl_2$ and $CdCl_3^-$ as 625, −1100 and 4600 cal. per mole, respectively. The exothermic formation of the uncharged species seemed unusual and worthy of re-examination, especially since the others were formed endothermally.

The work reported in this paper is part of a program underway in this Laboratory, concerned with the factors influencing the stability of complex ions and particularly with the heats of formation as they relate to differences between ligands and between various metal ions. Since heats of formation obtained from the variation of concentration stability constants with temperature will depend somewhat on the particular ionic strength used, it is important to determine the extent and direction of that dependence.

Stability constants were determined from observations of the e.m.f. of concentration cells of the type

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[1] In part from the M.S. thesis of Harold J. Dawson, Jr., May, 1952.

[2] I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941).

[3] E. L. King, THIS JOURNAL, **71**, 319 (1949).