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Abstract

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ON GERMANIUM ARSENATE

Arsenic-acid compounds of germanium have not been described in the literature. Meanwhile, the close similarity of H_3PO_4 and H_3AsO_4 and of many of their derivatives makes it possible to assume the existence of a germanium arsenate analogous to the described phosphate $Ge(HPO_4)_2 \cdot H_2O$ ([1],[2]).

Saturation of a solution of H_3AsO_4 with germanium dioxide did not lead to the formation of a metastable solution, as occurred in the interaction of GeO_2 and H_3PO_4. As a result of two weeks' stirring of a mixture of GeO_2 and H_3AsO_4 (4 mol/kg), a paste-like mass was formed. In the liquid phase, separated by suction on a porous filter No. 4, no germanium was found. Analysis of the solid phase, thoroughly washed with alcohol and ether and dried at 70°, established the following composition (in %): Ge 18.4; As 39.5; H_2O 9.5. For $GeO_2 \cdot As_2O_5 \cdot 2H_2O$ the calculated values are (in %): Ge 19.0; As 39.4; H_2O 9.7. Germanium was determined by the tannin method, arsenic iodometrically. The water content was determined directly from the loss in weight upon heating to 600°. As can be seen, the compound obtained has a composition analogous to that of the germanium phosphate separated from a metastable solution of GeO_2 in H_3PO_4.

(Figure: Fig. 1. Thermogram of $GeO_2 \cdot As_2O_5 \cdot 2H_2O$)

Fig. 1. Thermogram of $GeO_2 \cdot As_2O_5 \cdot 2H_2O$

$GeO_2 \cdot As_2O_5 \cdot 2H_2O$ is a finely crystalline powder, readily decomposed by water. Its thermogram is shown in Fig. 1. A series of successive endoeffects at 168, 224, and 275° corresponds to the removal of the first molecule of water; the crystalline structure changes hardly at all. At a temperature of 450° the remaining water is split off and the compound $GeO_2 \cdot As_2O_5$ is formed, which we designate as $GeAs_2O_7$-α.

The exothermic effect at 700°, as established by X-ray diffraction, is a consequence of a change in the crystalline structure. The compound formed at 700°, which we designate as $GeAs_2O_7$-β, is characterized by lower symmetry than $GeAs_2O_7$-α. Thermal decomposition of germanium pyroarsenate begins immediately after the exoeffect.

The endothermic effects at 835 and 925° are associated with the intense evolution of As_2O_5 and melting of the products formed. The composition of the product formed at 925° corresponds to the formula $4GeO_2 \cdot As_2O_5$. Complete splitting off of As_2O_5 occurs after prolonged heating at ~1000°. Analysis showed that the final product of heating is GeO_2.

Figure 2 gives the schemes of the X-ray diffraction patterns of $GeO_2 \cdot As_2O_5 \cdot 2H_2O$, $GeAs_2O_7$-α, and $GeAs_2O_7$-β. The values of the interplanar spacings d, the intensities I, and $\sin^2\theta$ are given in Table 1. The X-ray diffraction patterns were obtained with CuKα radiation in a camera 57.3 mm in diameter. The line intensities were estimated visually according to a nine-point system. Comparison of the X-ray diffraction pattern of $Ge(HPO_4)_2 \cdot H_2O$ and GeP_2O_7-α with the X-ray diffraction patterns of $GeO_2 \cdot As_2O_5 \cdot 2H_2O$ and $GeAs_2O_7$-α indicates their similarity (there is no isomorphism), which is possibly connected with the isostructural nature of the compounds being compared. Mixing

lines toward smaller angles θ (and, consequently, the increase in lattice periods), observed in the X-ray patterns of arsenic-acid compounds, is due to the increase in the radius of AsO_4^{3-} as compared with the radius of PO_4^{3-}.

In Fig. 3A the IR absorption spectrum of $GeO_2 \cdot As_2O_5 \cdot 2H_2O$ is shown (wave numbers of the maxima and inflections: 740, 780, 800, 815, 850, 890, 900, 935, 1260, 1635 cm^{-1}). The absorption band at 1635 cm^{-1} belongs to deformation vibrations of water. In the spectrum of the compound of composition $GeO_2 \cdot As_2O_5 \cdot H_2O$, obtained by heating to 250°, this absorption band is absent. Thus,

Fig. 2. Schemes of X-ray diffraction patterns of $GeO_2 \cdot As_2O_5 \cdot 2H_2O$ (1), $GeAs_2O_7$-α (2), $GeAs_2O_7$-β (3)

one of the two water molecules in $GeO_2 \cdot As_2O_5 \cdot 2H_2O$ is chemically bound and, evidently, enters into the composition of the compound in the form of two $HAsO_4^{2-}$ ions.

The character of the IR spectrum of $GeO_2 \cdot As_2O_5 \cdot 2H_2O$ does not contradict the statement made, since it is known from the literature ([3]) that in the spectra of acid arsenates, alongside the most intense band at 920–800 cm^{-1}, weaker bands are present to the left and to the right of it. On the basis

Table 1

$GeO_2 \cdot As_2O_5 \cdot 2H_2O$						$GeAs_2O_7$-α						$GeAs_2O_7$-β					
I	$\sin^2\theta$	d, Å	I	$\sin^2\theta$	d, Å	I	$\sin^2\theta$	d, Å	I	$\sin^2\theta$	d, Å	I	$\sin^2\theta$	d, Å	I	$\sin^2\theta$	d, Å
8	0.0097	7.8104	0.334	1.3326	0.0117	41806	0.011	7.418	4	0.173	1.85	1	0.430	1.17			
3	0.0324	4.2804	0.361	1.2829	0.037	3.9764	0.014	6.45	4	0.182	1.80	1	0.434	1.16			
4	0.0361	4.0481	0.377	1.2565	0.033	4.2253	0.022	5.17	2	0.189	1.77	1	0.465	1.13			
8	0.049	3.4804	0.392	1.2314	0.050	3.4334	0.032	4.28	3	0.201	1.72	1	0.481	1.11			
1	0.059	3.1632	0.399	1.2205	0.072	2.8799	0.038	3.94	3	0.212	1.67	2	0.505	1.08			
5	0.083	2.6685	0.442	1.1598	0.097	2.4751	0.039	3.84	3	0.228	1.61	3	0.530	1.06			
9	0.095	2.4932	0.475	1.1185	0.111	2.3135	0.047	3.54	1	0.234	1.59	1	0.540	1.05			

GeO$_2$ · As$_2$O$_5$ · 2H$_2$O	GeAs$_2$O$_7$-α	GeAs$_2$O$_7$-β												
1	0.101	2.4222	0.497	1.0944	0.135	2.0987	0.049	3.46	4	0.242	1.56	2	0.576	1.02
3	0.106	2.3611	0.530	1.0591	0.166	1.8904	0.060	3.15	4	0.248	1.55	1	0.591	1.003
2	0.119	2.2373	0.539	1.0502	0.209	1.6885	0.067	2.98	3	0.259	1.52	2	0.607	0.990
3	0.134	2.1071	0.599	0.9955	0.233	1.5964	0.074	2.83	3	0.272	1.48	2	0.630	0.966
5	0.146	2.0182	0.626	0.9753	0.269	1.4855	0.083	2.64	1	0.283	1.45	1	0.659	0.950
4	0.162	1.9123	0.638	0.9657	0.292	1.4266	0.091	2.55	5	0.291	1.43	1	0.694	0.926
3	0.180	1.8124	0.687	0.9304	0.307	1.3916	0.097	2.48	2	0.299	1.44	2	0.721	0.909
4	0.200	1.7232	0.694	0.9265	0.389	1.2346	0.109	2.34	2	0.309	1.39	1	0.750	0.891
1	0.211	1.6773	0.758	0.8854	0.429	1.1763	0.115	2.27	1	0.317	1.37	1	0.859	0.832
2	0.230	1.6071	0.795	0.864		1	0.127	2.16	3	0.340	1.32	1	0.883	0.821
6	0.244	1.5611	0.837	0.843		4	0.119	2.23	4	0.352	1.30	1	0.935	0.796
3	0.260	1.5101	0.848	0.837		4	0.141	2.05	2	0.379	1.25			
3	0.278	1.4634	0.885	0.819		3	0.150	1.99	3	0.392	1.23			
7	0.291	1.4273	0.921	0.803		1	0.160	1.93	3	0.407	1.21			
5	0.300	1.4063	0.935	0.797		3	0.168	1.88	1	0.417	1.19			

From the foregoing, the compound $GeO_2 \cdot As_2O_5 \cdot 2H_2O$ should be regarded as $Ge(HAsO_4)_2 \cdot H_2O$. It was established by X-ray diffraction that removal of the water molecule leads only to a slight distortion of the crystal lattice, which makes it possible to assume the presence in the structure of the compound of channels or voids occupied by water.

(Figure: Fig. 3. IR spectra of $GeO_2 \cdot As_2O_5 \cdot 2H_2O$ (A) and α-$GeAs_2O_7$ (B))

Fig. 3. IR spectra of $GeO_2 \cdot As_2O_5 \cdot 2H_2O$ (**A**) and $GeAs_2O_7$-α (**B**)

Figure 3B gives the IR spectrum of $GeAs_2O_7$-α, obtained by dehydration of $Ge(HAsO_4)_2$ at 500°. (Wave numbers of the maxima: 853, 910, and 1010 cm^{-1}.)

The IR spectra of $Ge(HPO_4)_2H_2O$ (?) and $Ge(HAsO_4)_2 \cdot H_2O$ are very similar in form, which, together with the similarity of the X-ray diffraction patterns of the indicated compounds, attests to the identity of their structures.

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Note: Figure translations are in progress. See original paper for figures.