THE PREPARATION OF THE SALTS OF HETEROPOLYACIDS BY TEMPERING A MIXTURE OF THE SOLID COMPONENTS

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The method of prolonged tempering of a mixture of the solid components $Na_4As_2O_7 + ZO_3 + Na_2ZO_4$ (Z = Mo, W) was successfully used to prepare new compounds in the pure state and thermoanalytical analysis yielded the empirical formula, $Na_{24}As_2Z_{22}O_{83}$. The two compounds melt congruently and have a melting point of 597°C (Z = Mo) and 691°C (Z = W). To make the determination of the empirical formula more objective, a computation method was developed for treatment of the thermoanalytical data and two computer programs were written.

This work is connected with a study[1,2] of the formation and preparation of the salts of heteropolyacids from the melts of alkali metal nitrates. These substances are formed in a nitrate melt by acidification of a solution of the Lux bases $Na_4X_2O_7 + Na_2ZO_4$ (X = P, As, V; Z = Mo, W) with a Lux acid. The formation of these substances was first indicated potentiometrically using an oxygen electrode[1]. Potentiometric titration yielded the probable composition[1] of the heteropolyanion, $[X_2Z_{24}O_{87}]^{20-}$. The separation of the compound, where X = As and Z = Mo from the nitrate melt, its analysis and properties were also studied. Impurities in the substance obtained by this procedure and further difficulties prevented exact determination of its stoichiometric composition, which analysis indicated lies in the range defined by the empirical formulae: $Na_{18}As_2Mo_{18}O_{68}$, $Na_{16}As_2Mo_{17}O_{54}$, and $Na_{16}As_2Mo_{18}O_{67}$ (ref.[2]). The means of formation of this substance and the molecular spectral analysis indicated that this is a new type of heteropolyanion based on the diarsenate anion containing the As—O—As bond which has not yet been described in the literature[3]. It was further found that this substance melts without decomposition at temperatures above 550°C and can be heated to temperatures of 600°C without structural change. Consequently, it is possible to obtain sodium molybdatodiarsenate by tempering a mixture of the solid components ($Na_4As_2O_7$, MoO_3, and Na_2MoO_4) in the ratio given by the above empirical formula for a period of about 50 hours. This work was carried out in order to study that part of the phase diagram of the triple system $Na_4As_2O_7$–MoO_3–Na_2MoO_4 in the region of assumed composition of the compound using differential thermal analysis and to

determine its composition and melting point and to attempt to carry out a similar study for the corresponding tungsten compound.

EXPERIMENTAL

Chemicals employed were all *p.a.* chemicals from Lachema Brno. Sodium diarsenate was prepared by dehydration of $Na_2HAsO_4.7 H_2O$ at a temperature of 130 to 300°C. Sodium molybdenate was prepared in a similar manner from $Na_2MoO_4.2 H_2O$ and sodium tungstate obtained from $Na_2WO_4.2 H_2O$.

Analytical methods. Sodium and molybdenum were determined by atomic absorption spectroscopy using a Varian Techtron instrument. Sodium was determined in the presence of CsCl (2 mg cm^{-3}) to eliminate interference at a wavelength of 589·0 nm in a flame with a ratio of acetylene : oxygen = 2 : 5·75. Molybdenum was determined at a wavelength of 313·2 nm in a flame with a ratio of acetylene : air = 3·25 : 5·75. Arsenic was determined gravimetrically as $Mg_2As_2O_7$ according to Levol and tungsten was determined gravimetrically as WO_3 (ref.[4]).

The tempering of the mixture of solid components, lasting tens of hours was carried out in platinum crucibles. Quartz crucibles had to be used in the recording of the thermoanalytical curves, as a special shape was required. As the recording of the heating or cooling curves lasts only tens of minutes, the danger of exchange of arsenic for silicon and consequent peak deformation are minimal.

Apparatus for differential thermal analysis. This instrument was constructed in the Department of Inorganic Chemistry of Charles University[5] and was used in connection with a compensation unit for elimination of the effect of changes in the ambient temperature and with a TZ 4 601 double-pen recorder (Laboratorní přístroje, Prague). Aluminium oxide was employed as a standard. The furnace temperature and temperature differences between the sample and standard were measured using a Ni–NiCr thermocouple. The thermocouples were calibrated[6] in the temperature range from 300 to 600°C using the phase transitions of the substances: $KClO_4$ (*s–s*), Cd (*s–l*), Zn (*s–l*), K_2SO_4 (*s–s*), and K_2CrO_4 (*s–s*). The samples were placed in quartz crucibles with a hollow base for fitting the thermocouple. (Commercially manufactured corundum crucibles for DTA measurements could not be used as the melt leaked and destroyed the thermocouple connection.) Samples with a weight of 1 g were used. The heating rate was linear, 4·4°C *per* minute. Where the peaks on the thermogram coalesced, the recording was repeated with a heating rate of 2·2°C *per* minute. The peak temperatures were read off according to the ICTA recommendations (ref.[6]).

The computation of the thermoanalytical data was carried out using a PC Sharp 1 500 computer.

Powder X-ray analysis. The formation of the heteropolyanions from the mixture of solid components was verified using X-ray analysis according to the Debye–Scherrer method using a Micrometa 2 instrument (Chirana) in a Siemens–Halske chamber with a diameter of 57·3 mm at the wavelength of the CuK_α radiation (154·178 pm, nickel filter), evaluated visually using a Hilger–Watts comparison instrument (London).

The Θ angles and interplanar distances d were determined for the pure compound using X-ray recordings obtained by the Bragg–Brentano method on a horizontal diffractogram with a radius of 150 mm. The CuK_α radiation was obtained using a curved quartz monochromator, recorded using a Geiger–Müller tube and a linear recorder. A shift of Θ from 5 to 50° and rate of 0·5° *per* minute were used.

RESULTS

The samples for thermoanalysis were prepared by tempering precisely weighed and homogenized mixtures of the pure initial substances $Na_4As_2O_7 + ZO_3 + Na_2ZO_4$ (Z = Mo, W) packed in platinum crucibles and closed with a quartz lid. The total amount was about 2 g of the mixture, very occasionally more. The crucibles with the weighed mixture were tempered in a crucible furnace, at a temperature of 570 to 600°C for an average of 30 hours for Z = Mo and at a temperature of 680−720°C for an average of 50 hours for Z = W. The time required for complete reaction of the components was verified by X-ray analysis for selected samples; however, completion of the reaction was satisfactorily indicated by liquefaction of the sample in the given temperature range.

Possible loss of MoO_3 during prolonged tempering of the sample was also considered as this would lead to a shift in the composition of the melt. Two samples of a mixture with identical composition (molar ratio of Na_2MoO_4 : MoO_3 : Na_4As_2. $.O_7 = 7 : 11 : 1$) were tempered. The first sample was completely homogenized, packed into a narrow platinum crucible and closed with a quartz lid. The second sample was not homogenized and was simply poured into an unclosed, wide-mouth platinum dish. The two samples were heated together in the furnace to 570°C, the crucible for 20 hours, and the dish for 80 hours. Thermoanalysis of the two samples (see below) indicated that they are completely identical, *i.e.* that no components were lost from the second sample. Chemical analysis of some samples confirmed this conclusion.

The compositions of the samples varied in a small region around the figurative points of the triple system $Na_4As_2O_7–ZO_3–Na_2ZO_4$, determined primarily by the empirical formulae given in Table VI in ref.[2] and also along two cross-sections through the triple system for Z = Mo, for a constant 10% concentration of $Na_4As_2O_7$ and for a constant 45% concentration of Na_2MoO_4. The results for measurement of these two cross-sections (Figs 1 and 2) permitted refining of the concentration range for the liquidus surface of the required compound. The positions of the figurative points were refined in thermoanalysis of the initial samples. A total of 48 samples with various compositions were prepared for Z = Mo (Tables I and II) and 25 samples for Z = W (Tables III and IV).

Thermoanalysis of the samples was employed to find the sample with the highest melting point and with a single endothermic peak on the heating recording or exothermic peak on the spontaneous cooling curve. However, as spontaneous cooling often led to marked supercooling or to a glass transition, only the heating curves were evaluated. The peak corresponding to the highest temperature (ϑ_P) indicated the temperature of the liquidus surface of the compound and the subsequent peaks indicated the temperatures of secondary (ϑ_S) or ternary (ϑ_T) crystallization. Exothermic peaks for glass-phase crystallization, which disappeared on repeated heating, were observed on some of the heating curves.

We based our considerations on the later confirmed assumption that the two compounds melt congruently and that their precise composition corresponds to the formula at the maximum melting point. Samples close to this composition did not exhibit any effects of secondary and ternary crystallization on the DTA curves, but the peak of primary crystallization was very marked. The position of the maximum melting point on the liquidus surface of the compound was refined by computation of the thermoanalytical data. Samples with compositions that were especially important for the computation were subjected to repeated measurements under identical conditions, *i.e.* in the same crucible over several days, to eliminate the effect of ageing of the characteristics of the thermocouple.

The liquidus surface of the compound has the shape of an irregular elliptical paraboloid (cone). The position of every point on this surface is determined by three spatial coordinates: ϑ (temperature), a (concentration of $Na_4As_2O_7$), and b (concentration of ZO_3). The calculation is based on data corresponding to coordinate b (independent variable) and ϑ (dependent variable) at constant value a_1. These points are fitted to function $f(\vartheta, b)$ and the position of the maxima, ϑ_1^{max} and b_1^{max}, are calculated. A similar procedure is followed for further cross-sections through points $a_2 \ldots a_n$, yielding a series of values of ϑ_i^{max} and corresponding b_i^{max}. The values of ϑ_i^{max} are fitted to function $F(\vartheta, a)$ with independent variable $a_1, a_2, \ldots, a_n$. This function is a projection of all apices ϑ_i^{max} onto plane ϑa. The calculated maximum
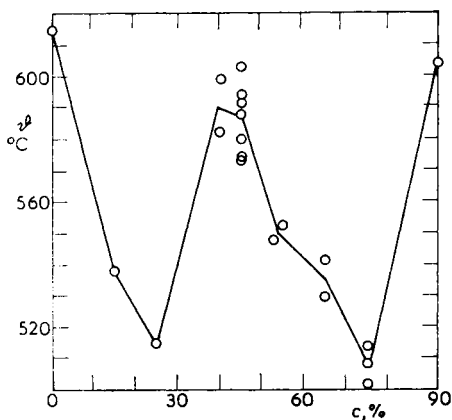

Fig. 1

Cross-section through the phase diagram of the $Na_4As_2O_7-MoO_3-Na_2MoO_4$ system for a constant 10% concentration of $Na_4As_2O_7$ (without computational interpolation)
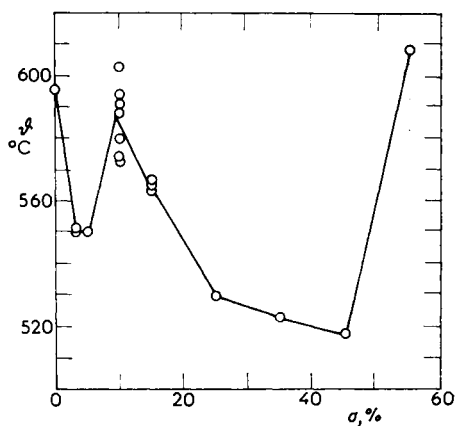

Fig. 2

Cross-section through the phase diagram of the $Na_4As_2O_7-MoO_3-Na_2MoO_4$ system for a constant 45% concentration of Na_2MoO_4 (without computational interpolation)

of function $F(\vartheta, a)$ is the apex of all ϑ_i^{max} and can be denoted as ϑ_{max}^{max}. The corresponding point on the a-axis is denoted as a_{max}^{max}. Thus two parameters are obtained for the apices of the three-dimensional space required. Then, all points b_i^{max} are fitted by function $\varphi(b, a)$ with independent vraiable a; this involves projection of points ϑ_i^{max} onto the ab plane. The value of a_{max}^{max} is substituted into calculated function $\varphi(b, a)$, yielding the third parameter b_{max}^{max} for the apex of the liquidus surface of the compound.

TABLE I

Compositions (%) of samples not used for computation and their phase transition temperatures (°C) in the system $Na_4As_2O_7$ (a)–MoO_3 (b)–Na_2MoO_4 (c)

a	b	c	$\vartheta_T{}^a$	$\vartheta_S{}^b$	$\vartheta_P{}^c$
—	55	45	—	514	596
7·99	45·51	46·50	—	520	579
8·14	39·74	52·12	—	498	581
8·26	43·67	48·07	—	—	587, 589
8·54	41·72	49·74	—	—	594, 596, 603
8·67	45·88	45·45	—	533	564, 564
8·85	39·62	51·53	—	527	577
8·99	43·90	47·11	—	—	577, 593, 593
9·49	46·50	44·01	—	540	587
10	—	90	—	458	615
10	15	75	—	503	538
10	65	25	487	522	530, 542
10	75	15	486, 498	—	515, 509
10	90	—	—	504	605
10·47	48·86	42·67	487	520	556
10·67	52·08	37·26	—	546	554
10·87	57·49	31·64	—	538	548
10·94	44·50	44·57	—	—	588, 588
11·15	49·90	38·95	—	526, 526	559, 559
11·37	55·53	33·10	—	512	531, 534
11·92	53·37	34·71	—	528	553
25	30	45	—	523	530
35	20	45	—	463	523
45	10	45	—	463	518
55	—	45	—	475	608

^{a} ϑ_T — temperature of ternary crystallization; ^{b} ϑ_S — temperature of secondary crystallization; ^{c} ϑ_P — temperature of primary crystallization. The significance of these symbols is retained in the other tables.

Functions $F(\vartheta, a)$, $f(\vartheta, b)$, and $\vartheta(b, a)$ were expressed in terms of a polynomial function. Calculations indicated that a second degree polynomial is completely sufficient for the data employed; for example, for $f(\vartheta, b)$,

$$\vartheta = K_1 + K_2 b + K_3 b^2 \ . \tag{1}$$

TABLE II

Compositions (%) of samples used in the computation, their phase transition temperatures (°C), and computation of the maxima in the system $Na_4As_2O_7$ (a)–MoO_3 (b)–Na_2MoO_4 (c)

a	b	c	ϑ_T	ϑ_S	ϑ_P	Regression b–ϑ^a
3	37	60	449	508	574, 578	
3	42	55	—	510	575, 583	$\vartheta^{max} = 580 \cdot 2 \pm 2 \cdot 9$
3	47	50	—	504	571, 575	$b^{max} = 41 \cdot 3$
3	52	45	—	504	551, 551	
5	35	60	461	508	579	
5	38	57	—	500	591	$\vartheta^{max} = 593 \cdot 2 \pm 5 \cdot 6$
5	40	55	—	524	590, 601	$b^{max} = 40 \cdot 2$
5	45	50	—	520	578, 582	
5	50	45	—	515	550	
7	33	60	426, 434	478	548, 552	
7	36	57	453, 453	502	579	$\vartheta^{max} = 595 \cdot 2 \pm 6 \cdot 9$
7	38	55	—	485	580, 580	$b^{max} = 40 \cdot 6$
7	40	53	—	509	601, 603	
7	43	50	—	—	584	
10	25	65	—	515	515	
10	40	50	—	—	582, 599	$\vartheta^{max} = 589 \cdot 0 \pm 5 \cdot 8$
10	45	45	—	518	574, 574, 580, 580, 591, 594	$b^{max} = 41 \cdot 9$
10	53	37	—	523	548	
10	55	35	—	525	553	
15	25	60	427	486, 494	486, 494	
15	30	55	433	484, 484	529	$\vartheta^{max} = 573 \cdot 5 \pm 9 \cdot 2$
15	35	50	—	494	570, 570	$b^{max} = 36 \cdot 6$
15	40	45	—	504	564, 564	

^{a} Regression a–ϑ^{max}: $\vartheta^{max}_{max} = 596 \cdot 7 \pm 5 \cdot 8$°C; $a^{max}_{max} = 8 \cdot 4\%$; regression a–b^{max}: $b^{max}_{max} = 40 \cdot 9 \pm 3 \cdot 3\%$; mass ratio for ϑ^{max}_{max} $a : b : c = 8 \cdot 4 : 41 \cdot 0 : 50 \cdot 6$; molar ratio for ϑ^{max}_{max} $a : b : c = 1 : 11 \cdot 9 : 10 \cdot 34$.

The values of ϑ_i^{max}, a_i^{max}, b_i^{max}, ϑ_{max}^{max}, a_{max}^{max}, and b_{max}^{max} were calculated by the least squares method, assuming that the values of a and b are determined accurately experimentally, while the experimental values of ϑ_{exp} deviate to a greater or lesser degree from the value of ϑ calculated from Eq. (1). Thus, the standard errors s_{max} of the ϑ_i^{max} values were taken as the squares of the reciprocal values $1/(s_{max})^2$ area weighing factor assigned to the individual values of ϑ_i for samples of identical composition to indicate their relative value. Two programs were written to solve the normal equations, one single-purpose and one general.

The computations were carried out using the samples listed in Tables II and IV and the corresponding primary crystallization temperature values. The results of the treatment are also listed in these tables and are indicated in Figs 3 and 4. The computation yielded the rounded-off molecular ratio $Na_2ZO_4 : ZO_3 : Na_4As_2O_7 \doteq 10 :$ $: 12 : 1$ for both compounds, corresponding to the empirical formula $Na_{24}As_2Z_{22}O_{83}$. The melting point for $Z = Mo$ equals 597°C and, for $Z = W$, 691°C.

Pure compounds with composition corresponding precisely to the derived empirical formula were subjected to X-ray analysis. The results, listed in Table V, indicate that both substances are isomorphous. The compound for $Z = Mo$ is poorly soluble in water, while that for $Z = W$ negligibly. In ethanol, ether or acetone both substances are insoluble. Both substances are colourless. Study of the thermal behaviour of the compound $Na_{24}As_2W_{22}O_{83}$ indicated that this substance does not decompose at a temperature of 850°C and that only a slight loss in weight occurs (6·84% after 10 hours) as a result of sublimation.

DISCUSSION

It was found in a previous work[2] that sodium molybdatodiarsenate prepared from a nitrate melt solution melts without decomposition at temperatures higher than 550°C. This was the melting point of the compound containing impurities in the

TABLE III

Compositions (%) of samples not used for computation and their phase transition temperatures (°C) in the system $Na_4As_2O_7$ (a)–WO_3 (b)–Na_2WO_4 (c)

a	b	c	ϑ_T	ϑ_S	ϑ_P
5·61	47·79	46·60	—	—	685
6·06	43·65	50·29	—	—	664, 668
6·12	48·13	45·75	—	—	686, 686
6·38	45·96	47·66	—	—	690, 692
7·48	49·03	43·49	—	—	683, 686

form of foreign elements and some of its components. Its composition could not be determined precisely by chemical analysis and thus the ratio of the initial components necessary for synthesis from a nitrate melt was not clear. Consequently, the empirical formula and exact melting point could not be determined. However, the fact that this substance melts without decomposition permitted synthesis in pure form by prolonged tempering of a mixture of the pure solid components, leading to determination of the empirical formula and the exact melting point. This method of preparation is simplified by the fact that the final compound is formed in liquid form at the tempering temperature, so that the solid components react thoroughly and comple-

TABLE IV

Compositions (%) of samples used in the computation, their phase transition temperatures (°C), and computation of the maxima in the system $Na_4As_2O_7$ (a)–WO_3 (b)–Na_2WO_4 (c)

a	b	c	ϑ_T	ϑ_S	ϑ_P	Regression b–ϑ^a
5	40	55	—	547	594	
5	45	50	—	—	670, 673	$\vartheta^{max} = 684\cdot6 \pm 17\cdot2$
5	50	45	—	—	568, 678	$b^{max} = 50\cdot8$
5	55	40	—	—	666, 686	
6	46	48	—	—	689, 701	$\vartheta^{max} = 695 \pm 11$
						$b^{max} = 46\cdot0$
7	33	60	—	536	572, 572	
7	38	55	—	540	654	$\vartheta^{max} = 688\cdot5 \pm 16\cdot53$
7	43	50	—	567	634, 650	$b^{max} = 54\cdot2$
7	48	45	—	—	684, 684	
10	30	60	477	547, 547, 563	547, 547, 563	
10	35	55	—	553, 557	623, 627	$\vartheta^{max} = 678\cdot7 \pm 4\cdot7$
10	40	50	—	549	666	$b^{max} = 45\cdot1$
10	45	45	—	—	668, 676	
10	50	40	—	—	672, 672	
10	55	35	—	555	622	
15	30	55	—	557, 565	577, 581	
15	35	50	—	555, 555	575, 598	$\vartheta^{max} = 627\cdot8 \pm 23\cdot1$
15	40	45	—	570	650, 653, 660	$b^{max} = 39\cdot8$
15	45	40	—	559	579, 595	
15	50	35	—	580	580	

^{a} Regression a–ϑ_{max}: $\vartheta_{max}^{max} = 691\cdot2 \pm 4\cdot38°C$; $a_{max}^{max} = 6\cdot1\%$; regression a–b^{max}: $b_{max}^{max} = 45\cdot8 \pm 0\cdot0\%$; mass ratio for ϑ_{max}^{max} $a : b : c = 6\cdot1 : 45\cdot8 : 48\cdot1$; molar ratio for ϑ_{max}^{max} $a : b : c = 1 : 11\cdot5 : 9\cdot5$.
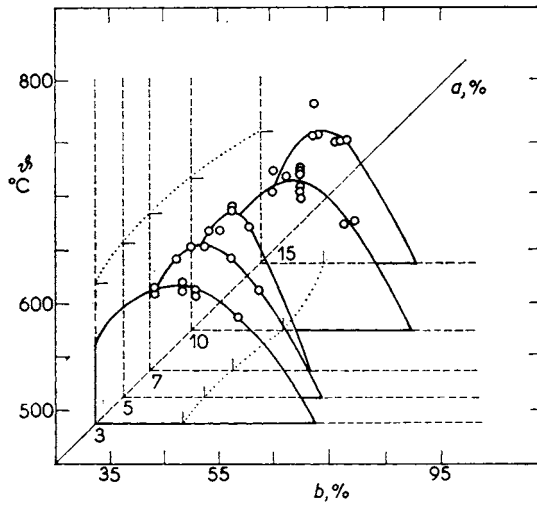
FIG. 3

Shape of the liquidus curves in the $Na_4As_2O_7$–MoO_3–Na_2MoO_4 system for a constant concentration of $Na_4As_2O_7$ and projection onto the ϑa and ab planes derived by computational interpolation
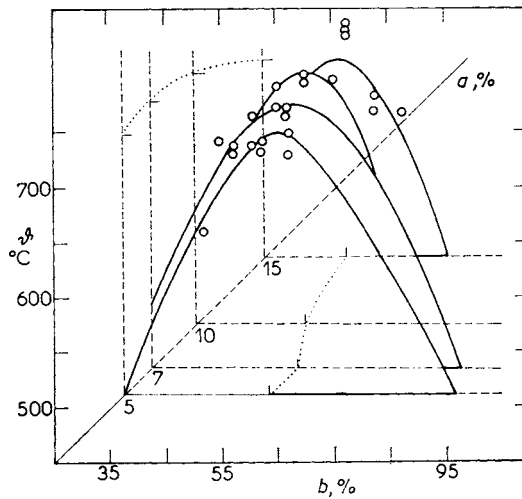

FIG. 4

Shape of the liquidus curves in the $Na_2As_2O_7$–WO_3–Na_2WO_4 system for constant concentration of $Na_4As_2O_7$ and projection onto the ϑa and ab planes derived by computational interpolation

tion of the reaction is indicated by conversion of the whole reacting mixture to liquid form.

Thermoanalysis of the $Na_4As_2O_7$–MoO_3–Na_2MoO_4 system was carried out in more detail than for the analogous tungsten system, for which a completely analogous composition of the substance formed was assumed and confirmed. The thermoanalysis was carried out to determine the composition of the pure, congruently melting substance, *i.e.* the composition of the sample whose DTA curve exhibits a single peak for primary crystallization at the highest temperature compared to samples with different compositions, where primary crystallization occurs at a lower temperature and peaks appear for secondary of tertiary crystallization; the

TABLE V

Comparison of the intensities and interplanar distances (pm) for sodium molybdatodiarsenate and tungstatodiarsenate

$Na_{24}As_2Mo_{22}O_{83}$				$Na_{24}As_2W_{22}O_{83}$			
I	*d*	*I*	*d*	*I*	*d*	*I*	*d*
61	725·0	35	197·3	21	737·4	47	198·1
—	—	22	191·4	21	592·1	26	191·7
71	544·0	—	—	88	553·9	6	184·4
53	467·0	—	—	56	474·4	19	181·0
47	457·0	23	179·4	50	462·2	18	180·3
58	357·4	22	175·5	49	378·5	14	177·1
—	—	—	—	11	367·7	10	171·5
41	320·9	34	167·0	48	323·1	22	169·2
100	311·0	—	—	100	314·2	19	163·1
52	305·8	20	162·1	53	309·9	20	162·6
27	298·8	18	160·8	33	301·7	—	—
20	290·3	19	155·8	27	292·1	17	157·0
19	273·8	24	153·9	29	274·6	28	154·6
24	263·2	—	—	24	265·1	11	150·9
25	252·2	—	—	26	253·5	13	148·3
—	—	—	—	19	245·5	12	147·9
13	238·6	18	144·3	—	—	9	145·0
25	229·8	18	143·1	34	232·0	13	142·6
—	—	15	136·1	16	229·8	19	136·6
15	225·4	14	132·9	—	—	11	133·4
22	214·6	11	126·2	22	216·0	—	—
—	—	16	122·5	9	213·1	18	122·7
13	208·0	13	119·6	11	208·4	8	119·6
		13	116·9			12	117·0

latter peaks become more marked with increasing distance of the figurative point of the sample from that of the pure compound. The treatment of the results was refined and made more objective by the use of a computation method permitting assigning weights to the various primary crystallization temperatures found in repeated measurements on a sample with given composition, to determine the most precise position of the apex of the liquidus surface of the compound.

The precise molar composition of the molybdenum compound would correspond to the empirical formula $Na_{24.68}As_2Mo_{22.24}O_{84.06}$ (Table II) and $Na_{23.00}As_2$. $.W_{21.00}O_{79.50}$ (Table IV) for the tungsten compound. As the previous work[1,2] and the X-ray study indicate that both substances have the same composition, the given compositions were rounded off to the common empirical formula $Na_{24}As_2$. $.Z_{22}O_{83}$. In this empirical formula, two As atoms correspond to an uneven number of oxygen atoms, so that the most probable structure is based on the diarsenate ion with the As—O—As bond, as given in the earlier work[2].

The scatter of the figurative points corresponding to the empirical formulae suggested in the previous works and here for the molybdenum compound is given in Fig. 5. It can be seen from the figure that the scatter of the formulae suggested in the earlier work is greater than for the samples that exhibited only a marked endothermic peak for the primary melting of the pure compound on the thermoanalytical recording. Thus, the thermoanalytical method is more precise for determination of the exact composition than chemical analysis. In addition, chemical analysis was carried out only for the molybdenum compound, while the thermoanalytical method yielded almost identical figurative points for the molybdenum and tungsten compounds. Fig. 5 also indicates that, compared to the figurative point of the precisely calculated empirical formula (point **9**), that of the rounded-off empirical formula (point **8**) is shifted only very slightly compared to the scatter of the remaining points.
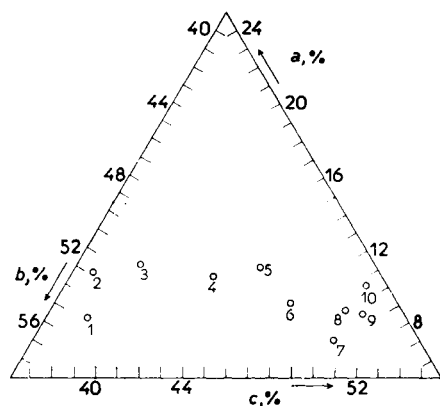

FIG. 5

The scatter of important figurative points in a detailed cross-section of the triple system $Na_4As_2O_7$–MoO_3–Na_2MoO_4. *1* $Na_{20}As_2Mo_{24}O_{87}$; *2* $Na_{16}As_2Mo_{18}O_{67}$; *3* $Na_{16}As_2Mo_{17}O_{64}$; *4* $Na_{18}As_2Mo_{17}O_{65}$; *5* Table I, 18th sample; *6* Table I, 8th sample; *7* Table II, 14th sample; *8* $Na_{24}As_2Mo_{22}$. $.O_{83}$; *9* $Na_{24.68}As_2Mo_{22.24}O_{84.06}$; *10* Table II, 16th sample

It can be expected that similar compounds will exist for X = P or V. The method described here can be used for other similar cases in the determination of the compositions of new compounds formed by tempering of the components, provided that these compounds melt congruently.

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